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REWIEW ARTICLE

GLYCOOMICS CLUSTERS OF LACTOSE AND ITS DERIVATIVES IN NANOTECHNOLOGY OF LIVING CULTURES

A. G. Khramtsov

North Caucasus Federal University,
ul. Pushkina 1, Stavropol, 355009 Russia,
e-mail: hramtsov@stv.runnet.ru

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Abstract: A paradigm of scientific perspective on one of the main components of raw milk - lactose (milk sugar) in terms of emerging views about milk science - LACTOOMICS with the logistic term GLYCOOMICS as a separate section on lactose and its derivatives is stated. The role of lactose and its derivatives in the biocenosis of living cultures is shown. The contribution of Nobel Prize winners in the development of the issues related to lactose as the "life sugar" is estimated. Optimized molecular lactose anomer structures and calculations of electrostatic potential are presented. The possibility of lactose derivatives synthesis with the use of molecular-kinetic patterns and neural network simulation is proved. These provisions allow us to establish a system of scientific views on one of the main components of raw milk at the level of post-genomic representations.

Keywords: Lactoomics, glycoomics, lactose (milk sugar), lactose derivatives, lactulose, molecular structures, neural network simulation.

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INTRODUCTION

On the assumptions of the declared LACTOOMICS postulates as the science of MILK [1] and the principles of dairy logistics [2] it seems appropriate to outline in a brief form some considerations in terms of innovation and information technology relating to one of the major components of milk – lactose (milk sugar) – an ideal nanocluster of the "dwarf" size – 1 nanometer. If whey can be considered a "universal agricultural raw material" (by Academician N. Lipatov), lactose (more than 70% of dry matter) should be referred to as an idealized model for the food nanotechnology of "Living Cultures". In this case, it is clear, especially in recent time that alongside with lactose its derivatives should be considered as natural products of directed and controlled modification. In summary, it seems quite logical to have an independent scientific section of LACTOOMICS - GLYCOOMICS designated by the article title. Certainly, along with GLYCOOMICS, it seems logical to establish LIPIDOMICS (milk fat) and PROTEOMICS (milk proteins - casein and whey).

OBJECT AND METHODS OF STUDY

The term GLYCOOMICS was formed on the basis of the published materials [3, 4] to the depth of more than 400 years (from the time of Fabrizio Bertholleti) and systematized in the collections of the Symposium of the International Dairy Federation (Russia, Moscow, May, 2007). They are also found in specialized monographs [5, 6] and the materials of the fifth (Paris, 2008), and the sixth (USA, 2011) International Conferences, devoted entirely to the primary lactose (milk) raw material – whey. Conference proceedings are published and in a systematic form (English and Russian versions) are available from the author.

From a genetic point of view, according to the theory of adequate nutrition and trophic ecology, lactose should be considered as LIFE SUGAR – naturally given component of the secretion (milk) of mammals and humans. It, like all carbohydrates, stands at the beginning and the end of the renewable energy and entropy flows passing through the biosphere.

It should be noted that lactose and its derivatives were in one way or another the object (subject) of the studies of prominent scientists honored with the highest award of the Earth civilization – Nobel Prize. As an exclusive example given below is a list of Nobel Prize winners (by year of awarding), whose works, in our opinion, are more or less relevant to the objects of the MMF Symposium.

E. Fischer (1902) studied carbohydrates, including lactose. He owns a brilliant solution to the problem of the synthesis of natural sugars and other compounds.

I. Pavlov (1904), studying the function of the digestive glands, found that the most useful and easily digestible for the body of mammals are the components of dairy products. Pavlov believed milk and its components to be amazing food prepared by nature due to all these advantages.

I. Mechnikov together with *P. Ehrlich* (1908) investigated the questions of immunity and health. In his book "Sketches of optimism" ("Life Extension"), *I. Mechnikov* examines the lactotherapy phenomenon as prevention of diseases and life extension, thanks to eating dairy products containing lactose and lactics.

A. Fleming, E. Chain, H. Flory (1945) who discovered penicillin and its curative effect in various infectious diseases, considered lactose to be a major component of nutrient medium used for the synthesis of antibiotics.

L. Pauling (1954) investigated the nature of chemical bond and its application to determine the structure of compounds. He is widely known for his work on orthomolecular medicine, elimination of lactose intolerance, as well as the development of the concept of dietary supplements.

F. Jacob, J. Monod, A. Lvov (1965) developed the theory of genetic control of enzyme synthesis on the example of the lactose operon (lac-operon) of *Escherichia coli* bacterium.

It is quite possible that the day when the next Nobel Prize will be awarded for the research related to this unique LIFE SUGAR is not far off then.

RESULTS AND DISCUSSION

The ancient Greeks, peering into the infinity of the sky, found an analogy on Earth – MILK, thus "Milky Way" and GALAXY were born. Our fellowmen *A. Bochkov, V. Afanasiev, G. Zaykov* [7], while considering the problem of carbohydrates in the Earth's biosphere, also associated the names hierarchy of e.g. milk glycals with the Universe: lactose (galactose) – Milky Way – GALAXY. What kind of an interesting, imaginative and important comparison for dairy science it is!

Aristotle in his extant treatise "On the Origin of Animals" already pointed out that milk "contains fire, i.e. the warmth of the body." Apparently as a fuel of this warmth we can assume with great certainty the presence of lactose in dairy raw materials, which is the first among the other components (fat and protein) to be subjected to bioenergy conversion. When comparing, lactose ability to "burn" (to be fermented) in a body is referred to as "oak wood" (monosaccharides "burn as stubble", sucrose as "birch wood"). Our "favorite" then – the promoter of bifidobacteria and prebiotic - lactulose, provides "fuel" for finishing sections of gastrointestinal tract (GIT) of the body, "burning" possible troubles. Figuratively speaking, lactose is the main "repository" of raw milk energy with the ratio of glucose: adenosine triphosphate (ATP) at the level of 35 : 1. The diagram below (Fig. 1) shows the uses of milk sugar (lactose). They are quite numerous and constantly expanding.

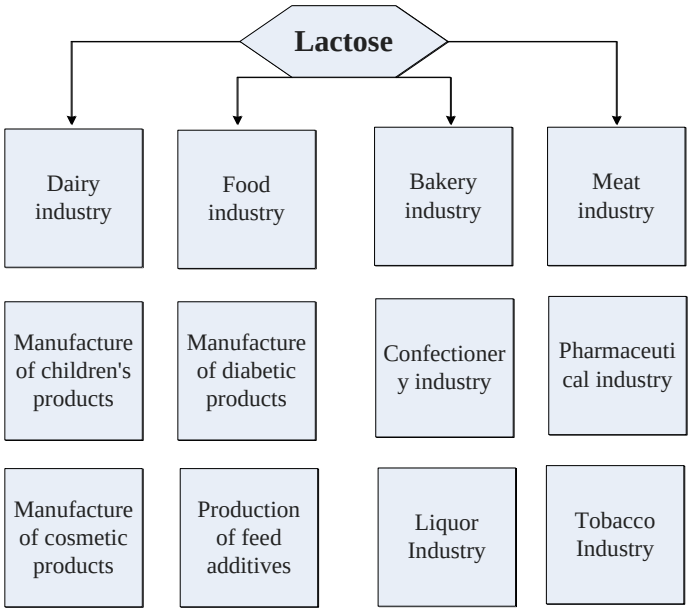


Fig. 1. Schematic diagram of some directions of milk sugar (lactose) usage.

Biological synthesis of lactose in the alveolus of female mammals is the subject of research by our colleagues – biologists and breeders. It is definitely identified that the health and the lactose content of lactating females are interrelated and can be used in genomics as a certain "life affirmation" test [8].

Chemical synthesis of lactose is still lying in the portfolio of possible innovative breakthroughs of the twenty-first century and is awaiting for its researchers. Therefore, the only source of the life sugar can only be some dairy, lactose bearing raw material**.** This is the heritage and a kind of industry reserve, which is yet to be evaluated by people.

Lactose in the life cycle of body metabolism is considered not only to perform energetic, but also plastic, immune, and some other not yet identified functions. For example, the founder of medicine Avicenna believed that "milk sugar" of the nurse forms the "thin" (now smutent) lining of the brain of infants which effects lipotropically on the choline. There had long been known “sweet powder”, which was prepared by nomads from mare whey. It was applied as a "magic remedy" for "feeding" children, the weak and the sick; giving them "life force" and health (immunity). According to the figurative expression of the outstanding twentieth century physiologist and Nobel Prize winner, Academician I. Pavlov, lactose should be considered as one of the three main components of the "amazing food prepared by nature itself." Lactose monosaccharide components also play an important

physiological role in the body, especially that of the newborn: glucose provides synthesis of reserve carbohydrate - GLYCOGEN (energy "safe" of a body), and galactose - brain GANGLIOSIDES.

Lactose intolerance in some representatives of the human race at the genetic level is still not fully decoded. Although it should be noted that at the MMF Symposium (Russia, Moscow, 2007), "the mystery of the veil" was ajar in numerous reports [3].

In everyday practice, Thilo Shleyp's slang – "Caution: lactose!" is apparently legitimate [9]. Milk sugar extraction in the so-called lactose-free products is still another significant source of lactose and its derivatives in future [10]. This is a separate, independent problem for researchers and practitioners.

Lactose ($C_{12}H_{22}O_{11}$) composition, properties, biocenosis and its solutions are well studied and published in the open literature [5, 6]. Recently its anomeric conformation has been identified, calculations of torsion angles and valence bonds for the prediction of chemical stability in terms of the synthesis of derivatives have been made. At the same time, the sphere of activity of physicists, chemists, biologists and engineers in this field is infinite - from the puzzle about the ratio of anomeric forms, such as in cow and human milk, to anomalies of solubility, crystallization and information capacity. Figure 2 shows the optimized structural formula of lactose alpha-isomer, which is extracted from lactose bearing raw material (mainly whey from cheese production – so-called cheese whey).

The results of calculation of molecular electrostatic potential distribution in two dimensions are shown in Fig. 3. The calculation of molecular electrostatic potential spatial distribution is shown in Fig. 4.

These patterns clearly show the areas of increased electron density, which may be first attacked by the electrophilic reagent, as well as the areas with minimum electron density, which can be attacked by nucleophilic reagents. The localization of domains with deficient electron density may serve to explain the direction of the attack of nucleophiles with the subsequent formation of oxynitrils, oxymes, hydrazones, endiols and other chemical derivatives.

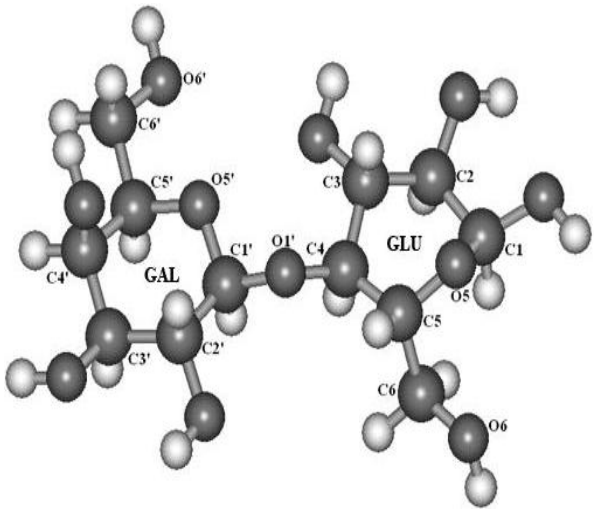


Fig. 2. The structure of α-lactose molecule (GAL, GLU).

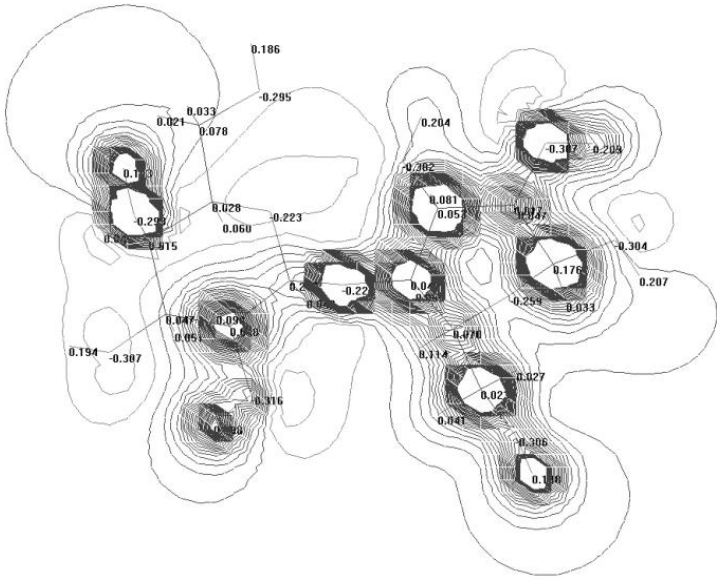


Fig. 3. α-D-lactose molecule. The distribution pattern of molecular electrostatic potential in semi- empirical calculation.

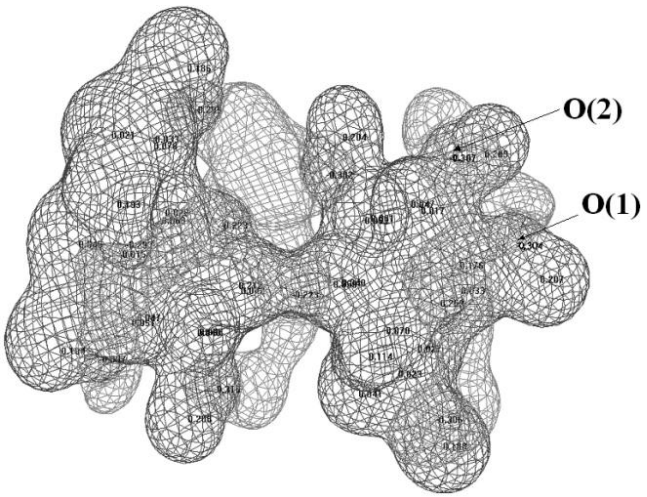


Fig. 4. α-D-lactose molecule. The spatial distribution pattern of molecular electrostatic potential.

Lactose polymorphism and uniqueness are to some extent confirmed by molecular structure of this natural carbohydrate, shown in Fig. 5.

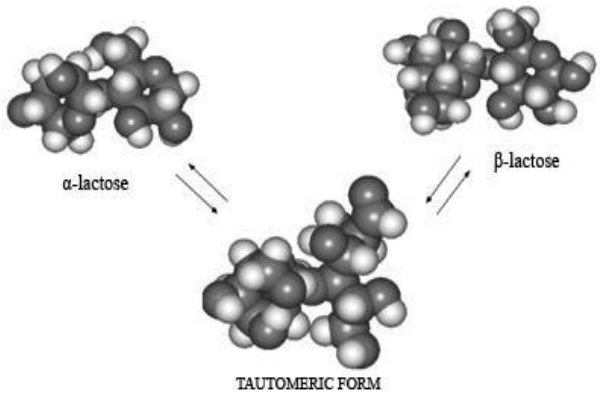


Fig. 5. The process of lactose mutarotation in aqueous solution.

Table 1 shows the main properties of geometrically optimized molecular structures of lactose anomers which were defined by quantum mechanics techniques. It should be noted that the heat of formation ΔH298 coincides with the known data, the dipole shows the uniformity of electron density distribution, and RMS gradient is close to zero.

Table 1. Molecular properties of α- and β-lactose

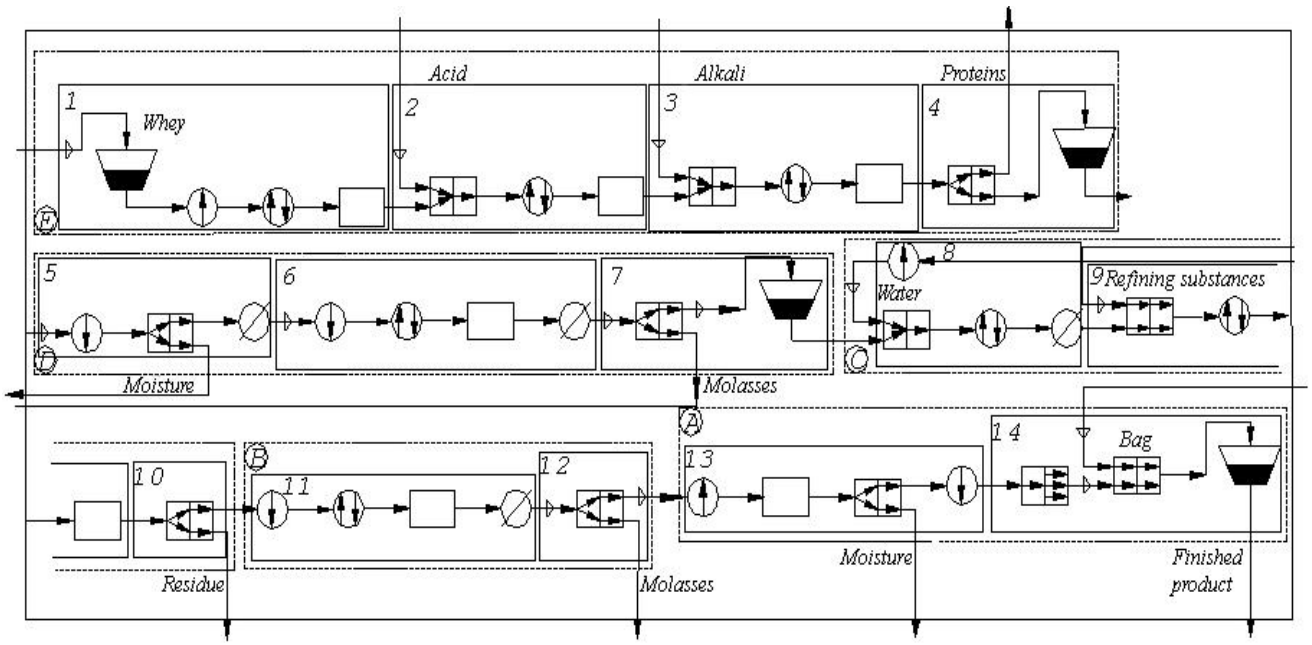
Name	The heat of formation, kcal / mol	Dipole moment, Debye	RMS gradient kcal/ (Å × mol)
α- lactose	-522.462	1.277	0.099950
β- lactose	-523.046	1.711	0.070530

Lactose resources in milk produced on the planet (more than 600 million tons per year) make up to about 27 million (those of sucrose are at the level of 100 million tons). Lactose bearing raw material (whey- more than 100 million tons per year) contains approximately 4.5 million tons of lactose - a potential raw material for the production of milk sugar. Using methodical approach of the company Fresenius Kabi, we have such fragmented information in terms of milk sugar production - at the level of 700 thousand tons per year; derivatives - 100 thousand tons per year, including lactulose - 50 thousand tons per year. Analyzing the number of figures (millions of tons): 600-100 - 27/4.5/0.7-0.1-0.05 we can confidently assert the possibilities of lactose (milk sugar) and its derivatives production to be practically unlimited. They may be of interest from the standpoint of global macroeconomics and dairy industry micromarketing, according to the president of MMF *Mr. D. Begg* [11].

Lactose removing from lactose bearing raw material is not now a secret (it was hidden in the period of the organization of antibiotics production). There is a worldwide large-scale commercial production but unfortunately, there has not even been a common technology yet. Figure 6 shows operator model for producing high-quality (refined, officinal) milk sugar, adopted in the world nowadays.

The degree of lactose extraction does not exceed 70%. Intensive technology of spray drying method requires industrial implementation. Molecular sieve filtration and biotransformation await for their researchers, particularly in terms of practice. The portfolio of innovations has lactosats studied at the school of the professor *Y. Zaikovskiy* [12] (Omsk AI, 40-s of the twentieth century), then a doctoral thesis of *M. Kovalenko* [13] (LTIHP, 60-s of the twentieth century). A separate theme is a full and efficient use of secondary (casein powder, cream cheese, whey proteins) and intermediate (condensate, molasses, "cake" from a filter press, mineralization substance) products. It should be emphasized that lactose production on the principles of non-waste technology helps to solve the environmental problems of complete cycle of raw milk industrial processing.

Lactose derivatives have always taken place in the technologies of living cultures (gastrointestinal tract - GIT) and fermented (lactic) products - beverages, cheese, cottage cheese, sour cream. They can be synthesized in the required direction and controlled from lactose. Figure 7 shows a diagram of possible directions of lactose derivatives synthesis. The approximate range of currently known lactose derivatives exceeds more than 50 names and is constantly updating.



Symbols of milk sugar production processes:

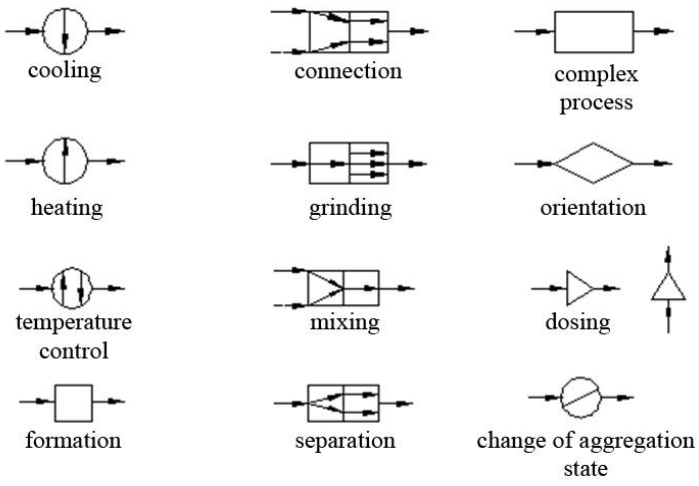


Fig. 6. Operator model of high-quality milk sugar production technology:
Designation of subsystems: (*A*) Finished product formation with desired physical, chemical and organoleptic characteristics; (*B*) Obtaining of wet crystals of a predetermined composition; (*C*) Obtaining of purified milk sugar solution of a given composition; (*D*) Obtaining of wet lactose crystals of a given composition; (*E*) Obtaining of purified whey of a given composition. Designation of operators: (*1*) Thermal denaturation of protein whey; (*2*) Thermal denaturation of whey proteins with acidification; (*3*) Thermal denaturation of whey proteins with deoxidation; (*4*) Discharge of precipitated whey proteins; (*5*) Concentration of purified whey; (*6*) Lactose crystallization in condensed whey; (*7*) Discharge of wet crystals; (*8*) Dissolution of wet crystals; (*9*) Refining of lactose solution; (*10*) Separation of refining substances; (*11)* Crystallization of purified lactose solution; (*12*) Discharge of wet crystals; (*13*) Drying of wet crystals; (*14*) Packing and packaging of a finished product.

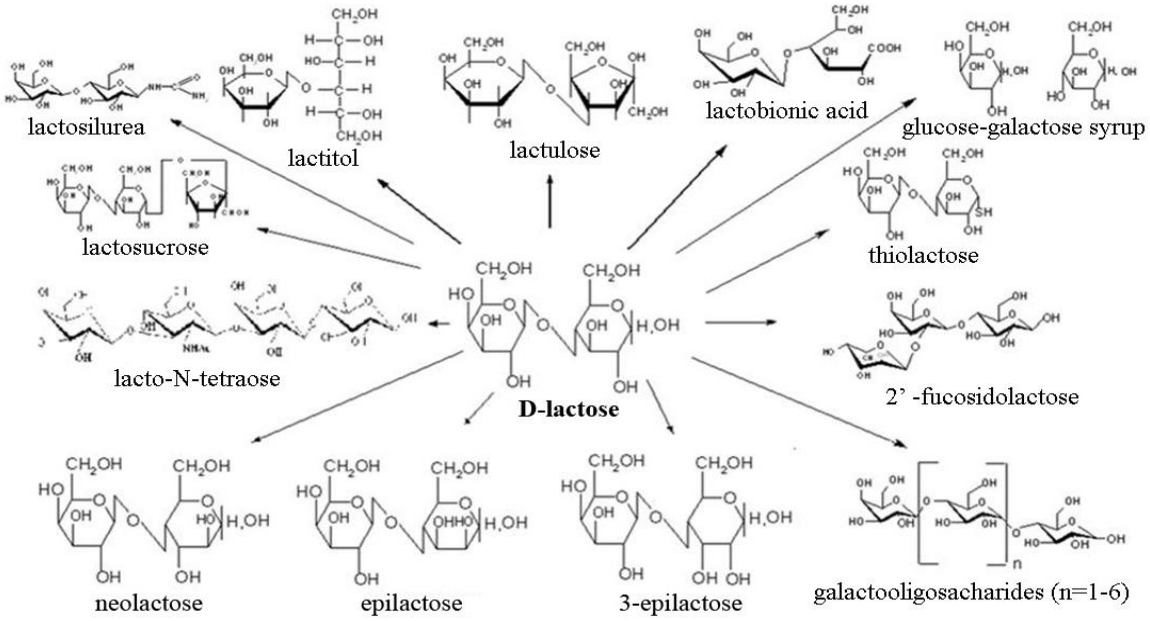


Fig. 7. Diagram of genetic relationship between lactose and its derivatives.

Lactulose, galactose and glucose syrup are worldwide known derivatives, as it was pointed out above. Lactitol, lactosucrose, galactooligosaccharides and some other derivatives are still little known even to professionals. Iodine-, sulfur-, and selen- derivatives are ready to come to life, noteworthy is the synthesis of ethanol and laktosilurea.

Lactose selectins - bacteriocines, fucose, tagatose and lactobionic acid are already in demand in the world market. It is assumed wherein that the economic potential of lactose derivatives not only pays for the cost of their creation, but also offsets all the costs of starting feedstock. Some of them, such as lactulose are necessary for the suffering.

The revival of such derivatives as oligosaccharides [14] started from the middle of the twentieth century, especially with regard to LACTULOSE, the latter being advisable to linger for consideration separately.

So what kind of "milk miracle" is lactulose, synthesis of which was awarded the prize of the Russian Federation Government in the field of science and technology?

The life cycle of lactulose began in the mid-twentieth century, and has a tendency to expand. An international body for its use – ILAG was established, which is a credit to the organizers and creates real perspectives - a precedent for other lactose derivatives. Lactulose molecular structure is shown in Fig. 8.

Similarly to lactose anomers the main properties of molecular structure of lactulose in an optimized geometric shape were defined by quantum mechanics techniques and are listed below: the heat of formation, kcal / mol 478.626; Dipole moment, Debye 1.981; RMS gradient kcal / (Å mol x) 0.004132.

The data and figures in Table 1 indicate the correctness of geometric optimization with the minimization of potential energy, energy balance of properties of the culture and the possibility of directed effect upon the molecules of aldose and ketosis.

Mechanism of reagent and nonchemical transformation of lactose (aldose) into lactulose (ketosis) is studied in detail [15] – bio-cluster nanotechnology on the proton level is assessed in terms of the energy activation on the Arrhenius formula and described by multiplicity perceptron with the help of "neural networks" methodology (Figs. 9-11).

In virtual experiments there was the degree of isomerization of 95% achieved. In future, biotransformation and directional heat-electro-physical effect on lactose molecule, e.g. by a laser beam in lactose solutions and dairy raw materials are possible.

Dozens of original (know-how) production methods of lactulose concentrates in liquid and dry forms - "Normase", "Dufalac", "Lactusan", "Alkosoft", "Lazet", "Lael" and others are worldwide known. Figure 12 shows the currently accepted technological scheme (operator model) of lactulose concentrate production.

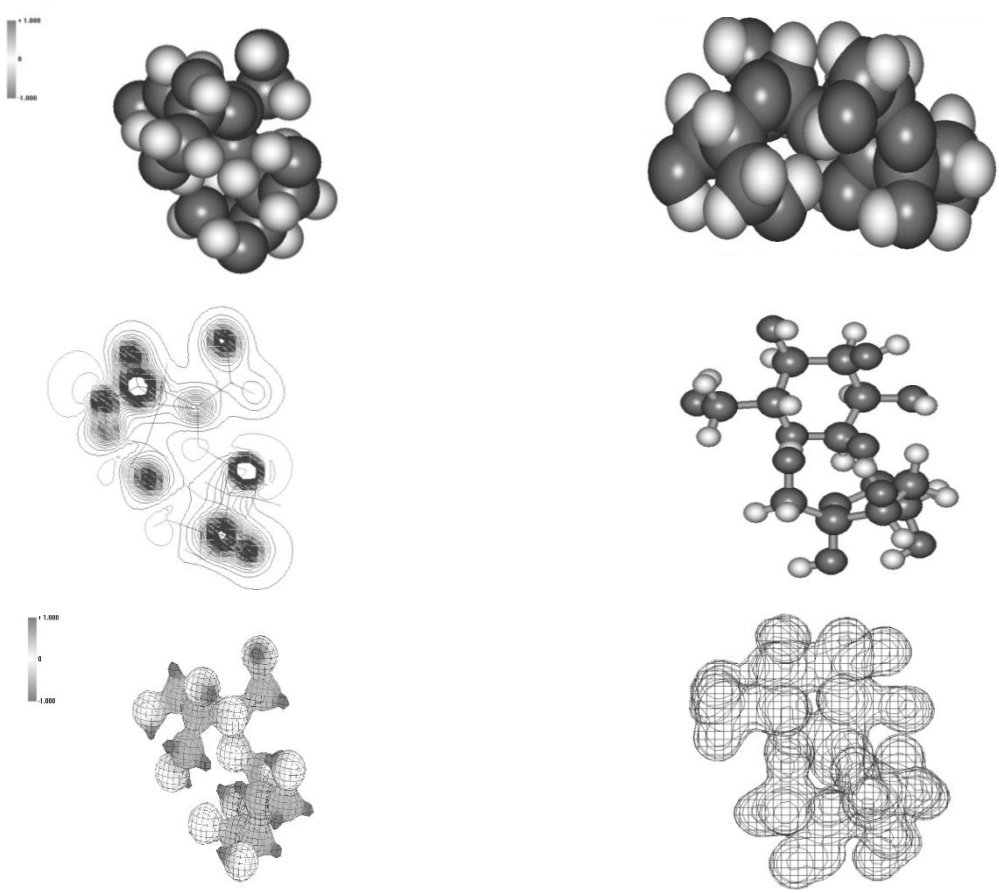


Fig. 8. Lactulose molecular structure.

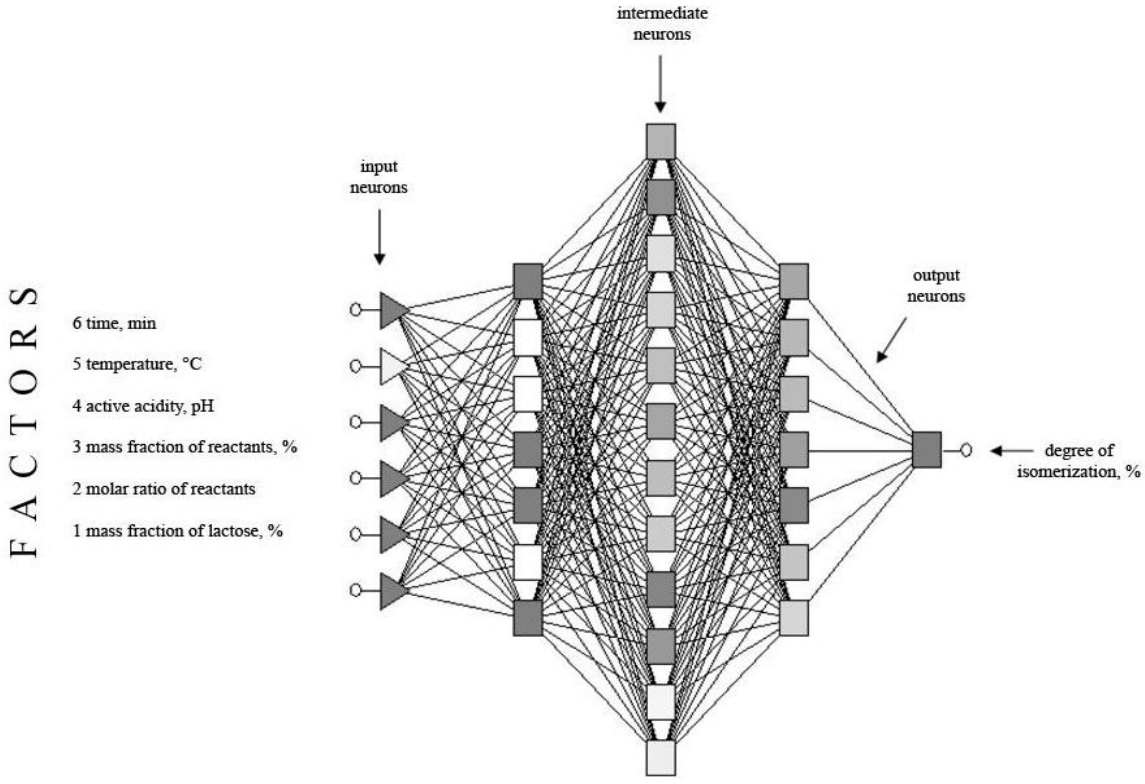
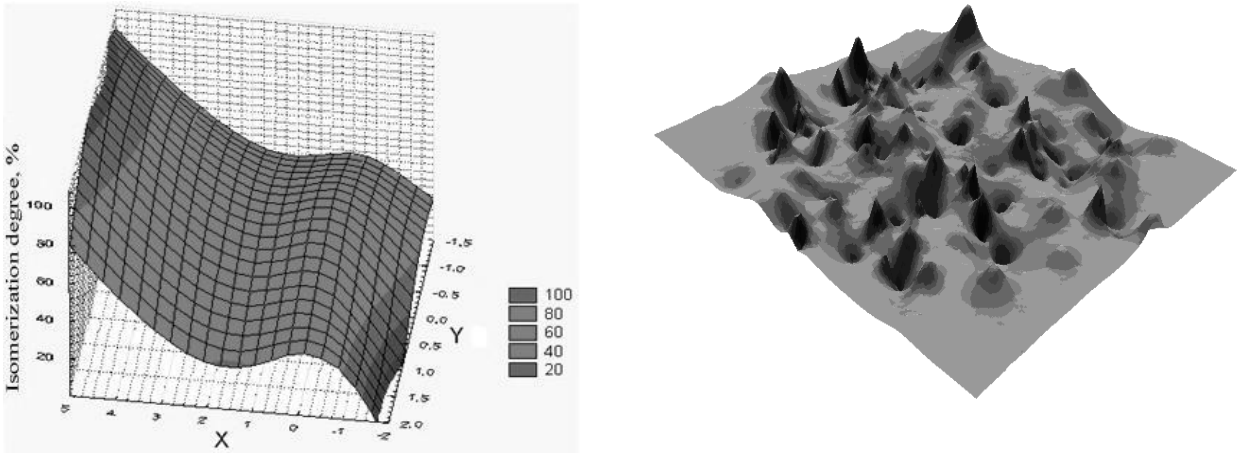
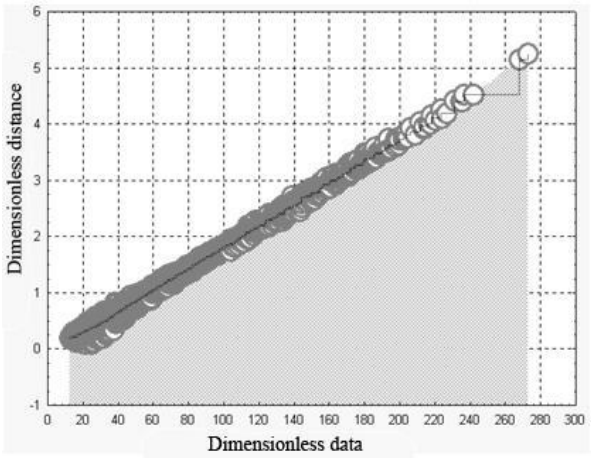


Fig. 9. Multiplicity perceptron of scaling lactose into lactulose.

Fig. 10. Conversion of lactose into lactulose with slice scaling techniques of neural networks.



(a) (b)



(c)

Fig. 11. (a) The response functions, (b) the efficiency of neural network approximation and (c) Sheapard scheme of isomerization conversion of lactose into lactulose.

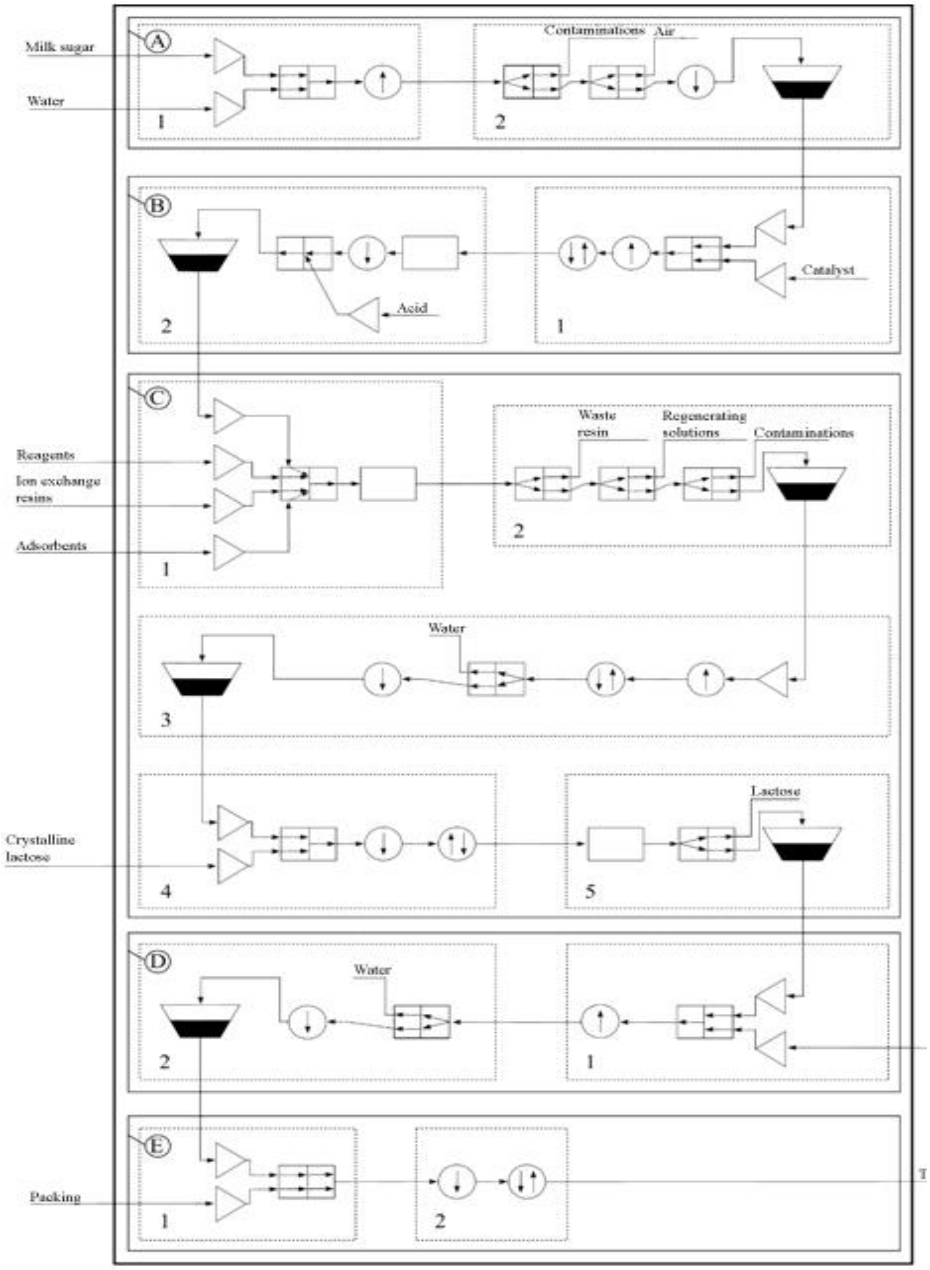


Fig. 12. An operator model of "Lactulose production technology": (A) subsystem of preparation of raw materials, which has operators: *1* – dilution, *2* – cleaning; (B) subsystem of lactose into lactulose isomerization which has operators: *1* – making catalysts, *2* – temperature control and neutralization; (C) subsystem of lactulose selection from reaction mixture which has operators: *1* – introducing reagents and exposure, *2* – departments of reagents and purification (separation of waste reagents), *3* – thickening, *4* – crystallization of lactose, *5* – discharge of crystallized lactose; (D) subsystem of lactulose solution drying which has the operators: *1* – addition of fillers, *2* – drying and cooling; (E) subsystem of finished product packing and cooling, which has operators: *1* – packing, *2* – cooling and intermediate storage.

As it was mentioned above, problems and prospects for other lactose derivatives obtaining are still to be solved in scientific research, and especially in practice.

The application of lactose and its derivatives is a separate, independent and rather large-scale topic for researchers and practitioners in various industries. It has just been marked in the form of a list and some samples of products. The calling card of lactose and therefore that of our dairy industry is on the shelves of nearly any pharmacy. That is the preparation of a vast array of medicines. Promising is lactitol and lactosucrose obtaining as an alternative to "white death" – sucrose. Lactulose may be considered as similar to a cigarette filter as a "safe threshold" of existing evils of mankind - alcohol.

Bioinformatic tablets based on the lactose or lactulose lattice, in principle, can change our perception of medicine. An anomer crystal biochip of lactose, in the apt words of the professional, can accommodate the entire Library of Congress. Finally, as a renewable byproduct resource of natural raw materials, lactose may be considered as an alternative to disappearing energy.

In general, you can imagine vividly illuminated the place and the role of lactose in the biosphere of our planet in the following algorithm:
– **Lactose around us** in lactose bearing raw materials and dairy products;
– **Lactose within us** in the form of the carbohydrate part of our diet and metabolism;
– **Lactose for us** in the form of milk sugar and its derivatives.

It should be noted that lactose is one of the most important and necessary components of functional foods (FF):
– Probiotics - nutrient medium for microorganisms;
– Prebiotics - starting raw material for synthesis;
– Synbiotics - a combination of pre- and probiotics in fermented dairy products of a new generation.

Certainly, the total consumption of lactose and its derivatives, especially lactulose, should not exceed the recommended standards similar to, for example, table salt.

All the information mentioned above is advisory by nature, as a possible motivation for the activity of researchers and practitioners within possible scientific section of milk science – LACTOOMICS in the rank of specific and separate section GLICOOMICS.

CONCLUSIONS

Assessing the place of lactose and its derivatives in the biosphere of our planet – Earth on the whole, the following factors can be systematically noted.

Utilization of the resulting lactose (milk sugar) in the annually produced milk in the world can be systematized in the following seven areas.
1. Rearing of newborn mammals (babies).
2. Production (obtaining) of dairy products.
3. Utilization of dairy products in human nutrition.
4. Production of fodder for livestock and poultry.
5. Utilization of fodder for livestock and poultry.
6. Production and use of milk sugar (lactose).
7. Obtaining and use of milk sugar derivatives (lactose).

Three (2, 6, 7) of the seven areas have in principle, a direct relation to the dairy industry, directly related is one more (4) and mediated are the other three (1 – substitutes, 3 - trade, 5 - utility livestock farms). Thus, the industry and its staffing should be focused on the whole range of possible uses of lactose dairy raw materials, which is especially important in a globalized world market, and for Russians – entry to WTO.

To the blessed memory of my unforgettable teacher, professor Mihail Sergeevich Kovalenko, (1906–1979)

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FOOD PRODUCTION TECHNOLOGY

STUDY OF ORGANOLEPTIC, PHYSICAL-CHEMICAL AND TECHNOLOGICAL PROPERTIES OF THE PLANT ANALOGUES OF PHARMACEUTICAL GELATIN PRODUCTION FOR SOFT CAPSULES

L. K. Asyakina[a,*], O. S. Belousova[a], A. N. Avstrievskih[b], L. A. Ostroumov[a]

[a] Kemerovo Institute of Food Science and Technology (University),
bul'v. Stroiteley 47, Kemerovo, 650056 Russia,
* e-mail: alk_kem@mail.ru

[b] Scientific and Production Association "Art Life",
Nakhimov St. 8/2, Tomsk, 634034 Russia

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Abstract: Factors causing the urgency of developing technology of capsules based on non-traditional raw materials, which are mainly plant analogues are considered. Carboxymethylcellulose (CMC), starches, agar, hydroxypropyl methylcellulose (HPMC) are those of economic viability due to cheaper raw materials, consumer demand for the encapsulated drugs and biologically active additives (BAA). New different characteristics that satisfy a wide range of consumers, including those who do not use animal products for religious and / or behavioral (vegetarians) reasons are presented. In the course of studies complex characteristics of organoleptic, physical- chemical, optical, buffering, rheological and structural-mechanical properties, chemical reactivity indices of plant analogues of pharmaceutical gelatin, and combinations thereof to produce capsules were determined. The tested plant analogues of pharmaceutical gelatin for capsules exhibit the properties of weak electrolytes. Active amount of titratable groups in plant analogues of pharmaceutical gelatin from agar and HPMC is small, that makes the contribution of these compounds impossible when predicting the properties of the acid-base complex mixtures or solutions. Plant analogues of pharmaceutical gelatin from starches exhibit sufficiently strong buffering properties, the average number of active groups in a 1% starch solution being 1.9 mM, and the solution's pKa of plant analogues of pharmaceutical gelatin from pectins in the range from 4.3 to 4.9 pH units respectively. Solutions of plant analogues of pharmaceutical gelatin from carrageenans are chemically unstable in the presence of acid in the solution. Acidity tests showed, that among the studied samples of plant analogues of pharmaceutical gelatin from starch all the starch samples proved to have satisfactory characteristics. The complex properties of plant analogues of pharmaceutical gelatin were examined and the possibility of using plant analogues of pharmaceutical gelatin for soft capsules was proved.

Keywords: Capsules, plant analogues of pharmaceutical gelatin, physical- chemical properties of hydrocolloids, microbiological parameters

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INTRODUCTION

Market analysis of encapsulated drugs and biologically active food additives (BAA) suggests close attention of capsule manufacturing companies to seek alternatives to traditionally used gelatin. This trend is based on the laws of development of the global consumer market: economic viability due to cheaper raw materials, consumer demand for the encapsulated drugs and dietary supplements with new and diverse characteristics that meet a wide range of needs, including those who do not use animal products for religious and/or behavioral (vegetarians) motives. All these factors cause the urgency of developing technology of capsules based on non-traditional raw materials, which can act as the composition of the hydrocolloids of plant origin [1].

This project aims to develop technological operations for obtaining of plant analogue of pharmaceutical gelatin and capsules out of it. Selection of materials for the production of pharmacological capsules must be based on the safety requirements for such products, technological requirements for raw materials at the production stage and basic requirements for capsules themselves – effective delivery and release of the drug or biologically active substance in a given location of gastrointestinal tract (stomach, gut). Ideally, the properties of the capsule as a vehicle for medicinal substances should facilitate the minimization of side effects of drugs, and, if necessary, prolong the effect of the drug due to its gradual release. Plant hydrocolloids – carboxymethylcellulose, sodium alginate, hydroxy-propyl methyl cellulose are used as raw materials and components to produce capsules in this project. The complex characteristics of raw materials to be used is a necessary step for the technology development of capsules production out of these components, including:

– organoleptic characteristics, physical-chemical properties and safety performance;
– analysis of the stability of raw materials and components for different operating conditions (temperature, pH, and others);
– characterization of the rheological properties of aqueous solutions of components, as this parameter is crucial for the preparation of capsules with the walls of specified and uniform thickness;
– analysis of the conditions of gelation (pH, temperature, concentration of the gelling agent, and others);
– analysis of gel dry conditions, structure and properties of resulting polymer films.

Natural hydrocolloids are widely used in the pharmaceutical and food industries for stabilizing of cultures, reducing weight loss of the feedstock, improving consistency and for preventing "oedema" products. Currently, carboxymethylcellulose, sodium alginate, gelatin, collagen, and hydroxypropylmethylcellulose are widely used [2, 3].

The finished product, consisting of biopolymers and mixtures thereof (including capsule walls) in the first approximation can be considered as a gel-like culture with a complicated distribution of water molecules. According to one known definition of a gel, it is a structured culture "polymer-solvent" with a stable system of bonds, which does not flow under its own weight. Gels are complex multicomponent cultures containing high-molecular substance (s) and low molecular weight liquid (water). Solutions for capsules usually contain from 80% to 90% water, gelling agents are mostly proteins, polysaccharides or mixtures thereof. The elastic properties of gels are due to the formation of the spatial network of interacting macromolecules-gelling agents or their units [4].

The study of individual components in real multicomponent gel cultures is a great challenge nowadays. The functional properties of polymer suspensions depend on pH, temperature, particle size and the nature of their surface, as well as the content of salts, lipids and other components. Thus, the practical application of biopolymers in real multicomponent cultures requires an assessment of a wide range of physical-chemical and functional properties.

The conditions of liquid – gel transfer system have great importance for the use of plant pharmaceutical analogues of gelatin. These conditions should provide sufficiently rapid gelation process under control. Methods of thermotropic gel formation are mostly suitable for bulk products (three-dimensional network of the gel). Due to the relatively low rates of diffusion of metal ions in the solutions of biopolymers ionotropic gelation processes are most effective in obtaining single- and two-dimensional gels, fibers and films [5, 6].

The scientific and technological research was carried out according to the Treaty №1, dated 01.01.2013 on the implementation of research, technological works with the Supplement №1 dated 02.13.2013 under the Integrated Project "Development of technology and organization of high-tech industrial production of pharmaceutical gelatin and its analogues for medicinal capsules" by the decision of the Government of the Russian Federation № 218, Phase 3.

The aim of this study was to determine the organoleptic, physical-chemical, optical, rheological, structural and mechanical properties of plant analogues of pharmaceutical gelatin for soft capsules, their complex characteristics.

OBJECTS AND METHODS OF STUDY

The main objects of research in the process of plant analogues production of pharmaceutical gelatin were [7, 8]: carboxymethyl cellulose, hydroxypropylmethyl cellulose, starch, agar, pectin, carrageenan.

Commercial preparations for plant analogues of pharmaceutical gelatin are presented in Table 1.

Table 1. List of components used to produce plant analogues of gelatin

Designation	Name
Starch	
K1	Nutritional supplement acetylated distarch adipate «C'Tex 06201», Cargill BV (Czech Republic)
Pectin	
P1	Pectin APS 105 (China)
P2	Apple pectin (Russia)
Carrageenan	
Ca1	Iota-carrageenan, half-refined LLC "Nord Plus" (Russia)
Agar	
A1	Agar type QP, Panreac (Belgium)
A2	Agar, Helicon (Russia)
Carboxymethyl cellulose	
C1	CMC (Ukraine)
Hydroxypropylmethylcellulose	
H1	HPMC (Netherlands)
H2	HPMC (Germany)

This paper presents the results of studies of plant analogues of pharmaceutical gelatin.

The main and supplementary raw materials for obtaining of plant analogues of pharmaceutical gelatin and subsequent manufacture of medicinal capsules were packed in polyethylene PE2NT 76-17 and polyethylene PE2NT 22-12. To study the organoleptic and physical-chemical properties of raw materials for the production of plant analogues of pharmaceutical gelatin there were used: temperature sensor, the reference module, open top UV quartz cell 10 mm, calcium Ca, Uncoded HC Lamp.

The mass fraction of water was determined using a thermostat COP-65 and analytical balance ATL-220-d4-1 (Acculab, USA). The mass fraction of total ash was determined using a muffle furnace PL 10/2.5 (Russia) and analytical balance ATL-220-d4-1 (Acculab, USA). To determine the mass fraction of nitrogen analytical balance ATL-220-d4-1 (Acculab, USA), digester D8 (Foss Tecator, Sweden) and a semi-automatic nitrogen / protein analyzer Kjeltec 8200 (Foss Tecator, Sweden) were applied. In order to predict the properties of the capsules produced from the initial compounds it is necessary to investigate the stability of pharmaceutical gelatin in solutions against the influence of acids and

alkalis, as well as their buffering properties. As a result it will be possible to estimate the average number of reactive groups per gram of dry matter component. Buffering capacity of obtained solutions depends directly on this characteristic. Buffering capacity is the amount of strong acid or alkali, which must be added to the test solution to displace the pH by one unit. In this case, the buffering capacity is determined by the minimum of the two values obtained by titration: titration with acid or alkali.

Another no less important in the practical aspect, value determined in the course of research, was the stability of compounds with different values of pH units. In this case, during the test a certain amount of acid and then an equivalent amount of alkali were added to the solution of a substance. If the pH value of the final solution proved similar to that of the initial solution, then, it showed the reversibility of the reactions. In other words, the test substance was chemically inert in the studied range of pH units. If there were differences between the values of the initial and final pH solutions, it indicated that the chemical substance was changed during the experiment and therefore was not stable in the range of studied pH units. The use of such substances in the industrial process with the unstable environment presented a number of difficulties.

The following reagents were used in the study: deionized water MillyQ, hydrochloric acid (Sigma Tek, highly pure, Russia), and sodium hydroxide (Sigma Aldrich) [9].

Hydrochloric acid was used as a 0.1 M solution in deionized water, sodium hydroxide - in a 0.1 M or 0.4 M solutions in deionized water. Dependences of pH solutions of the components to obtain capsules on the concentration of added acid or alkali were determined for polymer solutions whose concentrations are given in Table 2.

Table 2. Test solutions of gelatin and its analogues

Name of plant analogues	Designation of plant analogues	Concentration of alkali	pH of the solutions of plant analogues
Carboxymethylcellulose (Ukraine)	C1	0.3	1.2
Hydroxypropylmethylcellulose (Netherlands)	H1	0.5	1.5
Hydroxypropylmethylcellulose (Germany)	H2	0.5	1.5
Carrageenan (Russia)	Ca1	0.5	1.5
Agar (Belgium)	A1	0.5	1.5
Agar (Russia)	A2	0.5	1.5

These plant analogues of gelatin were dissolved in deionized water, then heated with stirring to 60°C and their solution was stirred vigorously on a magnetic stirrer for 30 min. After that, the bottle with the solution was placed in a water bath for 30 min, the solution temperature being between 97 to 100°C. The solution was then stirred vigorously on a magnetic stirrer for 30 min more, while maintaining the solution temperature at 60°C.

The pH values of the solutions were recorded continuously using a pH-meter S20 (Mettler Toledo, Switzerland). During the measurement, the test solution was constantly stirred with a magnetic stirrer (Biosan, MMS-3000). Hydrochloric acid solution was added with an automatic pipette, 1 ml. The solution of alkali was added with a syringe Hamilton. The portion of added alkali solution ranged from 10 to 25 microliters.

The general scheme of the experiment was the same for all test solutions. 15 ml of the test solution was placed in a glass weighing bottle, the electrode was dipped in a solution and mixing began. Mixing intensity was to form a funnel in the solution. The pH value was fixed. A 0.1 M solution of hydrochloric acid was added and pH value was fixed again. After that, portions of sodium hydroxide solution were successively added, and pH value was then fixed. Alkaline solution titration was continued until the pH value of the resulting solution exceeded 10.5.

The pH values of HPMC and CMC solutions were measured at room temperature (22 to 26°C), those of agar solution - at the temperature from 45 to 60°C. At lower temperatures, these materials form gels, and this prevents pH value and buffering capacity determination of the respective components. The pH-meter was equipped with a sensor and a temperature compensator, which provided the correct definition of the pH value in a wide range of temperatures. The results were evaluated using the program Origin 7.5.

The pH value of the test substance solution depends both on the chemical nature of the substance and its concentration, and may vary greatly. This must be considered when creating blends for capsules.

Before titration hydrochloric acid was added to the experimental solution, thereby shifting the pH value in the acidic region. Thereafter, the resulting solution was titrated with sodium hydroxide.

In the present study, when dealing with the concentration of components in the solution, it is advisable to operate with the mass fraction of the component in the solution, w%. Using such a value is justified from the point of view of practical approach, since the studied components are not uniform at the molecular level.

Nevertheless, the mass fraction of substance in the solution directly reflects its buffering properties, determines the average number of active functional groups per unit weight of the component. Analysis of titration curves allows the concentration of active groups to be determined. Thus, the number of active groups should be directly proportional to the concentration of test component in the solution [10].

The spectrophotometer Cary 50 For was used for detection of transparency at a wavelength of 650 nm.

The work was conducted by testing plant analogues of pharmaceutical gelatin to obtain capsules in terms of chemical and microbiological safety. Raw materials and components for the production of plant analogues of pharmaceutical gelatin were tested for heavy metals and toxic elements, radionuclides, pesticide residues and microbiological parameters.

One of the main methods of physical-chemical analysis of aqueous solutions and dispersions of biopolymers is highly sensitive differential scanning calorimetry (DSC). This method makes possible to determine the temperature and enthalpy of conformational transitions in solutions and dispersions of biopolymers and accurately characterize the gel forming ability of gelatin and its plant counterparts. In this section thermodynamic properties of aqueous solutions of plant analogues for the manufacture of pharmaceutical gelatin capsules (carboxymethyl-cellulose, hydroxypropyl methylcellulose, agar, pectin, starch, carrageenan) were investigated by DSC.

Thermodynamic characteristics of the solutions of plant analogues of gelatin were determined using a differential scanning microcalorimeter DASM-4 (Puschino, Russia) in the temperature range from 10 to 120°C, at the heating rate of 2°C/min and overpressure 2.5 bar. Milli-Q water served as a comparison sample. The scale of the excess heat capacity for each experiment was calibrated using the Joule-Lenz effect.

The following concentrations of the solutions (dispersions): starch - 0.5%, CMC - 1%, carrageenan - 0.5%, agar - 0.5% were chosen for studies. Concentration of CMC solution increases due to the fact, that it shows sufficiently weak calorimetric effects at the solution concentration of 0.5%. Samples of plant analogues of gelatin were dissolved in Milli-Q water at the temperatures from 25 to 30°C, and kept under constant stirring for several hours prior to the experiments.

The average values of thermodynamic parameters were determined using three measurements. The enthalpy of transfer was calculated per gram of dry matter. The experimental error in determining the phase transition temperature T_m was ±0.1 K for the heat of phase transition ΔH_m and the heat capacity of phase transition ΔC_p, experimental error was ±5% of the determined value.

These systems were studied for the following physicochemical parameters:
(1) Toxic elements;
(2) Microbiological parameters;
(3) Organoleptic characteristics;
(4) Mass fraction of moisture, ash, protein impurities;
(5) Acidity.

Studies were performed using standard techniques.

RESULTS AND DISCUSSION

1. *The organoleptic and physical and chemical characteristics of the plant analogue of pharmaceutical gelatin from starch*

The results of appearance, color and odor of test samples of plant analogues of pharmaceutical gelatin from starch are shown in Table 3, and in accordance with Appendix A1. The results obtained after the complex characteristic of organoleptic properties of all the samples of plant analogues of pharmaceutical gelatin from starch are shown in Table 3.

Table 3. Analysis results of the organoleptic characteristics of plant analogues of pharmaceutical gelatin from starches

Rate	Sample*				Requirements GOST 51985-2002	Analysis technique
	Starch Sample 1	Starch Sample 2	Starch Sample 3	Starch Sample 4		
Appearance	homogeneous powder	homogeneous powder	homogeneous powder	homogeneous powder	homogeneous powder	GOST 23058-89
Odor	odor characteristic of starch	odor characteristic of starch	odor characteristic of starch	odor characteristic of starch	odor characteristic of starch	
Colour	white	white	white	white	white	

Note. * Some average starch samples K1 were taken.

According to the analysis of organoleptic properties (Table 3) it was found that all investigated samples of plant analogues of pharmaceutical gelatin from starch are homogeneous cream powders with the smell of starch.

Results of the analysis of physical and chemical parameters of plant analogues of pharmaceutical gelatin from starch are presented in Table 4.

As seen from the data presented (Table 4), all the investigated samples of plant analogues of pharmaceutical gelatin from starch have shown a satisfactory performance by the mass fraction of water (from 8.9% to 11.2%), mass fraction of protein in the dry matter (from 0.15% to 0.31%), the number of specks per 1 dm^2 of flat starch surface. The presence of sulfur dioxide (sulphureous gas) was not detected in any of the test samples of plant analogues of pharmaceutical gelatin from starch, because it is likely not to be used during their production processes. Studied samples microscopy of plant analogues of pharmaceutical gelatin from starch were characterized by high uniformity, size and shape of the starch granules being consistent with starch, indicating the absence of impurities in their composition.

Table 4. Results of the analysis of physical-chemical parameters of plant analogues of pharmaceutical gelatin from starch

Index	Sample*				Requirements GOST 51985-2002	Analysis technique
	Starch Sample 1	Starch Sample 2	Starch Sample 3	Starch Sample 4		
Number of specks on 1 dm^2 of flat surface when considering the naked eye	79	70	36	24	no more than 300	GOST 23058-89
Moisture content, %	no more than 14	no more than 14	no more than 13	no more than 13	no more than 14	
Mass fraction of total ash, based on dry matter, %	0.19	0.19	0.15	0.16	no more than 0.20	
Mass fraction of protein based on dry matter, %	0.5	0.6	0.8	0.8	no more than 0.8	
Acidity cm^3 of 0.1 mol / dm^3 of sodium hydroxide and 100 g of dry matter	20.5 ± 0.1	20.2 ± 0.5	15.6 ± 0.1	13.7 ± 0.4	no more than 20	
Sulfur dioxide content in mg/kg	not detected	not detected	not detected	not detected	no more than 50	
Impurities	absent	absent	absent	absent	not allowed	

Note. * Some average starch samples K1 were taken.

2. *The results of the pH value of solutions of plant analogues of pharmaceutical gelatin*

The pH values of all solutions of plant analogues of pharmaceutical gelatin from starch, CMC, HPMC, agar and carrageenan are shown in Table 5.

Aqueous solutions of plant analogues of pharmaceutical gelatin from starch, CMC and HPMC were characterized by close pH values in the range from 3 to 4 pH units. It should be noted that the pH values of starch solutions are higher if they do not undergo a boiling stage. In this case the pH value of solutions with the concentration from 1% to 10% are in the range of 5 to 6 units. The pH value of collagen solution ranges from 3.0 to 3.5. Agar solutions, unlike the rest of the test compounds are alkaline. PH value of these solutions are in the range from 8.5 to 9.0.

Table 5. The pH values of aqueous solutions of the investigated components to obtain capsules

Substance	Sample*							
	Starch Sample 1		Starch Sample 2		Starch Sample 3		Starch Sample 4	
Concentration, %	1.0	5.0	1.0	5.0	1.0	5.0	1.0	5.0
pH value	3.5	3.4	3.6	3.3	4.0	3.8	3.6	3.5
Substance	CMC sample 1		CMC sample 2		CMC sample 3		CMC sample 4	
Concentration, %	0.3	1.2	0.3	1.2	0.3	1.2	0.3	1.2
pH value	3.5	3.8	3.6	3.9	3.7	3.9	3.6	3.8
Substance	HPMC Sample 1		HPMC Sample 2		HPMC Sample 1		HPMC Sample 2	
Concentration, %	0.5	1.5	0.5	1.5	0.5	1.5	0.5	1.5
pH value	3.8	3.8	3.0	3.2	3.4	3.2	3.3	3.2
Substance	Agar Sample 1		Agar Sample 2		Agar Sample 3		Agar sample 4	
Concentration, %	0.3	1.2	0.3	1.2	0.5	1.5	0.5	1.5
pH value	8.5	8.9	8.8	8.9	8.6	8.6	9.0	9.0

Note. * Average samples of pharmaceutical gelatin analogues listed above were taken.

Increasing the concentration of substances in solution results in case of plant analogues of pharmaceutical gelatin from starch to lower pH values, and in the case of CMC, on the contrary - to its increase. This is not observed for plant analogues of pharmaceutical gelatin from agar, carrageenan, and HPMC.

When preparing mixtures, complex solutions and in the manufacture of the final product it is preferable to deal with chemically stable cultures. The use of substances in mixtures, which in certain conditions demonstrate the least predicted properties are not acceptable. In the present study several conditions in which test substances are not chemically stable were revealed.

Firstly, the same thing can be said about the solutions of plant analogues of pharmaceutical gelatin of carrageenan. After the standard procedure in the first hours in the solutions there continued colloidal processes that do not let to accurately predict the properties of the solutions. However, solutions were left at room temperature for eight hours. Their behavior was predictable.

Secondly, attention should be paid to the unique solutions of plant analogues of pharmaceutical gelatin

from agar. These solutions stand out from the line of solutions of all the studied components, because they have alkaline pH values, somewhat from 8 to 9 units. Furthermore, adding an acid to the solution of agar does not lead to the expected reduction of pH value. The pH value changes more differently than it would have happened to the solutions of substances chemically inert to acid. Gradual addition of the acid and an equivalent amount of alkali solution to the plant analogues of pharmaceutical gelatin from agar did not give initial pH value. The use of solutions of plant analogues of pharmaceutical gelatin from agar in the range of 3 pH units lower as compared with its own pH values of these solutions is not desirable.

3. *The results of the concentration determination of active groups in the solution of the test plant analogues of pharmaceutical gelatin*

Concentrations of active groups for all the studied solutions of plant analogues of pharmaceutical gelatin from starch were similar and ranged from 1.6 to 2.2 mM for 0.3% solutions and from 6.2 to 8.2 mM for 1.2% aqueous solutions (Table 6). Solutions of all the samples of plant analogues of pharmaceutical gelatin from starch trace the stoichiometric ratio between the percentage concentration of the solutions and the concentration of active groups.

The average concentration of active groups in a 1% solution of plant analogues pharmaceutical gelatin from starch was 1.9 mM. This value can be used for a rough prediction of buffering properties of solutions with various starch samples.

Solutions of plant analogues of pharmaceutical gelatin from agar show very weak buffering properties so that the concentration of active groups was not possible to determine.

During the titration of solutions of plant analogues of pharmaceutical gelatin from carrageenan there were obtained non-reproducible results. The gradual addition of the acid and an equivalent amount of alkali to the solution of plant analogues of pharmaceutical gelatin from carrageenan did not reveal the initial pH value. After the addition of acid to the solution of collagen, continuous growth was observed (several hours) in the direction of pH value increasing. The observed phenomena indicate the presence of irreversible reactions with acid in the solution of plant analogues of pharmaceutical gelatin from carrageenan.

For the aqueous solutions of substances the following relationship is true:

$$\mathrm{pKa} = 2 \cdot \mathrm{pH} \cdot \mathrm{units} - \lg(\mathrm{C}), \quad (1)$$

where pKa is the negative logarithm of the dissociation constant of the acid active group of substance; C – the concentration of active groups in the solution.

Given the previously established data for the number of active groups in the solutions of plant analogues of pharmaceutical gelatin from agar with various concentrations (Table 6) there were calculated pKa values (Table 7).

pKa values of the solutions of plant analogues of pharmaceutical gelatin from agar are in the range from 4.3 to 4.9. pKa value was defined for CMC C1as well and was 11.76.

Table 6. The concentration of active groups in the solutions of plant analogues of pharmaceutical gelatin from starch

Index	Sample rate *							
	Sample 1		Sample 2		Sample 3		Sample 4	
Mass fraction of gelatin in solution, % w / w	0.3	1.2	0.3	1.2	0.3	1.2	0.3	1.2
Concentration of active groups, mM	1.5	6.1	2.1	7.7	2.1	8.1	1.8	7.2

Note. *Some average starch samples K 1 were taken.

Table 7. pKa value of the solutions of plant analogues of pharmaceutical gelatin from agar

Index	Sample rate *							
	Sample 1		Sample 2		Sample 3		Sample 4	
Concentration of solutions of plant analogue of pharmaceutical gelatin, agar solution, % w / w	0.3	1.2	0.3	1.2	0.3	1.2	0.3	1.2
Concentration of active groups, mM	1.5	6.1	2.1	7.7	2.1	8.1	1.8	7.2
pKa	4.30	4.39	4.60	4.39	4.87	4.41	4.58	4.76

Note. * 1 and 2 were taken from the agar samples, A1and 3 and three samples from agar A2.

4. *The resuls of determination of the optical density of the solutions of plant analogues of pharmaceutical gelatin*

As a result of determination of the optical density D of the solutions of plant analogues of pharmaceutical gelatin there were obtained data shown in Table 8.

Of all the samples of plant analogues of pharmaceutical gelatin from CMC, 1 CMC sample had the highest degree of absorption. For the remaining samples absorption at the wavelength of 650 nm is approximately the same. After the heat treatment (even when heated to 40˚C) sample 3 from CMC shows reduced absorption. After cooling to room temperature, the optical density D of the sample solution from CMC 3 does not return to the original state, in contrast to other samples from CMC. That is, the sample of plant analogue of pharmaceutical gelatin from 3 CMC undergoes

irreversible changes in the solution under heating. Solutions of all the test gelatin samples were characterized by high values of optical density D compared with other substances (about 2), due to turbidity of resulting solutions.

The studied samples of plant analogues of pharmaceutical gelatin from agar are almost identical in transparency. Among all the studied hydrocolloids solutions and gels based on one sample from carrageenan were characterized as the most transparent. At the same time, the sample 2 from carrageenan is the most turbid among the investigated plant analogues of pharmaceutical gelatin from agar and carrageenan.

The study of optical properties of components' solutions to obtain capsules showed that all of the test groups of the compounds, solutions of starch are the most turbid. The optical density D of these solutions at the concentration of 1% is greater than 1.5 optical units. For the other groups of the compound optical density D is less than 0.5 optical units for all of these solutions.

Optical absorption of the solutions of studied components was practically independent of the conditions, such as pH value and temperature. The solutions of plant analogues of pharmaceutical gelatin particularly can be distinguished from sample 3 CMC, which after heat treatment exhibited lower optical density D than before. That may be indicative of irreversible changes at the molecular level.

Table 8. The optical density of aqueous solutions of plant analogues of pharmaceutical gelatin at the wavelength $\lambda = 650$ nm

CMC								
Concentration, %	Sample 1		Sample 2		Sample 3		Sample 4	
	Temperature, °C							
	25	100	25	100	25	100	25	100
0.5	0.1368	0.1193	0.0419	0.0405	0.0306	0.0134	0.0440	0.0279
1.0	0.1878	0.1701	0.0634	0.0780	0.0803	0.0561	0.0739	0.0614
1.5	0.2592	0.2722	0.1104	0.1120	0.1250	0.0290	0.1210	0.0962
Concentration, %								
1.5	0.5918	0.5460	0.2667	0.2503	0.1627	0.0858	0.2412	0.1308
Concentration, %								
1.5	0.5621	0.5192	0.2584	0.2494	0.1593	0.0868	0.2261	0.1782
1.5	0.5869	0.5450	0.2660	0.2620	0.1742	0.1229	0.2333	0.1733
Starch								
	Sample 1		Sample 2		Sample 3		Sample 4	
Concentration, %								
1.0	1.6897		1.5278		1.7421		-	
3.0	2.0876		2.0786		2.2906		2.2102	
5.0	2.2632		2.2240		2.6404		2.4020	
Concentration, %								
5.0	1.7023		2.1446		2.1446		2.0288	
Agars and Carrageenans								
	Agar				Carrageenan			
	Sample 1		Sample 2		Sample 1		Sample 2	
Concentration, %								
0.5	0.1785		0.1535		0.0460		0.5039	

CONCLUSION

In the course of studies the complex characteristic of organoleptic, physical-chemical, optical, buffering, rheological and structural-mechanical properties, chemical reactivity indices of plant analogues of pharmaceutical gelatin, and combinations thereof to produce capsules were determined. Samples of plant analogues of pharmaceutical gelatin from starch, carboxymethyl cellulose, agar, carrageenan and hydroxypropyl were characterized.

Summarizing the results of these studies, it should be noted:

– Investigated plant analogues of pharmaceutical gelatin to obtain capsules exhibit the properties of weak electrolytes;

– The number of titratable active groups in plant analogues of pharmaceutical gelatin from agar and HPMC is small and this allow us not to take into account the contribution of these compounds in the prediction of acid-alkali properties of mixtures or complex solutions;

– The plant analogues of pharmaceutical gelatin from starches exhibit very strong buffering properties. The average number of active groups in a 1% starch solution was 1.9 mM, and the pKa rate of the solutions of plant analogues of pharmaceutical gelatin from pectins lies in the range from 4.3 to 4.9 pH units;

– The solutions of plant analogues of pharmaceutical gelatin from carrageenan are chemically unstable in the presence of acid in solutions.

The acidity test results revealed that all the starch samples showed satisfactory characteristics among the test samples of plant analogues of pharmaceutical gelatin from starch. All the samples of plant analogues of pharmaceutical gelatin from starch, carboxymethylcellulose, hydroxypropylmethylcellulose, agar, and carrageenan did not exceed the rated values of the mass fraction of the total quantity of ash

based on the dry weight. Thus, sensory analysis of organoleptic and physical-chemical properties showed the possibility to use any representative sample of starch, carboxymethyl cellulose, hydroxypropyl methylcellulose, agar and carrageenan for the subsequent preparation of the mixture to produce plant analogues of pharmaceutical gelatin and capsules out of it.

The complex properties of plant analogues of pharmaceutical gelatin were finally examined and the possibility of using plant analogues of pharmaceutical gelatin for soft capsules was proved.

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THE BEHAVIOR PREDICTION OF RAW MATERIAL SYSTEMS IN THE TECHNOLOGY OF WHEY BEVERAGES

E. B. Grek, E. A. Krasulya*

National University of Food Technologies,
Volodymyrska St. 68, Kiev-33, 01601 Ukraine,
* e-mail: olena_krasulya@ukr.net

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Abstract: The relevance of researches is due to the need to develop the technology of whey-based beverages with high viscosity. The paper presents the criteria for choosing a method of milk whey processing; a list of existing technologies as classification scheme is included. An alternative ingredient of plant origin - orange fiber Citri-Fi has been proposed to regulate the consistency of the beverage. Due to the special processing it has functional and technological properties - the ability to bind moisture up to 13 mass particles for 1 weight fraction of the fiber. Using mathematical modeling, the optimal conditions of including dietary fiber in the milk whey have been determined in order to predict the behavior of raw material systems in the production of beverages with high viscosity in the technological cycle. Samples of dietary fiber were studied using an ultraviolet microscope with the optical system of fluorescent illuminator. Indices of dynamic viscosity of hydrated whey plant mixtures were determined by Geppler viscometer. The visualization of the transformation of dry Citri-Fi while swelling in whey was shown, allowing you to observe a multiple increase in the volume of tubular fibers. The mechanism of water-retaining process is confirmed by the preservation of the fiber structure and a significant increase in the volume of the fragment of dietary fiber due to the absorption of the whey. The conditions for the preparation and application of orange dietary fiber in the milk whey to obtain beverages with high viscosity were studied. Optimum conditions for preparation and application of whey plant mixture in the bulk of whey are the amount of Citri-Fi - 4–5%, the stirring time - 10–15 min, the swelling temperature - 30–35°C. The rational amount of whey mixture is 10–12.5%, provided that the temperature - 50–60°C, the stirring time - 8–10 min. The rational parameters and technological scheme of whey beverages with high viscosity have been developed.

Keywords: Dry and hydrated samples of Citri-Fi, whey plant mixtures, mathematical models, viscosity characteristics, beverages with high viscosity

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INTRODUCTION

Beverage industry is one of the efficient ways of using milk whey, which is accessible form for the correction of human nutritional status by enriching physiological functional ingredients with a favorable effect on the metabolism and immunity. All non-alcoholic drinks, including whey, are refreshing products in the daily diet of people. Nutritional value of whey beverages is linked to ensuring the water balance of the body and the energy [1-3].

Criteria for selection of whey as a basis for beverages formulated in published data are the following [4, 5]:
– minimal pre-treatment with the existing equipment and the possibility of correction of technological processes;
– the properties and composition of whey, its relative availability and low cost, safety;
– seasonal peaks of coincidence of the beverage consumption and production of whey at dairy processing plants;
– ecological necessity of solving the problem of whey disposal;
– the possibility of combining with herbal ingredients at the organoleptic level and ensuring their technological properties.

The composition of whey predetermines its use for production of various beverages, including fermented ones. Beverages based on native whey have high value due to the preservation of all milk components. There are several classifications of whey beverages; one of the variants is shown in Fig. 1 [6, 7].

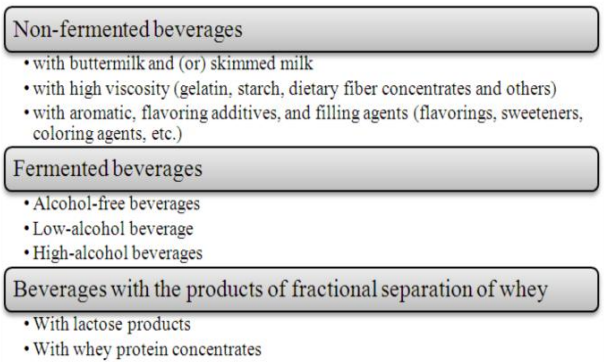


Fig.1. Classification of milk whey beverages.

There are a great number of technology solutions for complex processing of whey, including the production of beverages, however their implementation in the industrial process is insufficient [8-10]. This is due to the problem of ensuring production processes with modern expensive equipment, the lack of stringent en-

vironmental requirements, sanitary control and economic motivation, low awareness of both producers and consumers about the nutritional and prophylactic properties of whey and products based on it, and the possibility of biotransformation in the carbohydrate and nitrogen derivatives (lactulose, ethanol, lactic acid and others).

The addition of gelatin, starch, pectin, xanthan and guar gum, agar, carrageenan, protein concentrate and others of different quantities into milk whey provides whey products with different structured viscoelastic characteristics including high viscosity beverages [11].

Problems that require scientific evidence in the development of technologies of whey beverages with high viscosity are the selection of available plant ingredient; the regulation of the guaranteed content of the plant component; the rationalization of the production process.

Alternatively, the ingredients of plant origin for the regulation of the consistency of beverages may be dry citrus concentrates (Citri-Fi) – the series of improved natural dietary fibers. According to the manufacturer, the introduction of the latter in the recipe composition of dairy products has a positive effect not only on their biological value, but also on the technological properties. Orange fibers possess textural and antioxidant properties [12, 13]. Their addition in the recipe composition would stabilize the viscosity characteristics, enrich whey beverages with dietary fibers, emphasize the fullness of taste and expand the product range.

The above information about the properties and the previous investigations of Citri-Fi – the determination of their solubility (70.0 ± 2.1)%, and water-binding capacity (in water (96.0 ± 2.88)%), in whey – (95.0 ± 2.85)%), were used to study the conditions of preparation and application of plant whey mixtures into the main volume of whey to produce beverages with high viscosity. For rational mixing and obtaining homogeneous beverage it is advisable to introduce pretreatment with the testifying of this process [14, 15].

The aim of the paper is to develop whey beverages with high viscosity taking into account the possibility of predicting the behavior of raw material systems in the technological cycle.

OBJECTS AND METHODS OF RESEARCH

The object of research is orange fibers "Citri-Fi 200", the manufacturer - Fiberstar Inc., USA (The conclusion of the state sanitary-epidemiological examination № 05.03.02-03/50735 of 14.08.2009); whey plant mixtures, the beverage with high viscosity.

"Citri-Fi 200" is the citrus dietary fiber derived from cell tissue of dried orange pulp by the mechanical processing without the use of chemicals. The organoleptic indices of orange fibers are the powder of light cream color with a neutral taste and smell with a shelf life of 36 months at a temperature neither lower than 0°C nor higher than 32°C, relative humidity - 30-60%. According to the manufacturers, "Citri-Fi 200" is capable of absorbing from 8 to 13 mass particles of water for 1 mass fraction of the fiber, the pH is 4.0-5.0. Nutritional value of 100 g is 224 kcal. Physicochemical and microbiological indices of orange fibers "Citri-Fi 200" are shown in Table 1.

Table 1. Indices of "Citri-Fi 200"

Physicochemical indices		Microbiological indices	
Total fat, %	1.08	Amount of bacteria, COE/g	$<10^5$
Total carbohydrates, %	82.55	Yeast, mold in 1 g	<500
The total amount of fiber, %: - Soluble - Insoluble	75.3 39.6 35.7	Coliform bacillus in 1 g	<10
Sugar, %	5.38		
Proteins, %	7.38	Salmonella, in 1 g	negatively
Ash, %	2.46	E. coli, COE/g	<10

Samples of dietary fibers Citri-Fi were investigated by the ultraviolet microscope (Axioskop 40, Carl Zeiss, Germany) equipped with the optical system of the fluorescent illuminator and the universal condenser working in the zoom range from 1 to 100 with the ability of rapid change of the filters.

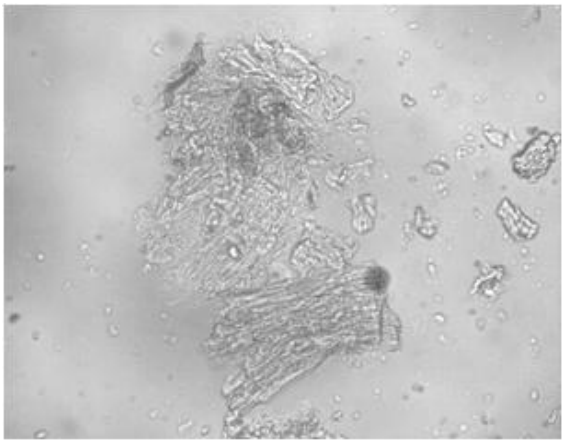


Fig.2. Visualization of Citri-Fi using autofluorescence.

While using autofluorescence a microphoto of "Citri-Fi 200" was obtained, visualizing an opened and dissolved structure of fiber cells links of which are able to bind a significant amount of fluid and keep it during the production process and product storage. It proves water - binding properties as it was claimed by the manufacturer.

The dynamic viscosity was selected as the main criterion of the efficient formation of viscous characteristics of whey plant mixtures and beverages.

With the application of mathematical package MathCad 15 three-dimensional regression models were constructed that adequately described the change of the dynamic viscosity of whey mixtures with Citri-Fi which were included in the main volume of whey to get beverages with a given consistency.

At the first stage for optimization and rationalization of the conditions for obtaining the homogeneous beverage with high viscosity model whey plant mixtures with different amounts of Citri-Fi (1–11%) were prepared. In native milk whey with the above indices heated to a temperature (30 ± 2)°C citrus fiber in various amounts was added and subjected to swelling from 5 to

15 minutes and different temperatures from 20 to 40°C. In hydrated whey plant mixtures the index of dynamic viscosity was determined using the viscometer Geppler BH-2. It was calculated by the formula:

$$\eta = K \cdot (\rho - \rho_0) \cdot \tau, \quad (1)$$

where η is the dynamic viscosity (poise); τ is the time of the ball movement; ρ is the density of the ball material, kg/m^3; ρ_0 is the density of the test product, g/cm^3; K is the ball constant (cP·cm^3/g·sec).

To convert units of dynamic viscosity in the SI system the following ratio was used: 1 poise = $1 \cdot 10^{-3}$ Pa•sec.

RESULTS AND DISCUSSION

Researches were conducted in two stages: at the first stage the mixtures with optimal proportion of Citri-Fi and whey with respect to viscosity characteristics were simulated. At the second - mixtures in a certain amount were added to the bulk and adjusted to quality parameters by mixing.

Multifactor mathematical models were obtained that adequately described the change of dynamic viscosity in whey plant mixtures with Citri-Fi while changing three independent factors. The coded form of the equation describing the model is the following:

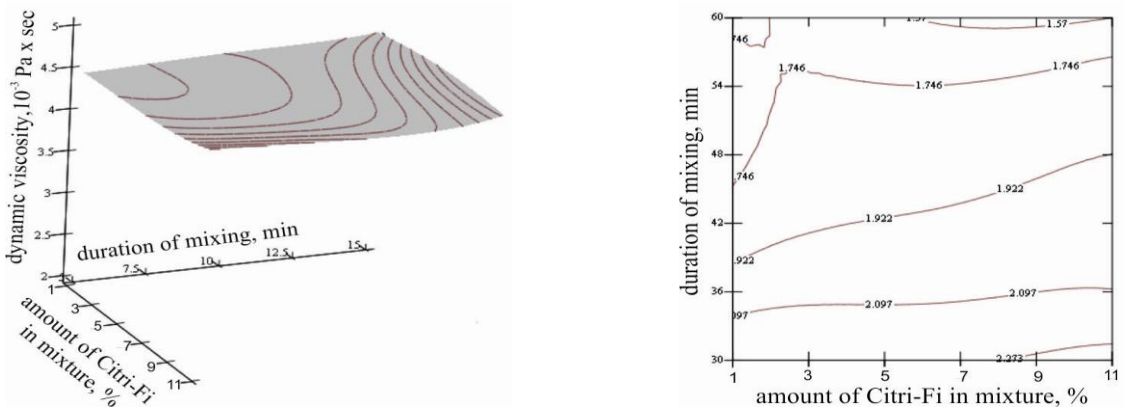
$$Y_1 = 2.545 + 0.0172\ C_1 + 0.0092\ C_2 + 0.0505\ C_3, \quad (2)$$

where Y_1 is the dynamic viscosity of whey plant mixtures with Citri-Fi, 10^{-3} Pa•sec; C_1 is the amount of dietary fiber in the whey plant mixture, %; C_2 is the mixing time, min; C_3 is the swelling temperature, °C.

The adequacy of the models was tested by the determination coefficient R^2Y_1 = 95%, testifying to the high quality characteristic of the connection of the system coefficients, as well as the examination was done by using the F-test (F-Fisher criterion) and the t-distribution to assess the reliability of the correlation coefficients.

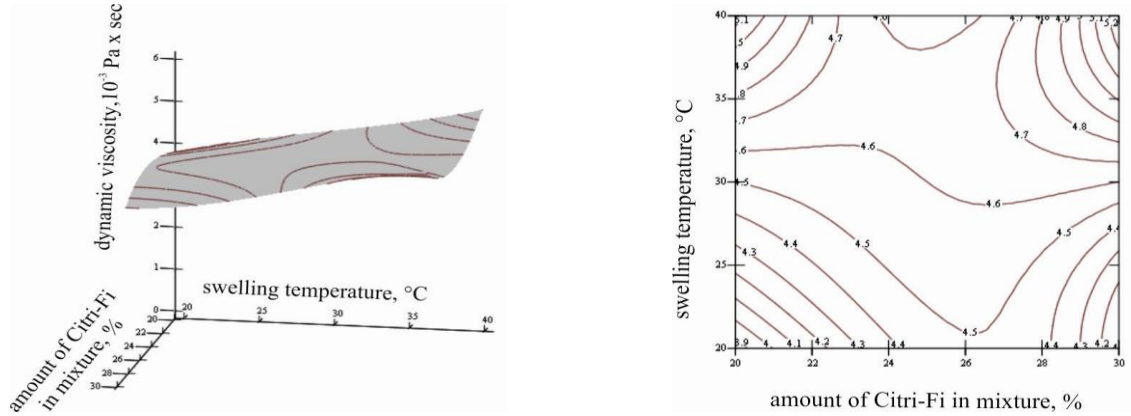
For a complex study and optimization of the component composition of whey plant mixtures three-dimensional regression models were constructed that adequately described the change of dynamic viscosity at the pair-wise change of two independent parameters ("the amount of Citri-Fi in whey plant mixture / the duration of mixing", "the amount of Citri -Fi in whey plant mixture / the swelling temperature"). For these models, the adequacy was tested by the method of root-mean-square deviation of calculated data from the experimental ones, which is less than unity.

Response surface and lines of constant values for the dynamic viscosity of whey plant mixtures with variable parameters of the swelling temperature, the duration of mixing and the amount of dietary fibers are shown in Fig. 3-4.



(a) (b)

Fig. 3. Response surface (a) and lines of constant values (b) of a dynamic viscosity index in whey plant mixture with Citri-Fi depending on the amount of dietary fibers (C_1, %) and the duration of mixing (C_2, min).



(a) (b)

Fig. 4. Response surface (a) and lines of constant values (b) of a dynamic viscosity index in whey plant mixture depending on MF (C_1, %) and the swelling temperature (C_3, °C).

As shown in Fig. 3-4 the analysis of mathematical models and their graphical interpretation give the reason to consider that the amount of Citri-Fi, the duration of mixing and temperature significantly influence the swelling index of the dynamic viscosity of whey plant mixtures. The optimum range of values of the basic characteristics (dynamic viscosity index) is greatly narrowed in the area of mixing - 10–15 min and the swelling temperature of 30–35°C.

Linear increase in the values of variable parameters (C_1, C_2, C_3) leads to the growth of the dynamic viscosity index. Quadratic effects indicate the presence of areas of the extrema of the response function: the maximum for the input parameters. When adding Citri-Fi more than 7%, there is a rapid increase in viscosity – the apparatus problems are possible when incorporated in the bulk of the whey.

The comparison of response surface of output parameters and their lines of constant values allowed to set the optimal parameters of the process of increasing the viscosity of whey plant mixtures with the best index of the dynamic viscosity: the number of Citri-Fi - 4–5%, the duration of mixing - 10–15 min, the swelling temperature - 30–35°C.

To visualize the changes taking place with dry Citri-Fi while swelling in the whey the coloring agent Acridine Orange was used, which made it possible to observe how the tubular fibers are increased in volume by several times when adsorbing moisture. Some parts are deformed due to changes in soluble fiber (Fig. 5).

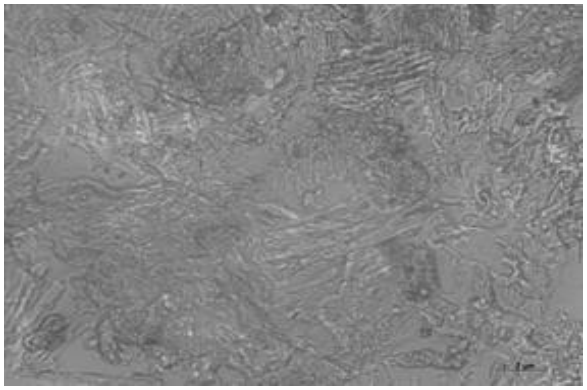


Fig. 5. Orange dietary fiber Citri-Fi.

It was found that orange fibers having a form of plates with a strong monolithic tubular structure like high-polymer complexes are damaged in some places due to mechanical processing (the cells were disclosed). Moreover, orange fiber in a non-hydrated state is characterized by a multilayer structure having the damaged walls of fiber with microcracks. This structure defines a high specific surface area of the carbohydrate matrix, and accordingly, increased moisture-absorbing capability. It is confirmed by the image of the hydrated sample Citri-Fi. There is a preservation of the fibrous structure and a sharp increase in fragment volume due to the absorption of whey as it was mentioned above.

The next stage of research is to determine the optimal amount of whey plant mixture for adding in the main volume of whey to obtain a beverage with high viscosity. The control beverage is a viscous drink with stabilizer that resembles a liquid jelly (such organoleptic feature corresponds to the index with a dynamic viscosity up to $(2.55 \pm 0.13)\ 10^{-3}$ Pa×sec). For obtaining the model beverage with high viscosity pretreated whey plant mixture in an amount of 5–15% with a particular amount of dietary fiber was added to milk whey. The mixing temperature was varied from 30 to 60°C, followed by mechanical processing of the obtained mixture for 6–10 min and then it was subjected to pasteurization at a temperature of (78 ± 2)°C with a maturation of 2–3 min.

To study the effect of three variables of the process (the amount of whey-plant mixture, the mixing time and the temperature for introducing the mixture into the bulk of whey) to the index of the dynamic viscosity the approach to modeling mentioned above was applied once more. In encoded form the equation for the beverage with whey plant mixture is the following:

$$Y_1 = 2.8262857 - 0.00061\ C_1 + \\ + 0.0095\ C_2 - 0.021267\ C_3, \quad (3)$$

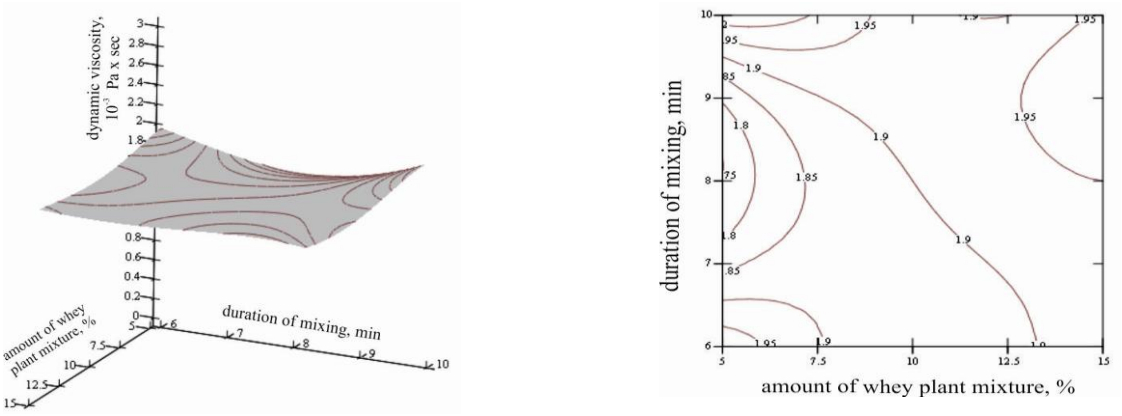
where Y_1 is the dynamic viscosity of the beverage with whey plant mixture, 10^{-3} Pa×sec; C_1 is the whey plant mixture, %; C_2 is the mixing time, min; C_3 is the temperature introducing into the whey, °C.

For a complex study of the influence of process conditions and optimization of the beverage composition with high viscosity when using the MathCad 15 three-dimensional regression models were constructed that adequately described the change of the dynamic viscosity of the beverage at the pair-wise change of two independent parameters ("the whey plant mixture / the mixing time within a total whey volume" and "the whey plant mixture / the temperature of introducing into the whey").

The obtained regression equations enable to predict the behavior of all systems throughout the technological process. Response surface and lines of constant values of the dynamic viscosity for the beverage with Citri-Fi with variable parameters – the temperature, the duration of mixing and the amount of whey plant mixture are shown in Fig. 6-7.

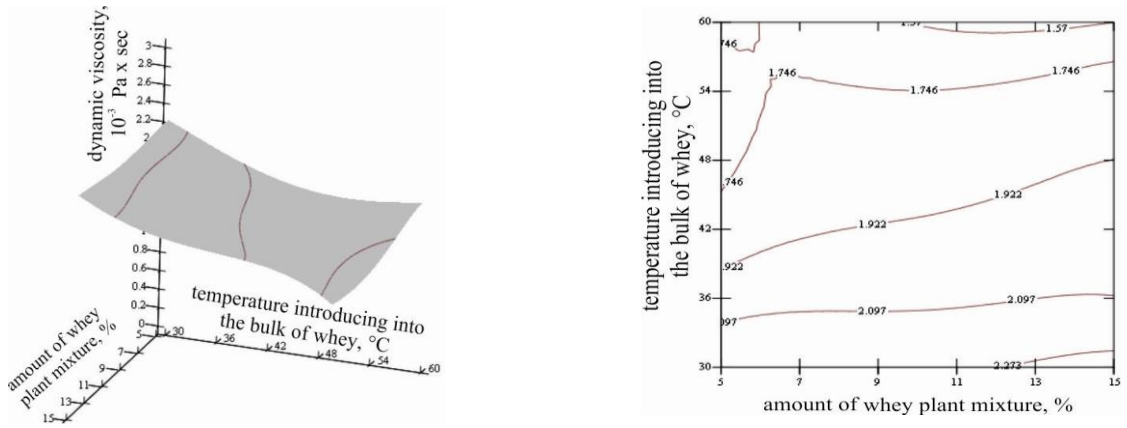
According to the analysis of the response surface shown in Figures 6-7, it was found that the optimum amount of whey plant mixture is 10–12.5%, with the introduction of the following modes in the bulk of whey: the temperature - 50–60°C, the stirring time - 8–10 min. Under these conditions, the dynamic viscosity index is $(2.64–2.68)\ x10^{-3}$ Pa×sec.

Based on the results of the research the technology of whey beverage with high viscosity was developed. Parametric production scheme is shown in Fig. 8.



(a) (b)

Fig. 6. Response surface (a) and lines of constant values (b) of a dynamic viscosity index of whey beverages depending on the amount of mixture with Citri-Fi (C_1, %) and the duration of mixing (C_2, min).



(a) (b)

Fig. 7. Response surface (a) and lines of constant values (b) of a dynamic viscosity index of whey beverages depending on the amount of mixture with Citri-Fi (C_1,%), and the temperature introducing into the bulk of whey (C_3,°C)

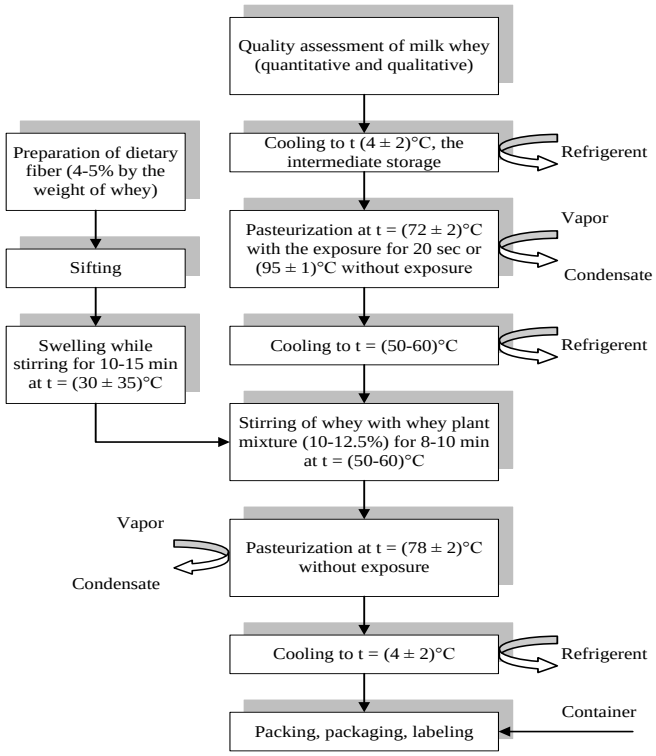


Fig. 8. Parametric production scheme of whey beverage with high viscosity.

CONCLUSIONS

The model is proposed to predict the behavior of raw material systems in the technological cycle to obtain whey beverages with high viscosity. The optimum parameters of the process of improving the viscosity in whey plant mixtures were determined. They are the amount of Citri-Fi - 4–5%, the stirring time - 10–15 min, the temperature of the swelling - 30–35°C. Also, a rational amount of whey plant mixture (10–12.5%) was found. The following modes of introducing this mixture into the bulk of whey are the temperature - 50–60°C, the stirring time - 8–10 min.

The paper shows the visualization of dry and hydrated orange fiber samples that are characterized by the presence of complex polyangular associates linked in a solid fibrous structure having a large number of fragments of orange dietary fiber. Also the parametric production scheme of whey beverages with high viscosity was proposed.

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SCIENTIFIC JUSTIFICATION OF HYDROMECHANICAL DISPERGATING IN FOOD PRODUCTION FROM HYDROBIONTS (CYST *ARTEMIA SALINA*)

O. K. Motovilov[a,*], V. M. Poznyakovskiy[b], K. Ya. Motovilov[a], E. V. Latkova[b]

[a] Siberian Research Institute of Technology and Processing of Agricultural Products, Krasnoobsk, Novosibirsk, 630501 Russia
* e-mail: gnu_ip@ngs.ru

[b] Kemerovo Institute of Food Science and Technology (University), bul'v. Stroiteley 47, Kemerovo, 650056 Russia

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Abstract: The problem of raising the level of protein supply in the diet of the population of the Russian Federation is still relevant. To solve this problem it is important to investigate protein food reserves, while priority is given to a combination of vegetable and animal proteins. Fish and non-fish water fishing is paid particular attention as a potential source of protein, because of almost inexhaustible world ocean reserves and the prospects for their use. The aim of the work is the scientific study and practical implementation of preparation and evaluation of the quality of pasty concentrates of aquatic organisms, as well as health food products based on them using hydro-mechanical dispersion. The scientific background of technological aspects of the production of aquatic pasty concentrate from hydrobionts (cyst *Artemia Salina*) using hydro-mechanical dispersion is presented in the article. Consumer characteristics, conditions and terms of the concentrate storage are identified. New data on the effectiveness evaluation of paste concentrate from cyst *Artemia* to increase the body's immune properties are obtained in the experiments with animals. The expediency of development and industrial production of cheese products using pasty concentrates of aquatic organisms is based. Regulated quality parameters, modes and terms of their storage are established.

Keywords: Hydrobionts, hydromechanical dispergation, cheeses, cavitation, foods, quality, safety, pasty concentrates

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INTRODUCTION

The modern concept of creating a sustainable food base comes from the need to search for and use of reserves of agricultural raw materials produced by deep processing of highly effective methods of physical and other kinds of actions [1].

The production of healthy food based on local raw materials is very important. These products are characterized by safety, high nutritional value, corresponding properties, meeting the needs of different population groups in necessary food, biologically active substances and energy [2].

The subject area is one of the priorities in the implementation of international and national programs in the field of diet correction and preservation of health, enshrined at the state level by laws and government regulations [3-7].

Existing technologies for processing are usually material- and energy-consuming, and often do not meet the requirements in terms of quality. Matters of general and function-based food production from pasty concentrates using hydro-mechanical dispersion deserve special attention as part of the discussed problem. The urgency and priority of these studies are shown in the work of scientists in the field of biotechnology – I.A. Rogov, T.K. Kalenik, in the field of hygiene and food biochemistry – V.A. Tutelian, B.P. Sukhanov, V.M. Poznyakovskiy, in the field of commodity science – L.G. Eliseeva, T.N. Ivanova, E.P. Kornena et al.

However, some aspects of this trend remain poorly studied, require scientific justification and practical solutions.

Currently, special attention is given to fish and non-fish water fishing as a potential source of protein, because of almost inexhaustible supply of the world's ocean and prospects for their use [8-11].

Artemia cysts are eggs of saltwater crustacean *Artemia Salina*. Biochemical composition of Artemia cysts (Table 1) indicates the presence of digestive lipids and unsaturated fatty acids in cysts. Artemia cysts are a source of vitamins, contain a set of vital mineral substances (Table 2 and 3). Vitamin E in cysts is 8.8 times more, compared to whole milk powder, B6 and B3 - 15 and 19 times respectively. The content of carotenoid averages 136 mg / 100 g [11].

Table 1. Chemical composition of undecapsulated Artemia cysts, % [11]

Index	Content
Moisture	9.14 ± 0.11
Protein	44.04 ± 1.29
Carbohydrates	30.72 ± 0.76
Lipids	7.22 ± 0.22
Ash	8.88 ± 0.17

Table 2. Mineral composition of undecapusulated Artemia cysts [11]

Index	Content
Macroelements, g/kg	
Calcium	0.24 ± 0.04
Phosphorus	0.46 ± 0.06
Potassium	2.40 ± 0.03
Sodium	8.70 ± 0.14
Magnesium	6.80 ± 0.09
Trace elements, mg/kg	
Iron	375.00 ± 7.93
Copper	17.50 ± 0.13
Zink	97.50 ± 0.68
Manganese	150.30 ± 3.20

Table 3. Vitamin composition of undecapusulated Artemia cysts [11]

Index	Content
Retinol	27.32 ± 0.18
Tocopherol	76.94 ± 2.91
Thiamin	7.69 ± 0.12
Riboflavin	23.08 ± 0.29
Pantothenic acid	38.00 ± 0.32
Pyrodixine	15.39 ± 0.14
Cobalamin	0.08 ± 0.01

Commercial processing of cysts *Artemia Salina* in Russia is practically absent. The main problems of implementation of existing technologies to process them are low efficiency, high cost and complexity of processing equipment.

The aim of the paper is scientific justification and practical implementation of preparation and evaluation of the quality of aquatic pasty concentrates, as well as health food products based on them using hydro-mechanical dispersion.

To achieve this objective there are the following tasks:

– to formulate scientific and methodological approaches to the formation of consumer properties of healthy food using hydrobionts;

– to substantiate the feasibility of hydro-mechanical dispersion for food raw materials and foodstuffs from the scientific point of view;

– to develop pasty concentrates on the basis of aquatic organisms;

– to evaluate the efficiency and functional orientation of pasty concentrates from Artemia cysts;

– to determine the direction of use of pasty materials from protein-containing concentrates, to develop formulations and technologies of cheese products, to explore their consumer properties;

– to develop and approve technical documentation for new products with pasty concentrates, to carry out their commercial approbation.

The scientific purpose of work is to develop a conceptual model of the system of food production with improved quality, safety and an integrated approach to the development of technologies using hydro-mechanical dispersion.

Scientific novelty. The main directions of improvement of food and biological value of food products are based.

Scientific and methodological approaches to the formation of consumer properties of food raw materials and food products obtained using hydro-mechanical dispersion are formulated.

The data on the nutritional value, functional properties and technological suitability of Artemia cysts, which served as the basis for the development of the technology of pasty concentrates are received.

Technological aspects of the production of pasty concentrates from Artemia cysts using hydromechanical dispersion are scientifically based, and its consumer characteristics, conditions and terms of storage are identified.

Regulated quality parameters, conditions and terms of storage are established.

Practical significance. Technical documentation is developed and approved. The novelty of technical decisions is confirmed by patents of the Russian Federation.

RESULTS AND DISCUSSION

In the first research stage, scientific and methodological approaches to the formation of consumer properties of healthy foods were formulated. To establish such products using plant and aquatic raw materials, a number of mandatory requirements were taken into account: access to raw materials, manufacturability of production, preservation of biologically active substances, storage stability, safety, nutritional value, balanced chemical combinations.

In the product development, along with safety indicators, attention was paid to the content of the feedstock and finished products of vital nutrients such as vitamins, macro- and microelements, fatty acids, and others.

In the second stage a method of hydro-mechanical dispersing for the processing of agricultural raw materials, obtaining pasty concentrates and finished products based on it with improved quality and safety was provided.

A unit based on MAG-50 was developed and tested in working conditions to implement this method. The novelty of the proposed method has a complex effect on the processed product of hydromechanical dispersion, the processes of homogenization, pasteurization and partial deodorization being carried out simultaneously. Rough grinding takes place owing to the stirrer equipped with additional cutting edges, pulverization and homogenization of the components to 6–12 micron are carried out with the working body. Pasteurization temperature is between 50 ... 55°C by ultrasonic cavitation arising during the rotation of body.

To develop paste concentrate (PC) of Artemia cysts, it was necessary to remove cyst chorion. It was found that decapsulation was effectively accomplished with calcium hypochlorite. Before decapsulation cysts are hydrated in fresh water at 25°C for 1 hour, then they are placed in the decapsulating solution where they are suspended. A complete chorion dissolution is confirmed by transition of dark brown color to orange.

Figure 1 shows the effect of the concentration of active chlorine solution, temperature and exposure time on the percentage of decapsulation.

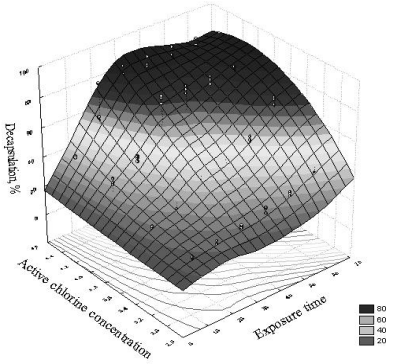

Fig. 1. The effect of the concentration of active chlorine solution, temperature and exposure time on the percentage of decapsulation.

The investigation of decapsulation process made it possible to establish rational parameters that provide the best removal of chorionic Artemia cysts at the lowest energy consumption: the concentration of active chlorine - 4.5%, processing time - 60 minutes, temperature - 35°C.

After decapsulation cysts were washed with decimolar hydrochloric acid, and processed with the hydromechanical dispersing vegetable oil being added in the ratio of 1 : 1. The result is a PC with desired properties.

Studies on the production of dry crushed concentrate from Artemia cysts on a jet mill MPV-1 were carried out. During cyst processing, the product is separated into two fractions: the first one is 90% (particle size up to10 microns), the second - 10% (undecapsulated empty cysts).

Comprehensive analysis of the chemical composition of concentrates was made, the results of which are presented in Table 4.

Table 4. Chemical composition of concentrates from Artemia cysts (n = 9)

Index c	PC from decapsulated Artemia cysts	Crushed concentrate
Moisture, %	20.20 ± 0.20	12.40 ± 0.80
Protein, %	49.60 ± 1.29	43.04 ± 1.29
Carbohydrates, %	23.24 ± 0.95	26.46 ± 1.30
Lipids, %	3.25 ± 0.15	4.90 ± 0.22
Ash, %	3.71 ± 0.21	13.20 ± 1.15
Vitamins, mg/100g:		
Retinol	35.02 ± 2.20	28.62 ± 1.18
Tocopherol	74.30 ± 3.30	74.94 ± 1.90
Thiamin	10.10 ± 0.17	8.89 ± 0.12
Riboflavin	24.42 ± 1.02	23.68 ± 0.19
Pantothenic acid	45.20 ± 1.62	38.43 ± 1.13
Pyridoxine	19.40 ± 0.72	17.09 ± 0.14
Cobalamin	0.09 ± 0.01	0.07 ± 0.01
Macroelements, g/kg:		
Calcium	0.18 ± 0.02	0.26 ± 0.04
Phosphorus	0.57 ± 0.10	0.46 ± 0.08
Potassium	2.21 ± 0.02	2.60 ± 0.03
Natrium	6.23 ± 0.16	8.54 ± 0.18
Magnesium	4.40 ± 0.09	6.45 ± 0.10
Trace elements, mg/kg:		
Iron	128.70 ± 2.40	380.40 ± 7.30
Copper	14.30 ± 0.20	16.20 ± 0.25
Zink	99.60 ± 2.30	94.30 ± 2.80
Manganese	136.21 ± 6.41	125.10 ± 5.30

To evaluate the effectiveness and functional directivity of PC from Artemia cysts laboratory animals - rats of Vistar line were experimentally studied through its inclusion in the diet of animals and investigation of immune system. Lysozyme, phagocytic and bactericidal activity increase, respectively 4–5, 2–4, and 11–13% compared to the animal group receiving common diet was determined. In rats, the test group showed a significant decrease in serum cholesterol levels (Table 5).

Table 5. The cholesterol content in blood serum, mmol / l (n = 5, P <0.01)

Group	Diet	M±m
1 – control	Basic	0.232 ± 0.0116
2 – experimental	Basic +undecapsulated	0.180 ± 0.0071
3 – experimental	Basic +crushed	0.176 ± 0.0092
4 – experimental	Basic +PC from decapsulated Artemia cysts	0.122 ± 0.0038

Laboratory animals treated with traditional vivarium diets have blood cholesterol content at the level of (0.232 mmol / l). When fed by cysts in the native state, the index declined by 28%, when fed by cysts, crushed on a jet mill, by 31% respectively. It is shown that the most efficient of the PCs are decapsulated Artemia cysts produced using hydromehanical dispersion: the introduction of this product to diet reduces cholesterol by 90%.

The obtained results testify to the effectiveness of Artemia cysts for the increase of immune properties of the body and the functional directivity of their active ingredients.

When developing a PC using hydromechanical dispersion, high keeping quality of nutrients in the feedstock was noted.

In the third stage, the possibility of using pasty concentrates as ingredients in food production was studied. Formulations and technologies of spreadable cheese products with the concentrate of Artemia cysts (PC "Artsalin") obtained using hydromehanical dispersion were developed. Process conditions and food production parameters were defined, consumer properties were investigated, quality regulation rates, time and storage conditions were established.

Rennet cheese with pasty concentrate from Artemia cysts (PC "Artsalin"). To study the qualitative indices of the developed product, the following cheese options were worked out: control; experimental 1 – cheese with 0.5% PC "Artsalin"; experimental 2 – cheese with 1.0% PC "Artsalin."

A method for producing hard rennet cheese comprises curd obtaining, filler introduction, making and pressing the cheese. PC "Artsalin" with the amount of 0.5–1.0% of curd was used as a filler. Components for the preparation of filler were taken in the following proportions, % of weight: raw milk 90–95, filler 0.5–1.0, vegetable oil 0.005–3.0, salt 0.005–2.0. The proposed method for producing solid rennet cheese can increase food value, due to the availability of vitamins, essential amino acids, polyunsaturated fatty acids and mineral substances in PC "Artsalin."

It was found that the number of amino acids including essential ones, both experimental variants differ from the reference sample in a positive way (Table 6).

Table 6. Amino acid composition of experimental hard rennet cheeses, g/100 g (averaged data, n = 7)

Amino acids	Control	Experimental 1	Experimental 2
Essential, including:			
Lysine	0.91	1.17	1.19
Threonine	0.61	0.74	0.82
Valine	1.48	1.89	1.98
Methionine + cystine	0.74	0.80	0.80
Isoleucine	0.20	0.26	0.35
Tyrosine + phenylalanine	1.41	1.44	1.51
Leucine	1.10	1.13	2.19
Total	6.45	7.43	8.84
Replaceable, including:			
Alanine	0.97	0.96	0.97
Arginine	0.75	0.69	0.78
Glycine	0.34	0.67	0.37
Glutamine	4.90	6.00	6.22
Proline	2.86	3.92	3.52
Serine	0.67	0.60	0.67
Total	10.49	12.84	12.53
Total quantity of amino acids	17.94	20.27	21.37

As part of the commodity evaluation, organoleptic characteristics: taste, smell, texture, pattern were investigated. Sample 1 was marked by delicious taste and peculiar smell of caviar, similar dependence was observed for consistency. The pattern did not reveal any significant differences between the experimental and control samples. In terms of integrated organoleptic characteristics, the maximum number of points - 72 is set for the 1st sample. The results show relatively high organoleptic virtues of composed cheeses.

The incorporation of PC "Artsalin" into the curd showed an increase of the amount of lactic microflora in test samples compared to that under control.

It was established that on the 10th day the content of lactic acid microflora in experimental samples increased by 13 and 21%. Subsequently, this pattern remained. After 60 days, marked difference made up 5 and 8.7%, respectively. We can assume that the PC "Artsalin" promotes higher microflora activization and the formation of lactic acid due to PC containing nutraceuticals, the latter being a breeding ground for these microorganisms.

High content of vitamins and minerals in cheeses produced with the addition of PC "Artsalin" compared with a control sample was noted as well.

To determine the biological value of blended cheese proteins, amino acid scores were calculated (Table 7), which indicate that the investigated product with 1.0% PC "Artsalin" does not yield to the reference protein in biological value.

Table 7. Amino acid score of hard rennet cheese with PC "Artsalin" (averaged data, n = 7)

Amino acid	Control		Experimental 1		Experimental 2		Ideal protein g/100g FAO/ WHO
	g/100g of protein	% to protein FAO/ WHO	g/100g of protein	% to protein FAO/ WHO	g/100g of protein	% to protein FAO/ WHO	
Lysine	5.1	93.0	5.4	97.5	5.4	98.7	5.5
Threonine	3.7	93.0	3.7	92.5	3.7	93.5	4.0
Valine	8.6	172.6	8.7	173.2	9.1	180.6	5.0
Methionine + cystin	3.4	97.1	3.7	104.6	3.7	104.3	3.5
Isoleucine	0.9	23.0	1.2	29.8	1.6	40.0	4.0
Phenylalanin	6.5	107.8	6.6	110.0	6.9	114.8	6.0
Total	28.2	100.8	29.2	104.2	30.3	108.4	28/100

Melted cheese with PC "Artsalin". The process of melted cheese production consists of the following main stages: selection and processing of raw materials, the removal of paraffin away from cheese crust, soaking and scraping, crushing and grinding of raw materials, mixture composition, incorporation of melting salts, mixture maturation, cheese-mass melting, PC "Artsalin" introduction, melted cheese prepacking and cooling, packaging of finished products.

To study the amino acid composition of the product under development experimental working out on options was carried out: experimental 1 – combined, 1.0% PC "Artsalin"; experimental 2 - combined, 0.5% PC "Artsalin."

The content of the water- and fat-soluble vitamins and minerals in cheeses with PC "Artsalin" was higher than that of the control sample.

Results comparing the amino acid composition of cheeses combined with optimal ideal protein composition give reason to believe that the products offered have a high biological value, especially leucine, phenylalanine and isoleucine (Table 8).

Table 8. Amino-acid score of melted cheese with PC "Artsalin" (averaged data, n = 5)

Amino acid	Control		Experimental 1		Experimental 2		Ideal protein g/100g FAO/ WHO
	g/100g of protein	% to protein FAO/ WHO	g/100g of protein	% to protein FAO/ WHO	g/100g of protein	% to protein FAO/ WHO	
Leucic	7.5	107.1	14.8	211.4	7.8	111.4	7.0
Lysin	10.1	183.6	10.8	196.4	10.7	194.5	5.5
Threonine	8.1	202.5	7.07	176.7	7.48	187.0	4.0
Valine	8.23	164.6	3.6	72.0	10.6	212.0	5.0
Methionine + cystin	3.4	97.1	4.2	120.0	3.5	100.0	35
Isoleucine	5.3	135.0	9.2	230.0	4.6	115.0	4.0
Phenylalanine	6.2	103.3	8.09	134.8	8.8	146.6	6.0
Total	48.83	139.5	57.76	165.02	53.48	152.8	35/100

As a result, sanitary and microbiological studies have shown that the introduction of PC "Artsalin" into cheese mass improves the quality of the experimental hard rennet and melted cheeses in storage in terms of safety. After 3 months of storage in the control samples of hard rennet and 1 month in melted cheese there were detected coliform bacteria; these microorganisms have not been identified in the test specimens. Antibacterial effect is due, apparently, to the PC "Artsalin" containing vitamin E which has an inhibitory effect on the development of coliforms.

There were no differences in the content of Salmonella, S. aureus, yeast and molds between the control and test samples of cheese.

CONCLUSIONS

1. The possibility of using hydro-mechanical dispersion for the production of food raw materials, semi-finished and pasty products with their application was based. Simultaneous use of cavitation effect and mechanical crushing makes it possible to obtain products with new quality characteristics and consumer properties. The results obtained were tested using apparatus with interrupting of the flow of treated medium, developed with mechanic-acoustic homogeneizator MAG-50.

3. The complex commodity assessment of Artemia cysts on physicochemical, microbiological indices, and other safety criteria were carried out. The data obtained served as the basis for their use in food production as a source of complete protein, polyunsaturated fatty acids, vitamins, minerals, whose presence enhances the nutritional value and determines the functional directivity of food.

4. The technologies for the production of pasty concentrates were developed. The dependence of the effect of temperature and time of treatment on quality of raw materials was defined. The features of the

chemical composition and consumer properties of concentrates of Artemia cysts were revealed. The conditions and terms of storage, nutritional value and safety factors were established.

5. A new range of cheese products with pasty concentrates has been developed and tested in the production environment. Dosages and methods of their application were defined. Regulated quality indices, nutritional value, terms and conditions of storage were established.

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THE STUDY OF FACTORS AFFECTING THE ACTIVITY OF MEAT ANTIOXIDANT SYSTEM

I. S. Patrakova*, G. V. Gurinovich

Kemerovo Institute of Food Science and Technology (University),
bul'v. Stroiteley 47, Kemerovo, 650056 Russia,
* e-mail meat@kemtipp.ru

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Abstract: Oxidation of lipids and myoglobin in raw meat are interrelated processes that affect the overall meat quality. The intensity of oxidation processes in meat raw material is regulated by its own antioxidant system (catalase, peroxidase, glutathione, etc.), the activity of which should be considered in the development of new technological solutions. Oxidation of lipids and myoglobin, directly affect the quality and safety of meat products, and reducing of the intensity of these processes contributes to the life time of raw meat, as well as that of finished products. The paper presents the study results of the salt curing mixture, including combination with yeast extract, affecting on the activity of the antioxidant system of the main types of raw meat - pork and beef. The basic systems, minced pork and beef being subjected to salting with curing salt (sodium chloride) and curing mixture consisting of 70% sodium chloride and 30% of composition KCl + $CaCl_2$ at the ratio of 1:1 are investigated. The influence of curing mixture on the intensity of oxidation of lipids and myoglobin of raw meat of different species is stated. It is found, that reducing the amount of sodium chloride in curing composition of the mixture brings down oxidative changes of heme pigments and meat lipids. Introduction of yeast extract into raw meat, in the amount of 2% enhances the inhibitory effect on oxidation in raw minced meat.

Keywords: Antioxidant system, antioxidant enzymes, catalase, peroxidase, meat, myoglobin, metmyoglobin, lipids, oxidation, yeast extract

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INTRODUCTION

The degree of lipids oxidation has a considerable influence on the formation of sensory, functional characteristics, nutritional value and safety of meat products. As a result of lipid oxidation, firstly, the accumulation of peroxides occurs, and also that of aldehydes and ketones, the presence of which adversely affects the security of raw materials; secondly, the degree of digestibility and protein content of essential fatty acids, amino acids, vitamins is reduced, affecting biological value; thirdly, the decrease of protein solubility, change of color, taste and odor is stated [1, 2, 6].

Peroxidation is the result of interaction of organic compounds, and molecular oxygen to form hydroperoxides and reactive free radicals. In muscle tissue polar and nonpolar lipids are subjected to oxidation and to a greater extent - phospholipids in membranes of muscle fibers, the composition of which contains the polyunsaturated fatty acids. The process of lipid oxidation begins immediately after slaughter and it is the result of the imbalance between pro-oxidant and antioxidant systems of raw meat [3, 4, 5, 8].

The proper antioxidant meat system includes enzymatic and non-enzymatic systems. Catalase, glutathione peroxidase, superoxide dismutase are distinguished from endogenous antioxidant enzymes. Their activity depends on the presence of antioxidants such as tocopherols, ascorbic acid, ubiquinone, glutathione, etc. [6].

Endogenous antioxidant enzymes, especially catalase and glutathione peroxidase can potentially inhibit the development of oxidation processes during storage of raw meat. Glutathione peroxidase is selenium-containing enzyme able to recover almost all types of organic hydroperoxides, as well as to prevent the accumulation of secondary peroxidation products [17, 18]. Catalase - heme-containing enzyme - is able to use one molecule as an electron donor, and another one - as an oxidizer, i.e. electron acceptor. It is a basic primary antioxidant, which catalyzes the decomposition of hydrogen peroxide to water, by combining this function with glutathione peroxidase. Protoheme is presented in peroxidase prosthetic group that, unlike most of the hemeproteins of heme groups is very weakly bound to the apo-enzyme. In the reaction catalyzed by peroxidase, hydrogen peroxide is restored by the compounds serving as electron donors, such as ascorbate, or quinines or cytochrome C. This enzyme has a high specificity and effectively neutralizes several hydroperoxide compounds: methyl and etilgidroperoxide, methyl, ethyl and other aliphatic alcohols. The mechanism of peroxidase and the action of glutathione peroxidase is to supplement each other, providing protection from the effects of lipid peroxidation at the stage of chain reactions branching and the formation of secondary peroxide products [18]. Both enzymes implement detoxification of enzyme active oxygen radicals, the formation of hydrogen peroxide from superoxide being catalyzed.

In addition to differences in their substrate specificity, these two enzymes differ in substrate affinity. At low concentrations of hydrogen peroxide, organic peroxides are preferably catalyzed by peroxidase, whereas at high concentrations catalases work [19].

Activity of antioxidant endogenous enzymes depends on several factors: the type of animal raw material, its localization, physiological function, on which in its turn depends the amount of heme pigment (myoglobin, hemoglobin) being active prooxidants. This is confirmed by the results of both domestic and foreign scholars. According to the data obtained by O.L. Golostyuhina, I.V. Golovina, and T.B. Vakhtina, the highest antioxidant enzyme activity is observed in gills, liver and red muscles of flounder, while the white muscles of observed fish are characterized by minimal activity of catalase and peroxidase. P. Hernandez, A. Lopez, M. Marco, A. Blasco have stated that the activity of catalase in the tested rabbit meat is lower than that in beef, pork and chicken thigh, but higher than in chicken breast [20, 21, 18]. Thus, it may be confirmed, that antioxidant endogenous enzyme activity is closely correlated with the concentration of heme pigments in muscle tissue and provides the stability of oxidation and restoration processes, greatly influencing oxidation changes which occur in meat.

Myoglobin is a complex protein – heme protein which plays an important role in the provision of animals with oxygen necessary for muscle metabolism and is the main meat pigment responsible for color formation. In the process of energy generation and in relation to oxygen, heme proteins perform such functions as oxygen transportation and tissue depositing, catalytic oxidation of organic compounds, decomposition of hydrogen peroxide and transfer of electrons [15].

Quantitative myoglobin content depends on the species, breed, sex and age, keeping and feeding conditions of an animal, type of muscles and their level of muscle activity. The ratio of such forms of myoglobin as dezoximioglobin (Fe^{2+}), oxymyoglobin (Fe^{2+}) and metmyoglobin (Fe^{3+}) is presented in meat synchronically, thus determining its color. In the presence of atmospheric oxygen myoglobin is oxidized to form oxidized oxymyoglobin - MbO_2, which gives the meat a nice bright pink-red color. However, this compound is unstable and transferred from ferrous to ferric state, thereby metmyoglobin of brown- gray color is formed (MetMb). When salting the meat in the presence of salt, which is an additional pro-oxidant factor, myoglobin or oxymyoglobin is oxidized and transformed into metform. As a result, then salted meat loses its natural color and becomes brown with different shades.

Myoglobin is a predominant iron compound in muscle tissue. Thus iron content in the heme myoglobin is 73.3%, 47.0% of the total concentration of iron in beef and pork, respectively, to the share of low molecular weight fraction of non-heme iron, and depending on the type of meat, it fits 2.4–3.9% of the total iron content, on average.

Organic and inorganic iron compounds act as catalysts in various stages of lipid peroxidation. It should be noted that the mechanism of catalytic effect and free iron ions involved in action, bound iron and heme iron in the oxidation of lipids, remains controversial. Though Kanner et al argued that the main catalysts for the oxidation of lipids are meat-free iron ions. At the same time during the research of Johns it was found that all inorganic forms of iron have low pro-oxidant activity compared to the heme iron [1, 4, 7, 8, 9, 10, 11].

Nowadays, myoglobin is one of the most powerful catalysts of lipid oxidation in meat raw material, which occurs in a certain sequence. At the initial stage oxidation of oxymyoglobin takes place and it is transformed into metmyoglobin with hydrogen peroxide, while with the increase of metmyoglobin in raw meat amount the rate of oxidation of lipids in muscle tissue increases. Baron et al have found that the maximum metmyoglobin pro-oxidant effect is manifested at low pH of raw meat and in the presence of hydroperoxides, whereas at physiological meaning of pH in the presence of lipids neutralization of metmyoglobin is observed, non-catalytic heme pigments being formed [8, 14]. On the next stage metmyoglobin is activated by hydrogen peroxide to parfirrylkation-radical containing tetravalent iron that turns into a short-lived parfirryl-myoglobin, and then into the long-life ferryl-myoglobin under the influence of which, at the final stage an oxidation process is initiated by lipids:

$$\text{Metmyoglobin} + H_2O_2 \rightarrow {}^{\circ}\text{MbFe IV} = O \rightarrow$$
$$\rightarrow \text{MbFe IV} = O.$$

It should be noted that pro-oxidant effect of ferryl-myoglobin, unlike metmyoglobin does not depend on pH and concentration of raw meat lipids [1, 6, 11, 12]. This scheme allows us to say that the metmyoglobin is able to exercise "pseudoperoxidase" activity to form erryl-myoglobin, being peroxidase analog which is an active oxidizer with respect to ascorbate, glutathione, cysteine, tyrosine.

There are evident data [3, 4], indicating the influence of physical condition, the degree of stress of an animal prior to slaughter, rigor characteristics, changes in pH, temperature, duration and conditions of maturation, which may occur at the intensive exposure, such as electrical stimulation of the antioxidant reactivity of the pro-oxidant meat systems. The rate of oxidation of meat lipids and meat products is also significantly affected by the composition of raw meat, the fatty-acid composition of lipids, the content of endogenous two-valent ferrum, technological processing methods, including grinding, emulsification and heat treatment.

At the same time, the question about the impact of processing additives on the activity of the antioxidant system of meat remains underinvestigated. Among the additives conventionally used in the technology of meat, special attention deserves salt (sodium chloride), which promotes the formation of organoleptic characteristics of the finished products and increase of their storage capacities. However, it is known that, depending on the concentration of salt used, it can have both pro-oxidant and also antioxidant effect.

It should be noted that the mechanism of sodium chloride pro-oxidant effect is not understood enough, to assume that its oxidative effect may be the result of the influence of reactive chlorine ion on lipids and heme pigments of muscle tissue. Pro-oxidant activity of sodium chloride is associated with its ability to disrupt the integrity of cell membranes, thereby ensuring the free access of heme and non-heme iron to lipids in muscle tissue. Besides, sodium chloride may promote the formation of metmyoglobin, which reacts with hydrogen peroxide to form ferrylmioglobin, being the catalyst of lipid peroxidation.

Analysis of available publications has revealed that the impact of sodium chloride on oxidation of heme pigments, which indirectly affect the antioxidant enzymes, has been studied to more extent. However, available data suggest that the catalyzing effect of sodium chloride - depends on its concentration in raw meat. Some scientists have found, that the pro-oxidant effect of sodium chloride concentrations up to 3% on the unit weight of raw material has a profound effect, whereas increasing it above 3% has, in contrast, an inhibitory effect on lipid oxidation [4, 7]. As regards to the effect of sodium chloride on antioxidant enzymes there is a well- known work of Lee S. K. et al, who found that the activity of catalase, glutathione peroxidase, and superoxide dismutase in its presence is reduced by 8%, 32%, 27%, which may be a prerequisite for the acceleration of lipid peroxidation [25]. Therefore, one of the possible ways to reduce the pro-oxidant effect of sodium chloride the decrease of its introduction into the technology of meat products should be considered.

Production of meat foodstuffs with reduced salt, and therefore sodium, fully meets the modern trends in healthy eating. A modern consumer among a wide variety of food products gives increasing preference to products, which are able to exert a positive effect on health, which ones are the functional foods. Production of functional foods involves the enrichment of both a traditional product by functional food ingredients during the manufacturing process and the decrease in product content of the components, being able to have a negative impact on human health [30]. One of these components, in accordance with the recommendations of the WHO, the sodium chloride has been declared, excessive intake of which may contribute to the development, primarily, of cardiovascular diseases [27].

By reducing the amount of sodium chloride added into meat products it is necessary to consider accompanying aspects related to the possible decrease of functional properties in meat systems, stability of meat products against the development of microorganisms.

The results of the analysis of domestic and foreign scientific publications suggest that the problem of effect of low-level introduction of sodium chloride, including its combination with different classes of commonly used food products, the activity of the antioxidant system of meat in relation to its oxidation processes of heme pigments remains poorly understood.

The aim of the research was to study the activity of beef and pork antioxidant enzymes, depending on the duration of salting, curing of ingredients composition as factors influencing the ratio of concentrations of oxidized and non-oxidized forms of heme pigments and intensity of lipid oxidation processes.

OBJECTS AND METHODS OF RESEARCH

Taking into account that oxidation intensity of lipid muscular tissue depends on the activity of the antioxidant enzyme systems of meat, and endogenous factors such as heme pigment number, points for investigation included: total pigment content and their oxidized form - metmyoglobin, the activity of catalase and peroxidase enzymes.

The objects of the study were beef of the first grade and half-fat pork meat, stored frozen up to 3 months. Raw meat was thawed to the temperature of (-1÷+1)°C, minced and mixed with 3% of sodium chloride (Sample K). In its prototypes sodium chloride in amount of 30% was replaced by the compound KCl + $CaCl_2$ at the ratio of 1 to 1 (Sample A1). In order to enhance the effect of antioxidant in the test sample yeast extract has then been added in an amount of 2% to the amount of raw materials (Sample A2).

Yeast extract is a natural source of natural antioxidant - glutathione (Table 1).

Table 1. Characteristics of yeast extract (Group of companies "Protein Ingredients Technologies ", Moscow)

Index type	Index value
Appearance	Powder, yellow and dark-brown color of varying intensity
Smell and taste	Yeast extract, characteristic without outward odor and taste
Extraneous admixtures	Not allowed
Mass fraction of protein, %, not less	37.5
Ash mass fraction, %, not more	15 (contains no salt)
Moisture mass fraction, %, not more	6
Nitrogen content (Kjeldahl method),%, not less than	6
Protein nitrogen content,% not less	2.5
Solubility of a 2% solution, %	100
pH of a 2% solution	4.5–6.5

Glutathione serves as a cofactor of glutathione peroxidase and antioxidant of primary cells having low molecular weight, it can be considered as one of the major players of the antioxidant system, rather active against a wide range of free radicals and lipid peroxidation products (hydrogen peroxide, organic radicals and reactive hydroxyl radical) [22].

The prepared samples were kept in salting at the temperature of (0–4)°C for 48 hours with sampling after 24 hours. Depth of oxidative changes in the raw meat was determined in accordance with the change of peroxide and thiobarbituric number during salting.

Research methods

The content of total amount of the pigments according to the method of Lee B.J., Hendricks D.G., & Cornforth D.P., is based on the extraction of meat pigments by aqueous solution of acetone and by consequent measuring of the extract optical density on SF PE 5400UF spectrophotometer at a wave length of 640 nm against acetone hydrochloride [31].

Total pigment content was determined by the formula

$$X = A640 * 680, \quad (1)$$

where A640 - optical density of solutions at wave length of 640 nm.

Determination of metmyoglobin by method of Krzywicki et al. is based on the extraction of pigments by ice phosphate buffered solution with consequent measurement of the optical density of the solution at the wave lengths of 525, 545, 565, 572 nm [32].

Metmyoglobin content, % relative to the total pigment content was calculated by the formula

$$X = [-2.51*(A_{572}/A_{525}+0.777*(A_{565}/A_{572})+ +0.8*(A_{545}/A_{572})1.098]*100, \quad (2)$$

where A_{572} - optical density of solutions at a wave length of 572nm; A_{525} - optical density of the solution at a wave length of 525nm; A_{565} - optical density of the solutions at a wavelength of 565 nm; A_{545} - optical density of the solution at a wave length of 545 nm.

Determination of peroxidase activity by a colorimetric method is based on determining the rate of the oxidation reaction to benzidine oxidation, to formation of a blue color dyeing in the presence of peroxide and peroxidase [26]. A weighed sample of meat was minced in a porcelain mortar with cold acetate buffer (pH 5.0). The homogenate was centrifuged for 5 minutes. The resulting supernatant liquid was filtered through filter paper and the filtrate was used for the reaction. The reaction mixture consisted of 0.2 M Na-acetate buffer (pH 5.0), 0.01% hydrochloric acid solution of benzidine extract, 0.3% of hydrogen peroxide. For the obtained solutions the optical density was determined at a wave length of 590 nm during 120 sec. on the spectrophotometer SF PE 5400 UF.

Calculation of peroxidase activity in relative units per 1 mg of protein was performed by the formula

$$A = ((\Delta D/T)*X)/(L*C), \quad (3)$$

where A is the activity of enzyme; ΔD - change in optical density (optical density to be subtracted at the end of the reaction from the optical density at the initial time point); X - final dilution in the cell extracts (reaction mix volume divided by the volume of inserted extract); T-reaction time, sec.; L - thickness, cm; C - protein content in the sample, mg.

Determination of catalase activity by spectrophotometry is based on determining the rate of decomposition of hydrogen peroxide by catalase of the tested sample to form water and oxygen [13].

A weighed sample of muscle tissue was triturated in a mortar with chilled extraction buffer (50 mM of K, Na-phosphate buffer (pH 7.8)). The homogenate was centrifuged for 5 minutes. The supernatant liquid was filtered through a paper filter, and the filtrate was used for the reaction process. The reaction mixture consisted of 50 mM of K, Na-phosphate buffer (pH 7.0), of extract and 0.6 M of hydrogen peroxide. Catalase activity was measured due to the change of optical density at the wave length of 240 nm every second for 100 sec. on the spectrophotometer SF PE-5400UF

Calculation of catalase activity in relative units on 1 mg of protein was performed by the formula (3).

Oxidative damage of raw meat lipids by definition of peroxidation number (PN) was performed by a standard method using chloroform extract obtained by the method of Piulskaya, B. [28], and by determining of thiobarbituric number (TBN) by the modified distillation method of Tarlagie, B. using sulfanilic reagent [29].

RESULTS AND DISCUSSION

The degree of activity of antioxidant enzymes is one of the key factors influencing the rate of lipid oxidation in meat. At the initial stage the evaluation of raw meat antioxidant system activity has been presented. The research results are shown in Table 2.

Table 2. Indices of the antioxidant activity of raw meat ($p < 0.05$)

Raw material	Catalase activity, U/g	Activity of peroxidase, U/g	Total pigments mg/100g	Number of metmyoglobin, % of total pigments	PN, mmol ½ O_2/kg	TBN
Beef	324.8 ± 6.4	12.5 ± 0.45	568.6 ± 4.2	30.7 ± 0.98	2.25 ± 0.18	0.207 ± 0.045
Pork	195.0 ± 3.8	7.5 ± 0.31	329.6 ± 5.6	22.5 ± 0.65	2.42 ± 0.13	0.342 ± 0.034

Due to the reported data, the activity of antioxidant enzymes, namely catalase and peroxidase in beef is higher than in pork by an average of 60%. The results can be explained by the whole complex of various factors.

Firstly, higher enzyme activity in beef may be attributed to higher protein content, generally, sarcoplasmic proteins in particular, which are the enzymes under investigation. Secondly, the activity of antioxidant enzymes depends on the types of muscle fibers. Muscle fibers, depending on their chemical composition and activity of enzymes can be divided into two metabolic types: oxidative (red) and glycolytic (white). Oxidative muscles are characterized by high content of mitochondria and their myoglobin content is higher than in muscles of glycolytic type. Oxidation is

used mainly by muscles fatty acids as a substrate having low activity of AT phase and phosphorylase, and glycolytic muscles use primarily glycogen as a source of energy and obtaining greater activity of the latter enzymes. It is generally believed that the muscle oxidative type shows higher antioxidant activity of enzymes such as catalase than that of glycolytic muscles [17].

Thirdly, high catalase and peroxidase activity may be the result of greater hydrogen peroxide content in the meat of beef. The process of converting heme pigments makes some contribution to the accumulation of hydrogen peroxide. Nowadays, there is the hypothesis that the oxidation of myoglobin increases the amount of metmyoglobin, which by showing pseudoperoxidase activity is converted into ferryl-mioglobin, actively involved in the oxidation of lipids. This results in the formation of accumulated peroxide and hydroperoxide - a compound being a substrate for catalase and peroxidase [17]. The total amount of pigments in beef is found to be 568.6 mg/100g, while the content of metmyoglobin is 30.7% of the total amount of pigments that corresponds to 174.6 mg/100g. Based on this result the amount of myoglobin (the total amount of myoglobin, oxymyoglobin and dezoksimioglobin) is 394 mg/100g. While the content of heme pigments in pork is 329.6 mg/100g at the content of 22.5%, i. e. metmyoglobin - 74.16 mg/100g and myoglobin - 255.4 mg/100g, respectively. These results are consistent with the published data describing the content of myoglobin in different kinds of raw meat [14].

High catalase activity in both types of materials explains the fact, that enzymes have a low affinity to hydrogen peroxide, and thus play a leading role in its inactivation at high concentrations. In contrast to catalase, peroxidase has high affinity with peroxide, which explains the lower activity index values. However, higher peroxidase activity in beef is the result of the fact, that metmyoglobin participates in the process of utilization of hydrogen peroxide, the former having pseudoperoxidase activity.

Obviously, the number of primary (peroxide number - PN) and secondary products of lipid oxidation (thiobarbituric number – TBN) determines the greatest antioxidant activity in beef. It is stated, that in beef peroxidation and thiobarbituric numbers value is lower than those in pork, by 7% and 65%, respectively.

Subsequently, we studied the effect of curing mixture and duration of salting on the catalytic ability of peroxidase and catalase.

It has been established (Table 3) that the addition of sodium chloride for 24 hours and 48 hours of salting, reduces the peroxidase activity to 16% and 21.5% in beef, respectively, relative to raw unsalted meat. A similar relationship has been established in relation to pork, the loss of peroxidase activity is 20.3% and 24%, respectively, after 24 and 48 hours of salting.

Table 3. Change of catalase and peroxidase activity, depending on the composition of curing mixture and salting duration ($p < 0.05$)

Sample	Beef		Pork	
	24 hours	48 hours	24 hours	48 hours
Peroxidase activity, U / g				
sample K	10.50 ± 0.14	9.81 ± 0.64	5.98 ± 0.31	5.70 ± 0.24
sample A1	10.42 ± 0.36	9.95 ± 0.72	6.01 ± 0.28	5.86 ± 0.32
sample A2	10.54 ± 0.41	9.98 ± 0.51	6.10 ± 0.39	5.92 ± 0.18
Catalase activity, U / g				
sample K	319.0 ± 4.5	311.3 ± 6.9	181.4 ± 2.6	179.5 ± 2.5
sample A1	320.1 ± 3.9	316.5 ± 5.4	187.5 ± 3.7	185.5 ± 3.4
sample A2	322.6 ± 4.6	318.7 ± 3.8	1916.0 ± 4.8	189.7 ± 5.7

Reduced activity of catalase in beef treated with sodium chloride is stated from 1.8% to 4.3% with respect to unsalted raw meat, respectively, after 24 and 48 hours of salting, in salted pork it is stated 7.5% and 8%.

Replacing 30% of sodium chloride in the composition on premix ($KCl + CaCl_2$) of curing mixture (sample A1) has a positive effect on the activity of the enzymes studied. Thus in sample A1 of beef increasing of peroxidase activity by 0.7% and 1.4% is observed relative to sample K at 24 hours and 48 hours, respectively. In samples A1 of pork peroxidase activity increased under salting relative to sample K in 24 hours and 48 hours, respectively from 0.5% to 2.8%.

A more pronounced increase of activity of catalase relative to sample K is observed in the pork sample A1, so the activity increase after 24 hours has been stated - 3.36%, after 48 hours - 3.34%, whereas in the beef sample A1 increased activity relative to the sample treated with sodium chloride, is 0.34% and 1.6% after 24 and 48 hours, respectively. Despite this, in general, catalase activity in samples of beef remains at a higher level as compared with pork.

Enhance of antioxidant enzyme reactivity in raw meat is facilitated by the use of yeast extract during salting, which is confirmed by the results obtained (Table 3). So peroxidase activity in beef has increased in sample K to 0.4% and 1.7% in the period under salting. In turn, the increase in catalase activity is 1.1% and 2.3% relative to sample K at 24, and 48 hours of salting. A similar dependence is observed for samples A2 of pork. The resulting dependence is explained by the fact that glutathione, as a substrate, in particular of true peroxidases, enhances their activity. [6]

The results of studies suggest a greater stability of catalase in the presence of chlorine-containing salts, which is consistent with available data in the literature [16].

Taking into account, that the heme pigments may have both an enhancing effect on the antioxidant system of raw meat, and be a catalyst for lipid peroxidation, the effect of salting on processes of meat pigments transformation has been studied (Table 4).

Table 4. Change in the number of heme pigments in meat according to curing composition of mixture and salting duration ($p < 0.05$)

Sample	Beef		Pork	
	24 hours	48 hours	24 hours	48 hours
Total pigments mg/100g				
sample K	565.8 ± 8.6	561.0 ± 7.1	318.5 ± 6.6	316.8 ± 7.6
sample A1	567.3 ± 7.3	562.3 ± 6.5	321.1 ± 5.9	319.6 ± 6.4
sample A2	567.9 ± 6.9	563.0 ± 6.8	320.6 ± 6.3	318.1 ± 7.8
Number of metmyoglobin,% of total pigments				
sample K	46.1 ± 1.3	50.8 ± 1.6	34.0 ± 1.2	36.7 ± 1.7
sample A1	45.1 ± 2.1	49.9 ± 1.4	33.7 ± 1.8	35.8 ± 1.2
sample A2	43.6 ± 1.6	48.6 ± 1.9	32.4 ± 1.6	34.6 ± 1.5

It is found that the composition of curing mixture and salting period does not affect the content of the total number of pigments, which remains almost constant throughout the period of salting for all the samples, the changes in the content of common pigments are within the limits of experimental error. However, it should be noted, that with the constant amount of total pigments, the quantitative changes are observed at the ratio of various forms of myoglobin.

According to the presented results, salting period for 24 hours is followed by an increase in the amount of metmyoglobin in sample A1 of beef and is stated 15.4% and 20.1% after 48 hours relative to that of raw meat unsalted, that of salted pork - from 11.5% to 14.2%, respectively. The data obtained are the result of influence of chlorine ions on myoglobin.

Reducing of the amount of sodium chloride in the composition of curing mixture on 30% decreases the amount of irreversibly oxidized form of myoglobin. So in sample A1 of beef regarding to sample K the number of metmyoglobin increases by 1% and 0.9% in the studied period of salting, and in samples of pork - by 0.3% and 0.9%, respectively.

In the systems observed the presence of the yeast extract has an additional inhibitory effect on the oxidation action of myoglobin. It has been found that in samples A2 of beef metmyoglobin number decreases by 2.5% and 2.2%, relative to the sample K - after 24 and 48 hours of salting. Similar values of metmyoglobin content are characteristic to the system of samples being used on the basis of pork. Reducing of the amount of metmyoglobin in test samples A1 and A2 may be the result of a greater activity of catalase and peroxidase.

Reducing of the amount of metmyoglobin is a positive precondition for the stabilization of lipid peroxidation. There is an assumption that the intensity of the lipid oxidation depends on the level of heme pigments in raw material. Since high content of oxymyoglobin and metmyoglobin promotes formation of hydrogen peroxide, and as a consequence, of ferrylmioglobin, these compounds have a strong pro-oxidant action. In this connection it will be of interest to study the effect of antioxidant enzyme activity and content of heme pigments on lipid peroxidation, depending on the composition of curing mixture.

The intensity of the formation of primary oxidation products has been evaluated by the change in peroxide number (PN).

Table 5. Dynamics of peroxide number changes in the process of salting ($p < 0.05$)

Duration of salting	PN mmol ½ O_2/kg		
	Sample K	Sample A1	Sample A2
Pork			
24 hours	4.02 ± 0.05	3.75 ± 0.02	3.53 ± 0.09
48 hours	4.69 ± 0.08	3.53 ± 0.06	4.02 ± 0.06
Beef			
24hours	3.98 ± 0.06	3.69 ± 0.04	3.41 ± 0.07
48 hours	4.53 ± 0.03	4.12 ± 0.07	3.94 ± 0.04

According to the study (Table 5) sodium chloride catalyzes the oxidative processes of lipids, while introduced in raw meat, since the value of PN relative to raw unsalted meat after 24 hours in samples K increases by 76.8% and 101.3%, for beef and pork - in 48 hours after salting by 66.1% and 93.8%, respectively.

Replacement of 30% of sodium chloride on premix ($KCl + CaCl_2$) in the curing mixture composition, helped to reduce the rate of oxidation. So in samples A1 of beef value PN relative to animal raw material increased by 64.0% and in pork - 54.9%. Over the next 24 hours of salting the number of primary oxidation products increased by 83.1% and 75.1% for beef and pork, respectively.

It has been found that the introduction of the minced yeast extract into the composition helps to reduce the intensity of accumulation of oxidation products. Thus, in sample A2 value of PN in beef decreased after 24 hours relative to the samples K and A1 - by 14.3% and 7.5%, to pork samples, - 12.1% and 5.8%, respectively. A similar dependence is retained after 48 hours of salting. The results are explained by the fact that yeast extract is a source of glutathione, which in turn is a low molecular weight antioxidant, able to carry out an independent antioxidant effect.

On the whole, the findings suggest the more intensive process of oxidation in the samples of beef, that may be the result of a greater heme pigment content in raw material [6, 11, 18]. In this case, the

absolute values of the test index for pork samples throughout the process of salting remain higher than in beef samples, which is the result of a greater content of fatty tissue. At the same time at the end of the term of salting the PN of all the samples taken under conditions is consistent with hygienic standards - no more than 10 mmol O_2/kg.

The transformation of primary products of oxidation into secondary oxidation products causes a further acceleration of oxidation. The intensity of secondary oxidation products formation was assessed by determining the number of thiobarbituric (TBN), which reflects the amount of malondialdehyde formed (Fig. 1).

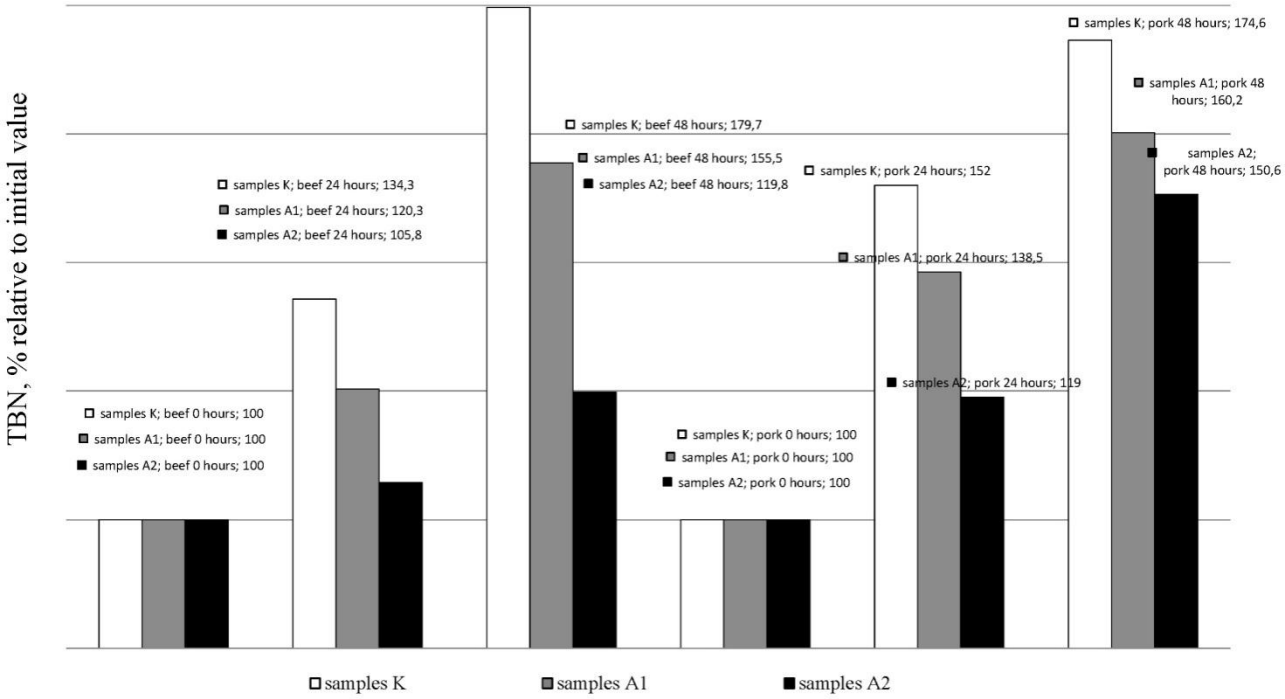

Fig. 1. Dynamics of TBN, of the samples in the process of salting.

According to the study results, the accumulation of products of secondary fat breakdown in the control samples is more intensive. Thus, after 24 hours of salting TBN increased by 34.3%, after 48 hours - 79.7% in the samples of beef and - 52.0% and 74.6% in the samples of pork, respectively.

Reducing the amount of salt in the composition of salting mixture and the presence of yeast extract helped to reduce the rate of formation of secondary oxidation products in the samples being based on beef and pork, which is consistent with the results of determination of TBN.

Oxidative stability of raw meat is the result of lipids and of myoglobin oxidation affecting each other. The intensity of these processes is regulated by its own antioxidant system, the activity of which depends on many factors, including the conditions of salting.

Analysis of the results suggests that beef is characterized by a more balanced ratio of active antioxidant complex. Peroxidase and catalase activity of beef is higher than that of corresponding enzymes in pork - by 60%. Reduction in traditional curing mixture of sodium chloride content by 30% contributes to the stabilization of antioxidant activity of the enzymes studied, which is reduced with respect to the initial values of 20.4% and 2.5% after 2 days of ripening in salting medium, whereas the use of sodium chloride is up to 21.5% and 4.1%, respectively. Combining of the curing mixture with a reduced content of sodium chloride and yeast extract does not lead to increase of antioxidant enzyme activity relative to the animal raw material, but contributes to further stabilization of the antioxidant system and reducing the intensity of lipids and processes of meat pigments oxidation. The obtained dependences are similar for both types of raw materials.

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TECHNOLOGICAL SUPPLEMENTARY MEANS FOR IMPROVEMENT OF BEVERAGE TECHNOLOGY

I. Yu. Sergeeva

Kemerovo Institute of Food Science and Technology (University),
bul'v. Stroiteley 47, Kemerovo, 650056 Russia,
e-mail: sergeeva.76@list.ru

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Abstract: Processing of raw materials, semi-finished and finished products with the help of a variety of aids is one of the most urgent methods of solving the problem of increasing beverage storage duration. The paper shows the state of a beverage as a disperse system during the process. In the semi-finished products at the beginning of technological chain the process of diffusion is not determined, thus the system of beverages experiences sedimentary instability. The processing of semi-finished and finished beverages before pre-packaging by various technological supplementary means leads to the formation of sedimentary stability, in which a sedimentation - diffusion equilibrium takes place. The hypothetical model of the state of beverage disperse system under the influence of technological supplementary means is demonstrated. Disperse system of beverages can be exposed in three main positions: sedimentary unstable, stable (equilibrium), excessively stable. The brief overview of characteristic features of supplementary means is presented, the latter being used in beverage technology to ensure the stability of products with the help of research data presented by domestic and foreign authors. One of the variants of classification of processing aids is the usage of hierarchical method. Structural and technological characteristics of the subsidiary materials used for durability of beverage upon storage are presented as a classification basis. Signs and stages of classification are marked. The presented embodiment of classification methodology can serve as a basis for the selection of processing with the help of supplementary methods, based on individual characteristics of the structural properties of complex means and substances involved in turbidity formation, as well as for indication of the parameters of materials rational usage in the production line as one of the fundamental factors for the formation of finished products quality.

Keywords: Drinks, durability, technological supplementary means, antioxidants, enzymes, sorbents, flocculants, hierarchical classification method.

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INTRODUCTION

A beverage, prepared from natural raw materials presents a complex multi-component, poly disperse system, being in certain equilibrium. A large proportion of beverage substances is arranged, due to their special characteristics (eg., taste, transparency) and is in a colloidal state. Being stored under the influence of various factors, an effect of violation of the physico-chemical equilibrium in the colloidal system of the beverage occurs, and turbidity is formed.

According to the terminology of technical regulations in accordance with the Customs Union "Safety of food additives, flavorings and processing supplementary technological means", substances or materials and their derivatives, which are not the components of food, intentionally are used in the processing of food raw material and in the production of food products for specific technological purposes, and they are removed after achieving the task from those materials, Such food products or residual amounts of them do not have the technological effect on the finished food product.

Processing methods, including the use of subsidiary materials designed to remove excess potential turbidity forming components, can intensify the clarification process and increase the terms of transparency in canned beverages. Processing of raw materials, semi-finished and finished products by a variety of aids is one of the important ways to solve the problem of increasing the resistance of beverages.

Supplementary means used in beverage technology to preserve the equilibrium of the colloidal system of drinks are quite diverse and differ in many ways.

The purpose of this research is to develop a classification of technological supplementary means (TSM), taking into account their structural features and technological orientation, as a methodological basis for the selection of (TSM), improvement of their processes and obtaining high-quality drinks.

OBJECTS AND METHODS OF STUDY

Objects of research are the scientific data of domestic and foreign sources of information. As for research methods, theoretical methods were used: a hypothetical method; methods of analysis and selection of information sources; generalization and systematization of information data; a hierarchical classification method [1].

RESULTS AND DISCUSSION

To achieve this goal it is necessary to solve the following problems:

– to review used to stabilize the beverage of opacities of variable origin;
– to develop a version of the classification of supplementary means by systematizing structural features and technological orientation of 100 stabilizers using hierarchical classification method.

According to the basics of colloid chemistry a disperse system is fundamentally thermodynamically unstable. Therefore, we can only talk about the relative thermodynamic stability of disperse systems. Relative stability is the ability of the system within a certain time to preserve its structure unchanged, i.e. particle sizes and their distribution in the system scope. Sedimentation (kinetic) and aggregate stability of the system are differentiated according to their mechanism. Under the sedimentation stability we understand the ability of the disperse system within a certain time to maintain unchanged particle distribution in the system volume, in other words, system's ability to resist the force of gravity.

Observing the process of sedimentation it is necessary to consider the Brownian motion, in which the microscopic and colloidal particles participate. Brownian motion is a consequence of diffusion, which tends to equalize the concentration of particles over the whole volume. These processes are in constant competition.

During the process the beverage as a disperse system passes through the following options for the competition of processes of sedimentation stability and diffusion:
– In the semi-prepared beverages at the beginning of the technological chain diffusion process is not determined, that is why the system is sedimentation-unstable;
– Processing of semi-finished and ready for pre-packaging beverages due to different technological methods and aids leads to the formation of sedimentation-stable system, in which there is a sedimentation-diffusion equilibrium, i. e., particle distribution is not uniform and stable.

Aggregate stability is the ability of disperse system to maintain the degree of dispersion constant in the course of time, i. e., particle size and its individuality. Under the violation of aggregate stability the coagulation process takes place. In the result of coagulation the system loses its aggregate stability. Due to it, the coagulation system loses its sedimentation stability, and the particles become too large to participate in Brownian motion. The coagulation process undergoes two stages: a hidden and an obvious coagulation during the process. During the former coagulation particles get larger, but do not lose their sedimentation stability. During the latter coagulation the apparent density of the particles is greater than the density of dispersion medium, and a precipitate is formed.

Any outward interference of sufficient intensity promotes the coagulation of disperse system. These effects include: changes in temperature; electric fields and electromagnetic fields attack; action of visible light; mechanical action; addition of electrolytes and so on. The temperature effect on the dispersion of beverages is laid into the basis of some technological methods, in order to coagulate large particles, for example, boiling of wort with hop and sharp cooling of semi-prepared liquors and others.

Figure 1 (in Table 1 there are explanations of the figure) shows a hypothetical model of the disperse system of beverage (DSB) state, when subjected to technological supplementary means (TSM).

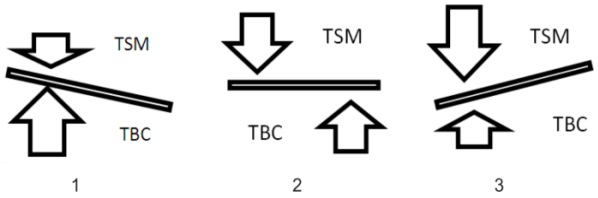

Fig. 1. Hypothetical model of the state of disperse system under the influence of technological supplementary means: (1) unstable DSB, (2) sustainable DSB, (3) "excessively" stable DSB (TBC - components of turbid beverages).

The use of technological supplementary means in the beverage industry allows to put a balance of the quantitative content of potential of turbidity-forming substances, i. e. to prevent hidden coagulation during storage of the beverage and as a consequence, to obtain dispersion equilibrium.

Table 1. Description of the disperse system of the beverage under the action of processing aids

Symbol	Clarification	The result of the effect of TSM on drink quality indices
(1) unstable DSB	The quantitative content of TBC exceeds the quantitative content of the TSM. The probability of suspensions is a maximum.	Violation of appearance of the beverage; visualization of opalescence and sediment; shortening storage
(2) stable DSB	Concentration of TBC is equivalent to the amount of TSM.	Indices of quality beverage meet regulatory requirements; provided warranty deadlines of storage
(3) "excessively" stable DSB	The quantitative content of TBC is excessive in relation to the number of unstable colloids in drink. Probability of suspension is minimal.	A decrease in the organoleptic characteristics of completeness of the beverage flavor and color; decrease of the nutritional value of a drink due to excessive excretion of physiologically active components of a product is observed

Preparing beverages from natural raw materials by application of beverage oxidation technology plays a non-uniform role from the point of view of the formation of organoleptic characteristics and durability of products. Thus, the study of home and foreign scholars in the field of study of biochemical reactions in production of red wines and specialized wines show

that micro-oxidation has a positive effect on the formation of complex flavor characteristics and aging of wine [2, 3].

To prevent turbidity, associated with the harmful effects of oxygen in the beverage technology *antioxidants* are used. A mechanism of interaction of antioxidants with a beverage is quite simple. These compounds interact primarily with oxygen, preventing its reaction with the product, active radicals are inactivated and peroxide forms are destroyed. In beverage industry natural and artificial antioxidants are used. Natural antioxidants include ascorbic and isoascorbic acid, ascorbates, tocopherols, rutin, quercitrin et al [4–7].

Widespread synthetic antioxidants are derivatives of phenols – gallateionol acid ethers, ionol and others [4, 5].

Foreign and home scientists are actively engaged in the research work on the production of antioxidants from natural herbal materials, such as skins and seeds of exotic fruits [8], apple pomace [9], flowers and stems of plants, or such as indigo, jasmine, corn silk [10–12].

In fermentation beverage technology they may use some sulphur compounds as antioxidants: suphfite, bi- and meta-sulphites and potassium metabisulphites. For example, when taking these additives an equilibrium between bound and free SO_2 in beer occurs, which depends primarily on the concentration of free oxygen, as well as physical factors (temperature, pH), and of course, the quality of the raw materials used [4, 5].

To improve the colloidal stability of drinks *enzyme preparations* are widely used, mainly of the hydrolase class - amylase, protease cellulase etc. [4, 14-16]. These biopolymers are used to hydrolyze high molecular components, resulting in formation of material of lower molecular weight, whereby the last are not able to participate in the formation of beverage turbidity.

Enzyme preparations are used to stabilize clear juices, wine, and fruit semis for liquors. Pectins, starch and phenolics are subjected to enzymatic hydrolysis. Pectin molecules are the part of the complex of particles of dregs remaining in juice after extraction. Enzyme activity of proper pectolytic enzymes is not enough for the hydrolysis of pectin dissolved in juice. Moreover, proper pectinmethylesteraza having certain residual activity can lead to the stabilization of the slurry. For the hydrolysis of pectin we use enzyme preparations with high activity of pektinmethyl-esteraza, endopoligalakturonaza, pektinliaza as well as collateral activity of arabinase, glycosidase and protease. Collateral activity is necessary for the enzymatic hydrolysis of the dissolved polysaccharides making up cellular walls. For the enzymatic hydrolysis of starch dissolved we applied enzyme preparations of alpha-amylase or amilogycozidase of filamentous bacterial origin. To remove phenolic compounds the use of enzyme complexes with laccase and difenoloksidaza activity is effective [5, 19].

Enzyme systems are also used to remove contained in beverages oxygen. Thus, glucoseoxidase enzyme system – catalase is used in beer production. Initially, the process of oxidation from glucose to gluconic acid is catalysed by glucoseoxidase. Catalase, in its turn, breaks up hydrogen peroxide obtained to form oxygen and water. Oxygen, released from the second reaction, is involved into the first reaction. Both reactions proceed until the expenditure of oxygen or glucose. This enzyme complex improves the biological stability of beer, not subjected to pasteurization, since under the shortage of oxygen the reproduction of yeast and other microorganisms is suspended [4].

The adsorption methods of beverage stabilization have become widespread. The basis of these methods of lightening substances is stipulated by the adsorption process of colloidal materials or neutralizing of electrical charges colloids of beverages due to introduction of substances with the opposite charge. For this purpose, we use materials of organic and inorganic origin (e.g., diatomite, bentonite, etc.).

Bentonite (bentonite clays) is an aluminosilicate, preferably consisting of a laminate material - montmorillonite mineral and beydelit. Montmorillonite is composed of oxides of silicon and aluminum at a ratio of 4 : 1. In domestic and foreign food industry sodium and calcium-magnesium bentonites are used. Their properties are slightly different [5, 17, 18, 20–22].

Sodium bentonites swell, repeatedly increasing volume somewhat less than those of calcium. The degree of swelling depends on the efficiency of the clarification process - the higher the degree of bentonites swelling, the more efficient lighting becomes. Alongside with the sorption of protein components bentonites remove phenolic compounds (tannins). This property of bentonite is associated with the structure of the bentonite mineral. Sorbent on the main surface of the plates has a negative charge and the edges are charged positively.

In food industries for an effective synersis and greater increase in clarification of beverages, using mineral sorbent, it is combined with a flocculant, in particular with polyacrylamide (PAA), activated carbon [5, 23].

For the adsorption of polyphenolic substances in beverage technology *compounds of organic nature* are used. The reaction between the aromatic hydroxyl group of polyphenols and -CO-NH- in the adsorbenthe is in the basis of interaction.

For instance, the polymer polyvinylpolypyrrolidone (PVPP) - white powder is composed of the same monomers as polyvinylpyrrolidone (PVP) has a ramified structure: PVPP is used in the world beverage brewing and stabilization to remove polyphenols, traditionally used for adding it to diatomite after application of the latter on the filter surface as a filter layer. PVPP absorbs as well nitrogenous substances in the composition of protein- polyphenol complexes [4, 5, 24–27].

PVPP action is analogous to that of the protein properties to bind with polyphenolic substances in the mechanism of turbidity formation. The difference lies in the fact that this process proceeds to considerably faster connections. That is why the introduction of PVPP on filtration stage of a drink takes the drink from the polyphenol fraction and prevents the formation of protein-tannin complexes, as well as the condensation and copolymerization of low molecular weight polyphenols.

To improve the colloidal stability of beverages in domestic and foreign practice *ionites* are also used**.** Ion-exchangers due to covalently bonded ionexchanging groups delay in controlled amounts of proteins and polyphenols.

According to the literature, mechanical density of the resin agarose is so great that it can be destroyed only with a huge mechanical force. Chemical stability of ionexchangers can be broken only by using strong oxidisers or enzymes [4, 5, 29].

The use of *drugs based on silicic acid* is widely distributed in domestic and foreign practice [4, 15, 28, 30-32]. Various industrial names of these drugs: kieselgur, kieselgel, silicasol, silicagel, silicasol - all silicic acid derivatives are related to the class of substances with a large surface area of contact. This means that the sorbent comprises a large number of fine pores. Among currently used stabilizing materials based on silicic acid, in accordance with water content there are distinguished: xerogel and gydrated kieselgel. Progress in the sorbent production technology significantly improved filtration properties by reducing the size of particles, leaving the range without changing the structure. Hydrogel is produced in the same manner as xerogel. However, the final drying process does not occur, so this product is marketed with the humidity of 65%. The only significant advantage of hydrogel with respect to xerogel is, that wherein it is applied the dust is not formed.

Starting component for the production of silicasol is waterglass - solution of special sand, soda ash and water. The choice of sand is the main factor which ensures optimum properties of the resulting silicasol. At later stages of processing liquid glass using ion exchange processes under the control of temperature, pH, pressure, hydrosol of silicic acid is obtained, that is a solution of the smallest silica dioxide nanoparticles. The initial molecule is the molecule of orthosilicic acid. Hydroxyl groups are disposed in a tetragonal form around the silicon atom and denote a silanol group. They are highly reactive compounds and in the formation of Si-O-Si are condensed into polysilicic acid and then form tiny spherical particles having on their surfaces a considerable amount of reactive silanol groups.

Use of kieselgel in brewing is based on the adsorption of protein and tannin compounds (and substances from which they are formed), followed by removal through precipitation of the beer filtration or before filling. Unknown cleavage products in beer or other products do not remain after the reaction, they are stored with some precipitants, such as tannin. For this reason, the use of kieselgel to stabilize the beer does not cause any discussions about its inadequacy to the laws of brewing (Reinheitsgebot - the requirement of product purity) and other requirements to food products. Technology of using Kieselgel to stabilize beer is constantly expanding and, that is of great interest, even in those countries, where there exist other processes and other supplementary means of stabilization of beer are allowed [15, 30-33].

To improve the colloidal stability and tasting berry juices *zeolites* are used [34]. Zeolite is a natural aluminosilicate, whose structure has a tetrahedral shape, and in the grounds of it there are aluminum and silicon ions located, bound by common oxygen ions. Zeolite and kieselguhr (diatomaceous earth), has a large number of fine pores, and wherein removing of the components due to clouding sorption occurs. Zeolite acts as a molecular sieve, it bears a negative charge, which is compensated by the presence in the structure of various metal cations. Cations can replace each other, at the same time zeolite has the properties of ion- exchanger. Zeolite cations are mobile and can be exchanged for other cations of different nature and valence. This property is the basis for modification. The outer surface of the zeolite crystals is small, as compared to the inner volume of adsorption that becomes available after dehydration of zeolite. Its density is low, it is 1.9-2.3 g/cm^3, cation exchange with heavy metals increases it. Furthermore, the density of zeolite depends on the extent, to which the structure is open and what cations are included in their composition. The high selectivity of zeolite adsorbents and their capacity in methabolism is due to molecular sieve effect. Such molecules as $(C_2F_5)_3N$, C_6H_6, $(C_4F_9)N$, C_6H_{12}, n-paraffins, some pesticides can penetrate inside the volume of zeolite.

One of the most important ways to change the properties of zeolites is their modification. The highest sorption capacity is typical for lithium, sodium, potassium, aluminum forms [34].

A certain niche among stabilizing agents is occupied by natural and synthetic *flocculants.* Flocculants are water-soluble macromolecular compounds which, when introduced in disperse systems, are chemically bound to the surface of dispersed particles, the particles are combined into agglomerates (floccules), promoting their rapid deposition. Gelatin is widely used among natural flocculants. It is used to lighten wine, juice, and other products. Gelatin is a protein drug that is extracted from the skin and bones of animals, purified, dried and milled. Gelatin is used in beverage processing for the deposition of polyphenols, which leads to an improvement in flavor, prevents reactions associated with the change in color (brown tone acquisition), and removes the blurred effect of phenol. When processing gelatin with polyphenols flakes are formed, which are deposited, and a fine suspension is carried away with them. The liquor is clarified and its filterability is improved. Efficiency of gelatin increases when used in conjunction with tannin or highly concentrated silica [3, 5, 35, 36].

In the technology of clarification of juices, wine materials and wines the use of natural flocculants, representing microorganisms biomass, such as fungi pleurotus ostreatus and fspergillus niger, takes place [37, 38].

In the domestic technology of preparation of fruit semi-finished products for liquor production polyacrylamide-based flocculants are used [36, 39-41]. Polyacrylamide (PAA) is a synthetic flocculant, amide copolymer of acrylic acid and its salts. The usage of partially hydrolyzed polyacrylamide having a degree of hydrolysis of about 30% is a common practice.

A synergistic effect of it when used in conjunction with coagulants flocculants, has been proved in practice. Application of PAA can reduce the dose of low molecular weight coagulant (e. g., bentonite) several times, greatly increase the rate of deposition of sediment, and the life of the product used for the clarification of the process equipment [36].

One of the applications of flocculants in the technologies of fermented beverages is the reduction of yeast biomass. Flocculants make possible to conglomerate yeast cells with further acceleration of their sedimentation, thereby helping to improve the biological resistance of drinks [39, 41].

In recent years it has become popular to use *hydrocolloids* in the food industry. Despite their very low concentration, they have a strong influence on the physico-chemical and organoleptic properties of food products [42].

Figure 2 shows the production of different hydrocolloids in the world market.

The leaders in the use of hydrocolloids in food products are by far the countries of Western Europe. More than 30% of all manufactured thickeners, gelling agents and stabilizers are consumed by European countries; the US share is approximately 32%, and Asian countries - about 25%. All other countries use about 10%, they include Russia [43].

Today among the most popular food hydrocolloids can be called pure natural substances of animal (gelatin) and vegetable (pectin, agar, gum) origin, as well as products of physical and chemical or enzymatic modification of natural substances - modified cellulose, starches, and others [43].

In the practice of brewing to adjust the quantitative content of polyphenols drugs carrageenan - virflok, Irish moss and others are used, which are introduced by boiling wort with hop. These drugs contribute to intensive formation of protein-tannin complexes [4, 15].

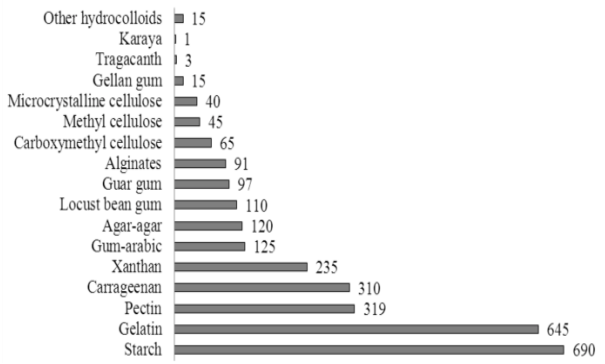

Fig. 2. World production of hydrocolloids, in billion $ [43].

One of the most promising hydrocolloids currently used in food industry is chitosan. Chitosan was at first obtained by Professor Roger C. in the middle of the 19th century. Chitosan is a polysaccharide, which is obtained from the shells of crabs or fungi by removing carbon compound [42].

Chitosan is biodegradable, non-toxic, non-immunogenic and biocompatible with animal tissues. In this connection, the prevailing amount of research has been directed to its use in medical applications. Chitosan is poorly soluble in water, because its bonds between chitosan molecules are stronger than those between molecules of chitosan and water. This hydrocolloid is soluble in acids, such as citric, acetic, oxalic and succinic acids. Chitosan has the ability to retain a solvent in its structure and substances dissolved therein. Flocculation properties of chitosan are exhibited better in solution than in insoluble state [42].

In foreign and domestic practice chitosan actively attracts researchers into the field of protection of food from microbiological spoilage instead of synthetic fungicides [44, 45], as well as a structural generator of nucleated food mixed with protein components in order to improve the physiological properties of medicinal drinks.

Nowadays, the research about the possibility of using chitosan in the beverage industry is conducted to regulate the qualitative composition in order to increase the resistance of the finished beverage [46-48]. Removal of excess beverage potential turbidity-formers as polyphenol and pectin components using chitosan can be explained by the chemical structure of hydrocolloid. In the chitosan molecule there exists a large number of free amino groups, which determines its property to bind hydrogen ions and acquire an excessive positive charge. Therefore, chitosan acts as an active cationic and effectively removes polyphenol and pectin from the reaction medium, bearing in it mostly a negative charge. Decrease in the concentration of protein fraction occurs, possibly due to the initial ion interaction of proteins with polyphenol pectin components followed by their passing into the sediment under the influence of chitosan.

As a glue material in the manufacture of beverages of fruit raw material, starch - potato and maize, are also used [36].

On the basis of the above mentioned data we may conclude that there are various tools to increase the resistance of drinks. Often, different means are used in combination with each other, and if used properly, the additional effect is obtained. At the same time, the ever-increasing production volumes require the search for newer and more effective ways to increase life time of various beverages.

In this paper, we propose a variant of classification of the technological supplementary means used in beverage technology, applying the hierarchical method (Table 2).

The term "classification" means the division of a set of objects into subsets according to certain similarities or differences. Here, under the noting element of "similarity" of the whole complex TSM, the purpose is meant, i.e., ensuring of guaranteed stable transparency of beverages. The division of TSM, according to the differentiation, includes the following subset categories: substances of antioxidant action (anti-oxidants), enzymes, flocculants and sorbents.

Differences between subset groups have different signs. Selection of signs is based on the purpose of classification.

Table 2. Classification of technological supplementary means used in beverage technology to eliminate turbidity

Sets	Sub-sets	Stage			Subset element
		1	2	3	
Additional technological means	Antioxdants, enzymes, flocculants, sorbents	1. Structural characteristic	1.1.Mechanism of action on the component opacities	1.1.1.Chemical interaction	Antioxidants
				1.1.2.Biocatalytic cleavage	Enzymes
				1.1.3.Flocculation	Flocculants
				1.1.4.Sorption	Sorbents
			1.2.Chemical organization	1.1.1. Organic	Antioxidants, enzymes, flocculants, sorbents
				1.1.2. Inorganic	Antioxidants, flocculants, sorbents
			1.3. A process for preparing / origin	1.3.1. Synthetic	Antioxidants, flocculants, sorbents
				1.3.2. Natural	Antioxidants, enzymes, flocculants, sorbents
			1.4. Molecular mass	1.4.1. Low molecular weight	Antioxidants, flocculants, sorbents
				1.4.2. Middle molecular weight	Antioxidants, flocculants, sorbents
				1.4.3.Macromolecular weight	Enzymes, flocculants
			1.5.Aggregate state in the reaction medium	1.5.1.Soluble	Antioxidants, enzymes, flocculants
				1.5.2.Insoluble	Flocculants, sorbents
				1.5.3.Colloidal	Flocculants
		2. Technological directivity	2.1. Impact on the overall	2.1.1. Raw materials	Antioxidants, enzymes
				2.1.2. Intermediate products, semi-finished products	Antioxidants, enzymes, flocculants, sorbents
				2.1.3. Finished product	Antioxidants, flocculants, sorbents
			2.2. Impact on component of production facility involved in the formation of turbidity	2.2.1. Polysaccharides	Enzymes, flocculants, sorbents
				2.2.2. Protein substances	Enzymes, flocculants, sorbents
				2.2.3. Pectic substance Islands	Enzymes, flocculants, sorbents
				2.2.4. Phenolics	Antioxidants, enzymes, occulants, sorbents
				2.2.5. Metals	Antioxidants, flocculants, sorbents
				2.2.6. Production microorganisms	Flocculants, sorbents
				2.2.7. Oxygen	Antioxidants

Signs of the classification are divided into teleological, genetic and technological. Teleological signs define the purpose and use; genetic - initial materials, raw materials, the main components of their chemical composition; processing - design, formulation, manufacturing processes, methods or finishing design.

In this case, the designation of the signs and stages of classification is based on the definition of TSM, regarding following methodological steps: identifying of production facility, then identifying of the component (or components), which will be the object of TSM, and then, on the basis of structural characteristics, making a selection of subset element, i. e., choosing TSM required for the process.

The first stage of the proposed classification is the division of TSM on the following grounds:

– Structural characteristics of accumulating genetic and technological signs of the classification;
– Technological direction - teleological sign.

Detailed classification criteria for the next step involve the properties of TSM, which provide the insight into the structural features of the agent used for the stabilization of beverages and, as a consequence, makes it possible to represent the methodology of interaction and stabilizer of beverages turbidity component. So, TSM is included into the classification of genetic features, with chemical stabilizer organization and the mechanism of action of turbidity component. In the process of preparing – origin, molecular weight and physical state in the reaction medium are the technological characteristics of classification.

There is a teleological sign of classification. In this case the use of (TSM) accumulates the two main aspects - impact on the manufactured object as a component of the flow process from raw materials to final products, and the impact on the actual components involved in the formation of beverage turbidity.

Analysis of the significance of classification contributes to solving production problems, connected with the use of the supplementary means, i.e., helps the manufacturer to identify some aspects of their application, to assess the advantages and disadvantages of a particular material.

In the analysis of the teleological signs of classification - the application of technological orientation of TSM, the specialist of production should initially assign the elements of the process stream, the regulation of composition, which determines the receipt of guaranteed durability in a product. Next, you need to specify a component, the presence or excessive content of which requires the introduction of TSM. The

outcome of these issues is the conclusion on the application of specific tools or complex use of several TSM in order to obtain a synergistic effect.

Technological awareness of a practical working mechanism of TSM in the turbal component allows you to define a rational process step. For example, consider the use of enzymes. Enzymes - is a tool, the use of which is possible in almost any stage of the process stream. Thus, the enzymes are used in brewing and for the treatment of raw materials (for malting), and in the preparation of the wort, and final fermentation compartment. Specialist on the basis of analyzing the components of a process stream determines the stage of the process, which regulates the qualitative composition of the product, will contribute to solving the problem - getting the finished beverage guaranteed durability.

Chemical TSM organization determines production losses related to specific consumption of TSM. For example, using bentonite as a stabilizer for semi-finished products of liquors, which by its chemical nature is an inorganic substance, there are large production losses with sediment during clarification semis. Thus effective dosages are measured in grams per cubic decimeter. While the use of an organic stabilizer, e.g., with the same purpose chitosan stipulates the formation of compact precipitate with introduced dose of TSM, many times smaller and is measured in milligrams per cubic decimeter [40].

Physical state, in which the stabilizer in the reaction medium, predetermines the mechanism of interaction, the method used in the process, allows to identify the stage of the process, which will make rational use of specific FA. For example, the use of flocculants and adsorbents would be the best on semi-holding stage before filtering process, and the use of antioxidants or enzymes does not require filtration after treatment.

A process of preparing / origin allows us to evaluate the economic component of the use of TVS. Thus, synthetic stabilizers, in most cases, are less natural. This, however, relates to enzyme preparations. Molecular mass plays a role in determining the aggregate state and the degree of solubility for the individual elements of a subset of stabilizing agents such as flocculants and sorbents.

We describe the algorithm of specialist actions in production of alcoholic beverages by analyzing the classification criteria of presented above version of classification. For example, we may consider the widespread sorbent – bentonite, used as an aid in the technologies of various drinks.

1. Analysis of teleological signs.

– We denote the production facility - or semi-finished liquors - alcoholized berry juice, fruit infusions. Consequence – element of subset is not defined;

– Morse component chemical composition, which requires adjustment of the quantitative content - the complex slurries that consist of polyphenol, pectin and proteins. Consequence - a subset of the excluded item "enzymes".

2. Analysis of genetic signs.

– Mechanism of action of the component haze - sorption or flocculation. Consequence - the specification of element subsets "sorbent" or "flocculent" as well as the stage of its use - treatment is available at the stage before filtration pasting semiproduct, we stop the choice, for example, on an element subset "sorbent" and denote a representative of this group – bentonite;

– Chemical organization - an inorganic substance.The investigation - necessity to consider losing semis with sediment.

3. Analysis of technological features.

– A process for preparing /in origin - natural, and has a low cost, which is one of the advantages of the assembly;

– The molecular weight - middle molecular;

– Physical state - insoluble sorbent in the reaction medium is a suspension.

Consequence of the analysis on this stage is the designation of specific use of bentonite to stabilize the fruit beverages (fruit infusions).

According to the above classification TSM, bentonite is a low molecular weight natural insoluble adsorbent of inorganic nature, used to stabilize the semi-finished products of alcohol beverages by the method of sorption turbid substances. Thus, in practice, the experts in this branch prefer to use bentonite in combination with any flocculant in order to obtain synergies and accelerate the process of infusion pasting.

Any supplementary means used in the practice of production for the equilibrium beverage system obtains signs, presented in this classification. Furthermore, within the element subsets, there are specimens, which have, for example, identical technological characteristics, while at the same time they have distinctive structural characteristics (e.g., bentonite and chitosan).

Thus, the shown embodiment of classification may serve as a methodological basis for selection of TSM, if taken into consideration individual structural characteristics of these means and properties of the substance complex involved into turbidity process, as well as to indicate the parameters of rational use of TSM in production line as one of fundamental factors for the formation of finished product quality.

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INFLUENCE OF VACUUM-PULSE DRYING ON THE CONTENT OF FREE AMINO ACIDS, TRYPSINE INHIBITOR ACTIVITY AND COMPOSITION OF VOLATILE COMPONENTS OF MUSHROOMS

I. V. Shcheglova, A. L. Vereshchagin*

Biysk Technological Institute (branch),
Altai State Technical University named after I. I. Polzunova,
ul. Trofimova 27, Biysk, 659305 Russia,
* e-mail: val@bti.secna.ru

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Abstract: Wild mushrooms traditionally are considered one of the sources of food fibers, vegetable proteins, macro - and - micronutrients, and also flavor components. However, the composition of mushrooms includes antinutritional substances capable to selectively reduce the absorption of certain nutrients. These are primarily antienzymes or proteinase inhibitors, which reduce the absorption of proteins. Previous studies have indicated applicability of vacuum-pulse drying to improve the nutritional value in the edible mushrooms (*Cantharellus cibarius Fr.*) autohydrolysis of bodies biopolymers of the mushrooms and increase of the rate of swelling in hot water. The possibility of applying a vacuum-pulse drying for increasing the content of free amino acids and reduction of the activity of trypsin inhibitors in edible mushrooms: chanterelles and autumn agarics (*Cantharellus cibarius Fr.*) is shown in this study. In addition, it is established, that the vacuum-pulse method of drying leads to reduction of flavor components content in the edible mushrooms. To study human body digestibility of vacuum-dried product further research is required. The effect of vacuum-pulse drying on flavor properties of mushrooms continues to be a controversial question.

Keywords: Mushrooms, vacuum-pulse drying, proteins, amino acids, trypsin inhibitors, volatile components

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ITRODUCTION

Nowadays there is a shortage of protein intake in different groups of population, which leads to a decrease in efficiency, metabolic disorders, and the emergence of a number of diseases. The proteins of mushrooms may play an important role in meeting the needs of food protein.

Mushrooms belong to vegetable products with a relatively high content of protein, which takes up to 40% solids, an average of 24.9 ± 1.75% [1]. However, up to date there is no consensus about the usefulness and comprehensibility of fungal proteins. Recognizing the great protein content in mushrooms, we cannot ignore the high content of dietary fiber and chitin. Definite proof of complexity of fungal protein digestibility by a human body can also be considered by the fact that the degree of extractability of the protein by various solvents, depending on the species of fungi is on the level 35–60% [2].

Biological value of food is determined by indication of protein quality, what reflects the extent to which its amino acid composition corresponds to the body needs in amino acids for protein synthesis. In fungal protein hydrolyzates up to 22 amino acids are revealed [3]. Essential amino acids are contained in mushrooms up to 33–44% of amino acids total sum. And their numbers are growing in direct proportion to an increase in protein content [4]. Alongside with the implementation of their biological function certain amino acids make great contribution into flavor properties of mushrooms [5].

It is also known that fungi include antinutritional substances capable to selectively reduce the assimilation of certain nutrients. They are primarily antienzymes or proteinase inhibitors, which block the activity of enzymes of the gastrointestinal tract, and reduce the absorption of protein substances [6, 7]. These are trypsin inhibitors capable to form inactive complexes with enzymes that break down proteins in a human body; wherein the enzymes lose their catalytic activity. Therefore, prolonged use of such food leads to hypertrophy of a pancreas and hence a slower growth. Thus, high levels of proteinase inhibitors content significantly lowers the nutritional value of proteins and has negative effects on the body.

According to studies [8] of the content of trypsin inhibitors, in 55 kinds of edible mushrooms a trypsin inhibitor activity is observed to be within 0.36–10.42 mg/g of dry weight.

L.A. Gzogyan showed that the fertile bodies of 18 different species of basidiomycetes in Krasnodar region contain these enzymes, with the exception of polypore (*Coriolus versicolor (Fr.) Karst*) and blackberries (*Hericium erinaceus (Fr.) Quel*). The highest level of activity of trypsin-like proteinases was found in fruit bodies of brown cap boletus (*Leccinum melanum (Fr.) Karst*) (5.3 mg/g), white mushrooms (*Boletus edulis*) (3.7 mg/g) and the chanterelles natural

(*Cantharellus cibarius Fr.*) (3.6 mg/g), autumn honey fungus (*Armillariella mellea (Fr.) Karst.*) (2 mg/d) [6].

Studies of V. I. Bakaytis and S. N. Basalaeva of seven species of wild mushrooms, grown in Novosibirsk Region and Altai territory, showed lower activity of trypsin inhibitors than in those of Krasnodar territory.

Thus, the highest activity of trypsin inhibitors is presented in white mushrooms (*Boletus edulis*) (0.97–1.20 mg/g), the average level of activity is stated in autumn honey agarics (*Armillariella mellea (Fr.) Karst.*), mokhoviki (*Boletus variegates*) and presented in natural chanterelles (*Cantharellus cibarius Fr.*) (0.67–0.44 mg/g), the minimum level of activity of trypsin inhibitors is in white podgruzdki (*Russula delica Fr.*) and real milk mushrooms (*Lactarius resimus Fr.*) (0.35–0.39 mg/g) [9].

It should be noted that trypsin inhibitors have sufficiently high resistance to inactivation. From some literature data we find trypsin [7, 10, 11], for example, after treatment of aqueous soy extract, containing trypsin inhibitors nearly for an hour, at 120°C their activity is reduced up to 30–35% [12]. The effect of heat treatment is increased by presoaking [13] and microionization [14].

Studies conducted earlier have shown the applicability of the method of vacuum-pulse drying to improve the nutritional value of chanterelles (*Cantharellus cibarius Fr.*) due to autohydrolysis of biopolymers of mushroom bodies and increase the rate of swelling in hot water [15].

Drying of mushrooms is an effective and popular way of their preservation and conservation. Dried mushrooms have unusually pleasant and strong aroma and flavor, thus they are considered delicacies.

During the drying process the composition of products significantly changes. Together with the removal of moisture, losses of volatile organic substances take place, concentration of low molecular weight compounds (peptides, amino acids, sugars, organic acids) significantly increases, and enzyme activity is also changed. All this leads to the change in aroma and taste of foods. Under high-temperature drying the reaction occurs between amino acids and sugars, leading to the synthesis of new organic compounds, including volatile products. That generates an aroma of fragrance-dried products. In dried products changes occur during storage, particularly in composition of volatile substances stipulated by their loss through volatilization or oxidation [16, 17].

As a result of research, in various kinds of mushrooms nearly 150 volatile substances have been found, belonging to different classes of organic compounds, liable to significant changes. Basic compounds forming raw mushroom flavor, are aliphatic alcohols and ketones with carbon numbers 8: 1-octen-3-ol, 2-octen-1-ol, 3-octanol, 1-octanol, 1-octen-3-one and 3-octanone [18-20].

The purpose of this study is to investigate the influence of vacuum-pulse drying on protein quality, trypsin inhibitor activity and composition of the volatile compounds of edible mushrooms.

OBJECTS AND METHODS OF STUDY

As research objects, we chose one of the most common precious wild mushrooms of the third category: chanterelles natural (*Cantharellus cibarius Fr.*) and autumn honey fungus (*Armillariella mellea (Fr.) Karst.*), collected in pine forest tracts "Soshnikovo" Priobsk forest massive, Altai territory. It is also known that these types of mushrooms contain the least amount of protein among the major harvested species [1].

Being cut into cubes of 5–10 mm in size lateral mushroom bodies were placed into the working chamber of a dryer and subjected to vacuum-pulse drying under temperature of 55°C. Processing was performed under certain pressure, lowering it from atmospheric pressure up to 100 Pa for the period of 30 seconds, and then again it was raised to atmospheric pressure and mushrooms were kept for 100 seconds. The process of successive vacuuming and holding mushrooms in contact with atmosphere was carried out periodically 2–5 times to constant weight, depending on the consistency of mushrooms with a definable age.

As a control sample the authors used the fruit body dried at atmospheric pressure, under temperature of 55°C bringing up to its constant weight (conventional convection drying).

Determination of mass fraction of the total protein in mushrooms sample was carried out by Dumas method on the express-analyzer Rapid N cube, the concentration of amino acids - by the method of ion exchange chromatography on an amino acid analyzer Aracus. Trypsin inhibitor activity (AIT) was determined by the method described in "Methods of biochemical research ..." (1987) [21]. Reagents of the firm ISN-Biomedical (US) were used, in particular a substrate - BAPA (Na-benzoyl-DL-arginine-p-nitroanilide) in accordance with the method of Iu.Ia. Gofmana and I.M. Vaysblaya (1975) [22]. The method used is based on the spectrophotometric measurement of proteinaceous substrate decay products optical density (BAPA) by an action of trypsin at a wavelength of 405 nm. The amount of inhibitors, extracted by distilled water from the air-dried mushroom flour (moisture content 6%) at the ratio of 1 : 50, was kept in a refrigerator for the whole night. The flour was obtained by grinding of dried mushrooms and their sieving through a sieve with a cell diameter of 0.1 mm. 0.05 M Tris-HCl-0.02 M $CaCl_2$ was used as a buffer. Determination of AIT was carried out at pH = 7.7; before operating all the solutions were incubated for an hour at 25°C.

Indices of the qualitative and quantitative composition of volatile aromatic mushrooms substances were determined by a gas chromatography. For this purpose, 5 g of crushed dried mushrooms were added in 100 ml of distilled water and 250 mg (5000 mg per 100 g of mushroom) of n-dodecane as an internal standard. The volatile components were removed within 45 min with 20 ml of diethyl ether, freshly distilled by continuous distillation-extraction. The extracts were dried with 2 g of anhydrous sodium sulfate and concentrated to a volume of 0.1 ml using ether distillation at 40°C with a Vigreux column on the length of 35 cm. The ether

extracts obtained were analyzed by gas-liquid chromatography.

For gas chromatography studies a capillary gas chromatograph with a HP 5730A with a flame-ionization detector, a quartz capillary column FFAP (50 m×0.32 mm, 0.5 micron layer of phase) were used. Analysis of the ethereal extracts was conducted at a column temperature programming mode as follows: isotherm at 77°C for 6.5 minutes, then the at temperature programming up to 210°C at a rate of 10°C/min.

RESULTS AND DISCUSSION

Experimental data on the determination of protein and amino acid composition are shown in Tables 1 and 2.

Table1. Mass fraction of total protein in mushroom samples

Mushrooms	Mass fraction of total protein in fungi samples, %	
	VIS	Control
Chanterelles	21.6	18.6
Honey fungus (autumn)	31.0	29.2

Table 2. Results of determining concentration of amino acids in samples

Name of determined amino acid	Amino acid concentration, mg/100 g dry substance			
	Chanterelles		Honey fungus	
	VIS	control	VIS	control
Aspartic acid	2890	2547	4575	4380
Threonine	495	466	1130	838
Serine	894	704	190	165
Glutamine acid	3585	3240	3679	3501
Proline + Glycine	605	570	2715	2556
Alanine	285	283	2778	2634
Umteine	1707	1238	2736	2566
Methionine	311	293	260	231
Isoleucine	966	916	1037	956
Leucine	1848	1515	1223	1159
Tyrosine	614	597	839	740
Phenilalanyl	3273	2988	2335	2206
Gistadin	2213	1860	2427	2307
Lysine	399	307	2715	2365
Arginine	1621	1230	2526	2334
Total content of amino acids	21706	18754	31165	28938

Note. Values are valid at P = 95%.

Thus we can see from Tables 1 and 2, as a result of pulsed-vacuum treatment, the total amount of protein and the content of individual amino acids increased. However, the degree of increase in a number of free amino acids is not the same. For example, in chanterelles the qualitative composition of real free amino acids varies with the destruction of glutamic acid, tyrosine and phenylalanine and with increasing proportion of cysteine and serine. In autumn honey fungus the relative content of aspartic and glutamic acids decreased, but lysine and threonine fraction increased.

Increase in the total amino acid content was 15.7% and 7.7% for chanterelles and honey fungus respectively. Changes in a proportion of essential amino acids are stated in the range of measurement error (less than 1%).

Table 3 shows the results of calculating the balance in composition of fungal amino acid protein according to the standard FAO (the calculations of tryptophan and valine were not involved, as their content was not determined).

Table 3. Amino-acid score of fungi protein

Amino acid	Amino-acid score of fungal protein, %			
	Chanterelles natural		Honey fungus	
	VIS	control	VIS	Control
Threonine	57	62	91	72
Methionine + cysteine	266	233	275	286
Isoleucine	111	122	83	83
Leucine	122	115	56	57
Phenilalanyl + tyrosine	298	319	180	170
Lysine	33	30	158	149
Total	887	881	843	816

These data suggest that limiting amino acids in chanterelles are lysine and threonine, and phenylalanine + tyrosine, while methionine + cysteine being predominant. In autumn honey fungus limiting amino acids are leucine, isoleucine and threonine, and methionine + cysteine are predominant. It should be noted, that no significant amino acid changes came soon after vacuum- pulse processing.

Thus, as a result of vacuum-pulse treatment, the qualitative and quantitative composition of the fungal protein varies. The data obtained can be attributed to the fact that by increasing water activity due to the vacuum treatment the pulse partial hydrolysis of chitin-glucan protein complexes and hard-digestive mushroom proteins occur. In this case free amino acids are generated.

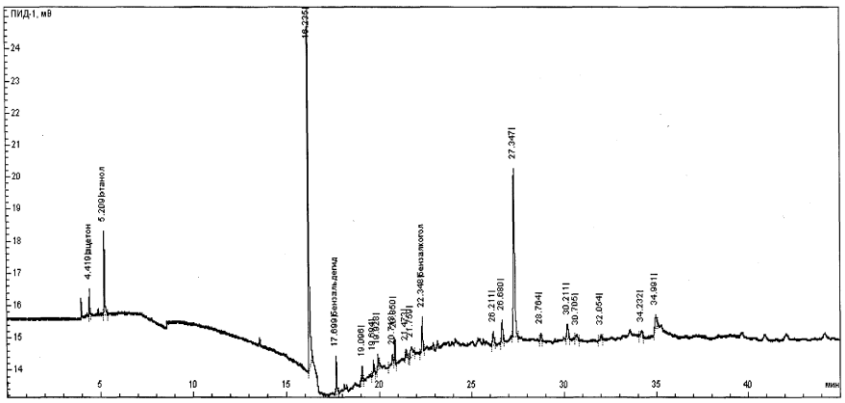
Experimental data on the determination of tripsin-inhibitor activity are shown in Table 4.

Table 4. The activity of trypsin inhibitors in mushrooms

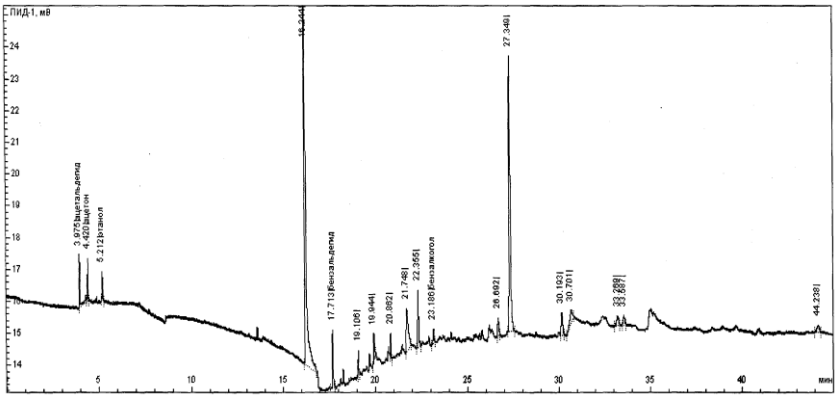
Mushrooms	AIT, mg/g dry weight		Trypsin inhibitor destruction degree versus control samples, %
	VIS	control	
Chanterelles real	0.45±0.03	0.77±0.05	41.6
Agarics autumn	0.57±0.04	0.77±0.05	26.0

These data show a decrease in the activity of trypsin inhibitors by 41.6 and 26.0% in natural chanterelles and honey agaric mushrooms (autumn) respectively.

Fig. 1 and 2 are chromatograms of volatile component samples.

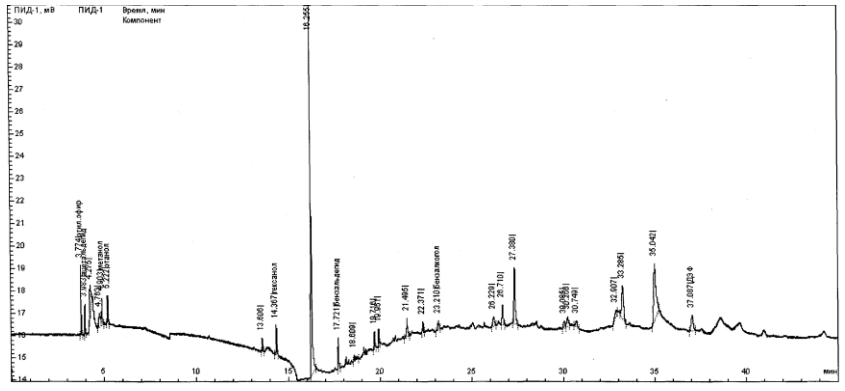


(a)

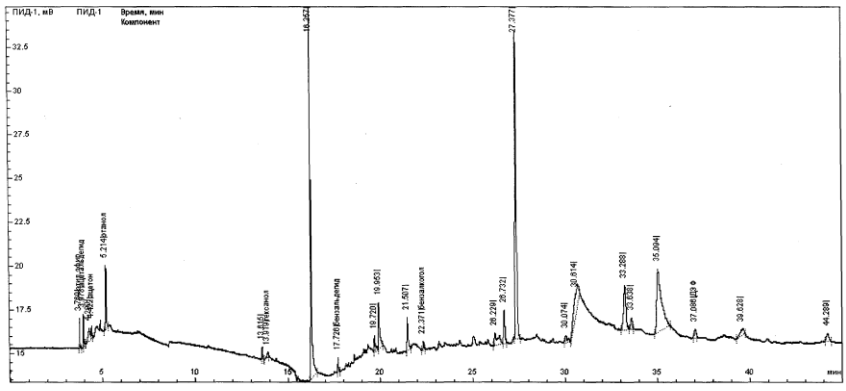


(b)

Fig. 1. Chromatograms of volatile samples of dried chanterelles: (a) vacuum impulse drying; (b) convective drying.



(a)



(b)

Fig. 2. Chromatograms of volatile samples of dried honey fungus: (a) vacuum-pulse drying; (b) convective drying.

In the study we found that treatment of mushrooms by vacuum-pulse method resulted in a decrease in comparison with the convective drying of the total volatile content of 45.7% and 55.6% in natural chanterelles and honey fungus respectively.

At the same time, the content of the treated samples increased in some volatile compounds: in agarics - hexanol benzalcohol, diethyl phthalate, benzaldehyde, ethyl ether, acetone; in chanterelles - ethanol and benzalcohol. Despite the fact that these substances are not key odorants of mushroom flavor, they can give an important and even decisive contribution to mushroom smell, changing it and adding new hints to it.

Thus, the vacuum-pulse treatment leads to increasing of free amino acids content and reducing the activity of trypsin inhibitors in edible mushrooms. Perhaps, this will increase the nutritional value of mushrooms, but the additional study of the product digestibility by a human body is needed.

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STUDY OF COMPOSITION AND BIOLOGICAL VALUE OF PINON KERNEL OF SIBERIAN PINE

M. A. Subbotina*, I. V. Dolgolyuk

Kemerovo Institute of Food Science and Technology (University),
bul'v. Stroiteley 47, Kemerovo, 650056 Russia,
* e-mail: smar08@mail.ru

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Abstract: The problem of rational use of natural resources and raw materials, and providing the population with nutritious foods is particularly important in regions that are characterized by bad environment. In this regard, unconventional plant material, in particular pinons of *Pinus sibirica* for the needs of the food industry will not only solve the problem of rational usage of natural resources and the creation of an additional amount of raw food, but also contribute to the extension of the range of general and functional food products. The purpose of study was to investigate protein, lipid, and mineral-vitamin complexes of pinon kernels. Molecular weight distribution of peptides and proteins was assessed by polyacrylamide-gel electrophoresis (PAGE) with Laemmli method. The quantitative content of water-soluble vitamins was determined using capillary electrophoresis system with the device Kapel-105", fat soluble vitamins - by high-performance reversed-phase liquid chromatography, mass fraction of macro- and microelements - by atomic absorption spectrophotometry. The relative content of individual fractions in the lipid complex was as follows: phospholipids - 7.9% mono- and diacylglycerols - 6.1%, respectively, sterols 2.7% - carotenoids - 0.9%, triterpene alcohols - 1.8%, free fatty acids - 1.1%, triacylglycerols - 71.2%. Proteins of pinon kernels are heterogeneous in composition, contain seventeen fractions, which have molecular weight ranging from 66.85 to 13.33 kDa. Carbohydrate complex consists essentially of digestible carbohydrates and has a high content of hydrolysable sugars from 4.6 to 5.0%, starch - 4.7±0.2%, pentosans - 1.8 ± 0.2%, and fiber - 2.3 ± 0.1%. In the mineral complex phosphorus, potassium and magnesium, iron, zinc, manganese, and copper are the predominant elements. The structure of vitamin complex includes tocopherols from 30.5 to 32.0 mg, vitamin A - 0.02 mg, and carotenoids - 0.8 mg per 100 g of lipids. The degree of meeting the daily need of human body in vitamins and minerals, when taking pinon kernels in food, is calculated. Research results allow us to recommend pinon kernels as poly-functional food raw materials with high content of technologically important components for the production of original premium products.

Key words: Pinon kernel, lipids, protein, mineral and vitamin complex, fatty acid composition, amino acid composition, polyunsaturated fatty acid of ω-6 family, linoleic acid, γ-linolenic acid

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INTRODUCTION

Climatic extremes and harsh working conditions, as well as high degree of anthropogenic and technogenic pollution have a significant impact on the health of the population of the Siberian region, contribute to the increased risk of formation of occupational and environmentally caused diseases. The negative effects of production and environmental factors are aggravated by improper nutrition. The nutritional status of the population of the Siberian region is characterized by insufficient in-take of proteins, dietary fiber, vitamins and minerals. The deficiency of vitamins B_1, B_2, B_6, C, E and minerals Ca, K, Zn and others was also revealed. In order to reduce the influence of physical factors of production and the effects of xenobiotics on the body it is necessary to include foods containing biologically important components of natural origin in the daily diet. When choosing such products, people should give preference to those that are made from local raw materials, most similar to geo- and biochemical composition of the human body, living in the particular climatic zone, and therefore more useful [1].

One of the most promising and innovative kinds of wild plant raw materials in the Siberian region are the seeds of Siberian pine (pinons). Pinons are widely known thanks to the unique food and biological value of their components. One of the tendencies of pinon kernels usage is their processing to produce cedar oil. Cake and hull remaining after oil extraction are secondary raw resources. From them you can get a diverse range of protein products both for direct consumption in human nutrition, and obtaining various types of food products.

In order to expand the areas of pinon kernel usage and their products in the food industry in the development of commercial, special, therapeutic and prophylactic foods, a deeper study of their chemical composition is necessary.

The chemical composition of the seeds of Siberian pine depends on the area of growth. The study of the composition and biological value of the seeds of Siberian pine (*Pinus sibirica Du Tour*) is going on to the present. It is high variability in composition and biological value of seeds of Siberian pine depending on

the zone of growth, which brings about an increased interest of scientists to their research. The knowledge of the composition and biological value of pinons kernel allows us to combine it with other plant and animal materials, and thus, approximate the contents of main nutrients in new products to the norms of physiological needs for the population of the Siberian region.

The purpose was to study the protein, lipid and mineral-vitamin complexes of pinon kernel of Siberian pine growing in the Kemerovo region.

OBJECTS AND METHODS

The object of study is the kernel extracted from different batches of seeds of Siberian pine growing in the Kemerovo region.

Mass fraction was determined by extracting them with the mixture of chloroform and ethanol in a Soxhlet apparatus, followed by the removal of the solvent, pre-drying at 103 ±2°C and weighing (GOST 23042).

The protein content was determined on the total nitrogen (protein) analyzer RAPID N ELEMENTAR, working according to Dumas techniques, the sample was burnt with the registration of total nitrogen in the thermal conductivity detector. To determine protein on the analyzer the sample was encapsulated, wherein the analysis accuracy was 0.5%.

For qualitative and quantitative determination of amino acid composition the system based on high performance liquid chromatography (amino acid analyzer) Aracus PMA GmbH was used. The method is based on post-column derivatization and consists in the separation of amino acids on the ion exchange column with the step gradient of pH and subsequent reaction with ninhydrin in the reactor. Detection of colored derivatives of amino acids is carried out using spectrophotometric detector with wavelengths 570 and 440 nm.

Molecular weight distribution of peptides and proteins was assessed by electrophoretic method in polyacrylamide gel (PAAG) by Laemmli techniques [2].

Special plates were prepared for PAAG polymerization, and chamber reservoirs for electrophoresis were filled with electrode buffering solution (0.066 M Tris, 0.19 M glycine, 0.1% SDS). Previously prepared sample analyzed was added to each well of the new-formed gel.

Sample preparation was as follows: 20 mkl of protein, 10 mkl of buffer for samples, and 10 mkl of distilled water were added to tubes of epindorf type. After the sample has been stirred and boiled for 5 minutes the device was turned on, and the separation of proteins was observed. Electrophoresis was performed at the current of 50 ± 0.1 mA and 75 ± 0.2 mA.

After electrophoretic separation the gel was washed and stained with the three reagents: first, with fixing solution, then with the solution of "washing" and only after that with the staining solution. Gel washing with each of the reagents was carried out for 10 minutes at the temperature of 80 ± 2°C. At the last stage gel bleaching was performed in distilled water at the temperature 25 ± 2°C.

Gels viewing and photographing was performed on UV transilluminator TCP 20M («Viber Lourmat»,) at the wavelength of radiation - 312 nm. Data storage and processing was carried out by gel-documenting system Vitran-Photo.

The obtained amino acid sequence of peptides was defined by automatic sequencer (Edman techniques). The method is based on the treatment of test phenyl isothiocyanate sample, which leads to the cleavage of one amino acid from the N-terminus of the sequence and its subsequent identification by liquid chromatography under pressure.

The separation of individual lipid fractions was performed by thin-layer chromatography. The system: hexane-diethyl ether-acetic acid in the ratio 80:20:1 was used as an eluent. Analysis was performed by ascending chromatography in a sealed chamber on the plates «Silufol». As the developer we used a 10% alcoholic solution of phosphomolybdic acid.

The quantitative content of water-soluble vitamins was determined by capillary electrophoresis on the device “Kapel 5”. This device is equipped with liquid capillary cooling system, and autosampler. Indications are determined off-line using spectrophotometrical detector based on the deuterium lamp and monochromator with the diffraction grating, the working range of wavelengths being from 190 to 400 nm.

Determination of fat-soluble vitamins was performed by reversed-phase high-performance liquid chromatography on chromatograph "Milichrom" with spectrophotometric detector in the spectral range 190-360 nm. The essence of the method lies in the extraction of vitamins from the sample under analysis by an extractant.

The mass fraction of macro- and microelements was determined by atomic absorption spectrophotometry on the device “Hitachi”.

RESULTS AND DISCUSSION

A distinctive feature of pinon kernels of Siberian pine is the variability of their composition, due to geologic and geographical, soil and climatic conditions of pine growth, pinon maturity, storage conditions, method of kernel separation and other factors [3, 4].

The chemical composition of pinon kernels of Siberian pine growing on the territory of the Kemerovo region is presented in Table 1.

Table 1. The chemical composition of pinon kernels of Siberian pine

Components	Mass fraction, % for absolutely dry matter		
	District		
	Yashkinsky	Tashtagolsky	Tisulsky
Protein	19.2±0.2	18.0±0.2	17.6±0.2
Lipids	60.5±0.5	62.5±0.5	62.6±0.5
Carbohydrates, including:	18.3±0.2	17.1±0.1	17.4±0.2
- hydrolysable sugars	5.2±0.2	4.8±0.5	5.0±0.3
- polysaccharides	13.4±0.2	12.3±0.4	12.4±0.2
Ash	2.5±0.1	2.4±0.1	2.4±0.1

The main component of the pinion kernels are lipids, the average content of which in studied raw materials was 62.5 ± 0.5% (based on absolutely dry matter). The absolute maximum of fat in the studied samples of pinon kernels of Siberian pine growing on the territory of the Kemerovo Region, amounted to 64.4% (pinons from Tisulsky District) and minimum to 60.5% (Yashkinsky district).

Lipid biological properties depend on the structure of triacylglycerols, as well as the presence of biologically active compounds, namely phospholipids and sterols. Phospholipids are involved in the construction of all cell membranes and cell organelles. Sterols and their esters are used for the synthesis of different physiologically active substances [5, 6].

Lipid complex of pinon kernels of Siberian pine appeared to be presented by spare and structural lipids. The relative content of individual lipid fractions in the complex was as follows: phospholipids - 7.9%, mono- and diacylglycerols - 6.1%, respectively, sterols - 2.7%, carotenoids - 0.9%, triterpene alcohols - 1.8%, free fatty acid - 1.1%, and triacylglycerols - 71.2%.

The biological efficiency of lipid complex of pinon kernels of Siberian pine is determined by the composition and amount of fatty acids (Table 2). The composition and the ratio of fatty acids in triacylglycerols of cedar oil define its physical-chemical, physiological properties, and digestibility.

Table 2. Fat - acid composition of cedar oil

Name of acids	Conditional Designation	Mass fraction,%	
		Average value	GOST 30623-98
Saturated, including:	-	7.7	-
- palmitic	$C_{16:0}$	4.4	3.0–3.9
- stearic	$C_{18:0}$	2.7	3.4–4.1
Monounsaturated, including:	-	24.1	
- oleic	$C_{18:1}$, ω-9	23.1	22.1–36.0
Polyunsaturated including:	-	67.9	-
- linoleic	$C_{18:2}$, ω-6	46.7	36.0–69.0
- α-linolenic	$C_{18:3}$, ω-3	0.3	0.3–0.4
- γ-linolenic	$C_{18:3}$, ω-6	20.1	18.0–24.3

Cedar oil extracted from the pinon kernels of Siberian pine contains acids of all groups - saturated, monounsaturated and polyunsaturated with a number of carbon atoms from 14 to 22. Palmitic acid prevails over other saturated ones in quantity, its maximum content in the studied samples of cedar oil does not exceed 4.4%. The ratio of stearic acid is almost two times smaller and ranged from 2.7%. Side by side with these saturated fatty acids in the cedar oil, there were identified myristic (0.2%), pektadecanoic (0.08%), arachic (0.2%), and behenic (0.1%) acids.

Oleic acid, the content of which was 23.1%, predominates over monounsaturated fatty acids in cedar oil. Oleic acid is involved in the synthesis of spare and structural lipids. Oils characterized by a high content of oleic acid contribute to the reduction of cholesterol and low density lipoproteins in blood [6]. Alongside with the cis-isomers of fatty acids cedar oil has in its composition a small amount of vaccenic acid (trans isomer) in an amount of 0.33 ± 0.02%.

Polyunsaturated fatty acids are contained in cedar oil mainly as those of acid ω-6 family: linoleic and γ-linolenic acid with high biological activity and are its essential nutrition factor. These acids are involved in the formation of structural lipids and various physiologically active substances. They are precursors of long-chain polyunsaturated fatty acids, the main natural source of which is the fish oil alone.

Since gamma-linolenic acid is associated with the increase in cholecystokynin and glucagon-like peptide hormone production, it causes the feeling of satiety and reducing food intake. Hypotensive, hypocholesterolemic, hypolipidemic, choleretic, wound healing action of cedar oil has also been associated with the activity of γ-linolenic acid. Despite the fact that the gamma-linolenic acid may be formed in the body from linoleic acid, its dietary intake is very important because the activity of enzymes (desaturases) converting linoleic to gamma-linolenic acid may be reduced with age under the influence of a number of factors [3, 7].

Phospholipids constitute the most complex and valuable group of structural lipids contained in vegetable oils. In lipid the complex of studied samples of pinon kernels, the amount of substances containing phosphorus compared to traditionally used in food oils is rather high and amounted to an average of 1.1 ± 0.1% in recalculation on stearooleolecitin. Furthermore, the unsaponifiable fraction of lipids of pinons kernel contains sterols (0.18%) and squalene (0.1%).

A relatively high protein content determines the nutritional value of the kernel of pinons. Protein content in pinon kernels is subjected to fluctuations and depends on the climatic conditions of growth and maturation [3, 4]. Within the Kemerovo region protein mass fraction averaged 18.2 ± 0.2% in the samples of pinon kernel. Protein fluctuations, depending on the zone of growth, ranged from 19.2 ± 0.2% (Yashkinsky district of the Kemerovo region) to 17.6 ± 0.2% (Tisulsky District of the Kemerovo Region).

Proteins of pinon kernels are spare proteins, and this determines their physical-chemical properties and the ability to be dissolved in various solvents. Qualitative and quantitative fractional composition of protein determines on the one hand the nutritional value and on the other, its functional properties.

The amount of extractable protein in the protein complex of pinon kernel is on average 71.5%, while the share of easily extractable proteins account for only 31.5% of the total protein. Salt-soluble protein fraction averaged 16.8%, water-soluble - no more than 14.7%, alkali-soluble - 40.0%. The amount of protein in the insoluble precipitate makes up 28.5%. This suggests that the consumption of pinon kernel as food protein will not be absorbed by more than 3/4.

Fractional composition of soluble proteins was evaluated using the method of Laemmli protein electrophoresis (Fig. 1).

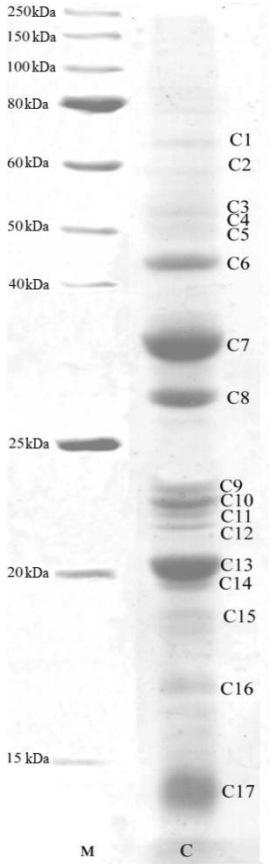

Fig. 1. Electrophoregram of aqueous extract by polyacrylamide gel electrophoresis (12% separating gel, 4% stacking gel): M - marker; C - in the rigging of low-fat kernels of pinons.

Electrophoretic studies of protein complex by method of Laemmli showed that proteins of pinons are heterogeneous in composition, contain seventeen fractions, the molecular weight of which fluctuates from 66.85 to 13.33 kDa (Fig. 1). The major proteins presented on electrophoretogram are proteins with the molecular weight of 32.16 kDa, 27.6 kDa, 20.14 kDa, 14.29 kDa. The amount of these protein fractions amounts to 49.76%. B6 fractions (molecular weight of 44.23 kDa) and B10 (molecular weight of 22.52 kDa) can also be attributed to the major proteins, as their percentage of the total amount is that of 8.70% and 6.88% respectively. According to their characteristics, they can be attributed to the hydrolysis products of larger protein fractions. Other proteins, whose content varies from 3.68 to 2.80%, have the molecular weight from about 13.33 to 66.85 kDa.

Nutritional value of pinon kernel is determined by its amino acid composition. The determination of the qualitative and quantitative composition of the amino acid protein complex of pinon kernel (Table 3) show that it contains all the essential amino acids, which accounted for not less than 36% and is characterized by high content of arginine, proline, aspartic acid and glutamic acid.

Table 3. The content of amino acids in the protein of pinons

Amino acid	Content, g / 100 g of skim dry matter	
	Average content	Fluctuation range
Essential amino acids:	36.14	36.1–36.25
valine	5.15	5.00–5.30
isoleucine	4.84	4.74–4.95
leucine	6.41	6.07–6.75
lysine	6.16	6.05–6.28
methionine	1.99	1.90–2.09
threonine	4.07	4.05–4.10
tryptophan	2.47	2.45–2.50
phenylalanine	5.05	4.95–5.16
nonessential amino acids	63.80	63.46–63.75
alanine	3.75	3.67–3.84
arginine	13.32	13.15–13.49
aspartic acid	13.04	12.98–13.11
histidine	2.68	2.65–2.72
glycine	4.42	4.40–4.45
glutamic acid	11.47	10.40–12.55
proline	7.50	6.74–8.26
serine	3.58	3.56–3.60
tyrosine	2.71	2.63–2.80
cysteine	1.33	1.15–1.51

Protein of pinon kernel surpasses wheat protein in the content of essential amino acids such as lysine, threonine, valine, methionine, tryptophan, and arginine, aspartic acid, and alanine as well. It is rather close to soybean protein in the content of valine, isoleucine, threonine, phenylalanine, and surpasses it in the content of tryptophan and arginine, but is inferior to soy protein in the content of leucine and glutamic acid from 1.2 to 1.5 times. Comparison of pinon kernel protein with animal proteins shows that the former like the majority of the vegetable proteins, is inferior to animal protein in the content of essential amino acids, but exceeds them in the content of arginine almost 2 (chicken egg) and 3 (cow's milk) times, being not inferior to the content of histidine and glutamic acid.

Carbohydrate complex of pinon kernel of Siberian pine growing on the territory of the Kemerovo Region, is characterized by high content of hydrolysable sugars and starches. In the group of sugars under consideration sucrose prevails from 4.6 to 5.0%. The amount of starch was 4.7% on average (the range of fluctuations is from 4.2 to 5.3%).

The content of individual fractions of dietary fiber, particularly fiber and swelling non-starch poly-

saccharides - pentosans. Pentosans are the building blocks of ribonucleic acids, which are concentrated in the kernel bud of pinons and ensure its special physiological function. According to the information received, the amount of pentosans averaged 1.8 ± 0.2%, fiber - 2.3 ± 0.1%. Thus, carbohydrate complex of pinon kernel consists essentially of digestible carbohydrates.

Phosphorus, potassium and magnesium are the predominant elements in the mineral complex of pinon kernel. High concentrations of these elements, as well as those of iron, zinc, manganese and copper favor the biological value of this kind of raw material. The mineral composition of pinon kernel is particularly low in calcium, potassium being predominant over sodium (Table 4).

Table 4. Mineral and vitamin complex of pinon kernel

Food substance	Average value of the food, mg / 100g	The degree of satisfaction of daily need of the human body, %
Macronutrients		
potassium	631.2 ± 0.2	25
calcium	26.6 ± 1.2	3
magnesium	306.0 ± 0.2	76
sodium	10.5 ± 0.7	1
phosphorus	986.7 ± 11.3	123
Trace elements		
iron	6.75 ± 0.8	67 – for males 37 – for females
manganese	8.8 ± 0.9	440
copper	1.3 ± 0.12	130
zinc	10.6 ± 0.9	88
Vitamins		
B_1	0.34 ± 0.02	23
B_2	1.07 ± 0.02	59
B_3	0.80 ± 0.05	16
B_5	2.50 ± 0.10	12
B_6	0.15 ± 0.05	7
E	30.20 ± 1.10	200

The data show that the degree of satisfaction of the daily needs of healthy adult male and female population in micronutrients is sufficient: the content of manganese and copper in 100 grams of kernels exceeds the needs of the individual and the content of zinc and iron is close to the standards. These elements possess important physiological functions: they have antioxidant properties and are involved in regulating the activity of several enzymes. Pinon kernels almost satisfy the daily needs in the content of magnesium and phosphorus being in excess quantity. Phosphorus is involved in many physiological processes, in cell regulation and regulation of acid-base balance. It is a part of phospholipids, nucleotides and nucleic acids and is required for the mineralization of bones and teeth. Magnesium is a cofactor of many enzymes involved in the synthesis of proteins and nucleic acids. It has the stabilizing effect for membranes and is required for calcium, potassium and sodium homeostasis support.

As food raw materials, pinon kernels are of interest in terms of their content of vitamins. By B-vitamin activity pinon kernels do not concede to such oilseeds as those of sunflower and soybeans, and exceed nut-like ones: walnuts, almonds, pistachios. It should be noted that in pinon kernel of Siberian pine in comparison with the above nut-like plants and oilseeds, vitamin B_2 (riboflavin) is 3 times more than thiamine. Vitamin B_2 is involved in redox reactions, increases the susceptibility of color visual analyzer and darkness adaptation [8, 9].

The consumption of 100 g of pinon kernels will satisfy the daily needs of human body per 59% in riboflavin, and per 23% in thiamine.

The structure of vitamin complex of pinon kernel include tocopherols from 30.5 to 32.0 mg per 100 g of product. Alongside with the total content the composition of tocopherol isomers is an important characteristic of the tocopherol isomers. In lipid complex of pinon kernels α-tocopherol share is on average of 52.2%, γ - 11.3%, δ - 36.5% of the total tocopherol amount. This ratio of various isomeric forms of tocopherols that differ between themselves by their biological and antioxidant activity, brings about adequate stand-bone lipid oxidation during storage and high biological activity of the product. The body can satisfy the daily consumption of vitamin E taking in 30-50 g of pinon kernels.

The content of vitamin A and carotenoids is insignificant - 0.8 and 0.02 mg, respectively per 100 g of lipids extracted from pinon kernels.

Research results allow us to recommend pinon kernels as multifunctional food raw materials with a high content of technologically important components for the production of original premium products.

Using seeds of Siberian cedar pine as a natural resource of many biologically and physiologically active components opens up great food industry perspectives to expand the range of products of high nutritional value and functionality.

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PROCESSES, EQUIPMENT AND APPARATUS FOR THE FOOD INDUSTRY

INTENSIFICATION OF BULK MATERIAL MIXING IN NEW DESIGNS OF DRUM, VIBRATORY AND CENTRIFUGAL MIXERS

V. N. Ivanets, D. M. Borodulin, A. B. Shushpannikov, D. V. Sukhorukov*

Kemerovo Institute of Food Science and Technology (University),
bul'v. Stroiteley 47, Kemerovo, 650056 Russia,
* e-mail: tppp@kemtipp.ru

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Abstract: Problem of obtaining mixtures from bulk materials is of current interest for various industries, thus, analysis of original designs of drum, vibratory and centrifugal continuous mixers is an actual scientific task. Mixers developed in Kemerovo Technological Institute of Food Industry (University) for processing of bulk materials are easy to manufacture, provide highly effective mixing of ingredients with a broad range of physical-mechanical properties in thin vibroboiling and disperse layers, with the organization of various leading (bypass) and recirculation flows. Presented designs of mixers have small dimensions and low energy costs. They make good smoothing ability of complex input fluctuations possible using volume dosing. Mixing process time in them does not exceed a few minutes, different bulk compositions resulting in a good quality. Drum mixers under consideration, are characterized by little influence on material to be mixed, and may be used in technological schemes requiring the minimum damage to particles. They have also small dimensions. To obtain bulk compounds with a high mixing ratio it is appropriate to apply centrifugal continuous mixers, characterized by high efficiency at small size and low energy consumption. The examined designs combine mixing processes in thin layers of diluted and dispersed flows and they have a high degree of smoothing ability of input material flows. Mixing process intensification in the designs of continuous mixers is carried out by organization of internal and external recirculation of leading flows and separation of input flows into several parts and their subsequent multiple intersection.

Keywords: Drum mixer, vibratory mixer, centrifugal mixer, mixing intensification, bulk material, mixing quality, recirculating of material flows

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INTRODUCTION

Present requirements to the quality of mixtures are characterized by a considerable increase of physical - mechanical and flavoring properties of a final product. It is therefore advisable to develop new designs of continuous mixers (CMs), equipped with appropriate dosing devices. The authors present a brief description and the analysis of new CM constructions of drum, vibratory and centrifugal types developed in Kemerovo Technological Institute of Food Industry (University). They are designed to receive bulk compounds with different ratios of ingredients. For example, drum mixers allow the mixture to obtain a good quality with the ratio of its constituent components not exceeding 1:40, vibratory - 1:100, and centrifugal from 1:100 to 1:500 respectively. These units are characterized by high smoothing ability (inertia), low specific metal and energy costs, high intensity of mixing process, due to the organization of guided movement of thin material flows in conjunction with timing and recirculating. These units are suitable as the basic components for continuous mixing both separately and in any combinations thereof. For this, it is required when producing mixtures, e.g., with the ratio of ingredients of 1:1000 to incorporate serially arranged continuous drum (mixing ratio 1:10) and vibratory (at the ratio of 1:100) mixers. The objective of the article is to acquaint the audience of scientists and engineers of food, chemical and allied industries with new constructions of drum, vibratory and centrifugal continuous mixers to produce bulk compounds with different ratios of ingredients.

OBJECTS OF STUDY

In the first stage, the construction of continuously operating drum mixers will be analyzed.

Continuous drum mixer manufactured by the Certificate of Authorship no. 1592024 [13] can be used for the production of bulk compositions in food, agricultural and other industries. This unit is the first in a series of drum mixers with Г - shaped blades inside a rotor. First, the design and operation of this machine will be considered.

A drum mixer (Fig. 1) consists of frame *1*, mixing drum *2*, in which central shaft *4* is fixed in the centering supports *3*. Blades 5 are located on the shaft. The frame is equipped with loading pipe *6*, drive *7* and mechanism *8*, allowing the drum angle to be changed.

Blades *5* in the cross-section are Г-shaped. Mixing unit performance is as follows. Powdery components are put into the mixer by loading pipe *6*. When drum *2* rotates, powdery components move down along Г-shaped blades, simultaneously along its two guides. In addition to the separation of bulk material into two unequal flows on each blade, there takes place its circulation along the length of the drum. The movement of material occurs in the axial direction towards the discharge because of the presence of long blade sides in the mixing area. At this point, there is some mixture internal circulation, making a good smoothing ability of input components pulsations possible.

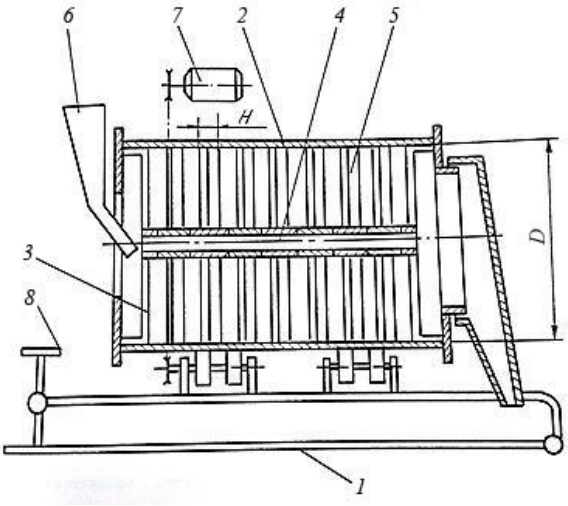

Fig. 1. Continuous drum mixer (Certificate of Authorship no.1592024): (*1*) frame, (*2*) drum, (*3*) centering supports, (*4*) shaft, (*5*) blades, (*6*) loading pipe, (*7*) drive, (*8*) tilting mechanism.

The analysis of this construction revealed inadequate longitudinal movement of the components to be mixed due to poor bulk material recirculating, resulting in a slight homogeneity of flows inside the drum. In addition, while stirring the particles having differences in density and dispersion are segregated. All this reduces the quality of the final mixture. To intensify the process of mixing and to increase the residence time of material particles in the unit, it is necessary to provide mixture recirculation. We propose to install Г – shaped blades on the shaft rotating relative to each other at 360°, being located in a spiral or staggered manner (RF Patent 2508937 [7]). This leads to an increase in the mixture chaotic transverse movement, favors its overall homogeneity, and improves the quality of final product.

The mixer (Fig. 2) consists of drum *1*, with fixed centering supports *2* therein, central shaft *3*, which has Г –shaped blades *4*. Frame *5* is provided with loading *6* and discharge *7* pipes.

The drum mixer performance is as follows. Powdery ingredients enter the mixer by loading pipe *6*. As the drum *1* rotates, they go down from the surfaces of Г-shaped blades while moving simultaneously along the two drum guides *1*. In addition to the separation of bulk material into two unequal flows on each blade, the circulation of mixed components takes place along the length of drum. The main flow of material moves towards the discharge in the axial direction, big sides of the blades being on this side. Turning Г-shaped blades relative to each other by 360°, we install them staggered (Fig. 3) or in a spiral manner (Fig. 4). When Г-shaped blades are installed staggered the bulk material is divided into two flows, one of which moves to the previous blade, and overlaps the second flow from thereof. As a result, split flows repeatedly overlap each other, favorably affecting the overall quality of mixture homogeneity. When the blades are installed in a spiral manner, part of the components is gradually returning to the original point of its movement. This provides three-dimensional internal circulation and smoothing of input materials pulsations. The final mixture is put out from the mixer through discharge pipe *7*.

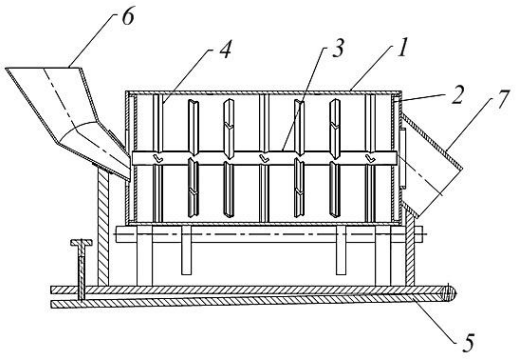

Fig. 2. Continuous drum mixer (Patent RF no. 2508937): (*1*) drum, (*2*) centering supports, (*3*) shaft, (*4*) Г– shaped blades, (*5*) frame; (*6*) loading pipe; (*7*) discharge pipe.

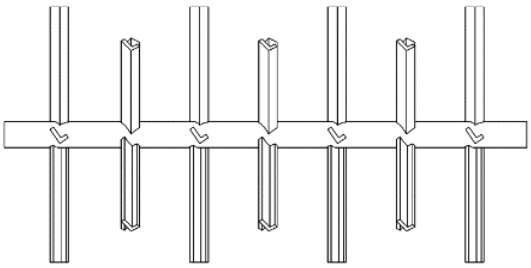

Fig. 3. Blades located staggered.

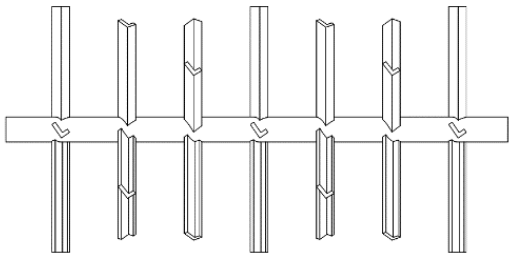

Fig. 4. Blades located in a spiral manner.

Thus, the multiple imposition of the flow of material inside the unit provides powder formulations of given quality. The proposed unit may operate in

batch mode too. In this case, the drum is installed horizontally. The circulation of flows along the length of the drum is retained therein as the axial flow generated by the difference in length and density is compensated by the counter flow obtained by the rolling of material at the angle of repose. Besides, the location of blades staggered increases the efficiency of material mixing with large fractions, while location of blades in a spiral manner provides material mixing with smaller fractions.

In the second stage, several constructions of continuous vibratory screw mixers that look like vertically mounted screws will be considered.

The first representative of this class is the mixer [9], schematically shown in Fig. 5. Components are put into the unit through pipe *1* to the upper chute of a perforated working body *2*, where under the influence of screw vibrations, they form a helical layer, and are simultaneously sieved through perforations to underlying chutes and discharge pipe *5*. One part of bulk material recirculates up through the chute. This flow is necessary to be reduced because it is influenced by local heterogeneity arising during mixture segregation and input flow fluctuations. The lower chute *6* performs the function of collecting, mixing, and guiding of final product to discharge pipe *5*. The movable plate *4* is intended to recover pipe *5* when we start mixing before initiating stationary operating mode. After achieving optimal "boiling layer" height (10-50 mm) on the chutes, the plate is removed. Optimal height of "boiling" layer on the working body is achieved by the vibration parameters change, which affects the amount of the main and reverse flows, and their adjusting by plate *4* to the discharge pipe active section.

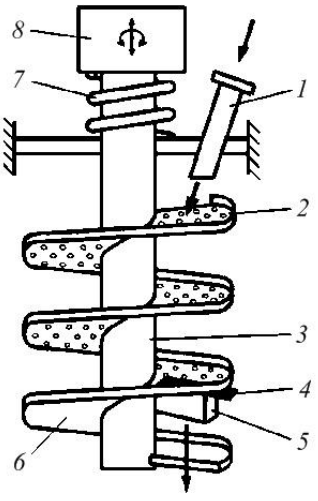

Fig. 5. In-line vertical screw vibratory CM with recirculation (Certificate of Authorship, USSR, no. 1674943): (*1*) loading pipe, (*2*) screw perforated tray, (*3*) bearing cylindrical column, (*4*) damper, (*5*) discharge pipe; (*6*) continuous spiral chute, (*7*) amortization connections, (*8*) vibrating drive.

Fig. 6 schematically shows an improved vibratory mixer with increased performance stability, protected by the USSR Certificate of Authorship, no.1793956 [10]. This stability is achieved in that the outer edge *7* of spiral chute is made inclined with alternating arrangement of perforated *8* and non-perforated *9* areas therein.

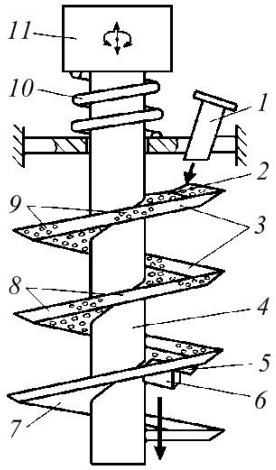

Fig. 6. In-line vertical screw vibratory CM with recirculation (Patent RF no.1793956): (*1*) loading pipe, (*2*) screw perforated chute, (*3*) outer inclined side, (*4*) bearing cylindrical column, (*5*) damper, (*6*) discharge pipe, (*7*) continuous screw chute, (*8*) non-perforated side areas, (*9*) perforated side areas, (*10*) amortization connections, (*11*) vibrating drive.

The ingredients are mixed simultaneously in the vibroboiling layer on the perforated working body in the unit and pour through the holes. The more is the humidity of components the less is their flow through the holes, causing a rise in the layer height on the chute. This phenomenon also occurs when the volume of input components entering through inlet *1* on to the upper chute of the working body increases. The growth of the height of bulk material layer leads to the increase of its width by tilting the external side *3*. The holes *9* located on its surface start to work too.

Due to this, there occurs a flow increase through the chute perforations with layer height decreasing thereon. Conversely, while reducing the humidity of components or the volume of material entering the mixer, chute height and width also decrease, and the number of perforations, involved in the process decrease respectively. There arises a "feedback", which adjusts the layer height of the material distributed on mixer chutes. Because of this, the stability of mixing process increases. Alternation of perforated *9* and non-perforated (solid) *8* sections, does not allow material particles to slip the mixer from upper chutes directly to discharge pipe under control. This construction (Fig. 6), as compared with the previous one (Fig. 5) provides increased yield of the final product due to increased process stability.

However, we failed to overcome the tendency of discussed screw mixers to uneven chute loading with bulk material. This contributed to the beginning of the development of a new series of units, which lack this drawback. They have constant height of dispersed phase layer on chutes, high stability and good smoothing ability of input concentration fluctuations of

ingredients. Vibratory mixer [11] shown in Fig. 7 is one of the latest representatives of this group. Its working body consists of two parts: the main part *3* mounted on a vertical bearing support 1 from outside and the additional one *5* mounted therein. The outer part has a lifting in the direction of the movement of bulk material, and the internal one – a slope. The input components are put into screw chute *5*. Under the influence of guided fluctuations, they roll over it to the hole in the pipe wall *1*. As a result of ingredients sifting through perforations on the bottom row of chutes, there occurs prior compound homogenization. Further, they go to the lower continuous chute of the main working body, on which mixture as it moves upward to outlet *5*, is graded up in vibroboiling layer. The availability of an additional working body *5*, leads to an increase not only in the unit performance, but also in the mixture quality by increasing the length of working surface.

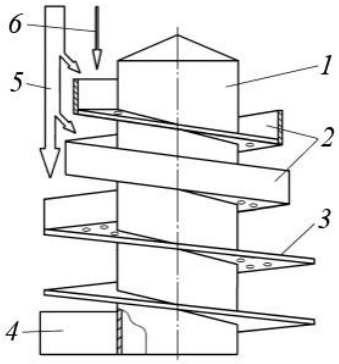

Fig. 8. Modernized additional working body: (*1*) cylinder, (*2*) narrow screw chute, (*3*) wide chutes, (*4*) guiding plate, (*5*) additional component, (*6*) key component.

To extend the range of ratios of mixed ingredients in the next invention a method of "serial dilution" is used. Thereby the width of upper chutes of additional working body [12] was reduced. On its narrow chutes *2* (Fig. 8) it is advisable to pre-mix ingredients, their share in the composition being small, or to add ingredients with the lowest consumption *6* and part of the bulk mass *5*. Later semi-finished product is incorporated to the remaining part. The amount of dilutions depends on the initial ratio and mixing conditions. There are two of them in Fig. 8. In this case, the chutes *2* are made with the width proportional to the total consumption of components. Vibrating layer thickness on the chute is maintained in the range of 10-30 mm. Under the influence of force impulses, components are transported along the inclined side and mix therein. Some of the material moves through the perforations to the lower chute, then, the next part goes in. The process of the components "serial dilution" on the narrow chutes *2* is followed by their pre-mixing on wide chutes *3*.The mixture moves through the hole (Fig. 7) on to the lower continuous chute of the outer spiral chute 4. Henceforth the process is similar to that of previous design.

In general, surface perforating of mixing elements is designed to smooth concentration fluctuations in compounds, which takes place due to its movement on the chutes. This is important for discrete measuring out of components. With vibrating layer being created due to air leaks through the holes underneath the layer there is an increase in the rate of bulk materials transportation and reduction of required vibration parameters.

At the final stage, we will analyze the constructions of continuously operating centrifugal mixers, different from those of other types of mixers. They have higher performance at low energy and material costs and are characterized by high mixing process intensity that takes place in thin layers under the influence of centrifugal force. Basic requirements for CMs (providing quality mixing, good smoothing ability, high capacity, low metal and energy costs and others) are satisfied in these centrifugal mixers. A number of these mixers developed by us meet all the above requirements through organization of guided flow movement structure of material in the working chamber of the mixer.

A distinctive feature of the developed CMs is the presence of a rotor, made in the form of a hollow truncated cone, or a combination of cones, as well as in the form of special devices to create recirculation or leading flows.

The first representative of the centrifugal CMs [8], we have developed is shown in Fig. 9.

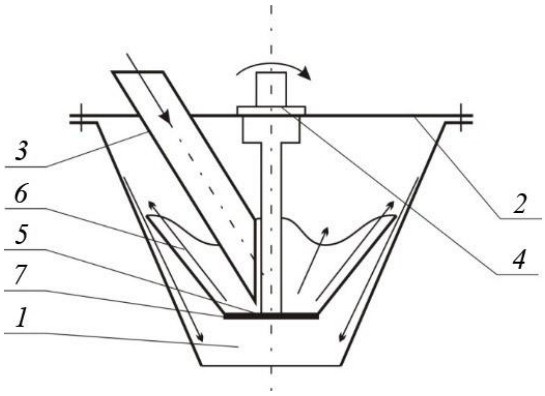

Fig. 9. Centrifugal mixer with wavy edged rotor (Patent RF no. 2361653): (*1*) casing, (*2*) cover, (*3*) loading pipe, (*4*) bearing connection, (*5*) shaft, (*6*) wavy edged rotor, (*7*) rotor disc.

The mixer operates as follows. Bulk materials are put into to spinning rotor disk *7* through pipe *3*. The weight of bulk components, under the influence of centrifugal force is distributed uniformly over disc *7*, moving to the inner surface of cone *6*. This results in a thin-layer movement of free-flowing components and facilitates partial mixing of materials. While "spreading" on the surface of cone *6*, bulk material moves to its upper wavy edge, the configuration of which facilitates the creation of an additional mixing effect in crossed material flows because the total annular material flow is poured from conical surface at different time intervals. Thereafter, dry bulk material flow is divided into several parts, overlapping each other subsequently in the annular space between the casing and the rotor of mixer. Thus, the unit's

smoothing ability and mixing intensity are greatly enhanced without additional energy consumption. The final mixture goes to the inner surface of casing 1 and is discharged from the unit.

Its disadvantage is low residence time of particles in the unit. This does not allow high-quality mixture to be obtained at the ratio of components to be mixed more than 1:80. To solve the problem we installed an extender on the shaft (below the rotor) in the form of perforated double stroke screw located in cylindrical pipe, which is connected with the outlet of conical casing (Fig. 2). This increases the residence time of material in the unit and, consequently, increases mixer smoothing ability that makes mixture components batch dosing possible.

Centrifugal - screw mixer performance (Fig. 10) [2] is as follows. Free-flowing materials are put into the spinning rotor disk *7* through pipe *3*. Bulk components, under the influence of centrifugal force are distributed uniformly over disc *7*, moving to the inner surface of cone *6*. Thus, the thin-layer movement of bulk components takes place facilitating partial material mixing. While "spreading" on the surface of cone *6*, bulk material moves to its upper wavy edge, the configuration of which facilitates the creation of an additional mixing effect in crossed material flows because the total annular material flow is poured from the conical surface at different time intervals. The material moves along the inner surface of the casing *1* to the outlet pipe *9* and goes to perforated screw *9*. Owing to the fact that when shaft rotates, screw chutes lift the material upwards, the latter is recirculated. Part of the material pours through screw perforations and a gap between the screw and the pipe down, and it goes out from the mixer as the final mixture form. The proposed constructive solution allows increasing material residence time in the mixer. The smoothing ability of the unit increases too. In other words, mixing process in the proposed construction takes place in two stages and makes batch dosing of components possible.

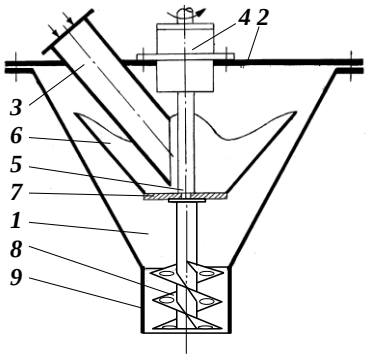

Fig. 10. Centrifugal-screw mixer (Patent RF no. 148608): (*1*) conical casing, (*2*) cover, (*3*) loading pipe, (*4*) bearing connection, (*5*) shaft, (*6*) cone, (*7*) disc, (*8*) perforated screw chute, (*9*) pipe.

Besides we increase residence time of material in the rotor and, consequently, improve the quality of final product by the engineering solution in accordance with RF patent no. 2496561 [1]. On the inner surface of cone there must be installed angle-like baffles located at different angles to the axis of rotation, on the outer one there must be fixed a scattering disk, and on the inner surface of the mixer casing - perforated guides. Due to the different lengths and angles of the angle-like guides, bulk material trajectories are repeatedly intersected, thereby increasing the residence time in the unit, and its smoothing ability.

The mixer, shown in Fig. 11 operates as follows. Bulk materials are put onto the base of rotating cone *8* through pipe *3*. Under the influence of centrifugal forces bulk particles move with acceleration from the central part to the periphery evenly spreading along its inner surface. Thus, the thickness of layer at the periphery becomes smaller. This is due to the increase of the surface of particle distribution. Material flows are reflected from angle-like baffles *9*, which vary in length and angle of slope. This design promotes formation of an additional mixing effect in crossed material flows as the annular flow of material is divided into pieces, overlapping each other subsequently. Thereby greatly increases smoothing ability of the unit and intensity of mixing process without additional energy consumption. Then, mixture, dropping through upper base of hollow truncated cone *8* is put into perforated guides *10*, and divided into two parts, one of which is poured through the holes to the bottom of the conical base of casing *6*, and the other part is supplied to scattering disc *11*. Material particles are cast away from the scattering disc to the walls of casing *1*. They are intersected with the flow which has passed through the holes in the perforated guides *10*, creating additional mixing thereby. The final mixture is discharged from the unit through pipe *7*.

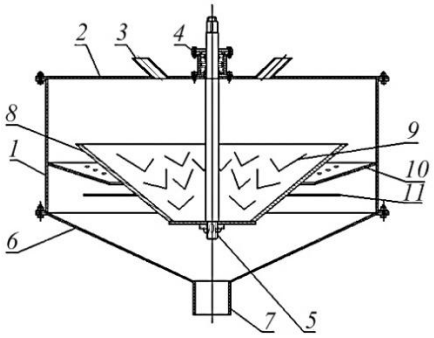

Fig. 11. Centrifugal mixer with angle-like baffles (Patent RF no. 2496561): (1) casing, (2) cover, (3) loading pipes, (4) bearing connection, (5) shaft, (6) conical bottom, (7) discharge pipe, (8) rotor, (9) angle-like baffles, (10) perforated guides, (11) scattering disc.

In addition, the intensification of mixing process can also be achieved through the installation of a flexible screw on the outside of the mixer (RF patent no. 2523576 [7]). This provides the external recirculation of material flow back into the working area, where it is mixed with the original components in the unit, the quality of resulting mixture being improved.

Centrifugal flexible screw mixer (Fig. 12) performance is as follows. Bulk components are fed through pipe *3* onto rotor base *8*. Under the influence

of centrifugal force, bulk material is evenly distributed across the base of rotor disc *8* from the center to the periphery, then, it moves to and along the cone surface upwards. The main annular material flow moves over cone surface, getting into the space between mixer casing and rotor. Material on the elliptical bottom *4* is divided into two parts, one of which (final mixture) is discharged from the unit through discharge pipe *9* by means of agitators *7*. Another one goes to flexible screw *10*, along which it rises and goes again to the basis of rotating rotor *8*, where it is mixed with the main material flow entering through loading pipe *3*. This results in the external flow recirculation and homogenization of material, the quality of the final mixture being increased.

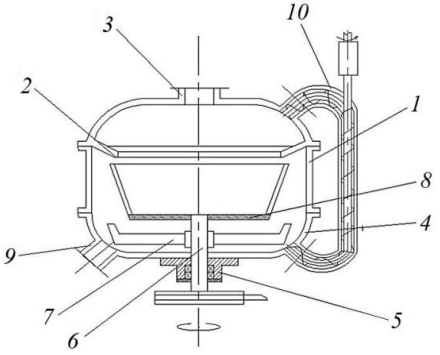

Fig. 12. Centrifugal mixer (Patent RF no. 2523576): (*1*) casing, (*2*) cover, (*3*) loading pipe, (*4*) elliptical bottom, (*5*) bearing connection, (*6*) shaft, (*7*) agitators, (*8*) rotor; (*9*) discharge pipe, (*10*) flexible screw.

A common shortcoming of centrifugal mixers is the fact that under the influence of centrifugal force finely dispersed components in mixture move upwards, leading to partial stratification (segregation).

To eliminate this drawback and to increase the intensity of mixing process, we propose to install a guiding diffuser in the mixer [3], which creates the predetermined movement of dusty flows. Besides, this engineering solution allows us to eliminate stagnant areas in the rotor center, increase the duration of material particles movement inside the unit, and significantly reduce the degree of segregation.

Fig. 13 is a perspective view of the centrifugal mixer with a guide diffuser, whose operation is as follows. Bulk components go to the rotating rotor disk base *9* through loading pipe *3* and uniformly spread out thereon, under the influence of centrifugal force. Hereinafter, the particles move upwards along the surface of thin-walled hollow truncated cone *10*. At the beginning of the movement of components along the cone *10* superfine particles start to go to dusty area, and the main material flow continues to move along its surface. After superfine particles have risen upwards, they go round the guide diffuser surface *4* and urge towards the center of rotor, where they are mixed with new material flow moving along the rotating cone surface *10*. Having reached its upper edge, under the influence of centrifugal force, the final mixture is discharged into the space between rotor and casing *1*, getting to the bottom of mixer *5*. The final mixture is removed from the unit by unloading blades *8* through discharge pipe *6*.

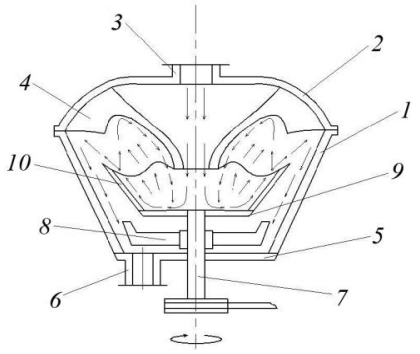

Fig. 13. Centrifugal mixer with guiding diffuser: (*1*) casing, (*2*) cover, (*3*) loading pipe, (*4*) guiding diffuser, (*5*) mixer bottom, (*6*) discharge pipe, (*7*) shaft, (*8*) blades, (*9*) rotor disc, (*10*) cone.

The above mentioned construction of one-cone centrifugal mixers allow us to obtain predetermined quality at the mixture ratio of mixed components in the range from 1:80 to 1:200, which is slightly reducing their application. When preparing mixtures with proportions of ingredients of about 1:400 it is necessary to increase significantly residence time in mixer working area while increasing unit smoothing ability. To achieve this goal, we propose to install additional cones, and to fix reflectors in the form of one-size individual elements of the torus on their inner surface, the latter being located on different cones staggered with respect to each other. When material passes over all the cone surfaces, residence time of particles in the unit increases. Besides, it increases because of mixture recirculation at the middle and outer cones, which beneficially affects the quality of finished product.

Fig. 14 is a perspective view of centrifugal continuous mixer [4] and its conical rotor isometric projection. The mixer operates as follows. Mixed materials go on to the inner cone base *8* through the loading pipe *3*. Cone angles of slope and guide height are increased from the center to the periphery of rotor. Bulk materials under the influence of centrifugal force move from the center to the periphery of disk, and then– to cone surface *8*. After that, they pass to the middle cone surface *9*, where the flow is partially split, one part of which is moved to reflectors *11* of the middle cone *9*, and to its base, resulting in bulk materials reverse recirculation and higher accumulating capacity of the unit. Under the influence of centrifugal force, the other part of material goes to the outer cone *10*, where the flow of material is similarly divided into parts, one of which is cast away to casing *1*, and the other, thanks to deflector elements - to cone base *10*. By mounting these reflectors staggered at the middle and outer cones *9* and *10* partial recirculation of material flow is generated. The final mixture is poured into the conical area of casing *1*, and is then put out from there through discharge pipe *4* with blades *12*.

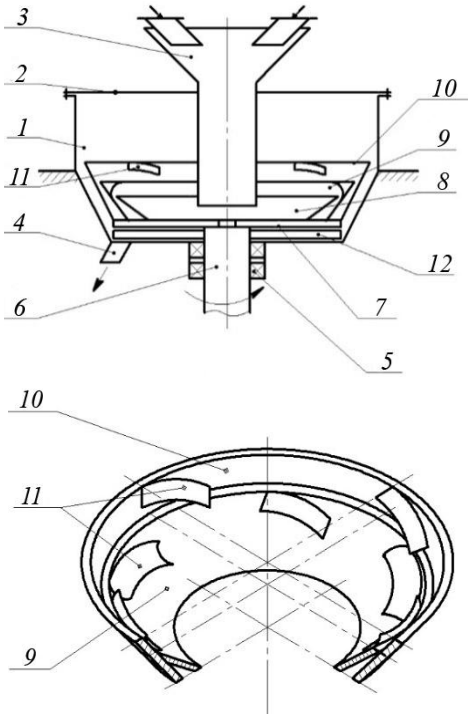

Fig. 14. Centrifugal mixer (Patent RF no. 2455058): (*1*) casing, (*2*) cover, (*3*) loading pipes, (*4*) discharge pipe, (*5*) bearing connection, (*6*) shaft, (*7*) rotor disc, (*8*) inner cone, (*9*) middle cone, (*10*) outer cone, (*11*) torus reflectors, (*12*) discharge agitations

When the influence on processed materials containing conglomerates is not intensive enough it is difficult to obtain a final product of high quality. Therefore, to increase the quality of final mixture, dispersing capacity of the mixer must be increased.

We propose to intensify the process of mixing and dispersing of dry bulk materials containing conglomerates by their multiple destruction and dispersion with conical blades installed on the rotor. This constructive solution makes mixing in thin dispersed layers of equal thickness possible, ensuring uniform loading in rotor cones, and mixing at the level of individual particles and micro-volumes.

A general view of a centrifugal mixer dispersant [5] and its isometric view of the rotor are shown in Fig. 15.

The mixer operates as follows. The input bulk materials go through loading pipe *3* to the rotating conical blade containing four agitators *11*, destroying conglomerates of bulk components. Thereafter, loosened and crushed mixture constituents under the influence of centrifugal force move along the inner surface of cone *8*. Mixed components move along the surface of the middle cone *9*. Having reached its periphery, material flows and the remaining conglomerates go to the surface of dispersing blades *12*, where additional destruction and mixing of bulk materials take place. Then, grinded and mixed components go to the surface of outer cone *10*, where the same process of mixing and dispersing is repeated. Under the influence of centrifugal force, mixture from cone *10* goes to the lower part of casing *1*, and is removed by agitators *13* through discharge pipe *4*.

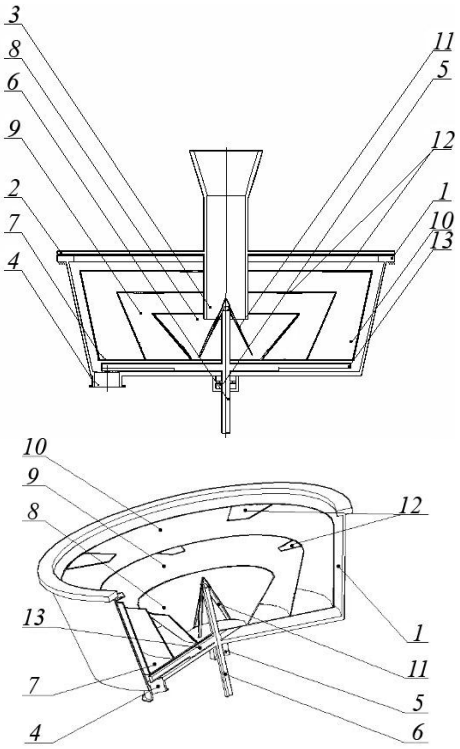

Fig. 15. Centrifugal diffuser mixer (Patent RF no. 2464078): (1) casing, (2) cover, (3) loading pipes, (4) discharge pipe, (5) bearing connection, (6) shaft, (7) rotor disc, (8) inner cone, (9) middle cone, (10) outer cone, (11) conical blade, (12) dispersing agitators, (13) discharge agitators.

CONCLUSIONS

1. Drum mixers under consideration are characterized by small influence on mixed material. Therefore, they should be used in the technological schemes, requiring the least damage to particles. They provide the maximum degree of smoothing of input flow fluctuations as compared with the vibratory and centrifugal mixers. These units can be used together with vibratory or centrifugal mixers to obtain mixtures with a large ratio of mixed ingredients.

2. CMs have the greatest practical importance among the constructions of vertical lift screw vibratory mixers presented in Fig. 7 and 8. They are easy to manufacture, can effectively mix ingredients with a wide range of physical-mechanical characteristics in a thin vibroboiling layer and have small dimensions.

3. To obtain bulk compounds with a large mixing ratio it is expedient to use continuous centrifugal mixers, characterized by overall high efficiency at low dimensions and energy consumption costs. CM constructions under consideration combine mixing processes in thin layers of diluted and dispersed flows and have a high degree of error smoothing in the input material flows.

4. The intensification of mixing process in the considered CM structures is carried out by the organization of internal and external recirculation of leading flows as well as the separation of input flows into several parts with their subsequent multiple intersection.

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FOOD HYGIENE

CONFECTIONERY GOODS FOR HEALTHY DIET

G. A. Dorn[a,*], T. V. Savenkova[b], O. S. Sidorova[c], O.V. Golub[d]

[a] State Agricultural University of Northern Zauralie,
Republic Street 7, Tyumen, 625003 Russia
*e-mail: tovar-kemtipp@mail.ru

[b] The State Scientific Universe Scientific Research Institute of the Confectionery Industry,
Elektrozavodskaya Street 20, Moscow, 107023 Russia

[c] Russian State University of Trade and Economics,
Kemerovo Institute (branch),
pr. Kuznetskiy 39, Kemerovo, 650992 Russia

[d] Siberian University of Consumer Cooperation,
pr. K. Marx 26, Novosibirsk, 630087 Russia

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Abstract: Confectionery goods are in great demand with different population groups, especially children both in Russia and other countries. This group of products can be considered as a convenient carrier of vital nutrients, the lack of which in the diet of the population in Russia, including preschoolers and school children is a serious problem. The market research of enriched confectionery goods has been carried out in the study. The relevance and demand of the development of given kinds of confectionery goods have been presented; their selection and recipe composition have been proved. The dynamics of the market development is carried out due to imported goods, which indicates the need for the production of domestic products. A group of specialized confectionery goods with various functional orientations was investigated. They are yogurt powder-based candies "Talantiki", enriched with vitamins and minerals; panned sweets "Dr. Konfetkin", sponge cakes and semi-finished goods with local herbs and vitamins. Their recipe composition was scientifically determined, taking into account the characteristics of the active ingredients and their synergistic effects on metabolic processes. The research of consumer properties of specialized goods has been made, which allowed to determine regulated quality indices, including the nutritional value and functional orientation. The testing has been put into practice in the conditions of commercial production. The developed products may be important for the correction of the nutrition and health of both children and adults with impaired nutritional status.

Keywords: Specialized confectionery goods, recipe composition, nutritional value, functional orientation

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INTRODUCTION

Confectionery goods represent a large group of high-calorie foods that are in great demand with different population groups, especially children. However, the physiological value of confectionery, as a source of essential nutrients is small. They contain large amounts of fat (from 5 to 35%), carbohydrates (47 to 100%), the main part of which is sucrose (39.6–100%), starch (34.7–66%) and small amounts of protein (from 3.2 to 10.4%). Energy value ranges from 350 to 528 Kcal, and depends mainly on the set of recipe ingredients (flour, egg and milk products, various additives - nuts, soybeans and others.)

Excessive consumption of these products disturbs the balance of the diet in terms of nutrients as well as energy value. A significant drawback of confectionery is the virtual absence of these important biologically active substances, like vitamins, carotenoids, macro- and microelements. Available scientific studies show that 100 grams of flour confectionery goods provide about 4–5% of the daily requirement of vitamins B1, B2, and PP. Also it is noted a slight mineral content. At the same time, their contribution to the total dietary energy intake at this level may reach 18-20%. A similar pattern is typical for other groups of confectionery goods [6–8].

The frequency of confectionery consumption by children and adult population in Russia is currently quite high. This is confirmed by the results of an epidemiological study conducted by the Research Laboratory of the structure and nutrition planning of RAMS led by Ph.D. A.K. Baturina.

It was found that 20–25% of children and 6-13% of adults regularly consumed commercial flour confectionary goods, 5–12% - sugar products. Among flour confectionery goods the preference is given to butter cookies (2.5–9.3% of respondents), cakes (3.8–6.4%), wafers and crackers (1.3–3.1%). Children

and teenagers prefer chocolates (more than 6% of respondents), older people – hard sugar sweets [6–7].

The transformations in the confectionery market that have occurred in recent years largely changed the traditional approaches to this group of products. Confectionery goods from high-calorie desserts are gradually becoming important and popular part in the diet of all age groups. They are increasingly being used in the school lunch assortment list. The demand for confectionery of dietary and prophylactic purposes is increasing [1–5].

The presented data strongly suggest that confectionery goods require substantial change of their chemical composition towards increasing the content of vitamins and minerals, dietary fiber and other essential nutrients, while reducing the energy value. This group of products can be considered as a convenient carrier of vital nutrients, the lack of which in the diet of the population, including preschoolers and school children is a serious problem.

OBJECTS AND METHODS OF RESEARCH

The objects of the study are the raw ingredients, semi-finished products, test and manufactured samples of confectionery goods; representative groups of the population.

The general and specific test methods of quality and safety of specialized products were used. To identify consumer preferences the questionnaires were applied. The studies were conducted in 5–7 multiple replicates and the obtained data were processed statistically using computer programs.

RESULTS AND DISCUSSION

To determine the assortment of products and the ways of usage the market research of flour and sugar confectionery goods has been conducted in Kemerovo.

Figure 1 shows the proportion of flour and sugar confectionery goods in the assortment of the investigated products. Flour confectionery is the largest share - 20 items, sugar - 8 items.

Figure 2 shows the prevalence of foreign manufactured goods - 56.6% compared with domestic products - 44.4%.

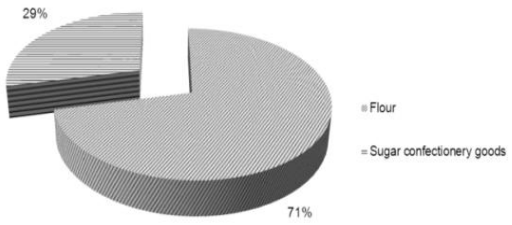

Fig. 1. Proportion of flour and sugar confectionery goods in the assortment.

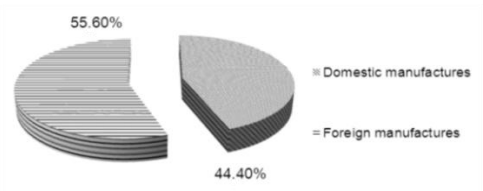

Fig. 2. Proportion of domestic and foreign manufactures.

Insufficient assortment of sugar confectionery goods of functional orientation was marked. They are hard sugar sweets and toffee candies as a rule. Such group of confectionery goods as panned sweets with high demand in the consumer market is virtually absent in the assortment.

Analysis of functional foods has shown that the enriching additives (%) are used such as iron - 7.25; calcium - 8.7; phosphorus - 2.9; magnesium - 1.44; iodine - 2.9; dietary fiber - 4.35; vitamin C - 15.94; B vitamins - 14.49; vitamin E - 14.49; vitamin A - 13.04; dietary bran - 1.45; folic acid - 1.45; inulin - 1.45; vitamin H - 1.45; pectin - 1.45; probiotics - 7.25.

It demonstrates the need for expanding the assortment of enriched confectionery goods from the point of view of modern Nutrition Science and demand for these products with the population.

A group of specialized confectionery goods with various functional orientations was investigated e.g. yogurt powder-based candies "Talantiki", enriched with vitamins and minerals.

The recipe composition of a candy in mg for one item is the following: premix of B vitamins 44–05 - 20, including: vitamin C (ascorbic acid) - 5, vitamin A (retinol acetate) - 0.0715, vitamin E (tocopherol) - 0.788, vitamin D3 (cholecalciferol) - 0.00036, vitamin B1 (thiamine) - 0.125, vitamin B2 (riboflavin) - 0.143, vitamin B3 (nicotinate) - 1.264, vitamin B5 (pantothenate) - 0.325, vitamin B6 (pyridoxine) - 0.144, vitamin B7 (biotin) - 0.0036, vitamin B9 (folic acid) - 0.0286, vitamin B12 (cyanocobalamin) - 0.0002; mineral premix - 87, including: iron - 1.45, zinc - 0.95, copper - 0.12, potassium iodide - 0.027 (20mkg); yoghurt powder "Jogufres S" - 340.973; maltodextrin "C" Dry MD 01915-250; Jerusalem artichokes dried - 70; crystalline fructose - 90; orange juice concentrate - 30; natural dyes "Beta carotene" - 2; natural flavoring "Orange essential oil" - 4; refined coconut oil - 100; gum - arabic "Fibregam" - 6.

Organoleptic, physicochemical, microbiological indices of quality and safety were investigated. Regulated indices of nutritional value were determined. The organoleptic quality indices are presented in Table 1.

Table 1. Organoleptic quality indices of yoghurt enriched candies "Talantiki with orange juice"

№	Index	Characteristic
1	Flavor and aroma	Clearly defined, characterized for given item, without off - flavor and odor. The flavor of enriching component is allowed.
2	Color	Candies “Talantiki with orange juice” vary from light orange to orange. The presence of inclusions is allowed.
3	Outer appearance	The surface is smooth. Slight damage of the surface due to automatic packing is allowed.
4	Shape	Round, biconvex, film-coated
5	Amount of items, having defects in appearance and color % (by weight), but no more than	2.0

The nutritional value (Table 2), indicating functional orientation of specialized products was determined. Recommended consumption portion is two candies a day for children aged from 3 to 7 years; three candies per day for children over 7 years.

The recipe of panned confectionery "Dr. Konfetkin" was scientifically determined. The recipe of developed product "Dr. Konfetkin" includes the following components, g/100 g of panned sweets: blueberry extract - 0.8; ascorbic acid - 0.29; vitamin A acetate (500ME/mg) - 0.024; cretaceous-toffee - 12.0; cocoa butter - 4.8; sugar - 9.6; dry milk substitute - 44.33; MCC - 8.0; flavor "Blueberry" - 0.16; sugar - 14.8; Gum Arabic "Quick Gum" - 0.48; cocoa powder- 4.7; bee wax - 0.016 (average weight of covered panned sweets is 1250 mg).

Organoleptic and physicochemical indices of specialized product were determined (Table 3).

Regulated indices of nutritional value of panned confectionery, the information about consumption rates and the adequacy to the percentage of consumer demand are presented in Tables 4 and 5.

Table 2. Nutritional value of yogurt enriched candies "Talantiki"

Nutritional value 100g of candies		% of normal physiological needs for children in a candy		
		3-7 years	7-11 years	11 years and older
Fats, g	10.00	-	-	-
Protein, g	11.59	-	-	-
Carbohydrates, g	51.00	-	-	-
Vitamin C (ascorbic acid), mg	500.00	10.0	8.3	7.7
Vitamin A (retinol), mg ER	7.15	14.3	10.2	7.9
Vitamin E (tocopherol) current. equiv., mg	78.80	11.3	7.9	6.6
Vitamin D3 (cholecalciferol), mg	0.036	3.6	3.6	3.6
Vitamin B1 (thiamine) mg	12.50	13.8	11.3	9.6
Vitamin B2 (riboflavin) mg	14.30	14.3	11.9	9.5
Vitamin B3 (nicotinate), mg	126.40	11.5	8.4	7.0
Vitamin B5 (pantothenate) mg	32.50	10.8	10.8	9.3
Vitamin B6 (pyridoxine), mg	14.40	12.0	9.6	8.7
Vitamin B7 (biotin), mg	0.36	23.7	17.8	14.2
Vitamin B9 (folic acid), mg	2.86	14.3	14.3	9.5
Vitamin B12 (cyanocobalamin), mg	0.02	13.3	10.0	6.7
Iron, mg	145.00	14.5	12.1	12.1
Zinc, mg	95.00	11.9	9.5	7.9
Copper, mg	12.00	19.6	16.8	14.7
Iodine, mg	2.00	20.0	16.7	14.3
Energy value, kcal	340.36			

Table 3. Organoleptic and physicochemical indices of panned sweet "Dr. Konfetkin"

Index	Characteristic
Taste and aroma	Clearly defined, characterized for this item, with cocoa flavor, without off-flavor and odor. The taste of enriching component is allowed.
Color	Color is from light brown to dark brown. The color of the body is in accordance with the recipe composition. The presence of inclusions in the shell and body is allowed.
Outer appearance	The surface is smooth, shiny.
Shape	Round, biconvex, sugar-coated with cocoa powder, pelleted body.
Amount of agglomerated and wrought items,% (by weight) of no more than	2.0
The average weight of a panned sweet, g	1.25 ± 15%
Moisture content,%, no more than	6.5

Table 4. Regulated indices of nutritional value of panned sweets "Dr. Konfetkin"

Indices 100 g	Nutritional value
Mass fraction of ascorbic acid, mg	288.0
Mass fraction of vitamin A, retinol mg	3.6
Carbohydrates, g	63.2
Fat, g	18.9
Energy value, kcal	428.0

Table 5. Consumption rates and the adequacy to the satisfying percentage of physiological needs of children and adults

Name of vitamin	Age group	Consumption rates, mg	30-50% from the standard	In a panned sweet, mg	Amount of panned sweets	Range of application, mg
Vitamin C	from 3 to7 years	50	15–25	3.6	4–5	14.4–18.0
	from 7 to 11 years	60	18–30		5–7	18.0–25.2
	from 11 to14 years	60–70	18–35		6–9	21.6–32.4
	from14to18 years	70–90	21–45			21.6–32.4
	adults	90	27–45		6–10	21.6–45.0
Name of Vitamin	Age group	Consumption rates, mkg/ret.eq	30–50% from the standard mkg/ret.eq.	In a panned sweet, mkg, retinol	Amount of panned sweets	Range of retinol application, mkg
Vitamin A	from 3 to 7 years	500	150–250	45	4–5	180–225
	from 7 to 11 years	700	210–350		5–7	225–315
	from 11 to 14 years	800–1000	240–500		6–9	270–405
	from 14 to 18 years					
	adults	900	270–450		6–10	270–450

As shown in the table the consumption of the recommended amount of confectionery provides the intake of at least 30–50% of the daily needs of children and adults in vitamins A and C.

The content of blueberries in confectionery recipes enhances its functional orientation towards the correction of visual function. Sponge cake for special purposes was developed; it was associated with the problem of carbohydrate metabolic disturbance due to excessive consumption of sugar. The latter is a risk factor for diabetes, cardiovascular diseases, cancer, atherosclerosis, overweight and obesity.

There is a need to prevent these diseases through the development and use of nutritional goods with sugar substitutes, one of them is sorbitol. Taking into account the objectives, consumer motivations and preferences when choosing products specialized confectionery goods were investigated. People with impaired carbohydrate metabolism were involved in the survey.

The results show that 72% of respondents acquire specialized confectionery goods. The most popular items are sweets (22%) - of sugar confectionery goods and biscuits (25%) - of flour confectionery goods (Figure 3). As for the other types of specialized confectionery either their assortment is limited, or they are not available due to the relatively high price.

Low popularity of cakes is due to the fact that they are relatively new and they are insufficiently presented in stores.

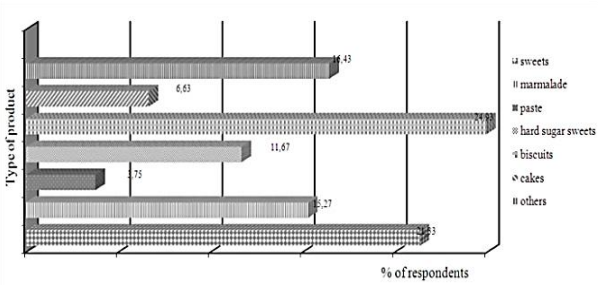

Fig. 3. Preferences to types of confectionery goods, % of respondents.

Figure 4 shows that 37% of respondents consume goods with sugar substitutes more than once a week, 28% - once a week, 25% - at least once a month.

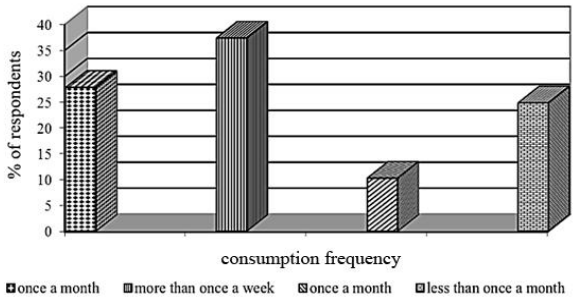

Fig. 4. Consumption of goods with sugar substitutes.

The criteria that are important to customers buying specialized confectionery goods are shown in Figure 5.

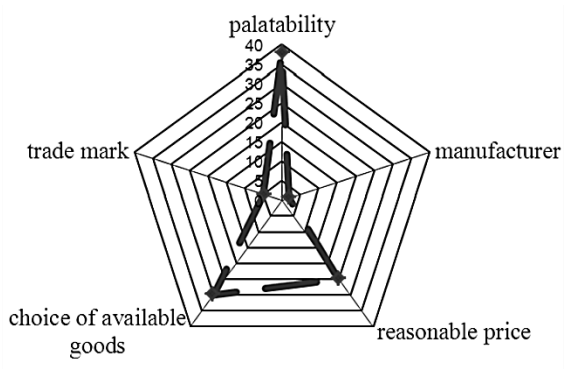

Fig. 5. Selection criteria when buying confectionery goods.

According to the data in Figure 5 it can be concluded that the main criterion when buying specialized confectionery goods is organoleptic qualities. The fact is that the trade organizations still present a small assortment of goods so the second criterion is its variety. The next criterion is the reasonable price of confectionery goods whereas the trade mark and the manufacturer are at the low position.

The greatest amount of respondents (55%) intakes from 100 to 250 g of goods containing sugar substitutes on a daily basis, 19% - from 250 to 500 g, 5% - more than 500 g. Consumers prefer to buy sponge confectionery goods with the sweeteners which were indicated in Figure 6.

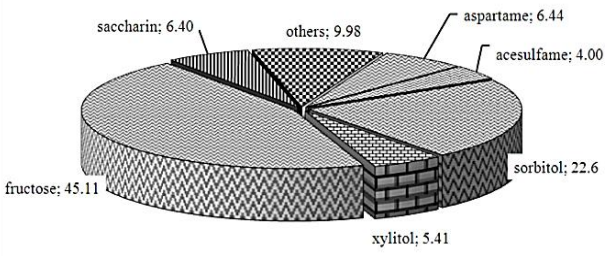

Fig. 6. Preferences to sweeteners.

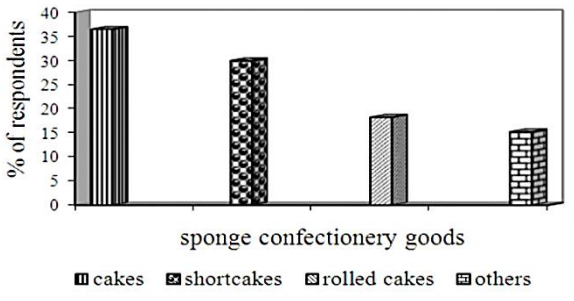

Fig. 7. Preferences to sponge confectionery goods.

Figure 7 shows 73% of respondents are ready to buy sponge confectionery goods with sweeteners, the most popular types of them are cakes (36.5%) and shortcakes (30%).

On the basis of market research we can conclude that the majority of respondents are ready to consume the sponge goods on sorbitol (cakes), as for decorating semi-finished products - fruits and berries; the most important criterion when choosing specialized flour confectionery goods is their organoleptic quality indices. Consumers are able to pay from 20 to 30 rubles for 100 g of this product.

Semi-finished sponge cakes and shortcakes were developed. "Weak" wheat flour, sorbitol, eggs, lecithin, whey, "paste for churning", vanilla were selected as the main raw materials.

In sponge goods intended for persons with impaired carbohydrate metabolism and tended to diabetes, sugar is replaced by sorbitol. The recipe composition has been developed taking into account the diet for diabetics, for them it is not recommended to eat more than seven units of bread per meal. The content of sweetener in the laboratory samples was taken as a percentage of the flour.

When selecting the amount of sorbitol the sweetness coefficient of 0.5-0.6 towards sucrose was taken into account.

Sorbitol having the characteristics and properties distinctive from sugar cannot fully ensure good egg whipping, so to improve the quality of the finished product the emulsifiers - 'the paste for churning" and lecithin are further included in the recipe composition. It is taken into account that the recommended amount of "the paste for churning" should not exceed 3%. Adding the paste not only improves the churning process and the distribution of the components in the recipe mixture, but also reduces the consumption of eggs with partial replacement for whey, thereby reducing the cost price of the finished products. Adding ‘‘the paste for churning’’ allows you to get products with high volume and uniformly porous structure, slows the staling and improves the quality of confectionery goods by increasing porosity. The use of lecithin reduces the viscosity of the dough, replaces sugar in the developed sponge product without decreasing quality indices of dough and finished products. It is considered that the permissible amount of soybean lecithin should not exceed 1%. Adding to the recipe "the paste for churning", whey and lecithin enables to reduce the amount of eggs by 25%.

The samples of sponge semi-finished goods with sorbitol content from 60 to 90% by weight of the flour and lecithin content of 0.1 to 1% were examined. To evaluate the organoleptic quality indices such as taste, color, smell, shape, appearance and crumb texture we developed a 30-point scale. The results obtained during the research of the organoleptic indices of the samples with different contents of sorbitol were processed using least - square method. The regression model is the following:

$$K = -0.0152\,c + 2.1701\,c - 48.121, \qquad (1)$$

where K - tasting assessment, c - percentage of added sorbitol.

The quality of the created model is proved by the coefficient of determination $R^2 = 0.93$, i.e. the change variation of the organoleptic indices depends on the change variation of the percentage of added sorbitol. The average approximation error $A_{average} = 10\%$,

indicating that the prediction accuracy for the created model is 90%.

The impact of the amount of sorbitol on organoleptic quality indices of sponge product is shown in Figure 8.

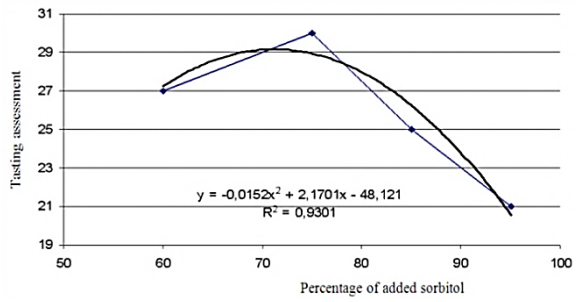

Fig. 8. Impact of the amount of sorbitol on the organoleptic quality indices of sponge product.

The optimum percentage of added sorbitol will correspond to the best organoleptic indices, i.e., Kopt = Kmax. The differential of organoleptic indices on the percentage of added sorbitol:

$$\frac{d \cdot c}{d \cdot c} = -0.0304\,c + 2.1701. \quad (2)$$

Extremum point, in this case is the maximum point:

$$-0.0304\,c + 2.1701 = 0, \quad (3)$$
$$c = 71.38.$$

The confidence interval with the reliability of 0.95: F(t) = 0.95/2 = 0.475, we find t = 1.96. Optimal percentage of added sorbitol is 75% by weight of the flour. The practical research is confirmed by mathematical calculations.

It is shown that the organoleptic sample with 75% of sorbitol has the best characteristics. The sample containing the least amount of sorbitol (60%) is characterized by insufficient sweetness. Samples containing more than 80% of sorbitol have a very sweet taste. Furthermore, the amount of sorbitol consumed by a man should not exceed 30 grams per day.

The samples of semi-finished sponge goods with different content of lecithin in the recipe were investigated. Analysis of the data obtained during the tasting assessment of samples using the least - square method allowed to determine the functional dependence of the organoleptic index of K on the percentage of added lecithin l ($R^2 = 0.93$):

$$K = -7.2765\,l_2 + 12.6612\,l + 16.21536. \quad (4)$$

To find the extremum points of created function the differential of organoleptic indices by the percentage of added lecithin was found and it was equated to zero:

$$\frac{d \cdot K}{d \cdot l} = -14.5531 \cdot l + 12.6612, \quad (5)$$

$$-14.5531 \cdot l + 12.6612 = 0, \quad (6)$$
$$l_{max} = 0.97.$$

The maximum value of organoleptic indices (in points) is achieved with 0.97% of lecithin. The commodity assessment of developed goods was given and the indices of their nutritional value were identified (Tables 6-8).

Table 6. Physicochemical indices of semi-finished sponge product

Index	Index value		
	With sugar	With sorbitol	IS 10-060-95
Humidity, %	24 ± 1	22 ± 1	25 ± 3
Mass fraction of total sugar (sucrose on) in terms of dry matter,% no more than	22.0 ± 1	8.0 ± 1	In accordance to the calculated content of the recipe with permissible deviations + 2.5%

Table 7. Indices of absorptivity and porosity

Index	Index value		
	With sugar	With sorbitol	According to TC 9134-133-02068315-10, no less
absorptivity, %	382 ± 3	352 ± 3	340
porosity, %	64 ± 3	73 ± 3	65

Table 8. Nutritional value of sponge semi-finished goods and shortcakes, g / 100g

Item	Proteins	Fats	Carbohydrates	Energy value, kcal/100g	Amount of bread units, g
Sponge semi-finished cake with sorbitol	5.0	3.5	39.2	208.0	3.3
Sponge semi-finished cake with sugar (test)	10.42	7.0	59.5	349.0	5.0
Sponge shortcake (with sugar) with a layer of black currant jam (with sugar)	4.6	7.3	64.7	343.0	9.2
Sponge shortcake (with sorbitol) with a layer of black currant jam (fructose)	5.2	3.5	61.1	293.0	5.0

The sponge shortcake (with sorbitol) with a layer of blackcurrant jam (not less 30% by weight of the product) possesses an energy value of 15% lower than the sponge shortcake (with sugar) with the same layer, the amount of bread units is 5g per 100g of a product. It is acceptable when feeding of persons suffering from diabetes, as for them it is recommended to consume not more than 7 bread units per meal.

The recipes and technology of confectionery goods were tested at enterprises NGO "SOUTH" (Biysk), they were certified under the requirements of international standards ISO 9000.

The developed confectionery goods may be important in ensuring a healthy diet of certain population groups taking into account the nutritional status.

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RELEVANT PROBLEMS OF SPORTS NUTRITION

N. Yu. Latkov[a,*], A. A. Vekovtsev[b], Yu. A. Koshelev[c], V. I. Bakaytis[d]

[a] Kemerovo Institute of Food Science and Technology (University),
bul'v. Stroiteley 47, Kemerovo, 650056 Russia,
* e-mail: tovar-kemtipp@mail.ru

[b] Scientific and Production Association "Art Life",
Nakhimov St. 8/2, Tomsk, 634034 Russia

[c] Pharmaceutical Company "Altayvitamins",
Zavodskaya St. 64, Biysk, 659325 Russia

[d] Siberian University of Consumer Cooperation,
pr. K. Marx 26, Novosibirsk, 630087 Russia

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Abstract: Nutrition is one of the primary factors of achievements in sports and sportsmen's health, on par with methodological and psychological aspects of training. A special place in sports nutrition is occupied by biologically active additives (BAA) made with plant and animal raw materials, amino acids, ferments, other irreplaceable nutrients and minor food constituents – energy, fat, protein and mineral exchange correctors, considering their efficiency and availability. Biologically active substances of the food components are also able to stimulate compensatory-adaptive reactions, prevent trauma and numerous diseases in professional sports, protect from common cold and other viral diseases before and during competitions. Great attention is paid to the scientific approbation of BAA formulae, with consideration of age, gender, sport type and synergic effect of separate components on metabolic processes in human organism. New types of BAA's for sports nutrition have been developed. The formulae have been created on the basis of data from literature and research on characteristics of active ingredients and their influence on the metabolic processes during training, competitions and recreational activities. Organoleptic, physical and chemical, hygienic and toxicological customer properties have been examined. Regulated quality indices (including nutritional value), which establish functional goals, have been determined. Considering the directions of BAA testing, the characteristic of several sport types has been given. The distinctive features of nutritional support have been investigated. The efficiency of specialized products has been determined by their inclusion into the diet and observation of specific properties, which characterize metabolic processes in sportsmen's organisms. The developed products have passed anti-doping control. They have been included into the Federal register and approved in the practice of sport competitions.

Keywords: Sports nutrition, principles of creation, specialized products, efficiency assessment

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INTRODUCTION

Modern sports and training of sportsmen of higher qualification are characterized by the availability of two factors:
– physical and psychological stress, which generally reaches the limits of physiological functions;
– the necessity of applying different approaches to achieve the final result.

The latter is associated with an increase in general and special performance of athletes during training and competitions, the recovery of the organism after overstress, prevention of possible complications and adaptation breakdowns.

One of the primary solutions of the presented problem is the development of scientifically approbated diets with consideration of type of sport, age, gender, and other basic factors. There is a need for new types of specialized products (including BAA), based on the achievements of modern pharmacology and nutrition sciences, which aim at the increase of sports achievements, prevention of professional disease and preservation of health [1–3, 9].

MATERIALS AND METHODS

The materials of research have been constituent components and created on their basis experimental and production samples of BAA's - "Vasoton", "Arovitol', "Vitalife", "Discovery", "Yohimbe Plus" complex, as well as representative groups of athletes.

Conventional assessment methods of organoleptic and physical and chemical quality indices have been used. Vitamin value tests have been performed with the use of spectrophotometry, high-efficiency liquid chromatography and fluorometry [8]. The criteria of safety have been estimated according to the requirements of technical regulations [11].

To evaluate the effectiveness of the developed products well-known and special clinical research methods have been used. They characterize the BAA

quality and the condition of metabolic processes of athletes.

The effectiveness evaluation of BAA "Discovery" and complex "Yohimbe Plus" was performed on a group of highly qualified swimmers (18 men, age 18.7 ± 1.7 years, height 1.86 ± 0.08 m, weight 74.6 ± 5.7 kg, experience 10.8 ± 1.7 years). Out of them 10 men were in the experimental group, and 8 were in the control group. The following parameters were investigated: level of performance using the electronic diagnostic complex "ART-2", external respiration analysis systems "BECKMEN" and "CORTEX", cardio-monitoring system POLAR ELECTRO "ACCUREX PLUS". The sportsmen performed rowing motions in several tests: 10 rows with maximal intensity (T-10), 1 minute with "competition" intensity (T-1) and multi-stage test - 10 tests 1 minute each with growing intensity. In these tests power measurements, heartbeat rate, oxygen consumption rate, lung ventilation were observed.

The effectiveness of BAA's "Discovery Strength" and "Lecitina" is studied on a group of 10 sportsmen during training for the Russia Championship and World Championship - 5 candidate masters of sports (a degree in Russian sporting awards scale), 4 masters of sports and 1 master of sports of the international level in skiing. The primary goal of training was the achievement of highest competitive condition of sportsmen by the middle of December and its retention until the middle of March.

RESULTS AND ANALYSIS

Present data from literature and research allowed composing the basic principles of sports nutrition [4–7, 10]:

– supply of the necessary amounts of energy to sportsmen according to energy expenditure during physical exertion;

– adherence to the principles of balanced nutrition in connection with certain types of sports and intensity of exercise, including the distribution of calories among basic food substances (which changes severely depending on the stage of preparation for the competitions); correlation of quantity and quality of amino acids composition in protein products; retention of expedient relations in fatty-acidic formula of diet, based on deep research of the influence of fats on lipidic metabolism in the whole organism or separate organs, cells and membranes; rational relations of mineral substances; balance of primary food substances, vitamins and microelements;

– choice of adequate forms of nutrition (products, food substances, their combinations) for periods of intense exercise, preparation for competitions, competitions themselves and recovery.

– use of inductive influence of food substances for activation of aerobic oxidization and associated phosphorylation, transglicosidatic processes, coenzymic forms, ATP reactions, accumulation of monoglobin and other metabolic processes that are especially important in physical exercise;

– use of food substances to build metabolic background, which is beneficial for bio-synthesis and realization of humoral regulators (catechins, prostaglandins, corticosteroids etc.);

– use of alimentary factors for accelerated muscle growth and strength increase;

– choice of adequate nutrition timetable , corresponding with the exercise schedule;

– use of alimentary factors for quick weight loss when adjusting the sportsman to the weight category;

– development of principles of nutrition individualization, depending on anthropomorphic-typometric, physiological and metabolic characteristics of the sportsman, condition of their digestive system, tastes and habits, allergic reactions to nutrients and their complexes.

Considering the principles mentioned, the specialized products of the examined function may serve the following purposes: nutrition in transit and between training sessions; acceleration of organism's recovery after training and competitions; mineral exchange regulation and thermal regulation; sportsman's weight correction; targeted development of muscle mass; reduction of daily ration during competitions; change of quality orientation of daily ration depending on the training exercise or during the preparations for competitions; individualization of nutrition, especially in cases of great psychological stress; urgent correction of unbalanced diet; increase of nutritional value during multi-step training.

It is shown, that correct sportsmen's diet allows increasing their capacity to adapt to extremely high levels of stress, achieving greater results, accelerating recovery processes of the organism, improving its function after intensive exercise, establishing higher psychological resilience[1–2].

Rational methodology of sports nutrition calls for specialized food rations, which include standard consumer food products combined with enriched products and BAA's that allow compensating a relative deficiency of necessary substrates, physiologically active substances and their complexes.

Consequently, the current accumulated experience in specialized sports nutrition enables to increase their capacity to adapt to extremely high levels of stress, achieving greater results, accelerating recovery processes of the organism, improving its function after intensive exercise, establishing higher psychological resilience.

In this work, scientifically approbated formulae and technology for specialized nutrition of sportsmen of different qualification in different activity periods were developed: BAA's "Discovery Strength", "Lecithin", "Yohimbe Plus", "Discovery", "Arovitol", "Vitalife".

Qualitative and quantative structure of the BAA formulae is developed on the basis of research of the pharmacological properties of their active components and their involvement in the metabolic processes in sportsman's organism with consideration of their combined synergic effect.

On the basis of organoleptic and physical-chemical research the regulated quality parameters of the developed product were determined (tables 1–4).

Formula of BAA "Discovery" consists of two pill forms, which include:

Form 1: manganic sulfate, cupric citrate, potassium iodate, ammonium vanadate, sodium molybdate sodium metasilicate, quercetin, calcium pantothenate, cholecalciferol, cyanocobalamin, thiamine mononitrate, papain, hesperidin, sodium selenite, rutin, nicotinamide, folic acid, pyridoxine chlorhydrate, riboflavin, tocopheryl acetate, retinol acetate, "CHROME-BIO" – raw material, alimentary trihydrate zinc zitrate, food additive "Sibel" (dihydroquercetin), ginkgo biloba (dry extract), hill saltwort (dry extract), beta-carotene 20% FS, food additive for protease "Bromeline 1200", coenzyme Q_{10}, ferric pyrophosphate, food additive "Sodium ascorbate", meal of milk thistle fruit (dried extract), silver sulphate, biotin, raw materials for BAA "FRUITEX-B™" – fruitoborate.

Form 2: parsley leaf, magnesium oxide, food additive "Redivivo (licopin)", alimentary trihydrate zinc zitrate, tea hedysarum (dry extract), prairieweed (dry extract), chinese magnolia vine (dry extract), reishi mushroom, damiana.

Regulated quality indices of the BAA are presented in tables 1–2.

Table 1. Regulated quality indices of the BAA "Discovery Strength" (Form 1)

Index name	Index value
Appearance	Pill
Color	Yellow
Taste and scent	Peculiar
Average mass, g	0.8±5%
Disintegration time, minutes, max	30
Durability to breaking, N, min	90
Durability to attrition, %, min	97
Content of one pill, mg:	
Vitamin A	0.50 (0.42–0.57)
Vitamin E	5.0 (4.2–5.7)
Vitamin D_3	0.0025 (0.0021–0.0028)
Vitamin C	35 (30–40)
Vitamin B_6	1.00 (0.85–1.15)
Vitamin B_1	0.75 (0.64–0.86)
Vitamin B_2	0.90 (0.76–1.04)
Vitamin B_3	10.0 (8.5–11.5)
Vitamin B_5	2.5 (2.1–2.8)
Vitamin B_9	0.10 (0.08–0.12)
Chromium	0.025 (0.021–0.028)
Selenium	0.035 (0.029–0.04)
Copper	0.50 (0.42–0.57)
Manganese	1.00 (0.85–1.15)
Iron	7.0 (5.9–8.0)
Zinc	7.5 (6.4–8.6)
Iodine	0.075 (0.064–0.086)
Vanadium, mcg	20 (15–25)
Boron	1.00 (0.85–1.15)
Silver, mcg	15 (10–20)
Silicon	2.5 (2.1–2.8)
Molybdenum, mcg	22 (18–33)
Rutin	15.0 (12.0–17.5)
Quercitin	15.0 (12.0–17.5)
Hesperdine	10.0 (8.5–11.5)
Flavone glycosides, min	2.4 (2.1–2.8)
Coenzyme Q_{10}	0.8 (0.5–1.0)
Flavolignanes (silibinin)	5.0 (4.2–5.7)
Beta-carotene	0.87 (0.74–1.00)
Proteolytic activity, F.I.P/g, min	3.0

Table 2. Regulated quality indices of BAA "Discovery Strength" (Form 2)

Index name	Index value
Appearance	Round pills
Color	Light grey
Taste and smell	Peculiar
Average mass, g	0.8 ± 0.5%
Disintegration time, minutes, max	30
Durability to breaking, N, min	90

Table 2. Ending. Regulated quality indices of BAA "Discovery Strength" (Form 2)

Index name	Index value
Durability to attrition, %, min	97
Content of one pill, mg:	
Lycopin	0.25 (0.21–0.29)
Zinc	0.25 (2.20–2.80)
Magnesium	200 (180–220)
Polysaccharides	9.5
Schizandrin	0.24
Tannins, min	1.6

Granular soya lecithin (corresponding to the requirements of SEC 77.99.916.Д.003770.06.03) was used as a raw material for BAA "Lecithin". Regulated quality indices of the developed product are presented in table 3. Complex "Yohimbe Plus" includes: starch, zinc oxide, royal jelly, ginger root, panthogematogen, vitamin E, ginseng root, flagroot, microcrystallic cellulose, carthamoid rhapontic, ginkgo biloba (extract), yohimbe (bark extract).

Regulated quality indices of the BAA are presented in table 4.

Formula of BAA "Discovery" includes: ferric sulfate, copper sulfate, potassium chloride, magnesium oxide, L-phenylamine, zinc oxide, sodium molybdate, cayenne pepper, parsley leaf, DNA, RNA, wheat sprouts, lactic bacteria, damiana, spirulina, raspberry leaf extract, maitake, nettle leaf, knot-grass, ginseng root, dandelion root, laminaria, lemon (bioflavonoids), histidine, aloe vera, calcium carbonate, pancreatin, microcrystallic cellulose, inositol, sodium selenite, L-glycin, papain, L-lysin, horse sorrel root, lipase, p-amino-benzoic acid, L-alanine, hesperidin, rutin, bromeline, lucerne grass, L-valine, L-threonine, L-tyrosyne, L-leucine, L-glutaminic acid, asparaginic acid, L-serine, L-proline, L-arginine, L-cysteine, premix 730/4, coenzyme Q_{10}, cola nut, choline bitartrate, chrome picolinate, cat's claw bark, pycnogenol, methionine.

Regulated quality indices of the BAA are presented in table 5.

Table 3. Regulated quality indices of BAA "Lecithin"

Index name	Index value
Appearance	Plain granules
Color	Yellow
Taste and smell	Peculiar
Phospholipids content, %, min	93
Peroxide value, moles of active oxygen/kg, max	10
Acid number, mg of KOH/g, max	35

Table 4. Regulated quality indices of BAA "Yohimbe Plus"

Index name	Index value
Appearance	Oval pill
Average mass, g	0.47 to 0.53
Color	Brown and red
Taste and smell	Peculiar, consistent with the formula
Disintegration time, minutes, max	30
Durability to breaking, N, min	90
Durability to attrition, %, min	97
Zinc content per 1 pill, mg, min	2.0
Vitamin E content per 1 pill, mg, min	10.0

Table 5. Regulated quality indices of BAA "Discovery"

Index name	Index value
Appearance	Oval pills
Average mass, g	0.47 to 0.53
Color	Green and grey
Taste and smell	Consistent with raw materials
Disintegration time, minutes, max	30
Durability to breaking, N, min	90
Durability to attrition, %, min	97
Content of one pill, min:	
Vitamin C, mg	12.5
Selenium, mcg	12.5
Chrome, mcg	42.0

Studying the safety parameters of the BAA has shown their correspondence with the actual sanitary-hygienic documentation.

Vasoton. A capsular BAA form, containing 0.5 g of L-arginine. The influence of the amino acid on the functional state of the organism is connectd to the following metabolic aspects:

– It is one of precursors of nitrogen oxide, which plays a key role in the functioning of CVS. L-arginine supplies with nitrogen the system of enzymes called NO-synthases, which synthesize NO, or nitrogen oxide. NO is a mediator of miorelaxation of arterial vessels. It is called an endothelial relaxation factor due to its ability to relax smooth muscles in blood vessels. It prevents adhesion and aggregation of thrombocytes - elements necessary for blood coagulation. In some cases their abundance may lead to heart disease and blood clots;

– It removes the dysfunction of blood vessel endothelium, restores the smooth muscles' relaxation ability (vasodilative, angioprotective, antiproliferative, disaggregative factors), thus ensuring the synthesis of NO;

– It is involved in the cycle of reamination (transamination) of amino acids, synthesis and extirpation of urea - the product of breakdown of proteins and amino acids. The blood vessels, the liver and the kidneys are cleared of toxic substances and may function normally;

– It stimulates the synthesis of the somatotropic hormone ("the growth hormone"), and through it the synthesis of proteins, regeneration of damaged tissue - tendon sprains, muscle trauma etc.;

– It plays a key role in the metabolism of muscles, able to increase their relative strength and muscle mass, at the same time decreasing fat;

– It stimulates the synthesis of anabolic hormone - insulin, serves as a precursor of creatine, which, joining with the phosphate group, creates phosphocreatine, which holds more energy and is necessary for maximal muscle power. All these factors support and stimulate the immune system.

– It possesses a psychotropic effect, intensifies spermatogenesis, giving a motivated mood, activity, and endurance - important factors for sport achievements.

Considering the role of L-arginine in metabolism, the following areas for utilizing of BAA "Vasoton" were designated:

– Optimization of coronary and periphery blood flow during extreme physical exertion, during training or competitions, especially with maximal or sub-maximal intensity;

– Acceleration of post-exertional restoration by synthesis of the metabolite - the product of breakdown of worked-out protein and amino acids.

– Stimulation and synthesis of hormones - somatotropic hormone and insulin for acceleration of protein synthesis, regeneration of damaged tissue, intensification of growth of young sportsmen, digestion of sugars and synthesis of glycogen;

– Intensification of synthesis of creatine (phosphor-creatine precursor) in liver, as well as glycine and methionine;

– Support of the immune system in times of great physical and psychological stress.

Recommendations for application were developed:

– Myocardial overstress (especially with symptoms of ischemia);

– Reduction of alactatic, lactatic, aerobic endurance, fatigue after extreme exertion, especially with maximal or sub-maximal intensity;

– Damage and inflammation of muscle tissue, tendons and connective tissue;

– Interruption of biological development with insufficient growth dynamic;

– Impairment of blood vessel function after intensive exertion;

The BAA is recommended for inclusion into the diet of the sportsmen, 1–2 capsules 2–3 times per day, for 2–3 months. The course can be repeated if necessary. It is classified as a substrate additive.

Arovitol - tableted form of BAA, a vitaminic complex in a form of chewing tablets 1.2 g each. It contains crushed fruit of the chokeberry tree and 12 vitamins (B1-0.6; B2-0.57; B6-0.6; E-2.5; C-60; B12-1.2 mcg; B5-0.12; Bc-0.12; H-0.073; niacene – 6.6; D3-147 IU; A – 166 IU; mg/1 tablet)

Chokeberry is a relatively rich natural source of biologically active substances: vitamins (P, C, E, K, B1, B2, B6, beta-carotene), macro- and microelements (iodine, iron, copper, manganese etc.), carbohydrates (glucose, fructose, sacharose), pectic and tannic substances, organic acids, bioflavonoids.

The content of P-vitamin active flavonoids in chokeberry is 2 times greater than in blackcurrant, 20 times greater than in apples or oranges. Those are catechins, flavones, hesperidin, rutin, quercetin, cyanidine etc., which are involved in bioregulation and stimulation of physiological functions in the organism, especially the reinforcement of blood vessel, increasing their elasticity and flexibility. The content of these substances may reach 2%.

Pectic substances of chokeberry (up to 0.5%), possess sorptive properties regarding heavy metals, toxic radioactive substances, remove various pathogenic microorganisms. Pectins normalize bowel functioning, improve the peristalsis of digestive system, accelerate mass peristaltic movement, remove spasms, improve the condition of large intestine, bind bile acids, provide the biligenic effect and reduce the probability of cholelithiasis.

Chokeberry exceeds tangerines, strawberry, raspberry and redcurrant in content of organic acids.

The content of iodine in chokeberry is 3-5 times greater than in blackcurrant, raspberry, gooseberry, strawberry and apples.

The natural properties of chokeberry are supported by the synergic influence of additional complex of vitamins, which protect the organism from various diseases, increase antioxidant properties, increase blood vessel flexibility, and normalize blood formation. The BAA is recommended for prevention and supportive therapy of cardiovascular diseases, correction of other impairments:

– strengthens blood vessels, increases their flexibility, increases tonicity;

– improves capillary blood flow;

– normalizes heightened arterial pressure;
– correct fat exchange, decreases cholesterol;
– normalizes intestine function;
– facilitates the removal of toxic metabolic products and radioactive substances;
– decreases the hyper-function of thyroid.

The BAA may be used for treatment of hypovitaminosis and avitaminosis, especially in winter and spring.

The total activity of natural components strengthened with the vitaminic complex, opens the possibility for sportsmen of any qualification (as well as people with active lifestyle) to use "Arovitol.". The maintenance of vitamin-mineral balance during training and competitions, as well as during restorative periods after exertion in aerobic and mixed areas of varying intensity and duration, allows achieving the following effects:
– removal of damage form toxic metabolites during restoration;
– improvement of capillary blood flow, prevention of cardiovascular diseases, chance of which may increase due to various biochemical and functional abnormalities, which appear with physical exertion of high intensity;
– facilitation of normalization of arterial pressure, which may increase during physical stress.

It is recommended to use the BAA on all stages of training and competitions: 1–2 tablets 2–3 times per day following meals for duration of 2–3 months. The course may be repeated after 2–4 months.

Vitalife. A series of vitaminized drink powders "Vitalife" are made using local natural materials. A selection of macro- and micronutrients is made with consideration of acquired experience in the field of sports nutrition and their synergic influence on metabolic processes in various periods of competitive activity.

Organoleptic and physical-chemical research was carried out during production and storage, which allowed establishing the regulated quality indicators (tables 6 and 7), including nutritional value (table 8).

Table 6. Organoleptic quality indices of vitaminized drink powder "Vitalife"

Index name	Characteristics
Appearance	Intimate plain dry substance. Clots are acceptable if they dissolve during intensive mixing
Color	Similar to the color of fruit and berry extracts used
Taste and smell	Smell of the corresponding flavoring agent, sour and sweet taste

Table 7. Physical-chemical quality indices of vitaminized drink powder "Vitalife"

Index name	Value of indicator
Mass fraction of moisture, %, max	3.0
Mass fraction of titrated acids (by malic acid), %, min	2.0
Preparation time, minutes, max	15.0

Table 8. Vitamin value of soft drink powder "Vitalife"

Content, mg	Per 100g of dry powder	Per one glass (100 cm^3) of the drink	% of daily requirement
Vitamin C	85.0	17.0	24.3
Nicotinamide	21.5	4.3	21.5
Vitamin E	12.5	2.5	25.0
Calcium pantothenate	8.75	1.75	25.0
Vitamin B6	2.5	0.5	25.0
Vitamin B2	2.125	0.425	24.0
Vitamin B1	1.75	0.35	23.4
Vitamin A	1.75	0.25	25.0
Folic acid	0.5	0.1	50.0
Biotin	0.25	0.05	33.4
Vitamin D3, IU	500.0	100.0	50.0
Vitamin B12, mcg	3.75	0.75	25.0

The drink also contains carbohydrates (sugar, glucose), extract (condensed juice) of sea buckthorn, chokeberry and viburnum.

Biologically active ingredients of sea buckthorn, chokeberry and viburnum (pectic substances, bioflavonoids, water-dissolving vitamins, organic acids, microelements) supplement the introduced vitaminic complex, increase their physiological influence on a human body:
– Replenishment of digestible carbohydrates;
– Prevention of hypovitaminosis;
– Increase of organism's resilience during psychological and physical stress, in adverse environments.

Bioflavonoids and pectic substances in extracts (condensed juices) of chokeberry:
– Normalize bowel functioning, improve the peristalsis of digestive system, accelerate mass peristaltic movement, remove spasms, improve the condition of large intestine;
– Bind bile acids, provide the biligenic effect and reduce the probability of cholelithiasis;

– Possess sorptive properties regarding heavy metals, toxic radioactive substances.

Considering the role of ingredients in metabolism, the following areas for utilizing of BAA were designated:

– Supplement of carbohydrates after exertion in aerobic and mixed areas of varying intensity and duration;

– Maintenance of vitamin-mineral balance during physical exertion in designated areas, as well as during restoration;

– Improvement of adaptation of sportsman's organism and acceleration of restoration after extreme physical and psychological stress by introduction of biologically active substances from extracts and juices.

Recommendations for application were developed:

– During exertion in aerobic area of energy supply: 30 g of drink powder in 300 ml of still water 30 minutes before exercise;

– During exertion in mixed area of energy supply: 30 g of drink powder in 200 ml of still water 30 minutes before exercise and 10 g of drink powder in 100 ml of water divided into 3–4 small portions during the exercise;

– 20 g of drink powder in 200 ml of water after the exercise to restore liquid balance and maintain vitamin-mineral balance.

Average recommended daily dosage during extreme physical stress is 60 g of drink powder in 600 ml of still water.

Not being restricted by any anti-drug regulations, the BAA is recommended for regular use in sports nutrition during training and exercise, including periods of extreme physical exertion as a means to maintain an energy supply, compensate the loss of liquids and vitamin-mineral substances, especially in cyclic or endurance sports to increase aerobic endurance, shorten the period of restoration after exertions.

The developed product has been analyzed with procedures of anti-doping control by methods of gas chromatography and mass-spectrometry in correspondence with the requirements of WADA. Expert resolutions for BAA usage in sports nutrition have been acquired from anti-doping center (Moscow), All-Russian Scientific Research Institute of Physical Culture and Sports (Moscow).

The choice of the separated or complex application of the developed BAA is made by sportsman's doctor and trainer with consideration of sportsman's state and specifics of training routine.

Merchantability evaluation of the specialized products including sports nutrition involves clinical studies, which are carried out to examine priority consumer properties. The natural observations are performed with consideration of specifics of the sport type, qualification level, the period of competition, age, gender and other factors that influence the metabolism in sportsman's organism.

Despite the abundance of methods of sports therapy, the key role is played by products with specialized metabolic effect, which are BAA's with scientifically approbated complex of vitamins, minerals, and other biologically active compounds with synergic influence. The efficiency of such BAA's is connected to different aspects of optimal relation between the processes of exertion and restoration, which are responsible for long-term physiological adaptation to physical stress. The ability to control said processes is one of the most important factors of training efficiency, improvement of sportsman's proficiency and sports achievements, at the same time preserving health during intensive training and competitions.

Considering the areas of BAA tests it is necessary to characterize particular sports disciplines - swimming and skiing.

Swimming. Swimming is a cyclic sport type, which has specific features in training and competitions.

The training process is characterized by high intensity, duration (up to 4 hours) and high movement frequency of exercises, which places special requirements upon sportsmen's nutrition (Sharp.2000):

– High energy supply (average energy loss during single 4-hour training session is 4000–5400 kcal for men and 3400–4000 kcal) (Sherman&Maglisho, 1992);

– Carbohydrate consumption not less than 600 g per day. Shortage of carbohydrates leads to insufficiency of glycogen in muscles, resulting in overstress and weaker results. Glycogen replenishment after physical stress is influenced by following factors: exercise type, carbohydrates quantity, their type, time of consumption of carbohydrate components and their quantity, combination with other nutritional components;

– Protein nutrition is highly important due to intensive training leading to the breakdown of proteins. Average protein consumption norm for swimmers is 1.5–2 g per kg of body weight, which ensure muscle catabolism at glycogen exhaustion.

Skiing. Considering present knowledge of muscle metabolism, this sport type may be characterized from the following standpoints:

– Muscle metabolism generally follows the aerobic path;

– Long duration of races leads to the exhaustion of glycogen;

– Maximal cardiovascular stress.

In skiing, the competitions are held on rugged terrain, which leads to functional and biochemical shifts in organism. Sportsmen of high qualification level develop high muscle metabolism, where high-oxide fibers with developed capillary network is dominating. This leads to faster gaseous metabolism and transfer of substances from blood to muscle cells, making aerobic metabolism more efficient.

High energy expenditure is characteristic to ski sportsmen during both training and competition. This problem is solved by three meals a day diet and additional nutrition.

Restoring the exhausted glycogen supply is also necessary after continuous and intensive work. Consumption of carbohydrate-rich products after exercise and before sleep is critical to glycogen resynthesis.

Liquid consumption of the sportsmen, despite low environment temperatures, reaches up to 8-10 l of water per day, which is justified by increased sweat secretion. Especially effective are carbohydrate drinks, consumed during the race.

The research performed and the present literature data enabled to define primary effects of components

of BAA "Discovery" and complex "Yohimbe Plus", which may serve as a nutritional supplement for the organism in addition to the regular diet.

Clinical studies of BAA's are performed on a group of highly qualified swimmers in collaboration with All-Russian Scientific Research Institute of Physical Culture and Sports Medicine (Saint-Petersburg).

Experimental group consisted of 10 swimmers; control group consisted of 8 swimmers.

The swimmers from experimental group consumed the BAA's in addition to the regular diet for duration of 20 days: BAA "Discovery" - 3 pills, complex "Yohimbe Plus" - 1 pill at breakfast and dinner. The control group received no BAA's. All examined received similar regular diet, were practically healthy and trained according to schedule. The research took place during the spring period. The sportsmen performed rowing motions in several tests: 10 rows with maximal intensity (T-10), 1 minute with "competition" intensity (T-1) and multi-stage test - 10 tests 1 minute each with growing intensity. In these tests power measurements, heartbeat rate, oxygen consumption rate, lung ventilation were observed.

The most prominent differences were observed in tests T-10 with maximal intensity and T-1 with competitive intensity. In experimental group the average cycle power has prominently changed from 171.3 ± 26.8 W (T-10) to 180.0 ± 31.8 W after receiving the treatment ($p<0.05$). In control group these changes were not prominent: from 148.3 ± 40.8 W to 146.4 ± 28.1 W.

In test T-1 average cycle power in experimental group prominently changed from 134.5 ± 20.3 W to 139.2 ± 23.4 W ($p<0.05$). In control group the value hasn't changed: 126.0 ± 17.8 W и 127.3 ± 17.4 W respectively.

It is known, that during developmental exercise the use of products, which regulate protein synthesis in muscle tissue, is recommended. During the experiment with BAA "Discovery" and complex "Yohimbe Plus" the increase in rowing motion power due to improved metathesis was observed. The creatine phosphokinase path of ATP resynthesis plays a key role in energy supply of a short-term work of maximal intensity for duration of 15–30 s (test T-1) (Volkov N.I. etc., 2000) ATP supply by creatine phosphate is limited by their supplies, which depend on creatine supply. The sources of creatine are meat, liver etc., and its synthesis in liver from amino acids arginine, glycine, and methionine. Consequently, one of the ways to increase the power of sportsmen's work (10 rows) may be introduction of BAA "Discovery", which supplies a complex of necessary amino acids (including creatine and methionine synthesizing), into the diet.

The acquired data show practicability of using the combination of BAA "Discovery" and complex "Yohimbe Plus" during the basic period of training, when one of the primary tasks of training exercise is increasing the power of swimmers' motions. It should be noted, that the comprised formula of used products allows foregoing the use of other vitaminic complexes, the amount of which is usually 5 or 6.

Unlike pharmaceuticals, which include biologically active substances in amounts 10–100 times higher than a daily dosage and which are introduced into the organism by mouth or parenterally, BAA's are designed for people with physical and psychological stress and are used to remove deficiency of these substances in limits of human physiological need and they are consumed only with food.

Clinical tests of efficiency of BAA "Discovery" and "Lecitina" are performed in collaboration with specialists from the regional sports prophylactic center by introduction of the BAA into the diet of skiers from the Krasnoyarsk State University team during training in preparation for the Russia championship and world championship in skiing. Ten sportsmen took part in the experiment: 5 candidate masters of sports (a degree in Russian sporting awards scale), 4 masters of sports and 1 master of sports of international level. The primary goal of training was the achievement of highest competitive condition of sportsmen by the middle of December and its retention until the middle of March. During this period several stages of major Russian and international competitions take place. Therefore the quantity, intensity and quality of training exercise during winter are constant.

The sportsmen used BAA "Lecitina" (1 teaspoon two times per day) and "Discovery" (1 pill two times per day) in their diet for the duration of 25 days. Recommendations were provided by nutritiologists from company "ArtLife". The quantity and quality of the completed work were compared with the corresponding values of the same sportsmen from the previous month. The functional exercise quantity of this group was determined with ECG control immediately after the exercise. A correction of the exercise quantity was performed to achieve the maximal training effect without overloading the sportsmen.

A prominent increase of cyclical load quantity by 30% during the experimental period was observed. The average load quantity increased from 478 km in January to 623 km in February. The change in work quality manifested itself in increase of high-intensity work percentage from 16% (77 km) in January to 33 % (204 km) in February. High-intensity work is a skiing exercise with heartbeat rate of 170 per minute or more. The dynamic of high-intensity performance in control and experimental periods is illustrated in Fig. 1.

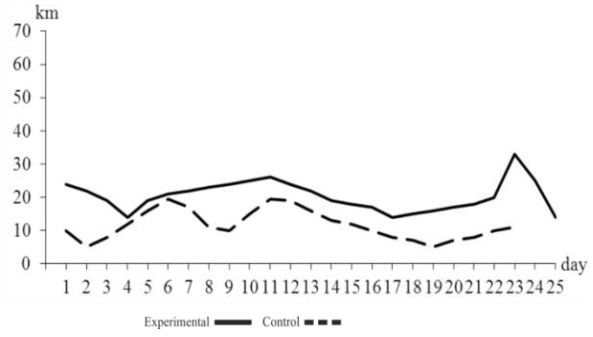

Fig. 1. The dynamic of high-intensity performance by training days in experimental and control periods.

The results of the experiment performed were not only the ability of sportsmen to withstand greater amounts of training work, but also the improvement of psychological resilience. It is evident from the achievements of the experiment participants in the world and state championships in skiing, which were the highest throughout the whole sports career.

The product has been tested and approved and is being produced by pharmaceutical company "Altaivitamins" (Biysk) and SPA "ArtLife" (Tomsk). The stability of the quality and safety of BAA's are ensured by the development and implementation of the management systems according to the requirements of the international standards ISO 9001:2000;22000:2005 and GMP rules.

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NUTRITIONAL FACTOR IN ENSURING HEALTH AND RELIABILITY INCREASE OF PROFESSIONAL ACTIVITIES OF INDUSTRIAL WORKERS

V. V. Trihina[a,*], V. B. Spirichev[b], V. Z. Koltun[c], A. N. Avstrievskih[d]

[a] Kemerovo Institute of Food Science and Technology (University),
bul'v. Stroiteley 47, Kemerovo, 650056 Russia,
* e-mail: tovar-kemtipp@mail.ru

[b] Scientific and Production Association "Valitek Prodimpex",
Gagarin St. 18a, Dedovsk, 143530 Russia

[c] Novokuznetsk State Institute of Improvement of Doctors,
Stroiteley Avenue 5, Novokuznetsk, 654005 Russia

[d] Scientific and Production Association "Art Life",
Nakhimov St. 8/2, Tomsk, 634034 Russia

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Abstract: Micronutrients (vitamins and minerals) play an important part in reducing the occupational and production related diseases among the workers of industrial enterprises. In this connection the ways of optimizing the preventive diets have been determined taking into account the specificity of jobs and the nature of effects of toxic compounds on the body. The results of research concerning the state of actual nutrition and vitamin supply of workers of metallurgical enterprises have been presented. Considering the nutritional status assessed the specialized drinks enriched with essential micronutrients have been developed. The results have been obtained in clinical studies of the efficiency of the instant drink "Vitalife" through its inclusion in the diet of workers for one month, twice a day. The excretion of vitamin C and vitamin B_2 in the urine, the content of the products of lipid peroxidation and the activity of antioxidant enzymes (TBA - active product – malonic dialdehyde, catalase activity and superoxide dismutase) have been studied. The program and methodic recommendations to optimize the preventive diets of workers of hot shops at metallurgical enterprises have been developed: 1 cup (200 cm^3) of ready-to-drink beverage made from the concentrate for soft drinks enriched with vitamins before work; 1 cup (200 cm^3) of fruit and berry kissel enriched with vitamins and calcium during lunchtime as the third course or as a separate dish; 4 cups (1 dm^3) of beverage from the mineral concentrate at the right time during the working shift. Products included in the program provide the water and salt balance and fill the micronutrient shortage. The use of specialized products in the preventive nutrition of workers has shown their efficiency in protecting the body from the unfavorable conditions of production. This can serve as a factor in the preservation of health and prevention of occupational and production related diseases.

Keywords: The actual food, specialized products, a preventive diet, prevention of occupational diseases

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INTRODUCTION

One of the preventive measures of occupational diseases of industrial workers and health preservation is the development of science-based diets and nutritional programs taking into account the specificity of jobs and the nature of effects of unfavorable production factors on the body [1, 18, 19]. The given direction is a priority in the current nutritiology which is confirmed by a number of government acts and regulations [21, 22].

It is known that when operating in the heating microclimate at metallurgical plants including aluminum production there is a considerable loss of water with the sweat, which leads to the increased consumption of vitamins and minerals by the body.

The characteristic combination of poor working conditions and the deficiency of vital micronutrients are the cause of psychosomatic disadaptation. As a result, the frequency of chronic diseases including occupational and production related ones increases.

The main vector of the problem solution is the creation and practical implementation of new types of specialized products, including soft drinks with directed functional properties. It is necessary to confirm the quality of the consumer properties of products by conducting experimental or clinical studies [19].

OBJECTS AND METHODS OF STUDY

The research objects have been diets of workers of the West - Siberian metallurgical plant and aluminum plant in Novokuznetsk of Kemerovo region, biological medium (saliva, urine), experimental and commercial samples of specialized products. The actual nutritional status has been studied with the help of questionnaire

using the method of 24 - hour playback and the computer program. The direct analysis of ascorbic acid in dishes and culinary products has been conducted for an objective assessment of vitamins in the diets.

The assessment of the body supply of workers with ascorbic acid, thiamine, riboflavin, niacin, tocopherol, retinol, beta-carotene has been achieved by the direct determination of vitamins and their metabolites in blood and daily urine. The activity of vitamin dependent enzymes in erythrocyte hemolysate has been examined: thiamine dependent enzyme of transketolase (TK) and the degree of its activation when adding thiamine diphosphate (TDP - effect), the activity of B_2 - a dependent enzyme of glutathione reductase (GR) and the degree of its activation when adding flavin adenine dinucleotide (FAD - effect), the activity of pyridoxine dependent enzyme of aspartate aminotransferase (ATF) and PALF - effect.

The analysis of vitamins has been performed with the help of fluorometric, spectro and photometric methods, highly effective liquid chromatography [2].

As a product of lipid peroxidation, malonic dialdehyde (MDA) has been investigated. The selection of this parameter is related to the fact that one of the main substrates of free radical oxidation is molecules of polyunsaturated fatty acids (PUFA) and lipid components of lipoproteids of low and very low density. Hydroperoxides (diene conjugates) are formed as a result of the oxidation of fatty acids which are metabolized into secondary products – malonic dialdehyde. In order to determine it the fluorometric method has been used. It is based on the fact that the final product of lipid peroxidation, MDA, reacts with thiobarbituric acid forming the fluorescent complex, the light intensity of which is directly proportional to the concentration of MDA.

The activity of two antioxidant enzymes - superoxide dismutase (SOD) and catalase has been studied. SOD activity has been determined by the chemiluminescent method according to the inhibition degree of nitroblue tetrazolium (NBT) reduction in the presence of NADH of phenazine methosulfate (PMS).

The principle of determining the catalase activity is based on the fact that the enzyme destroys H_2O_2 substrate. The undestroyed part of hydrogen peroxide is measured with the help of sodium molybdate.

The study of saliva has been used as the simplest and at the same time the most reliable way to determine the antioxidant capabilities of the body. Saliva contains free radicals that are formed during the antibacterial protection, as well as by the enzymatic way of peroxidase reactions. It has been shown that saliva possesses antioxidant properties, because it contains enzymes inhibiting the free radical oxidation.

The influence of saliva enzymes (catalase and superoxide dismutase) indicates the feedback between their activity and the amount of TBA - active products. Their content correlates with the similar indices in the red blood cells.

The research materials are subjected to the statistical analysis. Methods of parametric statistics have been used to process data about the actual state of the preventive nutrition, as well as the materials on the content of lipid peroxidation products in biological fluids (saliva) to determine average values, their errors and reliability by means of Student's test.

The investigations have been carried out on the basis of the accredited laboratories of vitamins and minerals of the Institute of Nutrition of the Russian Academy of Medical Sciences (Moscow), NPO "Art Life" (Tomsk), and a pharmaceutical company "Altayvitamins" (Biysk).

RESULTS AND DISCUSSION

The accumulated national and international experience shows that the insufficient intake of vitamins and some minerals from food is a common problem in all countries, regardless of their economic development.

The availability of vitamin deficiency is not limited to the inadequate intake of fruits and vegetables, although they are associated with vitamins for the majority of consumers. In fact, fruits and vegetables can only be a source of vitamin C, beta - carotene, other carotenoids, bioflavonoids (vitamin P) and, to some extent, folic acid only when having a great variety and a large number of their consumption.

The rest of the vitamins a person gets are from other products: B1, B6, PP - brown bread, lean meat, beans, nuts; B2 - milk and milk products; vitamin A - natural butter; vitamin E - unrefined vegetable oils.

The main reasons for the lack of vitamins, as well as other vitally important nutrients are:

– Reduction of the energy value of the diet and the amount of food consumed;

– Prevalence of canned food subjected to tough cooking and storage in the diet, poor in essential nutrients;

– Environmental stress, emotional stress and other negative factors of civilization, increasing the need for micronutrients;

– Bad habits such as smoking, heavy drinking, drug abuse;

– Low dieting culture, lack of public awareness about principles of healthy diets, lack of a financial opportunity to purchase a full food basket.

The prolonged vitamin deficiency leads to the failure of the body's adaptive capabilities and, as a result, it has an unfavorable impact on the human development, health and welfare.

Physical performance, resistance to the occupational and industrial diseases among the workers of industrial enterprises decrease, the negative effects of the harmful production factors on the body, nervous and emotional stress increase, professional injuries rises, active working life shortens.

The investigations conducted in the 60-ies by the scientists of the Institute of Nutrition of the Academy of Medical Sciences of the USSR under the leadership of professor V.V. Efremov at the Moscow Metallurgical Plant showed that the physical endurance of workers receiving a normal diet poor in vitamins was two times lower than that of workers taking a daily multivitamin preparation "Undevit".

The sickness rate of workers by the number of diseases and the total number of days missed was by 20-25% higher than that of workers provided with the right amount of vitamins corresponding to the recommended intake [6].

Similar results were obtained in the Moscow metro and in a number of similar studies in different regions of the country [27, 37, 25].

It has been determined that the stressful conditions of the professional activity and the effect of harmful production factors lead to the increased catabolism of vitamins and increased need for them [4, 11, 28]. For example, dispatchers and operators at the control panel need more thiamine and ascorbic acid by 30–40% [24].

The necessity for additional vitamins is sometimes specific depending on the factor effect. The UHF influence increases the body's need for riboflavin, folic acid, pyridoxine [36], when having vibration - for vitamins C, PP and B1 due to the reduction of their blood level [8, 20, 16, 23].

In some cases the vitamin deficiency occurs as a result of the combined action of several production factors [7, 13]. The training of astronauts is no exception [3, 4, 35].

All this indicates the need to optimize the preventive nutrition, especially vitamin provision of workers employed in the production with difficult and dangerous working conditions. The national and international experience considers it to be the most reliable and highly efficient means of improving their health and working capacity.

The relationship between the provision of the body with vitamins and its functional state have repeatedly been demonstrated in the works of V.V. Efremov and other authors [5, 6, 14]. It has been shown that the muscle weight of the workers of hot shops at the metallurgical plant having a normal diet is reduced by 17–26% in 2 hours after starting the operation, by the end of the working day – by 22–23%. The number of errors on the differential stimulus increases and the shortening of the latent period of visual - motor reactions is observed due to the weakening of the inhibitory process and the predominance of the excitatory one.

The muscular endurance of workers taking additionally the multivitamin preparation "Undevit", one pill a day, has remained at the initial level and only by the end of the working day it has decreased by 8–10%. There have been fewer errors on differentiation. The number of cases of acute catarrh of the upper respiratory tract has decreased by 25.6% and also the number of disability days (by 24.5%). The incidence of acute gastro-intestinal diseases has decreased by 34.5% and so the number of disability days (by 36.9%). A significant reduction in the incidence of myositis and radiculitis has been observed [6]. Loss of working days due to illness has decreased by 6–7% a year, including colds by 25% [35, 36].

The papers of other authors show the influence of vitaminization of diets of different professional groups on health care seeking for all diseases (the index has decreased by 28%), the cardio-vascular diseases have decreased by 32%. The reduction of labor losses has been respectively 30.7 and 42.6% in comparison with those workers who have not received extra vitamins [35, 36].

It has been found that the normalization of vitamin status can reduce the frequency of non-observance of some indices of lipid, protein, carbohydrate metabolism [10, 35, 36], and, in general, the negative impact of production factors on the human body [2, 3, 8, 20, 35, 36].

The additional vitaminization of employees of the locomotive crews at Lvov railways provides the improvement of adaptation to darkness, which is important for the prevention of general visual and color fatigue affecting the traffic safety [7].

Special attention is paid to ascorbic acid. The workers with the level of vitamin C in blood of 0.5 mg / 100 ml and higher have better reactimeter indices in comparison with the workers having lower concentrations [15]. Based on these data, the authors have concluded that the fatigue reduction, the increase of psychomotor reactivity and attention concentration can be achieved by consuming 120–150 mg of ascorbic acid per day with the level of its content in blood of 1 mg / 100 ml. These recommendations have been used to maintain the wake of transport drivers working at night [15, 43, 48].

The influence of relatively high doses of vitamin C has been studied by American scientists who have noted an increase in resistance to the stress effect of the intermittent light [47].

The additional inclusion of ascorbic acid in the diet for 2 years has reduced the sickness rate of employees of the locomotive crews of the electrodepot "Kaluzhskoe" of Moscow Metro compared with the previous period by 25% [13].

This paper deals with the analysis of the actual nutrition of workers of metallurgical enterprises, which has revealed the disbalance of the diet in a number of essential nutrients. The deficiency of vegetable fats was 50-75%. There was insufficient vitamin content, g / a day: C - 54 (39); B_1 - 1.4 (36); B_2 - 1.6 (36); PP - 20 (41); B_6 - 2.1 (16); A (based on beta - carotene) - 1.0 (+), in parentheses – percentage of deficiency.

The low level of vitamins established by the survey is consistent with the results of the analytical determination of ascorbic acid in the lunch diets of workers – 16.8 ± 1.9 mg (n=7). It makes up 23% of the daily requirement.

The concentration of vitamin C in blood serum is, on the average, 0.33 ± 0.01 and the norm is 0.7–1.2 mg / dl. In 95% of the examined workers it was lower than normalized values, including 85% who had the concentration lower more than twice. The number of workers with a deep deficiency amounted to 23–28% (<0.20 mg / dl). This situation with ascorbic acid took place in summer, in July, when the consumption of fruits and vegetables should be optimal. There is reason to believe that in winter and spring seasons the extent and depth of the vitamin C deficiency will be more expressed.

The content of vitamin B1 in the daily urine averaged 178 ± 5.7 mg / a day. 40–60% of the examined workers had the deficiency of the urinary excretion of thiamine. The TK activity of erythrocytes was at the level of 1.40 ± 0.02 mcmol Sedoheptulose

per 1 million of erythrocytes in an hour. THP effect was 23.5 ± 0.8%. Normally, the activation index of THP, a dependent enzyme of TK erythrocytes, should not exceed 10–15%.

The data obtained can be considered as the thiamine deficiency in the human body.

The daily excretion of riboflavin in the urine was below the lower limit of the norm - 290 ± 14.3 mcg / a day (the norm is more than 300 mcg /a day). The activity of GR erythrocytes was 21.0 ± 1.15 mcmol NADF2 per 1 million of red blood cells in an hour, FAD - effect - 1.4 ± 0.13% (the norm is less than 1.2). The index of FAD - effect equal to or above 1.2 was found in 63% of the total number of the examined workers. These data, along with the low excretion of vitamin B_2 in the same time period, indicate a lack of the adequate supply of riboflavin.

The supply with vitamin PP was estimated by the niacin metabolite excretion in daily urine - n-methyl-nicotinamide. Normally, this figure is 7–12 mg /a day. The deficiency of daily excretion with urinary niacin metabolite was 26–33% in the examined group. In general, for the whole group, the urinary excretion of n- methyinicotinamide was at the level of 4.9 mg /a day.

The revealed lack of nicotinic acid is not fully compensated due to its additional source - tryptophan.

The pyridoxine content in the body of workers was estimated by AST activity, which was at the level of 2.26 ± 0.11 micromoles of pyruvic acid per 1 g of Hb in a minute. The index value of PALF - effect was on average 1.9 ± 0.07%. According to several authors the index of PALF - effect in determining the activity of AST erythrocytes should not exceed 2.0, and the average is 1.5. In 26% of the examined workers the value of PALF - effect is equal to 2 or higher. The set value of PALF - effect indicates the marginal supply of the body with vitamin B_6.

The concentration of vitamin E in the blood serum was 0.8 ± 0.01 and it was at the lower limit of the norm (0.8–1.2 mg/100 ml). The highest frequency of the tocopherol deficiency occurred in the West - Siberian metallurgical plant (15%). In some cases, the level of vitamin E in blood was lower than 0.6 mg / 100 ml, reaching 0.54 mg / 100 ml.

The retinol supply of the majority of workers was within the normal limits: its average level in blood was 53 mg / 100 ml with the norm 30–70 mg / 100 ml. The content of vitamin A below the lower limit of the norm was observed in 3% of workers.

Unlike retinol, beta - carotene supply of workers of metallurgical enterprises was insufficient. The number of people with the level of beta - carotene below normal (80 mg / 100 ml) was on average 61%. There were some cases when its concentration in blood was 25–29 g / 100 ml, i.e. it was three times lower than the lower limit of the norm.

The excess consumption of animal fat, saturated fatty acids and cholesterol was observed with inadequate intake of phospholipids and polyunsaturated fatty acids with the diet, especially omega-3 family (the ratio of omega-6 / omega-3 is 28 : 1). There were low levels of dietary fiber, including pectins. The vitamin deficiency is characterized by the combined lack of vitamins C, B1, A, carotenoids, folic acid, and several minerals. In general, it was the basis to correct the preventive diet.

The main reason for low supply of the body with vitamins is their inadequate dietary intake, as evidenced by the assessment results of the actual diet and the content of ascorbic acid in dishes and culinary products. Equally important is the increased need of workers of metallurgical enterprises for vitamins due to the nature of work and the level of anthropogenic influence.

The identified deficiency reduces the activity of the immune system, the body's resistance to the unfavorable production conditions and the environment, accelerates aging and wear of the body, and reduces the duration of active working life.

The nutrition program for the workers of hot shops of metallurgical enterprises has been offered, which includes specialized products aimed at the prevention of occupational and production - related diseases.

The specialized products are presented by: a concentrate for soft drinks enriched with vitamins, a mineral concentrate for soft drinks and fruit and berry kissel enriched in vitamins and calcium, which have been developed in cooperation with the NPO "Art Life".

Tables 1 and 2 present regulated quality indices of the developed products with the addition of vitamins and minerals.

Table 1. Organoleptic quality indices of specialized products enriched with vitamins and minerals

Index name	Characteristics
Concentrate for soft drinks enriched with vitamins	
Product appearance	Thick, opaque liquid, there may be a precipitate
Color	From light brown to dark brown
Smell and taste	Smell of corresponding flavoring, sour and sweet taste
Solubility in water	Full, small opalescence in water is allowed
Mineral concentrate for soft drinks	
Appearance, color, smell, taste	Non-homogeneous white powder with crystals of different structure, odorless, bitter salty taste
Kissel of fruits and berries enriched with vitamins and calcium	
Appearance	Homogeneous, evenly colored granular mass, loose clots are allowed
Color and taste	Sweet and sour, corresponding to the raw materials used
Smell	Peculiar to the flavoring agent, odors are not allowed
Consistency of the product prepared by the method indicated on the label	Homogenous, viscous, without lumps, thickness of different degrees. Stratification of the product is not admitted, white inclusion is possible

Table 1. Ending. Organoleptic quality indices of specialized products enriched with vitamins and minerals

Index name	Characteristics
Drink powder with vitamins, «Vitalife»	
Appearance	Homogeneous, evenly colored, dry powder. Clots are acceptable if they dissolve during intensive mixing.
Color	Similar to the color of fruit and berry extracts used.
Smell and taste	Smell of the corresponding flavoring agent, sour and sweet taste.

Table 2. Physical and chemical quality indices of specialized products enriched with vitamins and minerals

Index name	Index value
Concentrate for soft drinks enriched with vitamins	
Mass fraction of soluble dry substances, % not less	55.0
Mass fraction of titratable acids (in terms of citric acid), %, not less	2.0
Sodium benzoate content, %, not more	0.1
Vitamin C content, mg /100 g, not less	450.0
Vitamin B_1 content, mg /100 g, not less	4.0
Flavonoid content, in terms of silibinin, %, not less	25.0
Tanning agents in terms of tannin, %, not less	0.5
Mineral concentrate for soft drinks	
Mass fraction of moisture, %, not more	10.0
Mass fraction of particles till 2 mm in size incl., %, not less	98.0
Mass fraction of metallic impurities, %, not more	$3 \cdot 10^{-4}$
Potassium content, g /100 g, not less	8.0
Magnesium content, g /100 g, not more	1.3
Readiness for use, min, not more	3.0
Fruit and berry kissel enriched with vitamins and calcium	
Mass fraction of moisture, % not more	5.0
Mass fraction of titratable acids (in terms of citric acid), %, not less	1.0
Mass fraction of sucrose, %, not less	48.0
Readiness for use, min, not more	3.0
Impurities and infestation with storage pests	Not allowed
Content of micronutrients, mg/100 g, not less	
vitamin A	3.4
vitamin E	100.0
vitamin B_1	12.7
vitamin B_2	20.0
vitamin B_6	48.8
vitamin PP	60.0
vitamin B_{12}	43.6
vitamin C	200.0
biotin, mcg /100 g, not less	0.32
Folic acid, mcg /100 g, not less	4.0
D-pantothenate of calcium	43.6
calcium	867.0
Beverage powder with vitamins «Vitalife»	
Mass fraction of moisture, % not more	3.0
Mass fraction of titratable acids (in terms of malic acid), %, not less	2.0
Readiness for use, min, not more	15.0
Vitamin content, mg / 100 g	
vitamin C	72.25-123.25
vitamin A	1.06-1.81
vitamin D_3, IU / 100 g	425-725
vitamin E	1.06-18.13
vitamin B_1	1.49-2.54
vitamin B_2	1.81-3.08
vitamin B_6	2.13-3.63
vitamin B_{12}, mcg / 100 g	3.19-5.44
nicotinamide	18.28-31.18
pantothenic acid	7.4-12.69
folic acid	0.43-0.73
biotin	0.21-0.36

Note. Physical and chemical indices are determined in the concentrate.

The program helps to optimize the water-drinking regime and vitamin and mineral balance throughout the working shift. It includes: an enriched concentrate for soft drinks (in stock); fruit and berry kissel enriched with vitamins and calcium (in stock); a mineral concentrate for soft drinks.

Table 3 shows the nutritional value of the program per employee during the working shift.

Table 3. Nutritional and energy value of the program

Product name	Daily norm of the finished product, cm^3	Nutritional and energy value of the daily norm of the finished products		% of daily requirements
Concentrate for soft drinks enriched with vitamins	200	Energy value, kcal	56.40	-
		Hydrocarbons, g	10.51	-
		Organic acids, g	0.40	-
		Vitamin A, mcg	270.00	30.0
		Vitamin C, mg	27.00	30.0
		Vitamin B_1, mg	0.45	30.0
		Vitamin B_2, mg	0.54	30.0
		Niacin, mg	6.00	30.0
		Tannin, mg	11.25	6.0
		Caffeine, mg	7.50	15.0
		Silybin, mg	18.00	60.0
Fruit and berry kissel, enriched with vitamins and calcium	200	Energy value, kcal	49.05	-
		Hydrocarbons, g	13.62	-
		Organic acids, mg	174.00	-
		Vitamin A, mcg	270.00	30.0
		Vitamin E, mg	9.00	60.0
		Vitamin B_1, mg	0.45	30.0
		Vitamin B_2, mg	0.54	30.0
		Vitamin B_6, mg	1.20	60.0
		Niacin, mg	6.00	30.0
		Pantothenic acid, mg	3.00	60.0
		Vitamin B_{12}, mcg	1.80	60.0
		Folates, mcg	240.00	60.0
		Biotin, mcg	30.00	60.0
		Vitamin C, mg	27.00	30.0
		Calcium, mg	130.00	13.0
Mineral concentrate for soft drinks	1000	Energy value, kcal	3.27	-
		Organic acids, g	1.35	-
		Sodium, mg	780.00	60.0
		Potassium, mg	1200.00	48.0
		Magnesium, mg	200.00	50.0
		Chlorides, mg	1300.00	60.0

Sanitary-epidemiological conclusions were obtained for these products. The program was approved by Federal State Scientific Organization «Novosibirsk Institute of Hygiene" of the Federal Service for controlling consumer rights and protecting the human welfare.

Methodic recommendations for the most effective and efficient use of the program have been developed.

The scheme of beverage consumption is shown in Fig. 1.

The consumption of recommended servings of the developed products - the concentrate for soft drinks enriched with vitamins in the amount of 20 g, the mineral concentrate for soft drinks and fruit and berry kissel enriched with vitamins and calcium in the amount of 15 g - provides from 6 to 60% of the daily requirements for essential nutrients.

The company "Valitek Prodimpex" has developed drinks and kissels under the brand name "Golden Ball", which protect the body from the influence of the unfavorable environmental and occupational factors. What do the products of fast (instant) preparation with the specified composition look like? Beverage powders are packaged in hermetically sealed packages of the metallized film from 9 g (drink) or 20 g (kissel) per one cup (200 cm^3) to larger pre-packing (5–10 kg) for public catering enterprises. Nutritional and energy value of specialized drinks are shown in Table 4.

The use of the "Golden Ball" with the natural pectin can solve 2 problems simultaneously - replacement of milk and additional introduction of pectin. Pectin promotes the excretion of lead, other heavy metals and radionuclides from the human body. Pectins connecting with heavy metals and radionuclides form insoluble complexes, which are excreted from the body not being absorbed through the mucous membrane of the gastrointestinal tract.

Taking into account the pharmacological characteristics of the formula components and their participation in the metabolic processes of the body the specialized drinks provide: strengthening of the immune system; reduction in overall sickness rate; protection against occupational hazards; excretion of toxic substances from the body; rehydration; increase of muscular endurance; increase of working capacity.

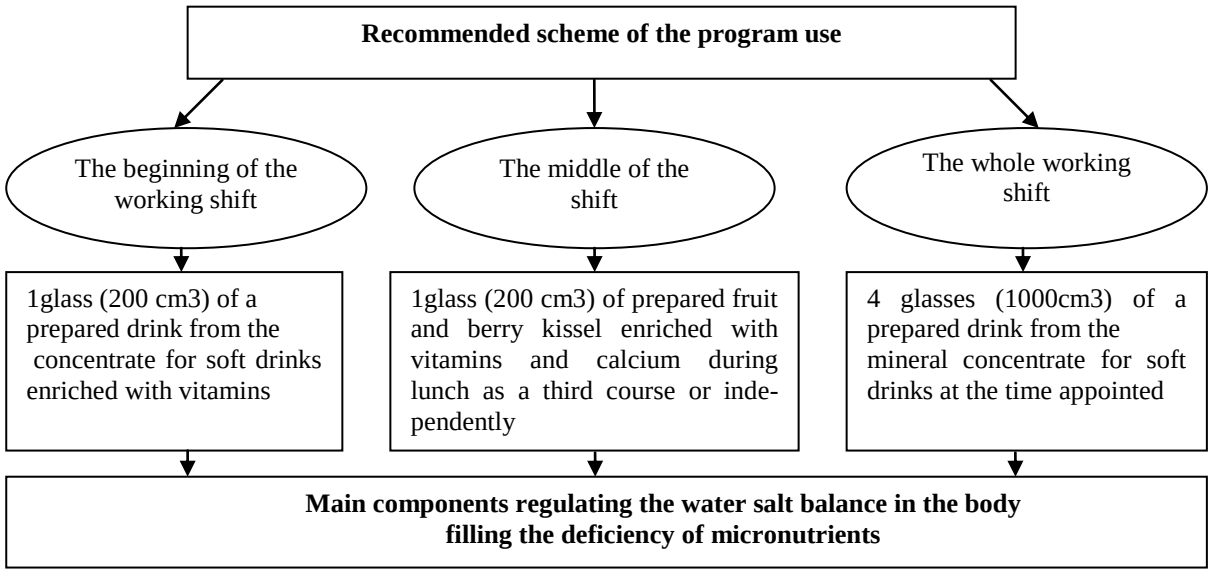

Fig. 1. The scheme of beverage consumption.

Table 4. Nutritional and energy value of the instant drink and kissel "Golden Ball" for the preventive nutrition of workers of metallurgical enterprises

Functional ingredients	Content of a prepared drink per glass (200 ml)	Recommended norm of consumption	% of recommended norm of consumption (RNC)
Vitamin C	30.0 mg	90 mg	33.3
Vitamin E	3.5 mg	15 mg	23.3
Vitamin B_1	0.5 mg	1.5 mg	33.3
Vitamin D_3	150 IU	400 IU	37.5
Vitamin B_2	0.6 mg	1.8 mg	33.3
Pantothenic acid	3.0 mg	5.0 mg	60.0
Vitamin B_6	0.6 mg	2.0 mg	30.0
Folic acid	0.2 mg	0.4 mg	50.0
Vitamin B_{12}	1.0 mcg	3.0 mcg	33.3
Biotin	0.07 mg	0.05 mg	……..140.0
Vitamin PP	6.5 mg	20.0 mg	32.5
Beta-carotene	1.0 mg	5.0 mg	20.0
Vitamin A	0.5 mg	0.9 mg	55.6
Pectin	2.0 g	25.0 g (pectin + fibre)	8.0
Hydrocarbons (drink)	8.5 g	-	-
Hydrocarbons (kissel)	27.6 g	-	-
Energy value (drink)	30 kcal	-	-
Energy value (kissel)	105 kcal	-	-

The chemical composition and energy value of the diet of workers of aluminum production have been estimated (Table 5).

On the basis of the research results the following peculiar properties of the actual supply of workers have been determined:

– the proportion of fat in the total calories exceeds the recommended norm, there is a significant excess of UFA intake, an insignificant level of PUFA intake, especially of the family of δ - 3 (the ratio of δ- 6 / δ - 3 is 28 : 1), and phospholipids and excess of cholesterol intake;

– insufficient amount of dietary fiber, especially pectin, which reduces the detoxication capabilities of workers in poor working conditions;

– the identified vitamin deficiency is characterized by the combined shortage of vitamins C, B_1, A, carotenoids, folic acid, and several minerals, i.e., it has the character of polyhypovitaminosis and polyhypomineralosis;

– taking into account a small amount of vegetables in the diets not subjected to heat treatment and fruits containing bioflavonoids, as well as the deficiency of vitamins and minerals with the antioxidant activity, it is necessary to pay attention to the problem of providing the workers with bioantioxidants, considering this trend to be a priority for the prevention of occupational and production related diseases.

Table 5. Chemical composition and nutritional value

Food products	Recommended norm	Indices
Proteins (g), including:	89	88.5 ± 6.2
Animal	49	40.6 ± 6.9
Vegetable	40	47.9 ± 3.7
Fats (all in all) g	104	141.3 ± 10.7
Animal	72	105.9 ± 9.5
Vegetable	32	35.4 ± 2.4
UFA	35	75.3 ± 8.5
MUFA	41	46.5 ± 4.8
PUFA	28	19.3 ± 2.7
PUFA/UF	0.7–0.8	0.26
Cholesterol	300	484.3 ± 43.6
Phospholipids	7.0	4.7 ± 0.4
Hydrocarbons (g),:	456	484.3 ± 28.2
MD – saccharides	50-100	126.7 ± 16.2
Food fibers	20-40	16.7 ± 1.5
Vitamins, mg		
A,mcg	1000	712.6 ± 51.4
E	15	12.5 ± 3.1
B1	1.6	1.2 ± 0.5
B2	2.0	1.5 ± 0.5
Niacin	22	17.9 ± 2.9
B6	2.0	2.2 ± 0.5
C	80	61.2 ± 10.3
Folic acid, mcg	200	171.8 ± 10.1
Minerals, mg		
Potassium, g	2.5-5.0	2250.9 ± 45.6
Calcium	800	767.5 ± 29.2
Phosphorus	1200	2148.9 ± 221.3
Magnesium	400	319.7 ± 16.3
Iron	10	15.2 ± 1.9
Zinc	15	12.4 ± 1.4
Chrome, mcg	50-200	45.7 ± 6.4
Iodine, mcg	150	46.5 ± 9.5
Energy value, kcal	3100	3562.9

The resulting materials have been the basis for the development together with the pharmaceutical company "Altayvitamins" of the concentrate for a soft drink "Vitalife" enriched with vitamins C, A, D, E, B2, B6, B12, nicotinamide, pantothenic and folic acids, biotin, and pectin.

A method for preparing beverage powder is: 20g (1 tablespoon) is poured into a glass (200 ml) of drinking water and dissolved when stirring. A glass of reconstituted beverage contains 0.25 part of the daily requirement of an adult in added nutrients. The double portion of the specialized product completely meets the daily needs of workers taking into account the availability of harmful environmental factors.

The intake of the beverage in the amount of 200 ml two times a day provides additional intake (mg) of vitamin C - 34.0; A - 0.5; D - 200 IU; E - 5.0; B1 - 0.70; B2 - 0.85; B6 - 1.0; B12 - 150 mcg; nicotinamide - 8.6; pantothenic acid - 3.5; folic acid - 0.2; biotin -1.1; pectin - 2.0 g.

Special preventive importance for the workers of aluminum production is given to the additional introduction of pectin into the diet.

The results of clinical studies have shown that taking drinks enriched with vitamins for one month in the right amount leads to a significant increase in the excretion of vitamins C and B_2 in the urine, while in the group of workers who have not taken drinks the essential changes have not been observed.

The content of products of lipid peroxidation and the activity of antioxidant enzymes in saliva in basic and control groups did not differ (Table 6).

Table 6. Content of products of lipid peroxidation and the activity of antioxidant enzymes (before vitaminization)

Groups	X±m		
	TBA-active product (MDA), nmol /cm^3	Catalase, IU /mg	Superoxide dismutase (SOD), IU /cm^3
Basic	19.3 ± 0.42	68.6 ± 5.1	25.4 ± 1.7
Control	18.7 ± 0.19	66.5± 6.3	26.7 ± 1.4

The negative links have been revealed characterizing the linear dependence among the content of malondialdehyde in saliva (r-0.65; p <0.05), the activity of catalase and superoxide dismutase (r-0.52; p <0.05).

When taking in drinks the workers obtained an additional complex of antioxidant substances in the form of vitamins, which served the basis for the study of lipid peroxidation and the activity of antioxidant enzymes (Table 7).

Table 7. Content of products of lipid peroxidation and the activity of antioxidant enzymes (after vitaminization)

Groups	X±m		
	TBA-active product (MDA), nmol /cm^3	Catalase, IU /mg	Superoxide dismutase (SOD), IU /cm^3
Basic	13.1 ± 0.29	89.8 ± 7.7	32.8 ± 1.7
Control	17.9 ± 0.31	68.7 ± 6.0	25.4 ± 2.5

Note. Difference is statistically significant (P<0.05).

The table shows the increase of the enzyme activity providing the antioxidant potential of the body and the improvement of the functional state in the basic group.

The protective effect of antioxidants in this case is provided with the following mechanisms:

– Direct interaction of oxidants with antioxidants (ascorbic acid);

– Capture of free radicals and singlet oxygen with vitamins E, B_1, B_6 (free radical scavengers);

– The protective effect of "structural" antioxidants preventing the contact of the active forms of oxygen with the functional cell components (vitamin E);

– Replacement and repair of damaged enzyme structures (vitamin E).

Vitamin E (tocopherol) performs a role of biological antioxidants in the tissues that inactivate free radicals, preventing the development of free-radical processes of peroxidation of unsaturated fatty acids.

Due to the fact that the PUFA is an essential component of biological membranes, this ability of vitamin E plays an important part in maintaining the structural integrity and the functional activity of the lipid layer of cell membranes and subcellular organelles.

Ascorbic acid has strong antioxidant properties and protection of biological membranes of phagocytes from the damaging action produced by the cells of active forms of oxygen and chlorine.

The materials of the clinical studies conducted enable to conclude that vitamins and pectin included in the beverage composition possess an effective potential to protect the body of workers from unfavorable working conditions of production, and can be a factor in preserving health and preventing occupational and production related diseases.

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STANDARDIZATION, CERTIFICATION, QUALITY AND SAFETY

SAFETY TONIC (ENERGY) BEVERAGES

T. V. Kotova[a,*], A. S. Razumov[b], A. S. Sukhikh[c], V. A. Polyakov[d]

[a] Russian State University of Trade and Economics, Kemerovo Institute (branch),
pr. Kuznetskiy 39, Kemerovo, 650992 Russia,
* e-mail: t_kotova@inbox.ru

[b] Kemerovo State Medical Academy,
st. Voroshilova 22a, Kemerovo, 650029 Russia

[c] Central Research Laboratory of Kemerovo State Medical Academy,
pr. Oktyabrskiy16a, Kemerovo, 650066 Russia

[d] All-Russian Scientific-Research Institute of Food Biotechnology,
st. Samokatnaya 4b, Moscow, 111033 Russia

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Abstract: Volume growth of consumption of tonic (energy) beverages determines the necessity to study safety criteria of the components used in their manufacture, having a tonic effect. Relevancy of the study is stipulated by the fact, that for the first time biological safety of prolonged use of the main components of non-alcoholic tonic (energy) beverages is evaluated by identifying biomarkers damage of cell membranes and integral parameters of metabolism, the results of which are applicable to humans. Under conditions in vivo the effect of prolonged use of the main components of tonic (energy) beverages - caffeine, taurine and herbal extracts (adaptogens in traditionally recommended quantities) on a model object was analyzed. The study was performed on 150 adult Wistar rats of both sexes (females, n = 75; males, n = 75). Experimental animals were divided into 5 groups according to the sort of components of tonic (energy) beverages consumed: 0.03% aqueous solution of caffeine and 0.25 % aqueous solution of taurine; ginseng extract; Rhodiola rosea extract; herbal extract of Schizandra chinense. In the control group the purified bottled water was used. In all groups of animals after three weeks of intake of (energy) beverage components, specific biomarkers of organ-and-tissue damage of cell membranes were determined in serum and tissue: alanine aminotransferase (ALT), aspartate aminotransferase (AST), creatine kinase (CK), lactate dehydrogenase (LDH) and integral basic metabolic parameters: glucose, uric acid, urea and total cholesterol. It was stated, that with prolonged daily use of aqueous solutions of caffeine and taurine in amounts corresponding to the content in tonic (energy) beverages, there was a significant increase in activity LDH and CK (twice and six times, respectively) concentration of urea and uric acid in serum. There is a tendency to increasing action of AST and hypoglycemia, reflecting subclinical pathogenetically for meaningful increase in metabolic rate with a predominance of catabolic processes. In the usage of herbal extracts as adaptogens metabolism is stimulated with a predominance of catabolic processes, mostly pronounced in the use of extracts of ginseng and lemongrass. However, the metabolic adjustment does not go beyond the range of physiological adaptation – not of a pathogenetically significant increase in the activity of enzymes, or biomarkers damage of cell membranes and hypoglycemia. On the contrary, there is a tendency to the development of hyperglycemia. Some specific gender metabolic reconstructions with prolonged use of restorative components of (energy) beverages are revealed.

Keywords: Biological safety, tonic beverages, caffeine, taurine, herbal extracts, biomarkers

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INTRODUCTION

A distinctive feature of non-alcoholic tonic (energy) beverages is the ability to have a tonic effect on the functional activity of individual organs and tissues of a human body as a whole, the effectiveness of which may vary depending on the physiological state, age and sex.

According to the results of numerous studies, the main consumers of tonic (energy) beverages are men aged 30–35 years. This is largely due to the peculiarities of life and social and community activities of the male population, in particular the need for more emotional stimulation, overcoming tiredness and stress, as well as compensation for the lack of so-called "healthy" food [1, 2, 3, 4, 5, 6].

Consumption and sales in this segment are growing. According to the results of previous studies that we reviewed, the level of consumption of tonic (energy) beverages in Russia will be increased by 1.5 liters per

capita compared to 2014, and it will be 2.9 liters by 2017. In highly developed countries, such as the USA, Germany, the UK, during the period from 2014 to 2017 level of tonic (energy) beverages consumption will be increased by 10.6 liters, 0.9 liters, 1.5 liters per capita respectively [7].

One of the main components of tonic (energy) beverages is caffeine. Its attractiveness for producers and consumers is stipulated by the availability and quite pronounced stimulating effect on mental and physical abilities of a person, which helps to keep fit during tiredness [8]. After intake of beverages with caffeine tiredness and drowsiness are temporarily eliminated or reduced. Caffeine has a great influence on the highest nervous activity of an organism, which largely depends on the applied dose and component and the type of humans nervous system. When used in small doses it is dominated by the stimulating effect, in large - depressing.

The results of the previous studies to determine presence and duration of tonic effect have confirmed the fact, that caffeinated beverages have a tonic effect lasting up to two or three hours, enhance efficiency and rapid involvement in the process, increase mental and physical performance. However, after drinking tonic (energy) beverages some deterioration of health is possible with the development of unpleasant subjective sensations (knock on his temples, nausea, physical weakness) and increased systolic and diastolic blood pressure, pulse rate [9]. Adverse effects occur with long-term consumption of caffeine-containing beverages in doses greater than 400 mg / day.

Consumption of caffeine-containing beverages is necessary to limit for the elderly and children.

For the elderly the effect on sleep is more pronounced: the coming slows down, the total sleep time is reduced, the frequency of awakenings increases, possibly due to the rapid metabolism of catecholamines of the central nervous system (CNS). Drinking caffeinated beverages can adversely affect the central nervous system.

Children, taking caffeine beverages with high doses of caffeine, may experience negative effects on the cardiovascular, genitourinary, nervous systems, gastrointestinal tract [8].

Another important component of tonic (energy) beverages is taurine, which helps to normalize the function of cell membranes, the optimization of energy and metabolic processes, maintain constant electrolytic composition of the cytoplasm of cells, inhibition of synaptic transmission. Taurine at high doses (greater than 1 g) has a suppressive effect on brains. In small doses, in combination with alcohol, caffeine and other stimulants of taurine containing drinks can cause excitation. Therefore it is not recommended to use taurine containing beverages to people with increased excitability and increased susceptibility to alcohol. One-time reception of taurine in a higher dose can cause a feeling of tiredness.

Of a particular interest are the studies of ginseng components influence on the immune system. Ginseng extract can have exertamodulatory effects on phagocytic cells and lymphocytes producing antibodies in humans and animals, increase the proliferative response of human lymphocytes in the minimum, inhibit concentrations and have the response to high concentrations [10, 11].

Ginseng has adaptogenic, metabolic, bio-stimulating, anti-emetic and tonic effects, stimulates the appetite. Around the world, ginseng and ginseng roots are widely used to improve mental and physical performance as a tonic and they are an effective tool in the treatment of amnesia [12].

It has been experimentally shown that after oral intake of ginseng powder, a significant improvement is observed in learning and mnemonic processes in old rats of both sexes having a sciatical damage of brain structures [13, 14]. Pharmacological activity is observed due to the content of ginsenosides: saponin glycosides and fatty ester oils, sterols and peptides, vitamins and minerals.

Almost for two thousand years Rhodiola rosea (golden root) was used in folk medicine. Rhodiola rosea extract optimizes the regenerative processes in the central nervous system, increases efficiency and adaptive capacity of an organism to extreme factors, helps to restore strength after tiredness. The main active ingredient is considered to be glycoside salidroside and its aglycone - tyrosol.

Rhodiola rosea roots have tonic, calming, fixing and hemostatic effect.

A long history of taking it as a tonic and an astringent in medicine of Asian countries is presented in fruits of Schisandra chinensis being a unique stimulant. This is one of the plants, which is commonly used for the treatment of coronary heart disease. What the magnolia extract activates, are estrogen-dependent luciferase genes from cells transiently transfected with the estrogen receptor [15].

Preparations from Schizandra raise excitation in the cerebral cortex and increase the reflex activity of the CNS. Toning, refreshing, stimulating effect of Schizandra (Chinese magnolia vine) is especially pronounced during intense mental occupation, what requires concentration, attentiveness, perception of wholeness. It is very important, that its tonic effect is not accompanied by depletion of nerve cells. Ginseng containing beverages increase visual acuity and ability of eyes to adapt to darkness. They reduce the heart rate, increasing its amplitude.

The tonic effect of Schizandra chinense beverages can be used as for practically healthy people (with tiredness, fatigue, reduced performance, lethargy, spring vitamin deficiency), and the people who suffer from hypotension, psychasthenia, vascular dystonia of hypotonic type.

However, despite the widespread consumption of tonic (energy) beverages and numerous studies of various aspects of this problem, the question of the biological safety of prolonged consumption of drinks containing tonic components remain unresolved, for example: of such as caffeine, taurine and herbal extracts - adaptogens.

The purpose of research is to analyze the impact of prolonged use of the main components of tonic

(energy) beverages - caffeine, taurine and herbal extracts (adaptogens in the traditionally recommended amounts) under in vivo conditions in the model object.

OBJECTS AND METHODS OF STUDY

The study was performed on 150 adult Wistar rats of both sexes (females, n = 75, male, n = 75), weighing 371 ± 26 g (females: 281 ± 29 g; males: 461 ± 23 g) in accordance with the requirements of the content and the humane treatment of experimental animals: Ministry of Health of the USSR from 12.08.1977 № 755 "On measures to further improve the organizational forms of work with the use of experimental animals"; "Rules of work with experimental animals" and "Rules for handling, maintenance, anesthesia and killing of experimental animals", approved by the Ministry of Health of the USSR (1977) and the Ministry of Health of the RSFSR (1977); principles of the European Convention (Strasbourg, 1986) and the Declaration of Helsinki of the World Medical Association on the humane treatment of animals (1996).

Study design was approved by the local ethics committee of Medical University "Kemerovo State Medical Academy" the Ministry of Health.

Criteria for inclusion animals in an experiment with are as follows: age 3–5 months, weight not less than 250 g and not more than 485 g of active animals without visible traumatic lesions and clinical manifestations of heart disease, liver and kidney.

Exclusion criteria were as follows: age less than 3 and more than 5 months, weighing less than 250 g and 485 g more, less active, painful animals.

All the animals were divided into 5 groups according to consumable components of tonic (energy) beverages (Table 1).

Table 1. Characteristics of groups of animals consuming tonic components of (energy) beverages

Group	Components of (energy) beverages	List on sex of animals	
		males	females
Group 1 (control, n = 30)	Distilled boiled water	15	15
Group 2 (n = 30)	Caffeine and taurine	15	15
Group 3 (n = 30)	Ginseng herbal extract	15	15
Group 4 (n = 30)	Rhodiola rosea extract	15	15
Group 5 (n = 30)	Schizandra chinense axtract	15	15

Group 1 (control): animals drank water (previously cleaned by filter "Barrier", heated to boiling and chilled to a room temperature) in amounts corresponding to those in groups 2–5.

Group 2: animals consumed aqueous solution of 0.03% caffeine and 0.25% aqueous solution of taurine (non-alcoholic tonic components of (energy) beverage) “Red Bull” in calculation of 0.04 mg and 0.03 mg per 100 g body weight, respectively.

Caffeine and taurine of brand Esarom (Essenzenfabrik Ges.mbH, Austria) was dissolved in pre-treated (by filter "Barrier"), boiled and cooled to room temperature water.

Group 3: The animals ate aqueous extract of ginseng Panax ginseng (20 g extract 100 ml of water) at the rate of 4 mg of extract per 100 g body weight.

Group 4: animals consumed aqueous extract of Rhodiola rosea, brand Rhodiola rosea (20 g extract 100 ml of water) at the rate of 4 mg of extract per 100 g body weight.

Group 5: animals consumed aqueous extract of Schizandra chinensis (Schizandra chinensis) (20 g extract 100 ml of water) at the rate of 4 mg of extract per 100 g body weight.

The choice of the dose usage in this study was based on recommendations according to the decision of the Customs Union dated 07.04.2011, № 622 and GOST R 52844-2007 "Soft tonic drinks. General specifications".

Animals used the prepared solutions of components tonic (energy) drinks daily in the morning for three weeks.

To put them from the experiment, the animals were given an overdose of diethyl ether (inhalation).

For the investigation samples of mixed blood were collected into sterile tubes containing EDTA. After centrifugation (16 TsLn, Polycom, Russia) at 4500 rev/min. for 10 minutes, plasma was collected into Eppendorf tubes and placed into a freezer, where it was kept at –18°C before the studies. Only a single freeze-thawing was allowed.

In the blood serum there has been determined alanine aminotransferase aspartamaminotransferaze (ALT and AST) activity spectrophotometrically (SF-2000, OKB Spektr, Russia) using reagent kits (JSC "Olvex Diagnosticum", Russia), of creatine kinase (CK) (HUMAN, Germany), of lactate dehydrogenase (LDH), the concentration of urea (JSC "Deacon-DS", Russia), glucose (JSC "Analysis-M", Russia), uric acid ("Vital Develonment Corporation", Russia), total cholesterol (JSC "Vector-Best" Russia) in accordance with the attached instructions. Thus it proceeded from the fact that more than two-three-fold increase in the activity of any of enzymes identified in blood is sufficiently reliable criterion of cell membranes damage, primarily hepatocytes, cardiomyocytes, as well as skeletal muscles and other cells, to a less extent. Aggregate analysis of changes in the concentrations

of glucose, urea, uric acid in the blood allows to evaluate integrally the metabolic rate, the ratio of anabolic and catabolic processes in the adaptive metabolic reconstructions, and increasing the concentration of total cholesterol - the degree of atherogenic food consumed.

Statistical analysis of the data was performed using the software package Microsoft Office Excel 2003 (license agreement 74017-640-0000106-57177) and Stat Soft Statistica 6.1 (EULA BXXR006 D092218FAN11). The distribution pattern of the data was assessed using the Shapiro-W Wilk. For indicators characterizing the quality of signs, the absolute number and relative value were indicated as a percentage ratio (%). For quantitative characteristics calculating arithmetic meaning (M) and standard deviation the calculation (m) was presented. To test the statistical hypothesis of the equality of the average rank of the two independent samples a Mann-Whitney test (Mann Whitney U-Test) was used.

Comparison of two related groups by quantitative variables, that are not normally distributed, was performed using Wilcoxon test for paired comparisons (Wilcoxon matched pairs test). In case of normal distribution of the characteristic data they are presented as a mean quantity and standard deviation, with comparisons using student's test for affiliated groups. The critical level of significance is $p < 0.001$.

RESULTS AND DISCUSSION

It was found that after three weeks of daily intake of aqueous solutions of caffeine and taurine, ginseng extract, Rhodiola rosea and Schisandra chinense extracts at doses corresponding to those in use of tonic (energy) beverages, ALT activity in serum did not change significantly regardless the consumption component and sex of animals (Table 2). However, activity of LDH 2-fold and CK 6-fold on the average increased in the use of aqueous solutions of caffeine and taurine. Activity of AST increased by 25–45% under use of aqueous solutions of caffeine and taurine, extracts of Rhodiola rosea and Schisandra chinense.

Table 2. Effect of prolonged use of restorative components of tonic (energy) beveragess on the activity of enzymes, biomarkers of cell damage in blood serum (M ± m)

Group	Enzyme Activity U/L			
	ALT	ACT	LDH	CK
1 (control; water)	33.4 ± 0.1	30.8 ± 0.1	268.7 ± 11.5	11.1 ± 0.3
2 (caffeine and taurine)	33.5 ± 0.2	37.2 ± 1.2*	544.2 ± 9.6*	66.6 ± 0.4*
3 (ginseng)	33.1 ± 0.1	30.5 ± 0.2	268.0 ± 11.2	10.6 ± 0.2
4 (Rhodiola rosea)	35.3 ± 0.3	44.4 ± 0.4*	231.0 ± 6.0*	11.0 ± 0.2
5 (Schizandra chinense)	37.3 ± 0.2*	43.3 ± 0.1*	249.4 ± 9.6	12.1 ± 0.4

Note. * $p<0.001$ as compared to (group 1).

In most cases, absence of significant pathogenetic (multiple) changes in the activity of investigated enzymes - biomarkers in serum indicated maintaining their intracellular pool and accordingly the functional integrity of cell membranes during prolonged daily use of energy drinks tonic components.

Subclinical increase (average 2-fold) in LDH with usage of aqueous solutions of caffeine and taurine reflected not so much damage of the cell membrane, as the stimulation of physiological and metabolic processes conjugated with the predominance of anaerobic incomplete oxidation of glucose and lactate, increased formation in peripheral tissues and red blood cells, increased gluconeogenesis, including that of lactate. As the consequence of these metabolic rearrangements LDH expression in cells increased, and in these conditions the inevitable increase in its extracellular translocations occured, the result of which was basically an increase of LDH activity in serum with prolonged use of caffeine and taurine.

However, with a very prolonged usage of aqueous solutions of caffeine and taurine pathogenetically significant (6-fold) increase in CK activity an having adverse effect has been detected, which could not only be the result of physiological rearrangement of metabolism and energy exchange. Moreover, in conjunction with subclinical increase in LDH, it is sufficiently strong reason to believe in the possibility of indirect excessive stimulation of catabolic processes, membrane damage cardiomyocytes, skeletal muscle and possibly to a less extent of hepatocytes during prolonged use of caffeine and taurine in traditionally recommended amounts.

Thus a trend reflecting the increased prevalence of metabolism in catabolic processes with prolonged use of caffeine and taurine was a more pronounced tendency to develop hypoglycemia against the increased formation of urea and uric acid, which reflects the prevalence of protein catabolism and synthesis of their nucleotide compared with the animals, drinking vegetable extracts (Table 3).

Table 3. Effect of prolonged use of restorative components of (energy) beverages on integrated indicators of metabolism (M ± m)

Group	Glucose, mmol/l	Urea, mmol/l	Uric acid, mg/100 ml	Total cholesterol, mmol/l
1 (control; water)	4.1 ± 0.1	6.2 ± 0.3	5.9 ± 0.2	1.3 ± 0.01
2 (caffeine and taurine)	3.4 ± 0.01*	9.9 ± 0.2*	7.8 ± 0.3*	1.1 ± 0.01
3 (ginseng)	5.1 ± 0.1*	10.0 ± 0.6*	6.0 ± 0.2	1.2 ± 0.01
4 (Rhodiola rosea)	5.2 ± 0.1*	9.3 ± 0.4*	7.8 ± 0.1*	1.3 ± 0.1
5 (Schizandra chinense)	5.5 ± 0.1*	5.7 ± 0.1	7.5 ± 0.2*	1.5 ± 0.1

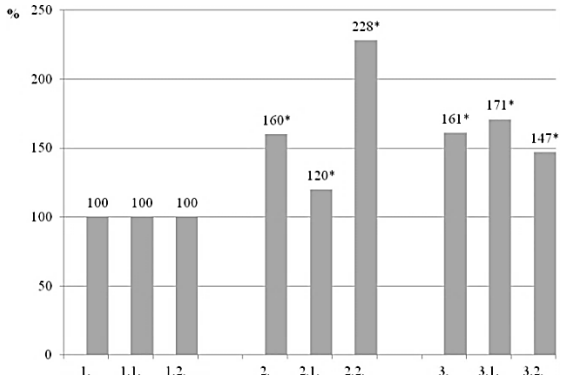
Note. * p<0.001 as compared to (group 1).

With prolonged daily intake of aqueous solutions of herbal extracts (ginseng, Rhodiola rosea and Schizandra chinensis) metabolic adjustment with the predominance of catabolic processes was carried out as well. However, against the background of increased catabolism of proteins and nucleotides, a reflection of what has been a significant increase in the concentration of urea and uric acid in blood, normoglycemia was maintained. Furthermore, to identify trends in the development of hyperglycemia, especially in the use of the extract of Chinese magnolia vine, with the animals in this group, the urea concentration increase in their blood was observed. Another feature revealed that influence of herbal extracts on the metabolism stated no significant increase in the concentration of uric acid in blood serum with prolonged use of ginseng extract. It may likely be, that at the bottom of the tonic effect of ginseng, Rhodiola and Schizandra there are several different metabolic reconstructions, including the provision of constancy of blood glucose at a higher degree of energy consumption.

Any significant increase in the concentration of total cholesterol in serum with prolonged use of aqueous solutions of caffeine with taurine, ginseng extract, Rhodiola and Schizandra have been identified, suggesting that the lack of direct atherogenic effect in all investigated in this study tonic components of (energy) beverages.

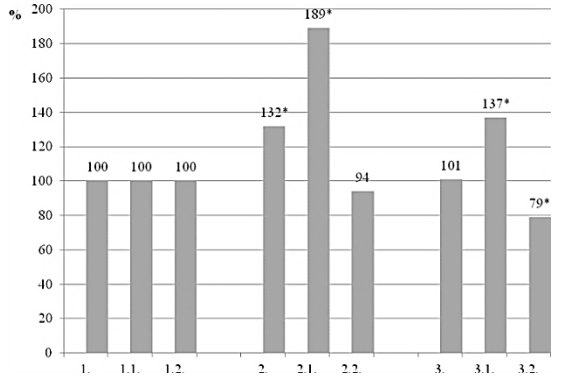
Taking into account the literature on gender peculiarities of tonic (energy) beverage consumption, an attempt was made for experimental evaluation of the influence of features of the major components on biomarkers of cell membrane integrity and integral indicators of metabolism depending on the sex of the animals.

Comparative analysis of the data obtained allowed to identify very important gender-specific peculiarities. In particular, when using an aqueous solution of caffeine with taurine greater concentrations of urea increased significantly in females, and in males - during prolonged use of an aqueous solution with ginseng extract (Figure 1). With prolonged use of aqueous solutions of caffeine with taurine and ginseng extract concentration of uric acid by males was significantly increased (Figure 2), whereas changes in the activity of enzymes, biomarkers of cell membrane integrity and some other features of males did not differ significantly, as well as the concentration of glucose.



Note. * p <0.001 compared with control group (Group 1).

Fig. 1. The effect of prolonged use of restorative components of (energy) beverages on the concentration of urea in the blood serum (% of control): (1.) Group 1 (control; water); (1.1.) Group of control. Males water intake; (1.2.) Group of control. Females water intake; (2.) Group 2; (2.1.) Females water solution intake with caffeine and taurine; (2.2.) Females water solution intake with caffeine and taurine; (3.) Group 3; (3.1.) Males water solution intake of ginseng extract; (3.2.) Males water solution intake of ginseng extract.



Note. * p <0.001 compared with control group (Group 1).

Fig. 2. The effect of prolonged use of restorative components of tonic (energy) beverages on the concentration of uric acid in the blood serum (% of control): (1.) Group 1 (control; water); (1.1.) Group of control. Males water intake; (1.2.) Group of control. Females water intake; (2.) Group 2; (2.1.) Females water solution intake with caffeine and taurine; (2.2.) Females water solution intake with caffeine and taurine; (3.) Group 3; (3.1.) Males water solution intake of ginseng extract; (3.2.) Males water solution intake of ginseng extract.

The concentration of urea in the blood serum of males with prolonged use of aqueous solutions in combination with caffeine and taurine as well as ginseng extract increased after 3 weeks 1.2 and 1.7 times on average respectively, as compared with the control group. With females, who consumed caffeine with the aqueous solution of taurine, this concentration increased twice more. After the use of ginseng it increased 1.5 times more. This could be due to gender characteristics of the hormonal status - prevalence of catecholamine stimulation and more muscle mass inherent to males.

However, the concentration of uric acid in the prolonged use of aqueous solutions of caffeine in combination with taurine increased significantly greater in males, possibly due to the increased exogenous methylated xanthine biotransformation in the liver.

With prolonged use of aqueous extract of ginseng gender differences in changes of uric acid concentration as well as the urea concentration in blood serum were although less pronounced, but nevertheless, concentration of urea increased in males more.

Thus, the comparative analysis of the results together with literature data allows us to conclude that, due to significantly higher body weight of males (461 ± 23 g and 281 ± 29 g, male and female respectively) and increased sympathetic-adrenal activity, stimulating effect of caffeine is accompanied by a pronounced intensification of metabolism and energy consumption, which inevitably leads to an increased consumption of glucose. To ensure constancy of glucose in these conditions, additional sources of initial substrates of gluconeogenesis from protein preparation are necessary, the formation of which from proteins and nucleotides is accompanied by the formation of final products of catabolism - urea and uric acid, a more pronounced increase in the concentration of the latter in males may result from rapid caffeine metabolism in a liver. The authors do not exclude, that due to it the fact of a more pronounced stimulatory effect of caffeine-containing soft beverages in men compared to women [4] is stipulated.

CONCLUSION

A prolonged (21 day) daily intake of aqueous solutions of extracts of ginseng, Rhodiola rosea and Chinese Schizandra in amounts corresponding to those in the use of tonic (energy) beverages, proved not to be accompanied by significant changes in pathogenesis of integrated metabolic parameters and biomarkers of cell membrane integrity, that is biologically safe.

(1) Prolonged daily use of aqueous solutions of caffeine with taurine in amounts, corresponding to those in the use of tonic (energy) beverages, carries a risk of structural and functional disorders of organs and tissues due to damage of the cell membrane mediated by excessive stimulation of energy metabolism and metabolism with a predominance of catabolic processes.

(2) Changes in metabolic rate with prolonged daily use of aqueous solutions of caffeine with taurine and ginseng extract are gender-sensitive, due to differences in body weight, respectively, the level of energy metabolism, gluconeogenesis and ensure its initial substrate due to enhanced catabolism of proteins and nucleotides, more pronounced in males.

(3) Long-term use of aqueous solutions of caffeine with taurine requires clinical and laboratory monitoring due to the risk of structural and functional disorders of organs and tissues as a result of the predominance of catabolic processes.

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ABOUT THE QUALITY OF MEAT WITH PSE AND DFD PROPERTIES

V. M. Poznyakovskiy[a], I. F. Gorlov[b], S. L. Tikhonov[c,*], V. G. Shelepov[d]

[a] Kemerovo Institute of Food Science and Technology (University),
bul'v. Stroiteley 47, Kemerovo, 650056 Russia

[b] Povolzhskiy (Volga) Research Institute of Production and Processing of Meat and Dairy Products,
ul. name Rokossovskogo 6, Volgograd, 400131 Russia

[c] Ural State University of Economics,
8th of March Str. 62, Ekaterinburg, 620219 Russia,
* e-mail: tihonov75@bk.ru

[d] Siberian Branch of Russian Academy of Agricultural Sciences,
Krasnoobsk, Novosibirsk Region, 630501 Russia

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Abstract: The use of modern technologies in meat production often leads to the formation of raw meat with uncharacteristic course of autolysis, one raw meat being characterized by a low pH value (less than 5.2), it is pale, flabby and watery (Pale, Soft, Exudative (PSE) with a loose consistency. Meat juice is allocated and meat has a sour smell. Other meat has a high ultimate pH (more than 6.2), it is dark, tough and dry (Dark, Firm, Dry (DFD) with coarse fiber and sticky. One of the quality indices enabling to identify meat into PSE and DFD groups is color. The pH of meat correlates with the loss of meat juice and color. Pork protein with PSE defect is characterized by a small amount of fractions with a high molecular weight and a large proportion of protein fractions with the molecular weight from 100 to 50 kDa. During meat production the technological solution for the rational use of raw meat with deviations in the autolysis process can be modes of heat treatment and the use of food additives. Stress causes a significant impact on the meat quality of slaughtered animals. The appearance of meat with PSE quality is associated with the animal susceptibility and its response to the stressful situation, and the specificity of biochemical processes in pork is caused by the development of a stress syndrome PSS (Porcine Stress Syndrome), the syndrome of poor adaptation. The meat quality is affected by breed, for example, hybrid pigs are superior to pure bred in technological properties and meat productivity. The meat of pigs of large white x Landrace x Duroc refers to NOR meat, which makes it more valuable. Due to the fact that the susceptibility of pigs to stress is inherited as a single recessive gene, the pigs are divided by genotype into two groups: stress sensitive and stress resistant. It has been shown that the activity of antiperoxide enzymes is higher in stress resistant broiler chickens than in stress sensitive ones.

Keywords: Meat quality, reasons of forming the nontraditional meat quality, autolysis, antioxidant system, lipid peroxidation

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INTRODUCTION

Modern technologies of feeding cattle and pigs enable to provide the realization of a genetic potential of meat productivity [1]. But during the intensification of livestock there appear some problems connected with the formation of raw meat with uncharacteristic course of autolysis, in particular, with a low pH value (less than 5.2). Such meat is pale, flabby and watery (Pale, Soft, Exudative (PSE) with a loose consistency, meat juice allocation and sour smell. The meat with a high ultimate pH (more than 6.2) is dark, tough and dry (Dark, Firm, Dry (DFD) with coarse fiber and sticky. [2] notices that the realization of pale, soft and exudative pork leads to the annual loss of $100 million for pig-breeding.

Characteristics, formation reasons and the rational use of raw meat with PSE and DFD properties.

The important identified index of meat with uncharacteristic course of autolysis is color which significantly affects the other characteristics and culinary and technological properties. Dark color is typical for DFD meat and the consumers consider it of poor quality by the visual observation.

[3] states that the index of light meat depends on the content of common pigments and the surface condition, and the yellowness and redness of meat depend on the ratio of myoglobin derivatives. Myoglobin in contact with the air oxygen turns into oxymyoglobin (MbO) which gives bright pink meat. Metmyoglobin (MetMb) is formed under the influence of light and air and meat acquires brown-grey color which indicates DFD evidence. It has been established that lightness of meat is a more stable parameter, less subjected to the action of external factors. Hence, it is more objective when determining raw meat into the definite quality group.

[4] recommends to break up meat into quality groups using the lightness index L, the value of which correlates with the change of pH value and the quantity of heme meat proteins. The scale "lightness pH24" has been proposed to identify the quality group of beef. The complex of pH indices, lightness (L) and redness index «A/B» can be used in addition to it.

To identify meat the reflection coefficient is used which reveals the real differences between PSE meat and DFD one.

A significant drawback of meat with DFD properties along with dark color is the fact that it is susceptible to spoilage because of high pH value and water binding capacity of meat.

The content of high molecular weight fractions increases during the storage of meat with high pH value, and there are no essential changes of the actin myosin fraction which maintain a relatively high and stable hydrophilicity level of this meat during the storage. This determines a high index value of water binding capacity of DFD meat [5].

A rapid breakdown of glycogen and increased accumulation of lactic acid take place in meat with PSE properties within the first hours after slaughter. It leads to the pH shift to the acid side and to the favorable background of microbiological contamination, but the low water binding capacity and color saturation make the technological processing difficult and decrease the yield of finished products [6].

[7] state that the products made of PSE meat possess a bad texture and bad water binding capacity. Therefore, to improve the quality it is necessary to investigate the texture and water binding capacity. Then, the amount of PSE pork included in the product can be increased.

[8] say that the ultimate pH values are the most convincing predictor of the meat quality. It is connected with a high degree of correlation between pH24 and water binding capacity [9]. The final pH between 5.5 and 5.7 is used to differentiate PSE meat from other indices. The correlation coefficients are calculated for the quality indication. Obviously, the highest correlation coefficients are observed between the ultimate pH value, the loss of meat juice and color of meat (paleness).

[10, 11] discovered a pattern in the ratio of the original and final pH values and the loss of meat juice in the samples of male pigs. The ratio of the final pH value and the loss of meat juice was described with the help of the linear equation. The loss of meat juice equals 33.6728 – 5.04 x pH24.

[12] notices that the reduction of meat freshness degree is associated with the accumulation of hexamethylcyclotrisiloxane (15.6–62.8 mg/kg), ethinyl ethylbenzene (32.1–40.0 mcg), cyclocycloheptatrien (82.6–94.9 mg/kg), ethylbenzaldehyde (9.9–31.9 kg/kg), diethylbenzene (0.9 – 20.5 mg/kg) and other substances. This causes the most pronounced changes in PSE and DFD meat. With a practical point of view the use of the method for the determination of histamine provides a more objective sorting of raw meat according to the freshness degree especially with signs of PSE and DFD defects.

[6] states that for pork with PSE properties the shear stress and increased cutting across the fibers are higher (89.4 kPa and respectively $1.55x10^{-5}$) in comparison with NOR pork (57.2 kPa and respectively $1.51x10^{-5}$). For DFD beef they are lower (57.4 kPa and respectively $1.45x10^{-5}$) as compared with NOR beef (68.3 kPa and respectively $1.57x10^{-5}$).

Decrease in the quality of meat occurs unequally in different parts of the carcass: the most affected are muscles of back and rounds that make up the most valuable meat parts of the carcass [13].

Muscle fibers are generally divided into three groups depending on their biochemical and functional properties:

– 13% of STO (slowly twitching and oxidizing) red fibers.

– 17% of FTO (fast twitching and oxidizing), they can be both white and red fibers.

– 70% of FTG (fast changing glycolysis) white fibers.

Clear differences in the muscle structure have been found between pigs of different stress tolerance in several studies [9, 10].

Pork protein with PSE defect is characterized by a small amount of fractions with molecular weight higher than 210 kDa and a large proportion of protein fractions with molecular weights from 100 to 50 kDa. The same is observed with regard to the protein fractions having a molecular weight from 50 to 15 kDa [14, 15].

Sixteen clearly defined protein fractions and four minor fractions are distinguished in the thermally processed PSE pork. Thus, with a molecular weight less than 100 kDa one can visualize two clearly defined protein fractions and one minor, from 50 to 100 kDa there are four protein fractions, one of which is minor. The largest amount of protein fractions is located in the area with molecular weights from 20 to 50 kDa, they are eleven. Two protein fractions one of which is minor can be marked in the area of low molecular weight protein fractions <20 kDa [16].

During meat production the technological solution for the rational use of raw meat with deviations in the autolysis process can be modes of temperature treatment and the use of food additives.

The destructive changes of proteins occur more intensively in meat of PSE group. For this meat it is necessary to find a way of lowering the end point of temperature treatment. [17] proposes to regulate the mode of thermal treatment to lower the denaturation changes of proteins and, as a result, to reduce the loss of mass, and to improve the tenderness and juiciness of PSE pork products. The emphasis should be on the critical temperature – 55°C in terms of denaturation and qualitative changes of proteins. For example, the mode of temperature treatment of pork with autolysis defects "Low temperature - longtime (LT - LT)" is a long thermal treatment of raw meat at low temperatures.

In addition to the appropriate thermal treatment, the technological solution for the rational use of raw materials with PSE and DFD properties may be the use of gums and other hydrocolloids, vegetable proteins.

Since the proteins possess the increased functional characteristics (formation and stabilization of emulsions, formation of gels), the use of vegetable protein to meet the challenges of raw PSE and DFD meat is very effective [18]. During the processing of meat with DFD properties it is recommended to apply low molecular regulators of pH medium (phosphates, GDL and others) and whey.

But at the same time the phosphate mixtures contribute to pH increase and water binding capacity of stuffing, but they do not solve the problems associated with other properties of raw materials, namely, emulsifying ability and intense color. Moreover, they add new problems (deterioration of the muscle tissue structure, the surface becomes slippery).

Whey is considered to be the best source for the nutritional value of people, but its application may be limited only because of its cost.

[18] considers that the alternative to the concentrated protein whey can be dairy protein complex highly functional additive "Newmil", produced by "Partner M" company according to Dutch technology.

Additionally, to improve the color characteristics and color stability of the product it is recommended to use HARMIX, the natural protein product from blood plasma of SONAC drug company. It is very beneficial to improve the color of the product, especially when using DFD meat, as it gives the natural color to the products, improves perception and emphasizes the contrast between fat and muscle tissues.

Furthermore, color stability ensured with the help of HARMIX is significantly higher than that created by the natural meat pigment myoglobin and its derivatives reacting with nitrite, it is used in cooked meat products [18].

The formation reasons of nontraditional meat quality are various: the impact of stressors, loading, transporting, unloading of animals for slaughter, joint keeping of cattle of different sexes for slaughter, the violation of the recommended duration period before slaughter, failure to comply with the parameters of electrocution, unbalanced diet, change of diet, genetic predisposition, and others.

Belgian researchers [7] have revealed the tendency of increasing meat with PSE properties during spring, summer and autumn months (April - September) compared with the winter period (December-March) on the basis of changes in pH meat, electrical conductivity and water binding capacity in 30 minutes and 24 hours after slaughter. Keeping animals for slaughter in summer for 2 and 4 hours and in winter for 2 hours reduces the share of PSE pork.

[19] notices that the composition of the diet, its balance in basic food and biological indices are an important factor in forming the quality of meat. The imbalance of diet in proteins affects the quality of meat, the autolysis speed is broken, pH changes, there appear PSE or DFD defects.

Stress causes a significant impact on the meat quality of slaughtered animals. Long distance transportation of animals for slaughter without feeding promotes the deterioration of the meat quality. Studies conducted in Spain [11] have shown that 3 hours for rest are sufficient to relieve fatigue from stressful transportation. Based on the research results carried out by [20] one can say that even the place within the trailer during the transportation can affect the meat quality of pigs.

It has been found that the appearance of PSE meat is associated with the animal susceptibility and its response to a stressful situation, and the specificity of biochemical processes in pork is due to the development of a stress syndrome PSS (Porcine Stress Syndrome), the syndrome of poor adaptation.

Pre-slaughter stress leads to the increased ante-mortem breakdown of glycogen and to the slight decrease of pH value in the muscle tissue during autolysis, while pH level of dark dry meat is within 6.4–6.8 [21]. In contrast, [22] have established that the pre-slaughter stress provokes an accelerated breakdown of glycogen and a significant shift of pH to the acid side. Thus, in 45 minutes after slaughter pH is 5.4 resulting in the formation of meat with PSE symptoms.

The accelerated glycolysis is associated with the damage of sarcoplasmic grid in PSE muscle tissue and release of Ca^{2+} according to [23].

Furthermore, [24] consider that in PSE muscle tissue during autolysis the calcium ions are released from the sarcoplasmic reticulum not so as in the NOR meat. This also prevents the development of rigor mortis in the exudative muscle tissue.

There is a reactionary attitude to the problem of meat with PSE and DFD properties instead of a warning one in the meat industry. Although it is possible to minimize the deterioration of meat quality by preventing the formation of raw meat with defects during autolysis, for example, by eliminating the stress before animal slaughter and by assessing the meat quality of each carcass with the information provided to optimize breeding stock [22].

[23] states that the use of anti-stress drugs enables to avoid the formation of meat with PSE signs, contributing to the normalization of the process of post-mortem glycogen breakdown in the muscle tissue of animals.

Slaughter of animals is one of the most crucial stages of meat production, and the appearance of PSE and DFD defects depends on the duration of the stunning. [2] believes that to ensure the quality of meat, it is necessary to stun animals only to fainting but still maintaining the functioning of heart.

The cattle breed affects the quality of meat, for example, hybrid pigs are more superior in technological properties and meat productivity than purebred. Pig meat of Large White x Landrace x Duroc refers to NOR meat, making it more valuable [19].

Since the susceptibility of pigs to stress is inherited as a single recessive gene, pigs are divided into two genotype groups: stress sensitive and stress resistant. Breeds like Perten, Swedish and Yorkshire belong to the first genotype, and Large White, Duroc, Chester - to the second [8].

[25] has found that the most stress resistant breeds are: Large White, the new type of "large white Konstantinovskaya", Landars, Hampshire and also

breed combinations: Large White x Landars, Large White x Hampshire, Large White x Duroc and others.

Pig selection which provides the intensive production of meat according to the data of a Finnish researcher [24] leads to the increase of pale, soft, watery PSE meat having a low water binding capacity.

Meat pigs have genetically expressed lack of metabolism in muscles, which is the basis for PSE pork [26].

Genetic predisposition is an equally significant reason for PSE and DFD meat, because the peculiarities of post-mortem biochemical processes in the muscle tissue are determined by genetic factors, breeding and selection by 20–40% [21].

[26] has established that the uncharacteristic post-mortem changes in the structural and functional properties of skeletal muscles leading to the deterioration of the meat quality occur among some animals. PSE signs prevail in pigs and poultry. It is caused by a genetic predisposition for PSS (porcine stress syndrome).

Pork producers should use all the available information in determining PSS gene in their herd.

Today the detection methods of PSS susceptible animals have become more technologically accessible. One of the means used by manufacturers of PSS pigs to determine the status of breeding herd is molecular DNA test. [28] has developed a fast, simple and accurate molecular test for PSS, enabling to distinguish all three PSS genotypes (NN, Nn and nn) with the accuracy of nearly 100 percent. Molecular test has been conducted on DNA extracted from the muscle tissue, hair, fatty tissue and blood drops. The molecular test has been patented at the University of Toronto. Blood from all animals has been analyzed in order to identify stress sensitive pigs. DNA test for pigs with a stress syndrome has shown the presence of Ryanodine gene (RYR-1).

Ryanodine is RN-receptor. According to [27] it is a main gene influencing the final pH value of meat.

The ryanodine gene of receptors [RYR1] has been established to be the causal mutation for PSS. The investigation of the structure of the skeletal muscle of pigs with different RYR1 - genotypes indicates the difference in diameter of all three types of muscle fibers. Stress sensitive animals have an increased diameter of muscle fibers. Much attention is paid to the genome analysis in the current research of the reasons for the formation of meat with defects in the autolysis process. This might help improve knowledge about the muscle biology and define the criteria for the selection of farm animals and poultry with favorable meat quality.

[27] notice that PSS gene has a negative effect on the reproduction and the carcass quality, so meat manufacturers should acquire or produce sows without PSS gene and gradually replace the old ones.

The use of gene technology enables to regulate the final pH value and other indices of the meat quality in the pig population.

Thus, the response to stress factors is caused by genetics and it is the main reason of forming raw meat with defects in the autolysis process. At the same time stress is a trigger for developing the oxidative stress in the body. Although there is no common definition of the oxidative stress, some researchers believe that the "oxidative stress" is the intensification of processes of free radical oxidation.

[29] define the "oxidative stress" as an imbalance between the production of oxidants initiating the free radical oxidation and the activity of the antioxidant protection system of the body neutralizing these processes.

During stress the processes of lipid peroxidation (LPO) are activated, the displacement of prooxidant-antioxidant balance takes place with the products of lipid peroxidation being both inductors and primary mediators of stress.

The impact of lipid peroxidation and antioxidant system (AO) of slaughtered animals and poultry on the meat quality remains insufficiently studied. Chicken meat is known to be the most susceptible to lipid peroxidation due to its high content of polyunsaturated, monounsaturated fatty acids and nonheme iron Fe^{3+} and Fe^{2+} in comparison with other types of meat.

In this connection, we have carried out studies on the influence of LPO processes and AO system of broiler chickens with different stress stability on the meat quality.

RESULTS AND DISCUSSION

LPO includes diene conjugates (DC), which are formed in the fatty acid molecule. They are compounds with conjugated double bonds. The increase of DC number in the blood plasma indicates the intensification of lipid peroxidation process.

Products of free radical oxidation of lipids are Schiff base, in which there is a fragment of -N = C < [30, 31].

In the research conducted it has been stated that the content of polyene bases in the heptane fraction of lipids in stress resistant chickens is significantly lower by 8.6%, diene conjugates - by 7.2%, ketodienes with conjugated trienes - by 21.2%, Schiff base is lower by 20.0%.

The chicken body has a protective mechanism in the form of the antioxidant system to prevent excessive accumulation of lipid peroxidation products. According to the present views the system consists of two links (Fig. 1):

– Enzymatic presented with oxidoreductase (glutathione reductase and others) and anti peroxide (catalase), superoxide dismutase (SOD) and others) and enzymes;

– Non-enzymatic presented with polypeptides, water-soluble and fat-soluble vitamins, amino acids containing thiol, flavonoids, carotenoids and other compounds.

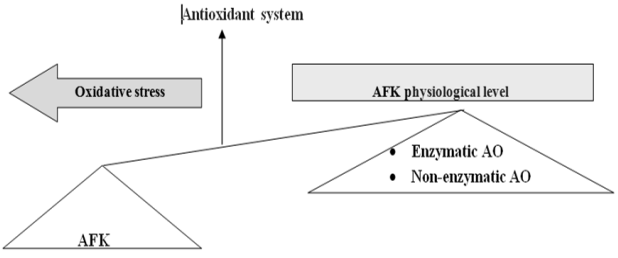

Fig. 1. Body antioxidant system.

The body antioxidant system is a complex of biologically active chemicals that can weaken the free radical oxidation of organic compounds by reactive oxygen (RO).

The figure shows that the enzymatic and non-enzymatic links of the antioxidant protection provide a stable physiological level of RO including free radicals, but if RO amount exceeds the norm, the oxidative stress occurs.

The study in the content of the main antioxidant enzymes, in particular, superoxide dismutase (SOD) and catalase (CAT) in chickens of different stress resistance has been conducted.

It is expedient to characterize the enzymes studied.

The role of SOD enzyme is to bind superoxide anion, wherein the transformation of highly reactive radicals is catalyzed into the less active hydrogen peroxide and molecular oxygen. The chemistry of the reaction is as follows:

$$M \cdot \ n+1 \ + -SOD + \ O_2 \cdot - \rightarrow$$
$$\rightarrow Mn + \ -SOD + \ O_2,$$

$$Mn + \ -SOD + \ O_2 \cdot - \ + 2H+ \rightarrow$$
$$\rightarrow M \cdot \ n+1 \ + -SOD + \ H_2O_2,$$

where M is the transition metal ion (Cu (n = 1); Mn (n = 2); Fe (n = 2). The oxidation state of the cation metal oscillates between n and n + 1.

It should be noted that the superoxide anion is less toxic in comparison with other RO, but it is the primary product of the oxygen reduction and the precursor of other RO forms. Its involvement in the enzymatic reactions of the synthesis of prostaglandin and xenobiotic metabolism enables to consider SOD as an enzyme performing not only protective, but also a regulatory function, because SOD is a key link in the regulation system of the steady-state concentration of superoxide anion [30].

Catalase (Cat) is a heme-containing enzyme from the hydro peroxide group that catalyzes the redox reaction of hydrogen peroxide decomposition:

$$Cat - Fe3 + \ + H_2O_2 = (\text{oxidized catalase}),$$

$$\text{oxidized catalase} \ + \ 2H_2O_2 =$$
$$= \ Cat - Fe3 + \ + 2H_2O_2 + O_2 \ ,$$

The Cat role in the antioxidant protection of the body is as follows: it prevents the accumulation of H_2O_2, therefore, it weakens the negative effect of oxidative stress on the cell [31, 32].

It has been established that the activity of antiperoxide enzymes in the stress resistant broiler chickens is higher than that in stress sensitive ones. Thus, the amount of catalase in the plasma of stress resistant chickens is higher by 17.1% and superoxide dismutase by 18.7%. The data obtained are consistent with the data on the formation of lipid peroxidation during the stress.

The main LPO substrate is mono- and polyunsaturated fatty acids (PUFA), which are a part of cell membranes and lipoproteins. The research has been conducted in the content of fatty acids in the meat of broiler chickens. It has been stated that the total amount of fatty acids including poly saturated and mono saturated ones in the meat samples of stress sensitive and stress resistant broiler chickens is not significantly different, therefore, the amount of mono saturated and poly saturated fatty acids does not affect the intensity of the meat oxidation.

The degree of the oxidative meat deterioration is judged by the peroxide value (PV).

The peroxide value in the meat samples increases during the meat storage. Thus, the peroxide value after 3, 5 and 7 days of storage in the samples of chilled meat of stress sensitive broiler chickens is 0.25; 0.38 and 0.78 mmol of active oxygen per 1 kg. The peroxide value in the meat samples of stress resistant broiler chickens is lower by 25.0%; 31.6% and 45.0% after 3, 5 and 7 days of storage, respectively.

The acid value is one of the main indices of the product quality. During meat production this index characterizes the depth of hydrolytic decomposition and during the storage it indicates the oxidative deterioration along with other characteristic indices.

The acid value of meat of stress resistant broiler chickens is lower by 14.3%; 28.0% and 32.5% after 3, 5 and 7 days of storage, respectively.

The marked increase of the oxidative spoilage of meat of stress sensitive broiler chickens reflects the actual oxidation at low activity of the antioxidant protection and high accumulation of lipid peroxidation products.

Thus, the results of the research conducted show that the degree of oxidative changes in the chilled meat depends on the reactivity of the antioxidant system of poultry and the formation of lipid peroxidation products. The weakening of the antioxidant activity and the activation of free radical oxidation of lipids in the blood plasma of broiler chickens increase the oxidation processes of meat.

There is a hypothesis that the level of intracellular enzymatic antioxidants is under the genetic control and it is caused by genetics. Hence, it can be assumed that the level of sensitivity to stress factors is controlled by genes. Based on the foregoing, it follows that the main reason of meat with defects in the autolysis process is stress. Since the development of stress is controlled by genes, then to prevent the formation of meat with PSE and DFD properties it is necessary to carry out the selection of farm animals and poultry not only in terms of productivity but also of the stress level.

CONCLUSION

The formation reasons of the nontraditional meat quality are various and they can occur both at the stage of production and in the processing. They are, in particular, the influence of stress factors, genetic predisposition, the violation of feeding rations and technological modes of farm animal breeding, and the stunning duration at slaughter. But the main reason for the formation of meat with PSE and DFD properties is the susceptibility of animals and poultry for slaughter to stress controlled by genes. Therefore, to prevent the formation of meat with defects in the autolysis process it is recommended to select farm animals and poultry not only in terms of productivity, but also of the stress level. It is necessary to include comprehensive nutritional additives in the formulation of meat products for the rational use of meat with PSE and DFD properties.

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THE DEVELOPMENT OF AN INTEGRATED MANAGEMENT SYSTEM TO ENSURE THE QUALITY STABILITY AND FOOD SAFETY

I. V. Surkov[a,*], V. M. Kantere[b], K. Ya. Motovilov[c], T. V. Renzyaeva[a]

[a] Kemerovo Institute of Food Science and Technology (University),
bul'v. Stroiteley 47, Kemerovo, 650056 Russia,
* e-mail: tovar-kemtipp@mail.ru

[b] Institute of Management, Quality, Safety and Environmental Enterprises Food,
Volokamskoe Highway 11, Moscow, 125080 Russia

[c] Siberian Research Institute of Technology and Processing of Agricultural Products,
Krasnoobsk 2b, Novosibirsk, 630501 Russia

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Abstract: Ensuring the competitiveness of Russian producers of food products is impossible without achieving the consistent quality and food safety. Special attention in this paper is paid to the introduction of relevant management systems at the enterprises of the food processing industry. A significant number of the currently available standards and specifications enables the management of any enterprise to choose the most appropriate variant for the given enterprise: to implement a single system or a set of systems which can represent the integrated management system (IMS). The main point in this choice is the idea of these types of management systems and of the potential, additional opportunities, and advantages that can be obtained due to their implementation at the enterprises. The responsibility of food manufacturers for the implementation and maintenance of procedures based on the principles of HACCP (Hazard Analysis and Critical Control Points) also determines the relevance of the topic. The evaluation of management systems, which are possible to implement at the food enterprises, has been conducted according to the following criteria: solvability of problems, applicability for the food enterprises and the possible effect from the implementation (a potential). The availability of fundamentals for the integration of management systems has been shown, the concept of IMS has been discussed and the need for IMS from the food enterprises has been identified The detailed plan of IMS development has been proposed. The possibility and the attractiveness of the development, implementation of other management systems in the food processing industry, in particular, the environmental management systems, management systems of occupational safety and health, energy management systems, models of ethical and social management have been established. The approach to the choice of IMS components has been confirmed on the basis of the utility definition and potential advantages of each management system separately. The model of the development and implementation of the "optimal" integrated management system of quality and safety for the food enterprises has been offered. The basic point of it is the process model as the main part of the "optimal" IMS of the food enterprise.

Keywords: Integrated management system, quality stability and food safety, quality and safety management systems, food industry

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INTRODUCTION

Food quality and safety are an important criterion of "quality of life" in all countries of the world. Such characteristics of food products as "quality" and "safety" determine to a large extent the "competitiveness" and "profitability" of the food enterprise. The development strategy of the food processing industry of the Russian Federation for the period up to 2020 proposes to implement modern management methods and integrated management systems of quality indices and safety of food raw materials and food products during the processing, transportation and storage to "solve the problem of increasing competitiveness of Russian food organizations, to create conditions for the import substitution for socially important foods and the export potential"[1].

The implementation and use of various management systems standardized in the documents of universally recognized organizations primarily the International Organization for Standardization (ISO) can certainly contribute to the successful realization of this direction. A significant part of the international standards ISO is universal: the standard requirements are general and applicable to all enterprises and companies, regardless of the industry sector, size and category of products. These include, for example, ISO 9001:2008 "Quality management systems. Requirements", ISO 14001:2004 "Environmental management systems. Requirements and instructions for use", ISO 50001:2011 "Management systems in power consumption. Requirements and instructions for use", and others.

The next group of standards can be characterized as the "industry standard", that is, with a clear field of application, for example: ISO 22000:2005 "Food safety management systems. Instructions for use", ISO 13485:2003 "Medical devices. Quality management system. Requirements for regulatory purposes", and others. The popularity of these ISO standards is shown by the statistics of a large number of certifications in the world, as well as in Russia. Table 1 presents the data on the quantity of certificates of conformity for the management systems at the enterprises of two groups: "agriculture and fishery" and "production of food, drinks and tobacco" according to the report «The ISO Survey - 2013» [2].

Table 1. Quantity of conformity certificates for management systems

№	Sphere of activity	ISO 9001				ISO 14001				ISO 22000			
		Worldwide		Russia		Worldwide		Russia		Worldwide		Russia	
		2012	2013	2012	2013	2012	2013	2012	2013	2012	2013	2012	2013
1	Agriculture fishery	4883	4953	4	9	1269	2467	1	1	22715	26284	171	279
2	Production o food, drinks and tobacco	33705	32519	120	677	5878	6890	35	56				

Statistics shows that the most popular standard is ISO 9001: 2008, followed by ISO 22000: 2005 and ISO 14001: 2004.

DATA GENERALIZATION ACCORDING TO THE MANAGEMENT SYSTEMS

In addition to the quantitative evaluation of the implementation of management systems at the food enterprises, and in order to understand what to implement and what management system, it is important to understand what each of the systems can potentially and actually give to the enterprise and whether there can be a synergistic effect from the integration of these management systems. The integration into the world economy creates certain risks for the domestic food industry. It requires the adoption of comprehensive measures to increase the competitiveness and the practical implementation of international standards in the field of food safety. At present, the perspective is not only the development and implementation of food safety management systems but also the development and implementation of integrated management systems (IMS).

ISO 9001: 2008 (GOST ISO 9001-2011 «Quality management systems. Requirements" [3]) - the quality management system according to the requirements of this standard aims the enterprise at achieving the customer satisfaction, while observing the compulsory requirements for the products supplied. The purpose and logic of this important standard is very simple because only a satisfied customer will always buy "our" products and give "us" his/her money, thus ensuring the profitability, viability and sustainability of "our" company. For the food enterprises the important elements that determine the category of "customer satisfaction" are the quality of products, to be more exact, the quality "in dynamics" , the stability of the quality index (regardless of the day of the week, time of the working shift and time of the year of production) and the product safety . It appears that the guarantee of the quality stability of the finished products will be the controlled sequence of processes, ranging from ensuring the consistent quality of raw materials till ensuring the planned characteristics of the shipped finished products based on the concept of controlling the "product life cycle" in accordance with the evaluation data of customer requirements, on the one hand (process input), and the evaluation data of the customer satisfaction, on the other hand (process output). The practice of a number of enterprises and some large companies shows that the success is largely determined by not only the achievement of customer requirements, based on the stable product quality but the possibilities of producers to anticipate the customer requirements, that is, actually to manufacture a new product, unexpected to some extent for the consumer, and accepted by him with appreciation. In achieving these approaches the important role plays the competent application of the concept of the cycle: “Plan (Planning) - Do (implementation) - Check (checking) - Act (action)”, (PDCA). "Product safety" being certainly an essential component of the concept of "food production quality" is the central category of the other management system, which is discussed below (ISO 22000: 2005 (GOST R ISO 22000-2007), but as an important component of the index of the "product quality" in the broadest sense, it has the full right to be controlled within the quality management system according to GOST ISO 9001-2011 at the food enterprises. Thus, the advantages of the implementation of quality management systems based on the requirements of the standards ISO 9000 are as follows:

– often - putting or at least improving the general order at the enterprise: in documents, on the territory, in the industrial and utility rooms, and so on;

– positive changes in the minds of the employees and the relationship between the divisions of the enterprise, the increase of responsibility level, the understanding that wages depend on the buyer of the company's products and his satisfaction, and not from the director or accountant of the company. To obtain the needed quality and the supply conditions of interesting

products for the buyer, it is necessary to achieve satisfaction of domestic consumers;
– ensuring a stable output and the required level of quality on the basis of effective processes of the quality management system of the enterprise;
– raising the level of consumer trust;
– improving the image of the enterprise;
– additional opportunities to retain existing customers and win the trust of new ones;
– improving the overall management system of the enterprise;
– additional opportunities and incentives to reduce costs and obtain more economic benefit;
– additional opportunities to increase the competetiveness of the enterprise.

ISO 22000: 2005 (GOST R ISO 22000-2007 "Food safety management systems. Requirements for organizations involved in the food chain" [4]). Food safety management system (FSMS) can be defined as a mechanism for the organization management to ensure the food safety during the production, storage and marketing. The important thing in understanding the requirements of this standard is that it applies only to the aspects of the food safety and its field of application relates to the ability of the enterprise to control the hazards of food production and guarantee its safety for the human consumption in accordance with applicable legal requirements. The main FSMS components at all stages of the product life cycle (PLC) are:
– interactive exchange of information;
– system management;
– programs of preliminary compulsory measures;
– principles of HACCP (Hazard Analysis and Critical Control Points).

The food safety is achieved by controlling all identified hazards (considering the probability and severity degree of their occurrence) with one of three established methods: PRP (preliminary programs), PRPo (operational preliminary program) and HACCP plan.

The standard recommends using the safety systems when realizing preliminary programs. They became widespread in the world, for example, GMP (Good Manufacturing Practices), GHP (Good Hygienic Practices), GLP (Good Laboratory Practices), and others. GMP system is considered to be one of the fundamental systems of the food quality and safety in the world. The food enterprises can use several elements of GMP system, in particular, the procedures in sanitizing rooms and equipment, in personnel hygiene, storage and others. The impact of GMP and GHP is aimed at the production on the whole, while the HACCP plan is developed for specific products, production lines and aimed at managing the significant and quite specific risks beyond the scope of GMP and GHP. To construct the effective FSMS it is important to understand all the distinctive features of these systems, their interrelationship (presented in Figure 1), aimed at achieving the single purpose - the safety of food products.

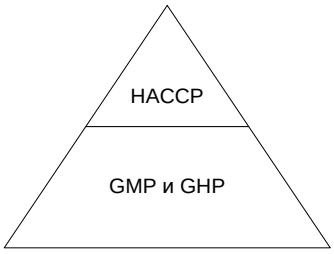

Fig. 1. Interrelationship of subsystems HACCP, GMP and GHP.

When using FSMS according to GOST R ISO 22000-2007 it is important to understand that the management system does not solve the issues that are considered in the quality management systems according to GOST ISO 9001-2011, namely, the achievement of customer satisfaction through the delivery of quality products. And this issue has been agreed by the authors who believe that FSMS is not a complete substitute for a quality management system [5].

FSMS implementation based on GOST R ISO 22000-2007 enables:
– customers to be sure that the products are manufactured in compliance with the hygiene requirements and that they are harmless;
– to demonstrate the intention to take all necessary precautions and to ensure the hygienic production of foods;
– to comply with the requirements for food safety of the legislation of the countries where the company exports its food products;
– to reduce significantly the number of evaluations made by the customer and, therefore, to save time and costs;
– to reduce rejects and return using the resource-saving technologies;
– to reduce costs by establishing better contacts with national food safety organizations;
– to increase the effectiveness of the management system concerning the food safety and to further develop the company.

The main advantages of the implementation of the food safety management system are the following:
– responsibility for the food safety;
– documented assurance concerning the food safety, which is especially important in trials;
– systems approach involving all the parameters of food safety from raw materials to end-users;
– more economical use of resources to control the safety; a significant reduction of the financial costs associated with the production of poor quality (dangerous) products;
– a significant increase of the consumer trust in the food products;
– optimization of the control systems and verification and, in particular, the company on the whole;
– new opportunities to enter new markets and to expand existing ones;
– the increase of the competitiveness level of the food production;
– competitive advantages in participating in important tenders;

– investors are more willing to invest;
– maintaining a reputation of a food safety manufacturer.

ISO 14001: 2004 (GOST R ISO 14001-2007 "Environmental management systems. Requirements and instructions for use" [6]) is an environmental management system. According to this standard the company focuses on reducing the negative impact on the environment, with the subsequent transition to the pollution prevention on the whole, the rational use of natural resources in balance with meeting social and economic needs. The environmental management system during its development is integrated into the overall management of the company, the integral part of which is the environmental protection system, acting at the enterprises in accordance with the legislation of the Russian Federation in this field. The problems of ensuring compliance with the requirements of the legislation in the environmental protection are in the foreground for many companies, implementing the environmental management system. In particular, the food processing industry affects the water resources most of all in the intensity degree of the negative impact on the environment. The enterprises annually emit about 400 thousand tons of harmful substances and only 44% are cleaned. As a rule, outdated treatment plants and equipment do not provide the required degree of purification. The proportion of wastewater contaminated with substances of chemical and microbiological composition is approximately 77% to the total volume of waste. It also confirms the low efficiency of the industrial wastewater treatment plants [7]. It turns out that the priority is providing the legal requirements, and only then - the implementation of the environmental management system, which will require significant resources in wastewater treatment plants, and possibly the reconstruction of production. Thus, for the implementation of environmental management systems more resources are expected to use than in the implementation of quality management systems, food safety management. The availability of the environmental management system gives additional opportunities to the enterprises:
– a better balance of environmental, economic and industrial components, opportunities to reduce costs;
– reduction of the level of risk environmental aspects;
– increase of the trust level on behalf of the controlling organizations, both state and public;
– strengthening of the positive image of the company, based on responsibility and environmental achievements;
– additional advantage in the eyes of potential investors, and in some cases - a prerequisite for the investment;
– the result of the previous advantages is synergistic effect, the increase of the competitiveness at the markets.

GOST R 54934-2012/OHSAS 18001:2007 "Management system of occupational safety and health. Requirements "[8] is a part of the general management system which is used to maintain the policy and management of its risks in the field of OHSAS (Occupational Health and Safety Assessment Series - a series of standards dealing with occupational safety and health). The management system developed by this standard is intended to meet the challenges of the systematic monitoring of hazards and risks in the workplace, continuous improvement of working conditions of employees and prevention of incidents, accidents and emergency situations. The management system of occupational safety and health in its philosophy, mission and methodological approaches is very similar to the environmental management system in the standard GOST R ISO 14001-2007. The benefits of implementing the management system of occupational health and safety are the opportunities to eliminate or reduce the risks of performers who may be exposed to hazards and risks associated with their work and, as a result, there is a reduction of losses (including financial) from accidents at work, monitoring for dangerous production factors, improvement of the psychological climate in the workplace, positive changes in the image of the company.

GOST R ISO 50001-2012 "Energy management systems. Requirements and instructions for use "[9] is a part of the general management system, which will optimize the process of energy consumption. The problem of limited energy resources, their high cost and the constant increase make the energy management systems attractive for the food processing industry. One can identify the potential benefits of the implementation of the energy management system:
– the system provides transparent and objective efficiency assessment of energy consumption;
– professional analysis of energy consumption makes it possible to reveal energy-consuming areas and so to reduce energy costs;
– reduction of risks with abrupt changes in energy prices and the high investment potential of energy efficient projects ultimately increase the competetiveness of the enterprise;
– origin and / or strengthening of the company's reputation as a socially responsible organization that cares about the environment and the rational use of non-renewable resources.

Currently there is no information about the practice of implementing the energy management systems at the food enterprises, but the potential of these systems enables to express confidence in the perspective of their implementation in the future.

GOST R ISO 26000-2012 "Instructions on Social Responsibility" [10]. A special feature of this standard is that it is not a management system standard and it is not intended for certification purposes, compulsory or contractual use. Lack of information about the practice of implementing the given standard at the food enterprises enables to say only about the potential benefits, which the implementation of the concept of social responsibility includes:
– strengthening of the positive image of the enterprise based on social responsibility of the food manufacturer;
– the possibility to attract and retain the qualified personnel, particularly in the context of an acute shortage;
– building confidence between the parties concerned, in particular, from the authorities, business partners;
– the opinion formation about the enterprise as a territory of social well-being [11].

An important element of the quality management system and ensuring the stability of the food quality is the sensor control system. The term "sensor" means "feeling" (derived from the Latin word “sensus” - feeling, sensation) and it is used with the term "organoleptic", which means "the identification with the help of senses". The so-called human factor plays a significant part in the sensor control. That is why, the results of organoleptic evaluation were considered insufficiently reliable for a long time. Modern methods, accumulated experience and the existing normative base, can essentially reduce the variability of estimates, increase the reproducibility of the results, which increase the level of trust and popularity of these estimates and enable to conclude that the sensor control is not an alternative, but an important part of the quality control along with the instrumental research methods (physical, chemical). Knowledge of the sensory characteristics of the incoming raw materials and products at all stages of their manufacture and maintenance of these characteristics at the required level are an important task of food workers responsible for the reception of raw materials, quality control and design of new food products. The application of the sensor control system at the food enterprise enables to obtain the following advantages:

– formation of food quality indices at the early stages of development: marketing research, the development of a new food product;

– ensuring the stability of organoleptic product characteristics at all stages of the product life cycle;

– the possibility of obtaining additional information about the characteristics of the food product by means of the descriptive sensory analysis.

All this shows the need to define the sensor evaluation method as an integral part of the unified system of the quality management of the food enterprise aimed at creating products of the stable quality, safe and attractive to the consumer.

The above data confirm not only the popularity and demand for these management systems, but also the fact that some enterprises have implemented not one but two or three management systems. In the situation of more than one implemented management system, there arises a question about the interaction of these systems, that is, these systems are combined to form a new unit from several components under a single governing body. Thus, the so-called "integrated management systems" are created. It is recognized that the integrated management system is a part of the general management of the enterprise corresponding to the requirements of two or more international standards for the management systems and functioning as one unit.

The modern manager has a wide range of possible management systems, which he can choose and integrate into the existing (or being created) concept of the general management of the enterprise. High attractiveness and individuality of each management system separately (it is potentially possible to obtain considerable benefit from the implementation of any particular system) promote the widespread implementation of IMS on the one hand and a sufficient number of common approaches on the other hand. In particular, the factors contributing to the integration of management systems may include the following general requirements:

– constructing a system based on achieving these goals;

– the concept of continuous improvement based on the application of PDCA cycle;

– principles of management (mostly) laid down into the quality management system according to the standards of ISO 9000: customer orientation (desire to achieve customer satisfaction, and each system has its own "customer"); leadership of the manager (the effectiveness of any system to a large extent depends on the level of realization of this principle); involvement of employees (involvement of relevant categories of employees for achieving the set goals is also true for almost all management systems); process approach (applicable for most management systems); system approach to management (without the implementation of this principle it is impossible to construct any effective systems); making decisions based on facts is a universal system-wide principle; mutually beneficial relations with suppliers (they can be interpreted as building mutually beneficial relations with stakeholders);

– requirements for documenting the management systems.

All this proves the validity of the approach to the choice of the foundations of the integrated management system. This foundation is the quality management system according to the requirements of ISO 9001.

Some support in the development and implementation of IMS can be GOST R 53893 - 2010 "Guidelines and requirements for integrated management systems" [12]. This document should be used together with the specific requirements of the management system standards to which the company joins during their development. It is expected that the implementation of the guidelines and requirements will help enterprises achieve the benefits when consolidating the general requirements for all standards of the management systems. The benefits include such factors such: improved business focus, a more holistic approach to the management of occupational risks, reduction of conflicts between systems, reduction of work duplication and bureaucracy, more efficient and productive internal and external audits.

The basis for the integration of management systems according to this standard is the general requirements established in the standards for the management systems: policy; planning; implementation and production; productivity evaluation; improvement; management review. This approach, according to the authors, basically does not contradict the above point of view. An important starting point in making decision about IMS development must be the understanding (identification) of the enterprise needs in the specific management systems and the anticipating of benefits that can be obtained from the integration.

The main IMS advantage is systematization of requirements for the enterprise activity in specific fields of management. It enables to minimize the functional dissociation of structural units, to eliminate

duplication in making management decisions, to optimize the number of external and internal connections.

It is important to understand the possible connection variants of different management systems, ways of IMS developing, difficulties and positive aspects within a single enterprise. The analysis shows that the construction of several management systems including those based on integration, is currently carried out in three fundamentally different ways:

(1) the parallel construction of several management systems, without any integration links;

(2) the so-called additive model when other systems based on the model of integration are consistently added to previously implemented management system;

(3) the model of the simultaneous creation of the integrated management system from a particular set of systems.

The first variant represents, in fact, the functioning of independent management systems isolated from each other. This model is characterized by duplication of processes (documents) and actions. This signify-cantly increases the pressure on the entire staff of the enterprise.

The complexity of a holistic perception of the management system by the enterprise management often arises with the additive model of construction and, consequently, low efficiency of planning, control and management in general. The volume of work, the need for resources and the development time of the integrated management system also increase in this case. A positive aspect of the given variant is the possibility of using the accumulated experience in the development of the first (basic) system during the implementation of the subsequent management systems. The historical prerequisite of this IMS development variant is the prolonged difference in the appearance of international standards and promptness in making decisions about their use by enterprise managers.

The third variant involves design, development and implementation of all management systems simulta-neously on the basis of the above mentioned principles of integration. The indisputable advantages of this model are: the elimination of duplicate elements of the implemented management systems, prevention of interrelationship confusion between management systems, a significant reduction of the creation terms of the integrated management system and labor intensity and resources; the processability of the entire development, implementation and further IMS functioning increase.

In general, the presence of several management systems has great appeal to consumers, stakeholders and investors.

The creation of the integrated management system to ensure the quality stability and food safety is almost identical to the implementation scheme of the separate management system [7, 13]. The following main stages of work are.

Stage 1: general organization of work in creating IMS (the formation of a strategic decision to establish IMS: understanding of the goals to be achieved, time and financial resources required for this task, the potential benefits as a result of IMS implementation (strategic, marketing, economic, image). It is recom-mendded to start the learning process of the development team already at this stage;

Stage 2: IMS design. The configuration of the future integrated management system is determined, a team of developers is finally formed, a detailed work plan is formed, the learning process continues;

Stage 3: IMS documentation. The working capacity of the formed integrated system and its effectiveness largely depend on the realization of this stage. The system-wide and specific documents are developed, the training of employees continues;

Step 4: IMS implementation. This stage includes the reconfiguration of the enterprise activities to fulfill the requirements of the developed IMS documentation, the correction of the documentation, which is not viable during the trial operation of IMS. It is crucial to achieve a positive perception of the changes that have made created IMS by all employees of the enterprise.

At the final stage of the implementation, it is recommended to conduct internal audits to determine the readiness of the developed and implemented integrated management system for the certification audit.

Stage 5: IMS certification. It is the logical culmination of the development and implementation processes, despite the optionality, along with the voluntary creation of all general management systems. An important aspect of this final stage is the choice of the certification body, which should be legitimate, significantly perceived at least by consumers of the developed management systems. It is economically expedient to choose the certification body that is able to certify all members of the IMS management systems. The successful result of this stage is to obtain a set of certificates of conformity for the management systems (for each system separately) within the created integrated management system of the enterprise.

The activity analysis of the food enterprises in developing, implementing and certifying the quality management systems and food safety has shown that the highest activity is observed in those sectors of the food industry, where there is the greatest competition, for example, in the beer industry. Breadmaking and confectionery industries on the contrary have objective reasons for the slow inclusion in creating the management systems - this is the low profitability of the industry and the lack of any subsidies. Although many enterprises now recognize the need for modern management systems and they are making efforts to implement them. Some enterprises, without having the right information about the financial and practical advantages to be obtained in a couple of years after the system implementation, consider it just a tribute to fashion and, of course, they are not in a hurry to invest in its development [14].

RECOMMENDATIONS IN USING IMS FOR THE FOOD PROCESSING INDUSTRY

The above mentioned evaluation, as well as the practice of development, implementation and certification of the management systems, allow to

formulate a group of "significant management systems for the food processing industry," which include: a quality management system, a food safety management system based on the principles of HACCP with GMP and GHP elements, a sensor control system forming a part of the integrated management system of the food enterprise to ensure the stability of quality and food safety and the important additions are an environmental management system, a management system of occupational safety and health, an energy management system, and the principles of social responsibility of business. The specified set of systems constitutes the "optimal" IMS, which can be recommended for a large number of food and processing enterprises. Taking the process model as the main forming part of the "optimal" IMS of the food enterprise, it can be represented as follows (Fig. 2). Figure 3 shows a graphical representation of the "optimal" IMS of the food enterprise as the most important part of the overall management of the enterprise.

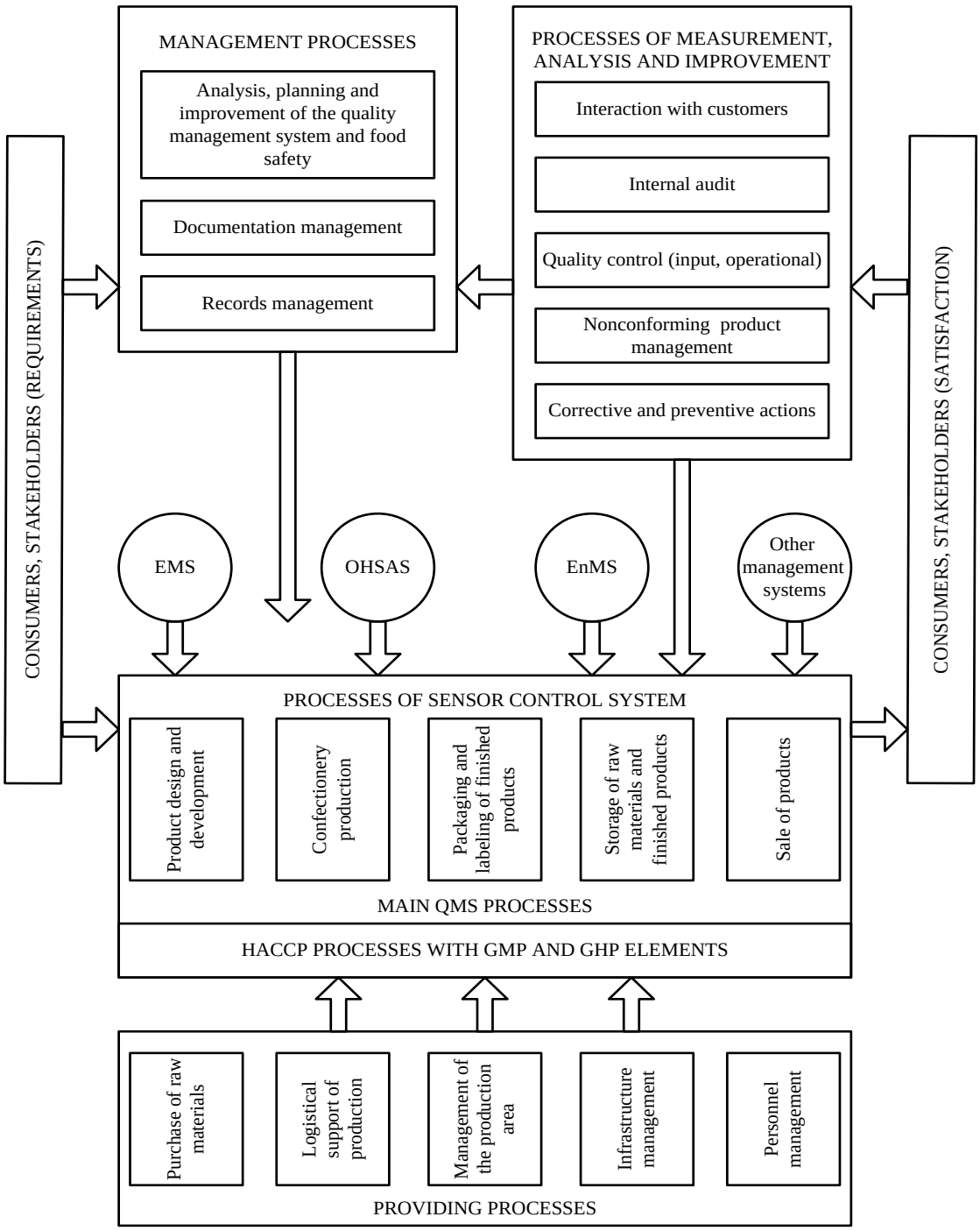

Fig. 2. Process model of the «optimal» IMS of the food enterprise.

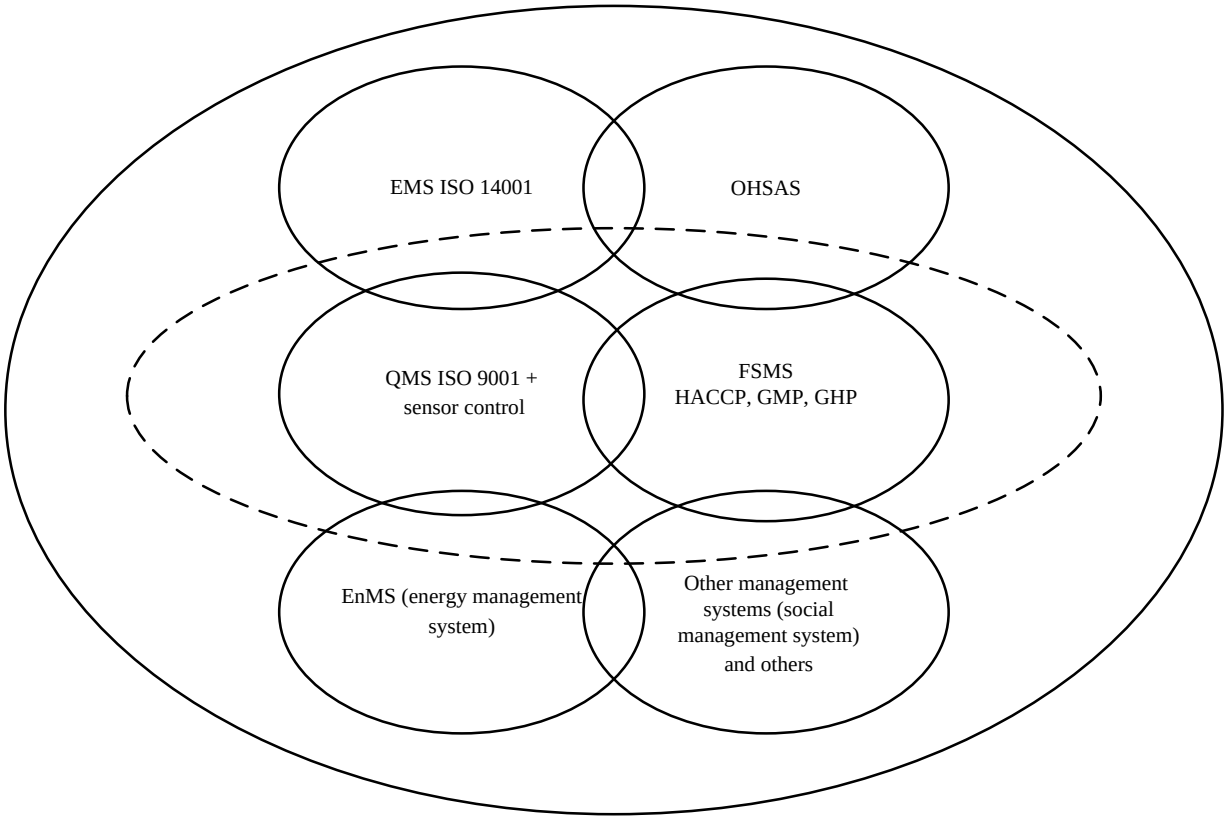

Fig. 3. «Optimal» IMS within the general management system of the food enterprise.

Ensuring the food production quality, which includes such important components as: safety, usefulness, attractiveness to consumers (taste, appearance, packaging, acceptable price), and the stability guarantee of these characteristics are the key to the success of the food enterprise, its effectiveness and long-term competitiveness. The management systems according to international standards and their highest form of realization that can provide a synergistic effect, the integrated management system, contribute to the solution of these tasks. It is possible to form the "optimal" IMS model for the food enterprise.

It is also important to realize that the work after certification audits does not finish there, and in fact, it is just beginning to achieve and maintain the stability of quality and safety of food products, finding the ways to enhance and improve them. If the food enterprise stops at some point, even at a high level, these gains and achievements could be lost in course of time, and the enterprise itself stops functioning.

Ensuring the continuous improvement of IMS functioning is the basis of the prosperity of the enterprise and the satisfaction of its customers.

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CHEMISTRY AND ECOLOGY

INFLUENCE OF PHYSICAL-CHEMICAL PROPERTIES OF ACTIVE CARBONS ON GALLIC ACID ADSORPTION

T. A. Krasnova, N. V. Gora, N. S. Golubeva*

Kemerovo Institute of Food Science and Technology (University),
bul'v. Stroiteley 47, Kemerovo, 650056 Russia,
* e-mail: ecolog1528@yandex.ru

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Abstract: The adsorption of gallic acid on active carbons of different ranks with different pore structure and chemical state of the surface is investigated. The regularities and features of the adsorption process are established. It is revealed that the adsorption isotherm of gallic acid from the aqueous solution with activated carbon of AG-OB-1 rank refers to the L-type isotherms by Giles's classification, and AC adsorption isotherm of ABG and Purolat-Standard ranks – to the S-type isotherms. L-type isotherm gives evidence concerning the flow of physical adsorption. With S-type isotherm is the adsorption described, at which the strength of the interaction between the solute and the adsorbent is less than the force of interaction between the adsorbed molecules, which can be explained by the formation of hydrogen bonds. It was found that the maximum adsorption of gallic acid with carbon sorbents changes in the following sequence - "Purolat-standard" > ABG > AG-OV-1. The mechanism of adsorption of gallic acid on active carbons is offered. Proceeding from the structure, the chemical state and the main adsorption parameters of active carbon, we can assume that the adsorption of gallic acid has physical nature. It can take place in pores, both due to dispersion interaction (of van der Waals forces) and due to the interaction between the active carbon surface functional groups, containing oxygen with carboxyl and hydroxyl groups of gallic acid. The values of adsorptive capacity testify to the dependence of the adsorption efficiency on the structure and physical-chemical properties of the sorbent. It has been determined that by the absorption of gallic acid specific interaction makes greater contribution. It is shown that the results obtained can be applied to create adsorption technologies on removing gallic acid from the sewage containing individual components and from the mixture with other polyphenols, including beer wort.

Keywords: Gallic acid, carbon sorbents, adsorption

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INTRODUCTION

Gallic acid (3.4.5-trihydroxybenzoic acid) is one of the most common plant acids. As a part of the plant usually in a bound form (esters, polymers) it is a precursor to a number of polyphenolic substances [1].

This acid is contained in the sewage of pharmaceutical factories, it is present as a component in the beer wort. Gallic acid and its derivatives have a pronounced astringent taste. When being boiled together with hops, they contribute to the formation of trub, reducing the colloidal stability and the quality of beer.

It has all the properties of hydroxycarbon acids. The most reactive is OH group in the position 4 (Fig. 1).

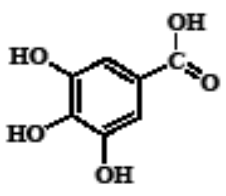


Fig. 1. Chemical structure of gallic acid.

Of the various reactions of gallic acid (oxidative coupling and esterification) there arise tannins. The tannins are divided into hydrolyzable tannins - carbohydrate and gallic acid esters (or its oligomers) and non-hydrolyzable condensed tannins.

Gallic acid forms oligomers of two types: with a carbon-carbon bond between the phenyl rings and with a complex ester linkage between the fragments. In this regard, gallic acids themselves are divided into non-hydrolyzable (diphenyl derivatives) and hydrolyzable (esters). Both these and those acids form hydrolyzable tannins with carbohydrates, because in an aqueous medium under conditions of enzymatic, alkaline or acid catalysis phenolic acids and carbohydrates are formed. These tannins are esters of monosaccharides with gallic or trigallic acids. Glucose esters with condensed gallic acid can be considered as tannins of dual nature, because they contain hydrolyzable fragments. These completely non-hydrolyzable tannins are derived from flavonols.

Under the influence of atmospheric oxygen tannins form stable black dyes [1].

Dimerization and polymerization of coniferyl alcohol compounds help to form such derivatives of phenolic acid or, to be more exact, phenolic alcohol

groups as lignans and lignins. Lignans are accumulated in all plant organs, they are present in dissolved form in resins and essential oils. Lignins in plants - important components of the cell wall of conducting and supporting tissues that act as tissue mechanical strengthening and cells protecting from biological, chemical and physical effects [1].

In practice, for the bleaching of natural water and food processing environments active carbons (AC) are used. In the production of beer to improve the properties of the final product active carbon of BAU-A, BAU-MF ranks is used [2]. For water treatment carbon AG-OB-1, with good performance is widely applied. Furthermore, in recent years the range of carbon materials has been expanded due to semi-cokes produced by the new technology. The difference of applied technology consists in replacing the traditional two-step process of carbonizing the raw material in an inert atmosphere, followed by activation for one-step process of air carbonization/activation. This reduces the final price of the sorbent due to the reduction of energy consumption for its production [3]. The use of these adsorbents will reduce the cost of production of beer and soft drinks as well.

The aim of the study was to investigate the adsorption of gallic acid by active carbons different in their structure and nature, to identify the possibility of their use in the process of improving the quality of beer.

OBJECTS AND METHODS OF RESEARCH

The objects of study are aqueous solutions of gallic acid, active carbons of the ranks: AG -OV-1 - granular AC (JSC "Sorbent", Perm) and semi-cokes ABG (PO "Carbonika F", Krasnoyarsk) and "Purolat-Standard "(JSC "Synthesis", Rostov-on-Don) [3]. General characteristics of carbon sorbents are shown in Table 2 [4]. All AC before study were washed with distilled water to remove dust particles. Then they were dried at room temperature (23 ± 2°C) during the day.

Table 2. Characteristics of carbon sorbents

AC rank	AG -OV-1	ABG	Purolat-Standard
Raw material	the mixture of coals, wood-chemical and coke pitch	brown coal	anthracite
Graining (form)	Granular (cylinder)	crushed	crushed
Carbonization and activation	Two-step	One-step	One-step
Particle size, mm	0.5–2.8	1.0–5.0	0.1–3.0
Bulk density, g/cm^3	0.52	0.49	0.68
Strength,%	70	70	70–80
Ash content, %	31	12	6
Mass fraction of Fe, %	0.62	0.13	0.02
Pore surface area, m^2/g	700–800	500	800
Total volume of pores on water, cm^3/g	0.76–0.84	0.50–0.57	0.24
Adsorptive activity on I_2, %	65	60	60
Adsorptive activity on new methylene blue, mg/g	-	160	140
Time of the protective effect on benzene, min	-	41	60
pH of the aqueous extract	6.8	7.5	8–9

Adsorption of the aqueous solution of gallic acid was studied at room temperature (23 ± 2°C) of limited volume under continuous stirring for 7–9 hours, in static conditions at concentrations ranging from 20 to 800 mg/dm^3 at the ratio of AC: an aqueous solution of gallic acid of 1 : 100.

Adsorption of gallic acid (Γ) was estimated by the equation

$$\Gamma = \frac{C_0 - C_p}{m} V_p \,, \qquad (1)$$

where C_0 is the concentration of the initial solution, mole/dm^3; C_p is the concentration of the equilibrium solution (after adsorption) mole/dm^3; V_p is the volume of the solution, dm^3; m is the mass of the adsorbent, g.

Determination of gallic acid in the solution was carried out by spectrophotometry at its own absorption.

For analysis, the wavelength was chosen according to the spectral curve registered on the instrument SF-46 for aqueous solution of individual substances (Fig. 2) [5].

The concentration of the solutions for the individual substances of gallic acid in the selection of optimum conditions of analysis was 20 mg/dm^3, distilled water was used as a reference solution. According to the analysis, light absorbing layer thickness of 10 mm, and the wavelength of 230 nm were chosen.

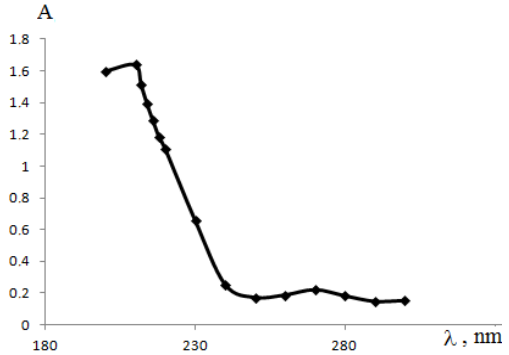


Fig. 2. The spectral dependence of the optical density of the gallic acid aqueous solution at the concentration of 20 mg/dm^3.

In a series of solutions with different concentrations there was determined the linear region for the construction of calibration curves. The dependence of

the optical density of the concentration is shown in Figure 3. The relative error in the determination of polyphenolic compounds is 4%.

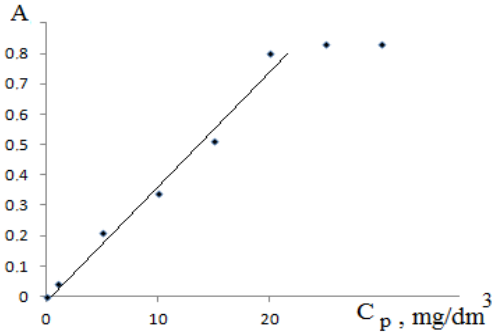


Fig. 3. The calibration dependence of the optical density on the concentration of gallic acid in the solution.

In the gallic acid determining, the test solutions with the concentration of more than 25 mg/dm^3 were diluted, for each solution dilution factor was chosen individually. The content of gallic acid in the test solution was calculated as follows:

$$C = X \cdot \frac{V_{mf}}{V_{al}}, \quad (2)$$

where X is the concentration of gallic acid in mg/dm^3, found from the graph; V_{al} is the aliquot of the test solution, cm^3; V_{mf} is the volume of measuring flask, cm^3.

The limiting value of the adsorptive capacity was calculated using the equation of Dubinin-Radushkevich:

$$\Gamma_0 = \frac{W_o}{V_m} exp \quad - \quad \frac{RT \ln \frac{C_s}{C_p}^2}{E\beta} \quad , \quad (3)$$

where Γ_0 is adsorbent maximum adsorptive capacity, mole/g; K is the universal gas constant, J/mole·K; T is temperature, K; E is characteristic adsorption energy, J/mole; β is coefficient of affinity; C_p is equilibrium concentration of the solution, mole/dm^3; C_s is the concentration of saturated solution, mole/dm^3; V_m is molar volume of the adsorbent, cm^3/mole; W_0 is the limiting volume of the adsorption space cm^3/g.

Structural characteristics of the adsorbents were determined by the low-temperature nitrogen adsorption on the specific surface area analyzer "Sorbtometer M" (production of Inst. of catalysis, Sib. Branch of RA of Sci., Novosibirsk).

The chemical state of the active coal surface - the amount of functional groups containing oxygen was determined by Boehm titration procedure.

The values of characteristic energies (E) and the size of the half-width slit-shaped pores (χ) have been determined taking into account the coefficient of affinity [6, 7].

$$E = \beta E^0, \quad (4)$$

where E is the characteristic adsorption energy of dissolved organic compounds, kJ/mole; E^0 is the characteristic adsorption energy of benzene vapor, kJ/mole; β is the affinity factor.

The affinity factor was calculated using the formula:

$$\beta = P \ P_0 = 0.97, \quad (5)$$

where P and P_0 is the parachors of the test substance and benzene, respectively [Tolmachev's hand-book].

These parachors of organic matter were calculated by the formula [6, 8]:

$$P = \frac{M}{\rho}\sigma^{1\ 4}, \quad (6)$$

where M is the molar mass of the matter, g/mole; ρ is the density of the matter, g/cm^3; σ is surface tension of the matter in the liquid state, N/m.

RESULTS AND DISCUSSION

The experimental adsorption isotherms of gallic acid from the aqueous solution are given in Figure 4.

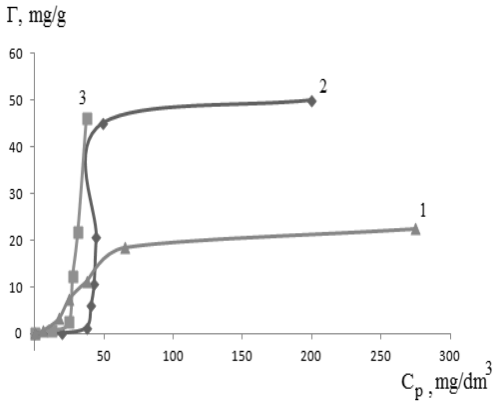
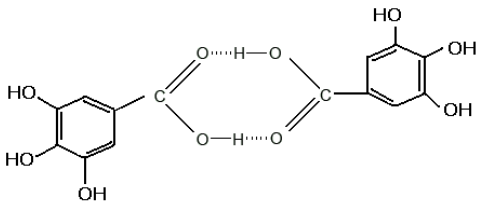


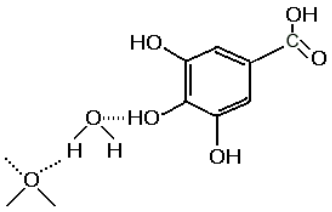
Fig. 4. Adsorption isotherms of gallic acid from the aqueous solution with adsorbents of (1)AG-OV-1, "Purolat-Standard" (2) and ABG (3) ranks.

The adsorption isotherm of gallic acid from the aqueous solution by active carbon of AG-OV-1 rank refers to the isotherms of L-type according to the Giles's classification, which testifies to physical adsorption. AC adsorption isotherms of ABG and Purolat-Standard ranks refer to the S-type isotherms. By the S-type isotherm the adsorption is described, at which the strength of the interaction between the solute and the adsorbent is less than the force of interaction between the adsorbed molecules, which can explain the formation of hydrogen bonds [4, 6, 9]. Succeeding from the structure and properties of gallic acid there can form hydrogen bonds both between molecules of the acid itself and with water (Fig. 5 a, b). The presence of a plateau with increasing adsorption (Fig. 4, isotherm 2.3) makes it possible to assume presence of a monomolecular layer at the AC followed by polymolecular layer sorption. In this regard, the adsorption of carbon sorbents is likely to be characterized by both primary and secondary interactions. Adsorbed molecules of gallic acid can act as active sites for secondary adsorption. Both separate molecules of gallic acid and clusters of polyphenolic

compounds may be adsorbed. High values of the adsorption can be explained by the fact, that it is the molecular aggregates that pass onto the activated carbon surface, not isolated macromolecular balls. The degree of aggregation of the molecules increases with increasing concentration, however with low content of gallic acid, there is large adsorption of the solvent in which similar structures begin to form first. When the concentration being increased the interaction of the macromolecules and supramolecular structures with each other becomes stronger, resulting in the occurrence of a spatial solution net.



(a)



(b)

Fig. 5. Possible schemes of the interaction of agents in the gallic acid – water system: (a) between the molecules of gallic acid, (b) between the molecules of gallic acid and water.

For a more complete characterization of carbon sorbents and calculation of adsorption parameters, the theories of monomolecular adsorption (Langmuir and Freundlich equations), polymolecular adsorption (equation of the Brunauer-Emmet-Teller (BET) type), the theory of volume filling of micropores (the equation of Dubinin-Radushkevich) were used [6, 9]. The adsorption isotherms in the corresponding linearization coordinates are shown in Fig. 6–8.

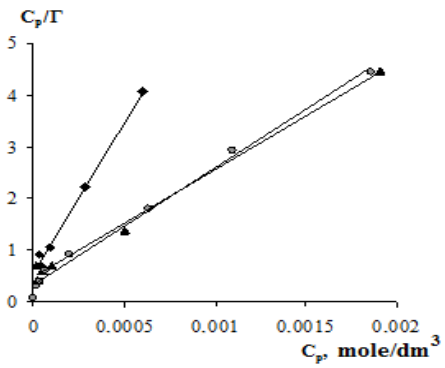


Fig. 6. The adsorption isotherms of gallic acid in the coordinates of Langmuir from the solutions on AC: ♦ - AG-OB-1; ▲ - ABG; ○ - Purolat-Standard.

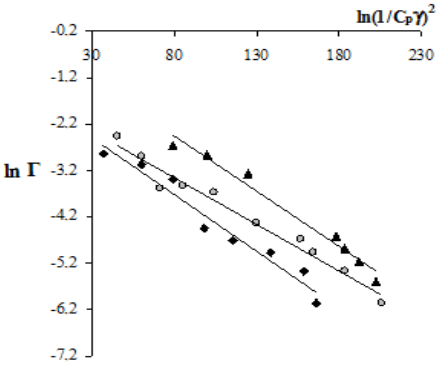


Fig. 7. The adsorption isotherms of gallic acid in the coordinates of Dubinin- Radushkevich from the solutions on AC: ♦ - AG-OB-1; ▲ - ABG; ○ - Purolat-Standard.

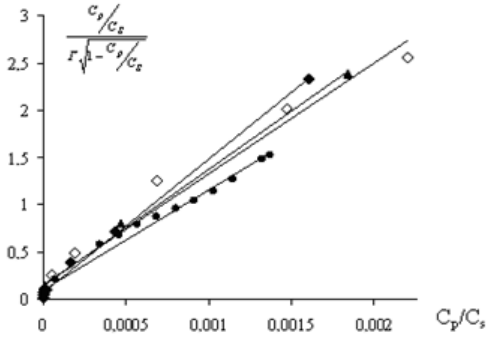


Fig. 8. Adsorption isotherms of gallic acid in the coordinates of BET from the solutions on AC: ♦- AG-OB-1; ▲ - ABG; ○ - Purolat-Standard.

The calculated values of adsorption parameters for all active carbons by monomolecular theory, generalized theory of BET and the theory of volume filling of micropores are shown in Table 3.4.

Table 3. Parametres of gallic acid adsorption by active carbons, calculated by the equations of Langmuir and Freundlich

Carbon rank	Langmuir		Freundlich	
	-G, кJ/mole	Γ_{max}, mole/g	1/n	b
AG-OB-1	30.72	0.00015	1.41	$6.1 \cdot 10^{-5}$
Purolat-Standard	30.19	0.00016	8.08	$6.6 \cdot 10^{-16}$
ABG	29.41	0.00012	4.27	$8.8 \cdot 10^{-9}$

Table 4. Parameters of gallic acid adsorption by active carbons, calculated by the equations of Dubinin - Radushkevich and BET

Carbon rank	Dubinin - Radushkevich		BET	
	Γ_0, g/g	E_0, кJ/mole	Q, кJ/mole	Γ_{max}, mole/g
AG-OB-1	0.1225	8.54	13.00	$1.5 \cdot 10^{-4}$
Purolat-Standard	0.0301	3.05	7.00	$9 \cdot 10^{-5}$
ABG	0.0024	4.60	12.50	$1.2 \cdot 10^{-4}$

Using obtained data, adsorption isotherms were calculated. Comparative analysis of experimental and theoretical adsorption isotherms showed that the BET, Langmuir, Freundlich and Dubinin-Radushkevich equations can be used to describe the adsorption process of gallic acid by active carbons from the aqueous solution (Fig. 9-12).

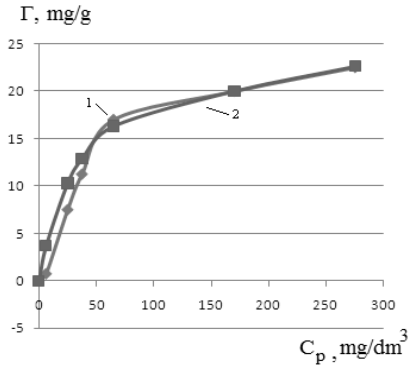


Fig. 9. The adsorption isotherms of gallic acid by of AC AG-OB-1 from the aqueous solution: (1) experi-mental; (2) calculated by the equation of Langmuir.

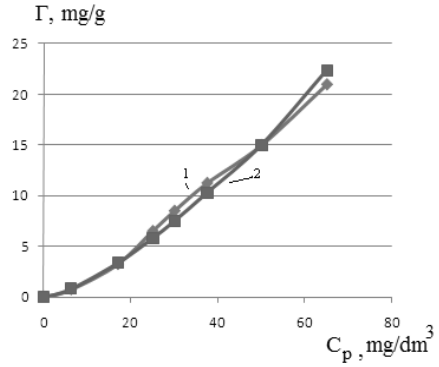


Fig. 10. Adsorption isotherms of gallic acid by AC of AG-OV-1 from the aqueous solution: (1) experimental; (2) calculated by the equation of Freundlich.

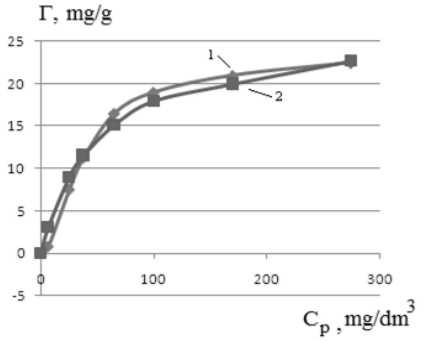


Fig. 11. Adsorption isotherms of gallic acid by AC of AG-OV-1 from the aqueous solution: (1) experimental; (2) calculated according to the BET theory.

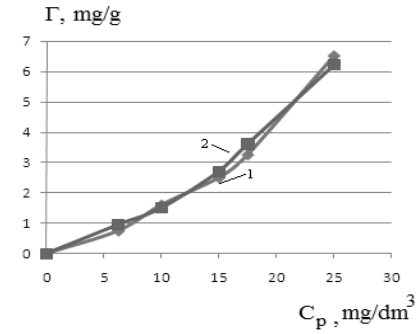


Fig. 12. Adsorption isotherms of gallic acid by AC of AG-OV-1 from the aqueous solution: (1) experimental; (2) calculated by the equation of Dubinin-Radushkevich.

Theoretical calculations showed that the maximum adsorption of gallic acid by carbon sorbents changes in the following sequence - "Purolat-Standard" > ABG > AG-OV-1.

The energy of the hydrogen bond (8-40 kJ/mole) is comparable with the values obtained by the Gibbs energy (-G, Table 3) in the adsorption on all active carbons, suggesting the specific interaction between the adsorbate and the adsorbent due to the formation of hydrogen bonds [7].

The values of the adsorption heat (Q, Table 4) confirm the physical nature of adsorption.

The value of characteristic energy (E0, Table 4) equal to (3.05–8.54 kJ/mole) testify to the fact that the adsorption of gallic acid takes place mainly in the meso- and macropores of the sorbent [6, 9].

The difference in the adsorption behavior of the studied sorbents is associated with their structural characteristics, and chemical state of the AC surface (Table 5, 6).

Table 5. Structural characteristics of active carbons

Active carbon rank	V_{micro}, cm^3/g	V_{meso}, cm^3/g	V_{macro}, cm^3/g	V_p, cm^3/g
AG-OB-1	0.22	0.24	0.57	1.03
Purolat-Standard	0.07	-	0.43	0.5
ABG	0.02	0.24	0.73	0.99

Table 6. The surface condition of active carbons

Sample	Content of elements*		N_{fgc}, mmole-equ/g (mmole-equ/$м^2$)			
	N+S+O	$O_{act.}$	*-OH*	$-COOH_{str.}$	*-COO-*	*> C=O*
AG-OB-1	2.71	2.28	0.213 (0.312)	0.032 (0.047)	0.078 (0.114)	2.08 (3.05)
ABG	7.05	2.76	0.130 (0.314)	0.020 (0.048)	0.040 (0.097)	3.70 (8.94)
Purolat-Standard	9.23	0.86	0.218 (0.700)	-	0.020 (0.064)	0.63 (2.02)

Note. * Percentage on the carbon organic mass.

AC of ABG rank can be attributed to mesoporous and Purolat - Standard - to macroporous adsorbents [3], which is also confirmed by the value of the heat of adsorption (7–13 kJ/mole) [6, 7]. AC of AG-OB-1 rank can be attributed to the sorbent having pores of mixed type (volumes of its micro- and mesopores are almost equal).

The presence of micropores provides physical adsorption due to van der Waals forces, and the functional groups containing oxygen - specific adsorption due to the interaction between the surface of the AC with the carboxyl and hydroxyl groups of gallic acid.

AC AGOB-1 contains the largest number of micropores. The highest total content of oxygen and the concentration of the active oxygen functional groups on the surface area is observed for the carbon sorbent of ABG rank, which is associated with the peculiarities of the production technology of the sorbent.

Adsorption is the result of the joint action of these factors. Obviously, in the case of gallic acid adsorption's greater contribution is made by specific interaction.

Analysis of experimental data has shown that the structure and physical-chemical properties of the sorbent have a significant impact on the adsorption of gallic acid.

Calculated from the experimental data the values of adsorption parameters for the studied carbon sorbents may be used in the data bank of sorption parameters of basic adsorbents at gallic acid adsorption.

The results can be used to make the adsorptive removal technologies of gallic acid from the sewage containing individual components and from the mixture with other polyphenols, including beer wort.

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CLUSTERS OF WATER IN THE COMPOSITION OF ANTIFREEZES

A. M. Miroshnikov[a,*], Z. N. Esina[b], A. A. Gushhin[a], N. N. Ushakova[a]

[a] Kemerovo Institute of Food Science and Technology (University),
bul'v. Stroiteley 47, Kemerovo, 650056 Russia,
* e-mail: alexandr_mirosh@mail.ru

[b] Kemerovo State University,
st. Krasnaya 6, Kemerovo, 650043 Russia,

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Abstract: Antifreezes based on water eutectics are widely spread in engineering and by crio-preservation of biological objects as well. Salts of inorganic and organic acids, alcohols, glycols, glycol ethers, glycerin, acids, bases, amino-acids, and other chemical compounds are suitable here as supplementary means. Part of these compounds is capable to take part in the formation of H-bonds with water molecules, the others do not form H-bonds ($CaCl_2$), but they are united into crystal-hydrates of $CaCl_2 \cdot 6\ H_2O$ type. In this case H-bond of water molecules can become the bond of intermolecular-cluster type. It is assumed that basic structural components of liquid water are cyclic penta- $(H_2O)_5$ and hexamers (H_2O_6), built with the participation of the long hydrogen bond and capable of producing the crown effect. Cyclic water clusters – short-range order of water in terms of cavity size and the number of oxygen atoms correspond to crown ethers: 15-crown-5 and 18-crown-6, sodium and calcium ions being absorbed into them. Energy estimation of water and ice (snow) interaction with the components of antifreezes: ethylene- and diethylene glycols, ethylene glycol ethers, hydrogen chloride and ammonia is made. Possibility of "ideal" solution formation with low freezing temperatures is shown. The analysis of the eutectics and diagrams of water antifreeze fusion based on the salts, alcohols, ethylene glycol, ethylene glycol ethers, hydrogen chloride and ammonia by comparison with an ideal solution of water concerning cryoscopic constant is carried out. It is established that the coefficient K in the equation of linear melting curve $y = K \cdot x + в$ for effective antifreezes, in terms of freezing temperature, exceeds the cryoscopic constant of water, that testifies to the destruction of long-range order of water. Penta- and hexamers of water responsible for short-range order of water pass into the eutectics as monomers or oligomers with the degree of cross linking equal to 2–4. To create effective antifreeze it is important to avoid the destruction of cyclic water clusters. It is desirable, as in the case with ethylene, to have the second component of water antifreeze in a cyclic form too. There is an analogy with naphthenic (cyclic) hydrocarbons of oil, which provide mobility of the condensed state. Promising are antifreezes based on mixtures of inorganic and organic compounds.

Keywords: Water clusters, penta- and hexamers, H-bond, antifreeze, water cryoscopic constant, crown-effect

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INTRODUCTION

Solutions with low freezing temperature based on water (antifreezes) are known in nature and are widely used in the technology of food production. The antifreeze composition comprises salts of inorganic and organic acids, alcohols, glycols, glycerin, acids and bases, amino acids and other compounds.

Formation of solutions is a spontaneous diffusion process proceeding from the thermal motion of constituent particles. Interaction force in the solution is evaluated by the osmotic pressure P, which depends on the concentration of the solute [1].

$$P = \frac{RT}{V_1} \times \ln\ 1 - x\ , \qquad (1)$$

or after simplification

$$P = RTc\ , \qquad (2)$$

where V_1 is the molar volume of the solvent, $V_1 = M/\rho$; M is the molecular weight; ρ is the density, x and c is the mole fraction of the solute.

This equation describes the ideal, that is, rather diluted (thin) solutions (10–6 - 10–2 mole / dm^3), in which osmotic pressure does not depend on the nature of the solvent and solute and is determined only by the number of interacting particles. Osmotic pressure is associated with the numerical average molecular weight of the solute:

$$M = RT\frac{m}{P}, \qquad (3)$$

where m is the molar concentration.

The osmotic properties of solutions include lowering the freezing point of the solvent (water) caused by the additive.

$$\Delta T_{fr.} = K \times m\ , \qquad (4)$$

where K is the cryoscopic constant of the solvent or the molar lowering of the solidification temperature of the solution. The indicator T characterizes the solvent and is independent of the nature of the solute (solid, liquid, gas). For water K = 1.86 °C/mole.

For concentrated solutions, it is necessary to introduce osmotic correction factors that reflect the relationship of real and theoretical values. The

composition of the resulting associates in the solution remains unknown, primary water clusters have not been established.

In quantum chemistry to assess the process of dissolution and the formation of associates pair interaction potentials in the system and their sign are used. If the sign is negative, the particles do not interact with each other the solution tends to the ideal and is described by the laws of physical chemistry. If the sign is positive, then the system can have colloidal phenomena in all the diversity [2]. Evaluation is performed by temperature. The upper temperature limit is the temperature of the onset of chemical transformations and the lower - the formation of the solid phase. In our work special points will be - 0°C ($T_{fr.}$ of water), minus 70°C ($T_{eut.}$), and 198°C ($T_{boil.}$ of ethylene glycol) for the system water-ethylene glycol. At the temperature of 198°C (more precisely from 180°C) there begins non-catalytic reaction of ethylene glycol formation from water and ethylene oxide or ethylene glycol dehydration to dioxan.

Our most studied compounds: water, alcohols, glycols, salts of mono- and dicarboxylic acids are compounds containing oxygen, capable through an oxygen atom to participate in the formation of H-bonds. At the same time other components of antifreezes (eutectic): $CaCl_2$, NaCl, HCl, NH_3 do not contain O atoms and formally they do not have H-bond via oxygen, although there are numerous hydrates: $CaCl_2$ 6H2O; $CaCl_2$ 4H2O; $CaCl_2$ 2H2O et al.

The aim of this work is to study the composition of water clusters (hydrates) in antifreezes in the temperature range of 100–200°C. One of the challenges of the work is to found the approaches for the creation of antifreeze formulations.

OBJECTS AND METHODS OF STUDY

The paper accepts:

– the main structural components of liquid water are cyclic penta (H_2O) 5 and hexa (H_2O) 6 steps, built at the expense of H-bonds [3];

– the concept of H-bond formed due to the shift of the valence electrons in the atom O, H atoms exchange between the water molecules to form cycles or chain structure. The formation of the bond [H-O-H ⋯ H-O-H] through two H atoms (long H-bond) that prevails in the ice is possible [4].

The sign (temperature) of the pair interaction in the ice (water) - antifreeze component and the possibility of solution formation $T_{fr.} < 0$°C was determined by mixing ice and water with the second component of antifreeze in Dewar flask. The results are shown in Fig. 1.

Interaction energy of HCl, the salts $CaCl_2$, NaCl and water was evaluated by the heat of mixing, taken from [5, 6]. Formation enthalpy of the hydrates $CaCl_2$ and HCl, containing 5–15 water molecules is virtually identical (Fig. 2).

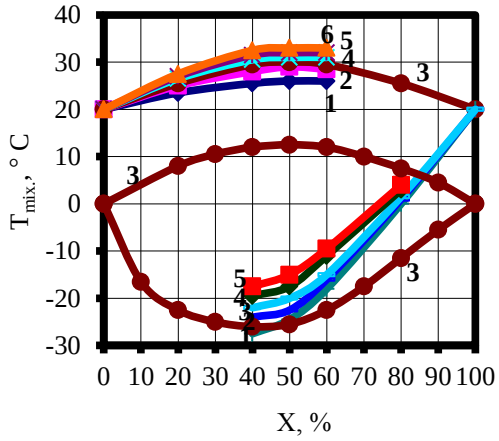

Fig. 1. The change of solution temperature depending on the concentration of the component, when mixed with ice and water: (1) ethylene glycol; (2) diethylene glycol; (3) ethyl ether of ethylene glycol; (4) ethyl ether of diethylene glycol; (5) ethyl ether of triethylene glycol; (6) ethyl ether of tetraethylene glycol.

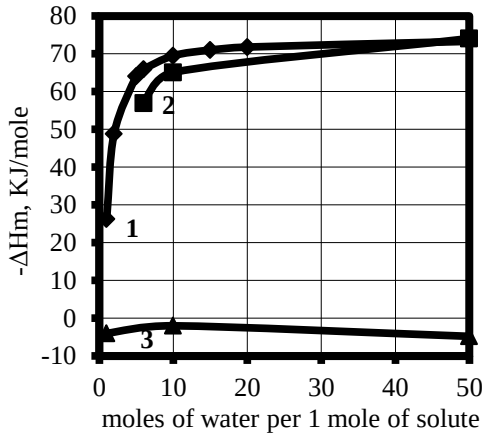

Fig. 2. The heat of dissolution (-ΔNm) in water: (1) hydrogen chloride; (2) calcium chloride; (3) sodium chloride.

The values for the charting of systems fusibility: HCl-H_2O, NaCl-H_2O, $CaCl_2$-H_2O, NH_3-H_2O, H_2O_2, H_2O, alcohols-water, ethylene glycol-water are drawn from the literature [6]. For ethyl cellosolve, ethylcarbitol, sodium adipate, phase equilibrium of aqueous solutions is studied using visual poly-thermal method of analysis. Sodium adipate was synthesized from adipinic acid and sodium hydroxide of reactive purity. The dependence of $T_{fr.}$ on the mole and mass fraction of additives is plotted. Fig. 3, 4 show the examples of eutectics with low and high content of the second component. Fig. 5 shows diagrams for tertiary butyl alcohol, ethylene oxide and propylene oxide, the first and third ones were obtained experimentally. For t-butanol the second eutectic is detected on the side of water.

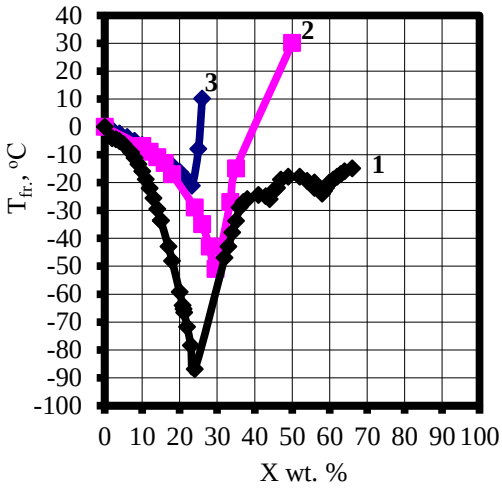

Fig. 3. The diagram of systems fusion: (1) HCl-H_2O; (2) $CaCl_2$-H2O; (3) NaCl - H_2O.

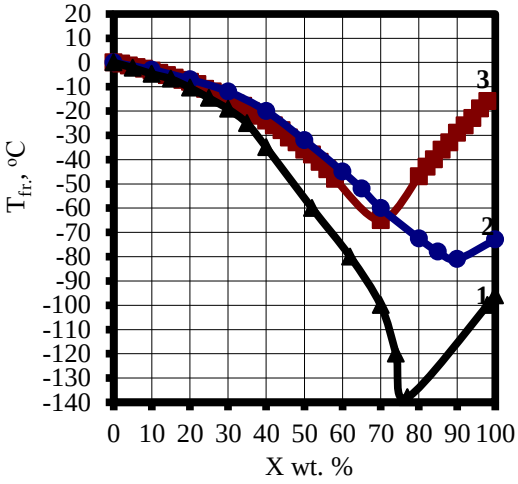

Fig. 4. The diagram of systems melting: (1) CH_3OH-H_2O; (2) C_2H_5 (OCH_2CH_2) OH-H_2O; (3) C_2H_4 $(OH)_2$-H_2O.

The program «Excel» linearizes fusion curves before eutectic in straight lines y = K·x + b. Points for concentration of less than 10% are excluded. Interpretation of graphs and equations of straight lines is based on the provisions:

– the slope of the line (K) for the ideal aqueous solution of 1.86 corresponds to cryoscopic constant of water;

– the intersection of the line with the y-axis is characterized by the coefficient b and corresponds to the water temperature of a particular cluster structure, these clusters become eutectic.

For the convenience of processing the results binary systems are numbered:

– Alcohols: methyl - 1 ethyl - 2, t-butyl - 3;

– Glycols: ethylene glycol - 4;

– Glycol ethers: ethylcellosolve - 5 ethylcarbitol - 6;

– Salts: sodium chloride - 14, calcium chloride - 15 potassium formiate - 7, potassium acetate - 8, sodium adipate - 9, sodium adipate (technological mixture) - 10, 11;

– Hydrogen chloride - 12;

– Ammonia - 13;

– Hydrogen peroxide - 16.

Equations, the coefficients K and b are shown in Table. 1, temperatures and the hydrate number of eutectics are indicated herein.

Table 1. Equations, the coefficients K and b, temperatures and the hydrate number of eutectics

№	Component	Equation of the line freezing	(minus)K	b	$T_{eut.}$,°C	Hydration number *	
1	CH_3OH	У= - 2.27x + 22.19	2.27	22.19	-138	-	0.5
2	C_2H_5OH	У= - 1.62x + 16.95	1.62	16.95	-130	-	0.2
3	T-C_4H_9OH	У= - 0.80x + 0.17	0.80	0.17	-6	15.0	0.5
4	$C_2H_4(OH)_2$	У= - 1.74x + 3.54	1.74	3.54	-71	-	2.0
5	$C_2H_5(OCH_2CH_2)$ OH	У= - 1.58x – 3.04	1.58	-3.04	-80	-	0.5
6	$C_2H_5(OCH_2CH_2)_2OH$	У= - 1.98x + 1.85	1.98	1.85	-64	-	0.8
7	KHCOO	У= - 3.49x + 7.52	3.49	7.52	-55	4.6	-
8	KCH_3COO	У= - 4.32x + 5.92	4.32	5.92	-62	5.4	-
9	$C_6H_8Na_2O_4$(ч)	У= - 4.00x + 3.61	4.00	3.61	-20	20.0	-
10	$C_6H_8Na_2O_4$(ц)	У= - 12.30x + 13.08	12.30	13.08	-46	-	-
12	HCl	У= - 8.45x + 32.06	8.45	32.06	-85	6.1	-
13	NH_3	У= - 4.15x + 46.01	4.15	46.01	-100	2.0	0.25
14	NaCl	У= - 2.48x + 1.01	2.48	1.01	-21	10.8	-
15	$CaCl_2$	У= - 9.23x + 12.55	9.23	12.55	-55	15.0	-
16	H_2O_2	У= - 1.70x + 6.02	1.70	6.02	-56	2.0	1.3

Note. * In the leftmost column on the water side, in the right one - from the second component.

RESULTS AND DISCUSSION

The analysis of the diagrams of aqueous solutions fusion.

Several studied systems 1, 2, 4, 5, 6, 14, 16 show: the convergence of the coefficient K and the cryoscopic constant of water (K = -1.86) (Fig. 6), but the difference in the eutectic temperature from minus 20 to minus 138 °C. For the system 14 (NaCl-H_2O) with K = -2.48 and b = 1.01 eutectic temperature is minus 21.1°C.

Thus, the approach of aqueous solutions to the "ideal" water according to K is a necessary but insufficient condition for the formation of eutectics with low fusion points. Small (hot) (b = 6–46) water

clusters should essentially be in the eutectic and the second eutectic component cluster join the structure of water clusters or voids between them. These are the systems H_2O-HCl; H_2O-NH_3; H_2O-$CaCl_2$; water-alcohols; water- salts of organic acids.

Clusters of liquid water stored in low-temperature eutectic have the water structure of the highest factors K and b. If K is less in absolute value than -1.86 and b is small, eutectic temperature of the system cannot be low. This example is given by the solution of t-butyl alcohol-water (K = -0.8; b = 0.17), wherein $T_{eut.}$ is only 6°C.

Consider fusion diagrams from water side (Fig. 3). The largest area is occupied by the system water-HCl, NaCl and $CaCl_2$ eutectics are absorbed into it. Eutectic temperatures of lithium and sodium hydroxyls are placed directly on the liquidus curve H_2O-HCl:

– LiOH-H_2O, $T_{eut.}$ minus18°C, composition LiOH×9,8H_2O;

– NaOH-H_2O, $T_{eut.}$ minus 28°C, composition NaOH×9,5H_2O.

Ammonia eutectic from water side (32% NH_3) has $T_{fr.}$ minus 100 °C, and hydrate number 2 (NH_3×2H_2O). Taking into account the association of ammonia molecules in the liquid state at low temperatures, we can only talk about the multiplicity of the number of molecules NH_3 and H_2O. The confirmation is the eutectic composition from ammonia side, where only 0.25 moles of H_2O falls at 1 mole of NH_3. In this case, the composition $4NN_3 \times H_2O$ is more likely.

For aqueous systems there has been previously identified the area of the formation of solid compounds such as clathrates [7], in which the "guest" and "host" are in the weak interaction: CH_4×6H_2O, C_3H_8 ×16N_2O, acetone $(C_3H_6O)_n$×$(17N_2O)_n$, dioxane $(C_4N_8O_2)_n$× $(18N_2O)_n$. Further on mixed clathrate-cluster structures based on the H-bond appear on the liquidus curve before eutectic temperature, which are dominated by the strongest associates of the water molecule, namely $(H_2O)_5$ and $(H_2O)_6$, as it has been now established. The formation of mixed structures is the cause of non-stoichiometric ratios in the hydrate, for example NaCl×10.8N_2O.

For the systems H_2O-NaCl; H_2O-$CaCl_2$ and H_2O-HCl eutectic hydrate numbers make up to: NaCl × 10.8N_2O (23.3 wt. %); $CaCl_2$ × 15N_2O (29.6 wt. %); HCl × 6H_2O (22 wt. %). Eutectic composition HCl × 6H_2O corresponds to the azeotrope composition of the second kind for hydrogen chloride and water, which is confirmed by the presence of the chemical (hydrogen) bond of the molecules HCl and H_2O.

Heat (enthalpy ΔHm) of HCl hydration qualifies as the maximum precisely at the ratio of 6 moles of water per 1 mol of HCI, calcium chloride behaves in the same way (Fig. 2), although the complete saturation is achieved with a larger number of molecules of water: HCl × (10-12) H_2O, $CaCl_2$ × (10-20) H_2O. Sodium chloride does not virtually interact with water, its ΔNm is less and has a different sign. The molecule of NaCl apparently absorbs into the structure of liquid water, but solid eutectic includes ice and NaCl × 2H_2O [8].

In the case of alcohols, eutectic from water was found only for t-butyl alcohol. It has $T_{fr.}$ 6 °C and contains 22% by weight of alcohol (RON × 15N_2O). From [3] it is known that at the concentration of 22% by weight t-butanol is converted from the structuring agent into its water crusher.

Increasing the basicity of the second component of the aqueous solution, for example, alongside with the transition to cyclic glycol ether - ethylene or propylene oxides, is accompanied by the formation of hydrates with positive freezing temperatures. Solid hydrates of ethylene oxide are present in the concentration range 10–70% by weight and have the freezing point plus 6–10.7 ° C. Of particular note is the composition C_2H_4O × 6H_2O close to 29 % by weight of ethylene oxide [9].

For propylene oxide, crystalline hydrate C_3H_6O × 5H_2O with the fusion temperature minus 6–7 °C is typical. In the system of propylene oxide-water, liquidus curve is parallel to the X-axis at this temperature (Fig. 5). While being stored crystalline hydrate C_3H_6O × 5H_2O loses its monoxide, passing into C_3H_6O × (10-20) H_2O. In the aqueous solution of propylene oxide there occurs delamination, the lower layer corresponds to C_3H_6O × 5H_2O. The structures of liquid and that of crystalline hydrate will differ, they can be built according to the type of complex compounds with a different coordination sphere.

From the alcohol side eutectic of tertiary alcohol S_4N_9ON has $T_{fr.}$ -5 °C, and corresponds to the formula 2ROH × H_2O and its composition is close to the composition of azeotrope. Depression of the eutectic freezing point as compared with the alcohol freezing point is 30 °C, water substantially destroys the structure of alcohol.

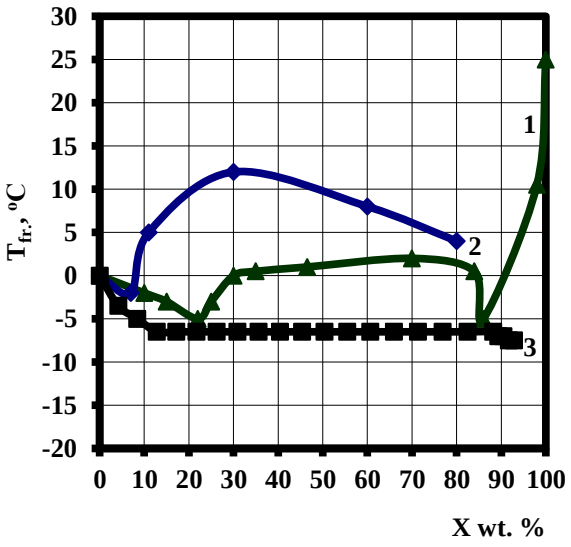

Fig. 5. Diagram of systems fusion: 1 – C_4H_9OH-H_2O; 2 – C_2H_4O-H_2O; 3 – C_3H_8O-H_2O.

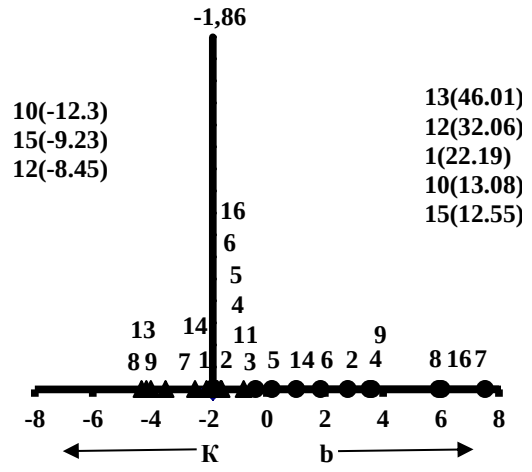

Fig. 6. Dependence of the coefficients K and b on the nature of the second component of water eutectics.

It is known [10] that the alcohols in the liquid state are associated as ROH × n, where n ranges from 3 to 30: methanol 30; ethanol 25; butanol 15; t-butanol 3.

While boiling the trimer of t-butanol is destroyed, an azeotrope of the 1st kind is formed with water, in which dimer 2ROH × H_2O dominates. Methanol has the eutectic 2ROH × H_2O with the freezing temperature minus 120 °C. Methyl and cellosolves also have eutectics from the alcohol side with low water content 2ROH×H_2O.

The greatest water influence on alcohols can be seen in the case of cyclohexanol. The eutectic ($T_{eut.}$ minus 56 °C, water content of 5 wt. %) is formed by the alcohol-water ratio of 3.4: 1. With water, cyclohexanol forms the azeotrope of the 1st kind containing 21 wt. % of alcohol (ROH × 20.9N_2O).

For ethylene glycol (Fig. 4), the range of known eutectics is described by us with the formula $2C_2N_4$ (OH) $_2$ × (2–5) H_2O. Eutectic composition with the minimum $T_{fr.}$, obtained by extrapolating of published results and calculated by the special method of thermodynamic similarity [11, 12] coincided and was 69 wt. % of glycol and 31 wt. % of water. This corresponds to the formula $2C_2N_4$ (OH) $_2$ × $3H_2O$ or 2 [$2C_2N_4$ (OH) $_2$] × $6H_2O$. The formulation allows for dimerization of ethylene in the vapor and the diluted solutions and the cluster cyclization that manifests in the IK- spectrum as the doublet of intramolecular hydrogen bond (3604 and 3614 cm^{-1}). Addition of water in the amount of 1–2 moles per mole of glycol does not lead to the destruction of the cyclic bond.

The temperature of this eutectic by extrapolation method is minus 68 ° C, by calculation - minus 73,7 ° C. The developed eutectic calculation algorithm is used for the aqueous solutions of propylene glycol, diethylene glycol, ethyl cellosolve, and several other esters and gives satisfactory results. The increase in viscosity of eutectic solutions with the temperature lowering requires the introduction of the coefficient of association (polymerization) of homogeneous fragments. Then the formula becomes $\{2[2C_2H_4(OH)_2]\times 6H_2O\}_n$.

Concentrated glycols (ethylene glycol) at room temperature form interaction solids, both with acids and bases (ethylene glycol + boric acid; ethylene glycol + dicyclohexilamine). Dicyclohexilamine also reacts with water, but the solid adduct is melted before its equivalent with ethylene glycol [13]. Glycol alkyl substituents prevent the formation of solid adduct or lower $T_{fr.}$. Glycols and glycol ethers may be part of a cluster, but the acting molecular weight herewith is less than that calculated by the rule of proportionality. For mixtures, there is a decrease of viscosity, $T_{fr.}$, but the increase in hygroscopicity. There is no volume contraction, and mixes dissolve water well enough. The greatest asymmetry of molecules and clusters based on them, and the minimum freezing temperature are attained in the clusters containing primary OH-group and hydrocarbon radical (CH_3-, C_2H_5-) in oxyethylene unit.The ether CH_3-O-CH_2-CH_2-O-CH(CH_3) - CH_2OH has the$T_{fr.}$ minus 80°C. The symmetrical disecondary dipropylenglycol CH_3-CH(OH)-CH_2-O-CH_2-CH(OH)-CH_3] melts at plus 46 ° C in the inert atmosphere and cyclizes due to intramolecular H-bonds when being diluted. The addition of water does not destroy the intramolecular loop, the band 3610 cm^{-1} is preserved, but almost completely suppresses the intermolecular hydrogen bonds (the band 3420 and 3480 cm^{-1}) of glycol molecules [14].

The interaction of glycols and their esters with water is exothermic. The thermal effect per unit weight of the compound added to water increases in the series: ethylene glycol < diethylene glycol < ethylene glycol ether < diethylene glycol ether < triethylene glycol ether < tetraethylene glycol ether (Fig. 1).

When ice being added to glycols, temperature decreases and passes through 0 °C in the series: tetraethylene glycol ether < triethylene glycol ether < diethyleneglycol ether < ethylene glycol ether < diethylene glycol < ethylene glycol. Ethylene glycol produces the greatest destruction of ice structure (melting capacity) and transfer to the liquid, the temperature reaching minus 28 °C (Fig. 1). Such behavior is described for $CaCl_2$ × $6H_2O$, when calcium hexahydrate is mixed with snow or crushed ice to obtain low temperatures. Anhydrous calcium chloride when mixed with snow or water is heated.

If the drop in temperature leads to the preservation of the "ideal" solutions - antifreezes at water level and the coefficient K in the equation of linealized liquidus curve is close to the cryoscopic constant of water, then we can talk about saving the water structure in antifreeze.

As it is currently established, in liquid water there dominate cyclic penta- and hexamers based on hydrogen bond. The diameter of the pentamer cavity is 2.8 Å. If we use the model of a long H bond, the structure of cyclic penta- and hexamers corresponds to the crown ethers: 15-crown-5; 18-crown-6 [15]. The diameter of the cavity of these ethers constitutes from 1.7 to 3.2 Å, they absorb into sodium, potassium, calcium ions. If the size of the cavity is not completely consistent, laminate complex is formed, wherein each cation has two or more crown ethers.

CONCLUSIONS AND RECOMMENDATIONS

Analysis of eutectics and diagrams of aqueous antifreeze fusion, based on salts of inorganic and organic acids, alcohols, ethylene glycol and its ethers, consisted in the comparison with an ideal water solution on cryoscopic constant. It made it possible to reveal cyclic water clusters of $(H_2O)_5$ and $(H_2O)_6$, which pass into the eutectics as monomers or oligomers with the degree of cross linking 2–4.

Cyclic water clusters can interact with the components of antifreezes (salts, acids, bases, neutral molecules) by the type of crown-ethers therefore it is necessary to consider the proportionality of used chemicals.

To create effective antifreezes it is important to avoid the destruction of cyclic water clusters, it is desirable to have, as in the case of ethylene glycol, the second component of water antifreeze and in a cyclic form as well.

Promising are the antifreezes based on mixtures of inorganic and organic compounds.

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ECONOMY OF THE AGROINDUSTRIAL COMPLEX

MARKET CAPACITY AS THE BASIS OF MARKETING RESEARCH FOOD MARKET OF KEMEROVO REGION

O. E. Brese[a,*], N. L. Grjaznova[a], V. A. Brese[a], A. K. Angersbach[b]

[a] Kemerovo Institute of Food Science and Technology (University),
bul'v. Stroiteley 47, Kemerovo, 650056 Russia,
* e-mail: brese@mail.ru

[b] EloSystems GbR,
Alt-Reinickendorf 28, Berlin, 13407 Germany

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Abstract: One of the main tasks of marketing research is to identify the capacity of food market. Market capacity, concerning its quantitative characteristics, demonstrates the capabilities of food market volume of sales. It is a common practice to distinguish between two levels of market capacity: potential and actual. The actual capacity of a market is the first level. Potential level is determined by personal and social needs, and it reflects an adequate volume of sales of goods. The capacity, which is really establishing in a market may not correspond to its potential capacity. Market capacity may be calculated in cash and in kind. Knowing the capacity of a market and its trend changes, it is possible to assess the prospects for the development of the food market. Different methods are used for the market capacity calculation, each of which is most suitable in the given context, this paper presents a comparative analysis of the choice of a calculation method of the food market, food market potential capacity of Kemerovo region is justified. The capacity of its food market in the period from 2001 to 2013 is calculated. The calculations take into account the demographic situation in the region and rational consumption norms of foods, recommended by the Ministry of Health and Social Development, what meets the modern requirements of a healthy diet. Conclusions on the data are formulated.

Key words: Marketing research, real and potential market capacity, rational consumption norms (rates)

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INTRODUCTION

Marketing is a hierarchically organized system of management activities in a market, regulation of market processes and market research. One of the basic requirements of marketing is to ensure the "transparency" of a market and the "predictability" of its development. Without the collection of reliable information and its subsequent analysis marketing cannot fully perform its mission. To do this, you must conduct marketing research. All marketing research is carried out in two sections: evaluation of various marketing options for the given time and getting their predicted values. Collection of information, its interpretation, evaluation and forecast calculations are assumed to call a marketing research.

When conducting marketing research, you should pay attention to the principles which you should follow – regularity, consistency, comprehensiveness, coherence and commitment, the multiplicity of information sources, versatility, and scientific character.

(1) Systematic character – studies should be carried out systematically, rather than in a disposable nature.

(2) System character – should cover the entire market and all the structural hierarchy of market processes: facts, their dynamics and interactions.

(3) Complexity – on the one hand, includes a set of actions or processes (collection, processing, analysis), on the other hand - an integrated approach to the study of objects (their relationships with other processes and objects).

(4) Coherence and commitment – the direction, magnitude, depth; the details of research should be organically linked to the goals and objectives of this market, entity reflect its real needs in specific analytical information.

(5) Plurality of sources of information – receipt of market information not from one but from several sources is advisable, allowing you to have a comprehensive "overlapping" each other's data and thereby to clarify and verify information, excluding questionable data.

(6) Versatility – research can be conducted on the basis of all the needs of obtaining any market information to make rational decisions.

(7) Scientific character – accuracy, objectivity, conditionality.

Non-objective, groundless investigations lead to wrong, distorted recommendations. Each of these principles is important in itself, but taken together they make such interaction possible and prepare such market research, which can become a reliable basis for making well-informed, thoughtful management decisions.

The main purpose of marketing research is reducing the uncertainty and risk in management and business decisions. We study the trends and developments of a market, its capacity, dynamics of sales, the actions of competitors, attractive sides and risks. Consumer research allows us to determine the motives of their behavior; and commodity research - the competitiveness of products; the effectiveness of incentives and advertising are investigated as well. The effectiveness of distribution channels, an important area of marketing research is to identify the strengths and weaknesses of business activities and others.

Marketing research can provide information on many aspects of a market. The study of the food market of Kemerovo region by marketing research is aimed at the discovery of effective means of market management on the basis of objective understanding of the situation on it.

Parameters of stable development of the regional food market can be determined through marketing research: one of the tasks of marketing research of the food market in the region is to determine its capacity. The calculation of food market potential capacity reflects the total needs of the region based on the highest possible level of consumption.

Food product is a specific product, used by consumers on a daily basis in certain amounts, which depends on a variety of factors: economic, demographical, natural and climatic, national and routine. The inclusion of real consumption and the size of the impact of these and other factors, determining these volumes allow us to calculate the demand of local market on a particular food product. Necessity (presenting as aggregate demand) is a potential consumer market, which, in its turn, is characterized by the capacity of the market.

In economic literature [1, 2, 3, 4] different ways of calculating the capacity of a market are suggested. Market capacity is a key parameter characterizing the total demand for products and being of interest. Market capacity of certain products is the volume of production of one kind or commodity group in a given area at a given time. In marketing interpretation of a market size (market capacity) it is the aggregate effective demand of customers for a particular product at the current price level. Real knowledge of market capacity allows us to build the right strategy of obtaining a market niche, or make a reasonable program of attainment of the leading position in the branch market. The option was recently enriched with a new content, expanding the scope of application: within the space of integration into the world community; within the market segment.

We may determine market capacity as a real and potential one. In the result of generalization of several works the following definition of market capacity is proposed - it is the cumulative number of certain goods or services, which for a certain period of time is provided in a market (or will be provided) by current demand, required supply structure and appropriate level of prices in the specific marketing environment. [5] The use of specific numbers in a certain period indicates the actual use of the concept of market capacity.

The potential capacity of a market is the maximum aggregate amount of certain goods and services, which is able to absorb this market for predetermined period of time under conditions of maximum consumption of all potential users and the maximum intensification of marketing campaigns. [5]

Procedure of determining the capacity of a market provides for special marketing research or calculations based on the published and borrowed information. Such studies are performed by specialized centers and more seldom marketing departments.

Estimation accounts based on the published data and calculation methods stated here (Table 1) may be made by market research and marketing departments, and where they do not exist – by economic analysis and accounting departments.

OBJECTS AND METHODS OF RESEARCH

To choose the right way, you must know exactly what the purpose is, and answer the question: why do you need to find the capacity of a market? Selection criteria determination method lies in the reply. In this work, we need to determine the capacity of the market in order to find out, what should be the saturation of the market (potential market capacity) of some food products.

From Table 1, we may state, that method 4 is the most suitable, since it takes into account the market capacity depending on the number of users. To achieve the objectives of the study, we need to modernize this method by making the following changes:

– It is necessary to determine not only the total number of users, but their age group;

– When determining consumption rates we consider the consumption coefficient, specific for a certain age category.

Thus, the formula 1 determining the potential market capacity will be as follows:

$$E = \Sigma (H_i \, x \, N \, x_I \, R_i), \quad (1)$$

where E is the number (in kind) of goods, products for consumption for the period in accordance with the norms of rational consumption; H_i is the number of the i-th consumers group; R_i is the consumption coefficient of specific age groups the i-th group; N is the physiological norms of products consumption (goods).

As a basis for calculating the demand amount for a particular food product physiological consumption rates were made, calculated for a specific region, in particular for the temperate continental climate zone of Siberia.

Thus, to calculate the needs of the regional market in food, the following data are necessary: the population of Kemerovo region, the rate of consumption of certain foods, consumption peculiarities of age categories. Consumption norms are defined as physiologically required amount of food for one person per year of normal life. Rates of consumption of some food items are shown in Table 2. When the consumption norms are taken for further calculations in the present work, we choose the maximum value due to the fact that, as mentioned earlier, the potential capacity of a market is determined by the maximum level of consumption.

These volumes of consumption of products by consumers of different age groups are not the same, so consumption rates were adjusted for age-specific consumption (Table 3).

Table 1. Methods for determining market capacity [3]

Description of the method	Formalized view
On the treatment of production volumes	
Method 1. Base: accounting of production, import, export and balances.	$M = P - E + I + (O_E – O_B) + (R_E - R_B)$, where P is the volume of production for the year of specific product or product group; I is the volume of imports of state and private structures; O_B, O_E is the residues at the beginning and end of the period, respectively; E is the exports of state and private structures; R_B, R_E is the state reserve at the beginning and the end of the period, respectively (not always taken into account, but only for specific types of products); M is the market capacity.
Method 2. Base: selecting the major manufacturers in the branch. Absolute and relative volumes may be considered. Supply of imported goods is valued on a par with that of manufacturers of domestic products.	$M = M_1 + M_2 + ... + M_i$
Method 3. Base: selective account of the major enterprises. It is used in a large number of enterprises. Sampling should be done by categories of producers: largest or regions. The calculation is possible in both absolute and relative terms.	$M = P_1 x K_1 + P_2 x K_2 + ... + P_i x K_i$, where P_1, P_2, ..., P_i is the production of an individual sample, the most typical enterprises within each category of producers, taking into account residues; K_1, K_2, ..., K_i is the coefficients within each group of samples manufacturers.
By the method of accounting standards expenditure and consumption	
Method 4. Base: accounting standards in expenses of consumers Essentially, this is theoretical or potential capacity of the market. Used for rapid expenditure of goods, which are purchased regularly.	$M = C \times W \times T_i$, where C is the consumption of goods per person; W is the number of users of the goods; T is the life time of the product.
Method 5. Base: norms for expenditure mechanisms. Inquire, that in one category are several mechanisms that should be considered separately in each category, and then summarize these data.	$M = C \times N \times T$, where C is the consumption of one mechanism over time T in a month; N is the number of mechanisms.
Method 6. Base: rates of consumption of food products, raw materials and other consumables.	$M = A_1 \times U_1 + A_2 \times U_2 + ... + A_i \times U_i$, where H is the annual rate of consumption per capita; U is the number of users of products or raw materials.
On the treatment of sales	
Method 7. Base: a sample of trade enterprises and accounting the norms of the volume of their sales (index sequential panels).	$M = P + (O_K - O_N) \times 12N / N_F \times T$, where P is the volume of sales; N_F is the number of the sample of trade enterprises; N is the total number of trading companies; T is the life time in months; $(B_E – B_B)$ is the life time in months different balances at the beginning and the end of the period, respectively, for the enterprise.
Method 8. Base: the value of all sales in the branch is on one single product or product group. Usually used for district or city, it is difficult to determine all trading enterprises in the country.	$M = (P_1 + P_2 + ... + P_i) \times 12 / T$, where P_1 P_2, ..., P_i is the life time in months amount of sales of various companies in the period T during a month.
Method 9. Base: accounting the amount of primary, secondary and additional sales. Consumer goods are divided into those who acquires the product for the first time, thus they form the primary market sales of M_F; for those who re-buy the item for the replacement of the old one, they form secondary market sales – M_S; for those who buy goods in addition, that is the second, third, etc. instances of the same product – M_A.	$M_F = P / T$, where T is the life time.

Table 1. Ending. Methods for determining market capacity [3]

Description of the method	Formalized view
Method 10. Base: transfer of the experience in terms of sales from one region to another, taking into account population and average salary (based on factor coefficients of sales driving).	$M = M_0 \times K_1 \times K_2 \times K_3$, where M_0 is the known capacity of one of the regional markets; K_1 is the first reduction coefficient equal to the ratio of the population of a new region to the number of well-known, that defines the size of the market; K_2 is the second reduction factor equal to the ratio of the average earnings of the new region to the known ones, K_3 is the for regions of the same type is 1.0, and to compare the new region with the big city urbanization ratio is 0.35.
On the treatment of nomenclature, prices, advertising volume with reference to the parameters well-known enterprises	
Method 11. Base: comparison of the sum of the range of all commercial enterprises bound to nomenclature and the range and volume of sales of their firm or a famous company. The method is applicable for industries with high nomenclature: for household goods, pharmaceuticals, electrical products and others.	$M = (K_1 + K_2 + ... + K_i) \times P_0 / K_0$, where K_1, K_2, ..., K_i is the nomenclature of companies on investigated industry; K_0 is the nomenclature of its own, or well-known company; P_0 is the sales of own or well-known company.
Method 12. Base - comparing the amount of advertising in the industry with the volume of advertising your own firm, or a well known one, tied to sales.	True for all firms. All calculations are similar to the previous case, except that, when instead of the nomenclature of the advertising volume equal to the product of the area of ads on the frequency of repetition or playing time on the frequency of repetition is taken.
Method 13. Base: finding a sales volume of the company with reference to the nomenclature of the average price and average commodity stocks. Preferred is the method for companies with significant nomenclature.	$M = K_1C_1R_1 + K_2C_2R_2 + ... + K_iC_iR_i$, where K_1 is the nomenclature of the first company; C_1 is the average price for the first item of the enterprise; R_1 is the average goods reserve for the first enterprise.
By the method of comparison with the previous period	
Method 14. Base: taking performance equal to the previous period, under conditions close to the stable.	$M_P = M_N$, where M_P is the market capacity for the previous period; M_N is the market capacity of the new period.
Method 15. Base: taking rates of the prior period, after adjusting for changes in certain economic solvency, the rate of ruble exchange, energy costs and other factors.	$M_N = M_P \times K_N$, where M_N is the market capacity of the new period; M_P is the market capacity of the previous period; K_N is the factor of economic change.
Method 16. Base: mainstreaming the previous period, adjusted for the share of imports K_I, and export K_E share of the internal volume K_P	$M_N = M_P \times (K_P + K_I - K_E)$ or only to the internal volume indicators $M_N = M_P \times K_P$
Method 17. Base: taking the rates for the previous accounting period, adjusted for the change in the market saturation.	$M_N = E_P \times (1 + S_N - S_P)$, where S_N, S_P is the respectively the new and old rates saturation.

Table 2. Physiological consumption rates of certain food products

Food products	Consumption rates,kg / year / person*	Consumption rates,kg / year / person**
Bread and pasta in terms of flour	95–105	105
Milk and dairy products in terms of milk	320–340	340
Meat and meat products	70–75	75
Potato	95–100	100
Vegetables and water- melons	120–140	140
Eggs	260 pcs.	260 pcs.
Sugar	24–28	28
Fish and fish products	18–22	22
Fruit and berries	90–100	100

Notes. * According to [6], ** Rates of consumption taken for further calculations in this paper.

Table 3. Scale of age groups consumption coefficients*

Age of customers	Up to 1 year	1 – 3 year	3 – 7 year old	7 – 11 year old	11 – 15 year old	15 – 18 year old	Grown ups	In the pension age
Coefficients	0.20	0.35	0.50	0.65	0.80	0.90	1.00	0.90

Notes. * According to [7].

More accurate baseline information on the calculation of the needs of the regional market in foods makes possible the adjustment of physiological norms of consumption of a particular age group in accordance with the scale of the specific age category. Arrangement of the data on the distribution of the region's population by age groups according to the age-specific coefficient of consumption intervals is presented in Table 4. Calculation (data given in Tables 2, 3, 4) of the needs of the region's commodity food groups (Table 2) is presented in Table 5 (the potential capacity of the food market of Kemerovo Region for 2001-2013).

Table 4. Population distribution by consumption groups for the 2001-2013 biennium*

Age of customers	Group size (on January 1)						
	2001	2002	2003	2004	2005	2006	2007
Up to 1 year	26 235	27 352	30 102	30 255	30 430	30 605	31 838
1 - 3 years	75 137	76 265	81 052	87 720	86 622	88 520	90 812
3 - 7 years	112 256	106 379	101 295	102 120	102 906	103 697	106 399
7 - 11 years	139 118	135 744	117 243	109 529	107 905	106 284	104 113
11 -15 years	196 520	194 348	170 318	155 308	147 610	139 911	127 303
15 -18 years	153 375	154 648	155 390	153 369	148 721	144 073	132 088
Grown Ups	1 672 516	1 688 677	1 681 018	1 691 118	1 695 600	1 700 086	1 708 033
In the pension Age	542 678	540 754	535 646	528 624	526 990	555 673	525 709
Total	2 917 835	2 924 167	2 872 064	2 858 043	2 846 784	2 868 849	2 826 295

Notes.* In accordance with Kemerovostat.

Table 4. Ending. Population distribution by consumption groups for the 2001-2013 biennium*

Age of customers	Group size (on January 1)					
	2008	2009	2010	2011	2012	2013
Up to 1 year	34 050	36 501	37 433	35 169	34 854	37 598
1 - 3 years	92 654	96 240	102 494	106 229	107 519	106 513
3 - 7 years	111 858	115 961	120 325	122 603	126 633	132 294
7 - 11 years	101 950	103 190	104 901	107 755	112 798	115 522
11 -15 years	118 053	110 654	107 483	104 597	101 608	102 877
15 -18 years	121 004	110 474	98 019	90 497	85 066	80 740
Grown Ups	1 713 187	1 710 074	1 703 773	1 636 090	1 610 431	1 582 508
In the pension Age	530 783	538 398	546 208	558 315	571 920	584 298
Total	2 823 539	2 821 492	2 820 636	2 761 255	2 750 829	2 742 350

Notes.* In accordance with Kemerovostat.

Table 5. The potential capacity of the food market of Kemerovo region for 2001-2013 years*

Trading group		2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013
Meat and meat products, thous. Tons	need	197.57	198.27	195.03	194.11	193.49	194.99	192.07	191.68	191.15	190.60	185.94	184.82	183.70
	deflection in previous year		+0.7	-3.24	-0.92	-0.62	+1.5	-2.92	-0.39	-0.53	-0.55	-4.65	-1.12	-1.12
Milk and dairy products in terms of milk, thous. Tons	need	895.65	898.83	884.15	879.98	877.14	883.90	870.72	868.93	866.53	864.03	842.95	837.84	832.79
	deflection in previous year		+3.18	-14.68	-4.17	-2.84	+6.76	-13.18	-1.79	-2.40	-2.50	-21.09	-5.11	-5.05
Bread and pasta in terms of flour, thous. Tons	need	276.60	277.58	273.05	271.76	270.88	272.98	268.90	268.35	267.61	266.83	260.32	258.75	257.18
	deflection in previous year		+0.98	-4.53	-1.29	-0.88	+2.1	-4.08	-0.55	-0.74	-0.77	-6.51	-1.57	-1.57
Fish and fish-products, thous. Tons	need	57.95	58.16	57.21	56.94	56.76	57.2	56.34	56.23	56.07	55.91	54.54	54.21	53.89
	deflection in previous year		+0.21	-0.95	-0.27	-0.18	+0.44	-0.86	-0.12	-0.16	-0.16	-1.37	-0.33	-0.32
Potato, thous. Tons	need	263.43	264.36	260.04	258.82	257.98	259.98	256.09	255.57	254.86	254.13	247.93	246.42	244.94
	deflection in previous year		+0.93	-4.32	-1.22	-0.84	+2.0	-3.89	-0.52	-0.71	-0.73	-6.20	-1.51	-1.48
Vegetables and melons, thous. Tons	need	368.80	370.10	364.06	362.34	361.18	363.98	358.53	357.79	356.81	355.78	347.10	344.99	342.91
	deflection in previous year		+1.3	-6.04	-1.72	-1.16	+2.8	-5.45	-0.73	-0.99	-1.03	-8.68	-2.11	-2.08
Eggs, million. pcs.	need	684.91	687.34	676.12	672.92	670.75	675.95	665.84	664.48	662.64	660.73	644.61	640.70	636.84
	deflection in previous year		+2.43	-11.22	-3.2	-2.17	+5.2	-10.11	-1.36	-1.83	-1.91	-16.12	-3.91	-3.86
Sugar, thous. Tons	need	73.76	74.02	72.81	72.47	72.24	72.80	71.71	71.56	71.36	71.16	69.42	69.00	68.58
	deflection in previous year		+0.26	-1.21	-0.34	-0.23	+0.56	-1.09	-0.15	-0.20	-0.21	-1.74	-0.42	-0.42
Fruits and berries, thous. Tons	need	263.43	264.36	260.04	258.82	257.98	259.98	256.09	255.57	254.86	254.13	247.93	246.42	244.94
	deflection in previous year		+0.93	-4.32	-1.22	-0.84	+2.0	-3.89	-0.52	-0.71	-0.73	-6.20	-1.51	-1.48

Notes. *In accordance Kemerovostat and Tables 2 – 4.

RESULTS AND DISCUSSION

Development of a region is primarily determined by the life standard of population and the degree of satisfaction of human needs for food. Availability of information on the potential capacity of the food market in the region allows the management of the region to respond to food crises in proper time, such as the global food crisis of 2007-2008.

In Kemerovo region the level of its own food production provision is about 70%, the rest is imported from neighboring regions, i. e., natural-resource potential of the region is not used to the full extent. Ensuring food self-sufficiency in the region is possible only when the mobilization of resource potential of agriculture and the creation of the industry of effective organizations is attainable. Over the years of agricultural reform in Kemerovo region, a broad range of agricultural commodity producers has been generated with different variety of forms of ownership and management, but not all of them are effective [8].

Recommended actions to ensure food security are to increase investment in agricultural production and productivity growth [9, 10].

In this work, to determine the potential market capacity we upgraded mode 4 (Table 1). These changes take into account the age group structure of the region's population and age consumption coefficient [11].

Not only agricultural production in rural areas plays an important role in the food market saturation, but also the so-called urban agriculture, which contributes to the improvement of the local population. The garden plots of urban population, urban fruit and vegetables gardens for growing fruit (currants, raspberries and others) require a minimum initial investment [12].

The potential of meat and dairy foods sales [13] in Russia is very large and requires further filling by domestic products. The problem of import substitution, especially in the developed in our country recent situation when we announced the international sanctions, is highly relevant for all industries, including food.

Being based on the calculated data decline in the needs of the regional market can be stated for the period of 2001-2013, also it is stipulated by consideration of some food products. It should also be noted, that slowdown needs of the regional market in foods in the years 2009-2013, particularly in 2011, are connected with the reduction in the total population of the region, in particular with a significant decrease in population in the category of "adult" (with a high rate of consumption of 1.0 to the general rules).

The relationship between the demographic situation in Kemerovo region and the capacity of the regional food market is obvious. Over the past 10 years, no increase in population is observed. Therefore, under these conditions, we can draw some conclusions, namely, for the improvement of situation it is necessary:

– To improve the standards of life of the region's population;
– To increase the birth rate and reduce mortality;
– To improve health and safety of labor in hazardous occupations;
– To raise awareness of the attractiveness of the area for citizens of other regions, etc.

Solving of these problems should become the priority task of leaders at all the levels: businesses and public organizations.

Thus, market research can provide information on many aspects of a market, since in this case we study trends and development processes of a market: its capacity, the dynamics of sales, the actions of competitors, attractive sides, the risks and others. The parameters of sustainable development of the regional food market of Kemerovo region can be determined by market research. Determination of market capacity is one of the main prior tasks of the marketing research of food market in the region. The knowledge of market capacity and trends of its change, makes it possible to assess the prospects for further development of the food market of Kemerovo region, as well as the adoption of competent management decisions for the development of the region as a whole.

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BOOK REVIEW

TRADITIONS AND INNOVATIONS OF DAIRY INDUSTRY

A. G. Khramtsov

North Caucasus Federal University,
ul. Pushkina 1, Stavropol, 355009 Russia,
e-mail: hramtsov@stv.runnet.ru

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Abstract: Brief information-review provides an analysis of the textbook for students of higher educational institutions, authorized by Ministry of Agriculture to study "Foods of plant origin" and "Foods of animal origin" by N.B. Gavrilova, M.P. Schetinin - "Technology of milk and dairy products: traditions and innovations", Moscow: Colossus, 2012, 544 p.

Keywords: Dairy raw materials, methods of processing, range of dairy products

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The authors of the textbook – famous Russian scientists of dairy industry – Natalja B. Gavrilova (Professor of the Department of Food and Biotechnology, Omsk State Agrarian University after P.A. Stolypin, Hon. Worker HS RF) and Michail P. Schetinin (Head of the Department of Food Production, Altai State Technical University after I.I. Polzunov and now a senator of the Federal Assembly of the Altai Territory) in accordance with the standard program for special disciplines for higher schools "Technology of milk and dairy products", of specialty standard 260303 managed to fit a huge file information on the complete range of products from raw milk on 544 pp. (44, 20 conv. printer's sheets). The book has an attractive design, good type and is neatly filed.

Substantial portion includes seven chapters (essentially parts), preface of the authors, introduction, conclusion and the reference list with the space for notes. Each chapter within the intellectual training ends with control questions and tasks. In general, the material in its form and substance matches to the XXI century brand textbooks, adopted in Russia.

In the preface and introduction, the authors outlined their position on the issue of the textbook, the contribution of predecessors and industry achievements. For example, they formulated the theme of food nanotechnologies related to dairy science. Students and industry professionals are to understand and accept it as an axiom for the modernization of technology of dairy products.

In the first chapter, departing from the traditional postulate, the authors first "dared" to begin with the presentation of raw milk monitoring and its technological modification processes. Given the limited scope of the textbook, they summarize information on the composition and properties of cow raw milk and that of other animals at the present legislative level. Further described are all currently known traditional (purification and separation, cooling, normalization, homogenization, thermization, pasteurization, sterilization, concentration, drying) and new, innovative (molecular sieve separation – micro-, ultra-, nanofiltration, reverse osmosis, electro-membrane treatment – electro dialysis, high pressure, cryogenic freezing) techniques and methods for processing feedstock. Equipment sanitizing is referred too. In the future, this chapter seems to light the problem of raw milk conditioning and apparently characterize all industry's raw complex – cream, skim milk, buttermilk and whey.

In the next five chapters, systematically presented is the technology of milk and dairy products by currently accepted product groups. Just list them: milk products and ice cream, including cottage cheese and sour cream; canned condensed and dried milk, baby foods; butter, butter pastes and spreads; cheese and cheese products. Each chapter in all groups and subgroups provides a clear basic concept, adopted by the Technical Regulations (TR), in accordance with federal law, terms and definitions. The authors state (briefly) the theoretical backgrounds of processing line and describe technological schemes with a focus on some of the regularities of the processes and operations in classics and innovations. In the future, this information allows for us to form systematically Technological Platforms for the production of dairy products by world standards in the context of the world market globalization and WTO membership.

The seventh chapter specifically shows very detailed and qualified information on the so-called (according to TR) secondary raw milk material (SRM) and virtually the single current industry reserve to ensure food security for our country indispensable health (functional) food products. Besides logistics of this presentation allows us to obtain products with the full use of all the components their individual removing and synthesis of derivatives from SRM. This is fundamentally important to the technological

(without waste), environmental (environmental protection) and marketing (economics) aspects of the Engineer (BSc, MSc) activities.

The textbook conclusion appealing to students – go for it, is worthy of admiration. List of recommended literature in Russian is quite complete. On the whole, the authors managed to do an impossible thing (in terms of publication volume) – to create a modern textbook, which organically "interlaces" traditions and innovations of AIC dairy industry. The textbook is certainly of great interest for dairy science professionals as well.

INFORMATION FOR AUTHORS

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The article's textual file is to include the title of the article, an abstract, a structured text, references, a separate sheet of captions for the diagrams, and tables (each on a separate sheet). Structural chemical formulae are placed in the body of text.

The articles are accepted in the text editor Microsoft Word using the font Times New Roman for texts, Symbol for Greek letters, and MathematicalPi2 for handwritten and gothic symbols. The standard font size is 14.

For tables, use Word (Table – Add Table) or MS Excel.

Recommendations for typewriting formulae

Mathematical equations forming a separate line should be typed in the MathType formula editor as a whole.

It is not allowed to combine a table, a text, and an inserted frame within the same unit. For the equations printed in the MathType, it is necessary to keep to the standard style of symbols and indices, their size and placing. Forced manual changing of individual symbols and formula elements is not allowable!

Dimensions

They are separated from the figure by a space (100 kPa, 77 K, 10.34(2) A), except for degrees, percent, and permille: 90°, 20°C, 50%, 10‰. Fraction dimensions: 58 J/mol, 50 m/c2.

For complex dimensions, it is allowed to use both negative degrees and parentheses (J/ mol-1 K-1), {J/ (mol K) or J(mol K)-1}, if it makes reading easier. The main requirement is the unified manner of writing dimensions.

While enumerating and giving numerical spaces, the dimension is set for the last number (18-20 J/mol), with the exception of angular degrees.

For Celsius degrees: 5°C, not 5°. Angular degrees are not omitted: 5°–10°, not 5–10°.

Dimensions for variables are written with a comma (E, kJ/mol); for logarithms, in square brackets without a comma: ln t [min].

Spaces between words

References to diagrams and tables are typed with spaces (Fig. 1, tab. 2).

Inverted commas and brackets are not separated by spaces from the included words: (at 300 K), (a); not (at 300 K), (a).

There should be a space between the № or § sign: (№ 1; § 5.65), but no space in numbers with letters: (IVd; 1.3.14a; Fig. 1d).

In geographical names, there is a space after the period: р. Енисей, г. Новосибирск.

References to cited works

Initials are put after authors' and editors' names and are not separated by spaces: Иванов, А.А., Petrov, B.B.

The year, volume, number, etc. are separated from one another and from the figures by spaces: 1992, n. 29, № 2, С. 213. or 1992, vol. 29, no. 2, pp. 213.

To refer to the issue number of both Russian and foreign journal, use the № sign. In the titles, the word *journal* is shortened for Journ. / Журн.

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