ISSN 2310-9599

КемТИПП

FOODS AND RAW MATERIALS

Vol.5, №1, 2017

The Ministry of Education and Science of the Russian Federation

Kemerovo Institute of Food Science and Technology (University)

FOODS AND RAW MATERIALS

Vol. 5, No. 1, 2017

ISSN 2308-4057 (Print)
ISSN 2310-9599 (Online)

Published twice a year.

Founder:
Kemerovo Institute of Food Science and Technology (University), KemIFST
Stroiteley blvd. 47, Kemerovo, 650056 Russian Federation

Editorial Office, Publishing Office:
office 1212, Stroiteley blvd. 47, Kemerovo, 650056 Russian Federation,
phone/fax: +7(3842)39-68-45

http:frm-kemtipp.ru

e-mail: fjournal@mail.ru

Printing Office:
office 2006, Institutskaya Str. 7, Kemerovo,
650002 Russian Federation,
phone: +7(3842)39-09-81

ISSN 2308-4057 (Print)
ISSN 2310-9599 (Online)

The Edition is registered by Federal Service for Supervision in the Sphere of Telecom, Information Technologies and Mass Communications (Media Registration Certificate EL no. FS77-61611 dated April 30, 2015)

The Journal is included in the International Databases: Emerging Sources Citation Index (Web of Science Core Collection), Scopus, Agris, CAS, FSTA, EBSCOhost, ResearchBib, ProQuest, CABI, Agricola, Ulrich's, Google Scholar, OCLC WorldCat, BASE.

The journal is included in the SQC list of leading peer-reviewed journals

The Edition «Foods and Raw Materials» is included in the Russian index of scientific citation (RISC) and registered in the Scientific electronic library **eLIBRARY.RU**

CONTENTS

REVIEW

FOOD PRODUCTION TECHNOLOGY

BIOTECHNOLOGY

PROCESSES, EQUIPMENT, AND APPARATUS FOR FOOD PRODUCTION

Signet for publishing
June 29, 2017
Date of publishing
June 29, 2017
Circulation 100 ex.
Open price.

Subscription index:
for the unified "Russian Press" catalogue – 41672,
for the "Informnauka" catalogue – 40539

Kemerovo Institute of Food Science and Technology (University), KemIFST, Stroiteley blvd. 47, Kemerovo, 650056 Russian Federation

REVIEW

USE OF FOOD RESOURCES AND DEVELOPMENT OF FOOD PRODUCTION TECHNOLOGY

V. A. Aret

Saint Petersburg National Research University of Information Technologies, Mechanics and Optics (ITMO University), Lomonosov Str. 9, Saint Petersburg, 191002, Russian Federation

e-mail: valdurtera@rambler.ru

Received February 09, 2017; Accepted in revised form April 10, 2017; Published June 29, 2017

Abstract: Various changes in demographic models of world population and evolution of food production technologies have been considered. Numerical constant values in the hyperbolic model of Heinz's cybernetics are defined as per the CurveExpert program and based on statistical data of the global population increased for the certain period at the mean square deviation of S = 74.8 of one million people a year and the correlation ratio of r = 0.994. Note at the same time that the calculated Heinz`s "Doomsday" falls on the 115th year of the life and the date of birth of this model developer. The relation of the world population growth to stages to develop food production technologies has been analyzed. The marginal population is evaluated in terms of the direct energy considerations. A variety of development hypotheses is proposed throughout the human development history based on the Darwin's model, astrophysics of the solar system and the policy.

Keywords: The von Foerster's model, the world population, the food technology

DOI 10.21179/2308-4057-2017-1-4-10 *Foods and Raw Materials*, 2017, vol. 5, no. 1, pp. 4–10.

INTRODUCTION

This article is aimed to clarify historical, economic and philosophical experience in production and consumption of food and to evaluate prospects for further development in this field of human activity. Currently we face some desperate predictions which make the subject and purpose of our research urgent upon the analysis. For instance, Professor John Beddington [1], UK Government's scientific adviser, predicted that by 2030 we would face disastrous scarcity of vital resources. By this time, the population will reach 8.3 billion people; the need in energy will jeopardize by 50% where the demand for fresh water will grow by 30%. V.I. Arnold [2], one of the Soviet mathematicians, developed the theory of catastrophes. The mathematical aspect of this poses certain doubts even where such intricate phenomenon as the cataclysm is fully covered addressing the bifurcation theory of differential equations and the theory of smooth reflection peculiarities, though it accentuates the urgency of mathematical analysis of problems, in addition. Ilya Prigogine, the Nobel laureate, in collaboration with Isabelle Stengers [3] looked for methods to restore the union between humans and nature based on new principles to be the solidarity of science, culture and so in addition to the union of humankind and nature.

OBJECTS AND METHODS OF RESEARCH

The research is focused on critical periods in history of technology for food production industry. In 1960, Heinz von Foerster, the scholar [4], published an article in the "Science" Magazine titled "Doomsday. Friday 13, November 2026". Based on the data on global population growth in 1958 he built a hyperbolic model as per which the world population by 2026 would be unlimited

$$N(t) = \frac{C}{t_0 - t}, \quad (1)$$

where $N(t)$ is the dependence of the global population N on time t; t_0 is the time constant by Heinz; C = 199686.86 is the constant of the global population by demographic data prior to 1950 that we calculated using a mathematic software product. Then the formula (1) takes on the form:

$$N(t) = \frac{199686.86}{2026 - t}. \quad (2)$$

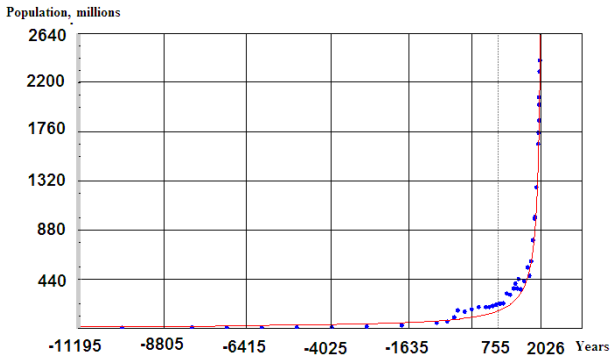


Fig. 1. Graph plotted on the global population based on statistic data up to 1950 using the CurveExpert software for the empirical formula (2). The standard deviation of the plotted data makes S = 74.8 and the correlation coefficient r is equal to 0.994.

RESULTS AND DISCUSSION

Kremer M. (1993) [5] proposed the similar global population-associated graph in 1993. Up to 1970s, the global population actually grows as per the hyperbolic law.

However, since 1989 the absolute growth rate of the global population tends to decline (US Census Bureau (USCB), 2008) [6]. By 2100, the growth rate could decline to less than 5 million people a decade. As some demographers limit the growth rate, the modeling will reach 10–12 billion people and some predict on the lower level of the global population stabilization. In this case, for example, the logistic law (Kapitza, 1996 [7]; Verhulst, 1845 [8]; Lotka, 1925 [9]; Volterra, 1926 [10]; Haub, 1995[11]) seems to be more appropriate.

The final scenario of population development is still vague. But it is clear that the Doomsday by Heinz would not occur in 2026 due to the global drive to perpetuity and it may occur for quite different reasons.

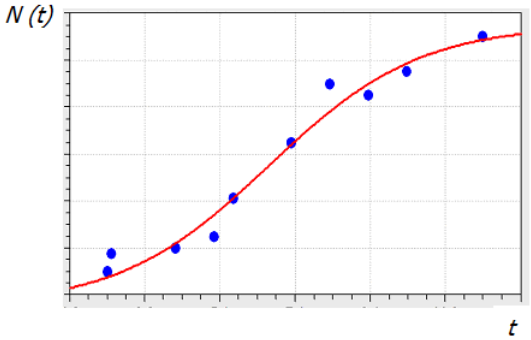


Fig. 2 . Standard graph of the logistic law.
(Today: 09-02-2017 13:08:49 Word population amounts to 7 496 359 712, http://countrymeters.info/ru/World [12]).

The astrophysical concept of the solar system and the Darwinian evolution model basis compile the following arguments on the development of food production technologies.

Photosynthesis is the main source of biological energy, the photosynthetic autotrophs (mainly, the green plants) use solar energy to synthesize organic compounds of inorganic, the heterotrophs (including humans) exist due to energy stored as autotrophic chemical relations. The Sun's energy resources are not endless. As it radiates, the mass of the Sun is reduced by 4.3 million tons per second (K.–P. Schröder and R. Connon Smith, 2008) [13]. The Sun can generate the energy for photosynthesis on the Earth for about 100 billion years, but the energy required will be "cut off" someday.

Let us consider the process of photosynthesis in detail. There are three stages of photosynthesis: photophysical, photochemical and chemical. At the photophysical stage, the light quanta pigments are absorbed, they transform to the excited state and the energy is transferred to other molecules of the photosystem. At the photochemical stage, the charges separate in the reactive center of the photosynthetic electron transport. The first two stages are jointly called the light-dependent stage of photosynthesis. The third stage takes place with no commitment of the outer world and includes biochemical reactions of organic compound synthesis using the energy stored at the light-dependent stage. Most such reactions as observed in Calvin cycle (J. Bassham, A. Benson, and M. Calvin, 1950) [14] are the processes of gluconeogenesis formation of sugars and starches from carbon dioxide in the air.

In 1941, Melvin Calvin, the American biochemist, proved that the water molecule photolysis is the primary photosynthetic process resulting in oxygen formation released in the atmosphere, and hydrogen used to reduce the carbon dioxide to organic substances. Using the radioactive carbon isotope, 14C, paper chromatography, and conventional methods of the organic chemistry, Calvin and his team managed to trace biosynthetic paths of photochemical processes. By 1956, the pathway of full carbon conversion in the photosynthesis was clarified. In 1961, Calvin was awarded the Nobel Prize in chemistry for researches on carbon dioxide assimilation at plants. The chemical photosynthesis formula may be submitted as follows:

$$6CO_2 + 6H_2O = C_6H_{12}O_6 + 6O_2 . \qquad (3)$$

Based on such reaction over 1017 kcal of free energy has been stored in the world each year that matches with assimilation over 1010 tons of carbon as carbohydrates and other organic substances (Stayer L., 1985) [15]. If such considerations are deemed correct, the maximum theoretical number of people to be supported by photosynthesis may be calculated at ease. Considering that there are 365 days a year and 1 person needs about 3,000 calories of energy per day, we obtain

$$\frac{10^{17}}{365 \cdot 3000} = 9132420913 \approx 10^{10} . \qquad (4)$$

Apparently, humans and other Earth creatures cannot, for various reasons, use all the stored energy (E.J. Kormondy 1996) [16]. Each link of the trophic chain lost about 90% of useful energy where the mankind still uses reserves of energy as the coal, oil, gas and other energy sources. However, the most

global population fails to receive the adequate quantity and quality of food recently. The food security is the urgent economic challenge for many countries and the global population approaches to photosynthesis energy capacity limits on the planet.

Let us consider the evolutionary classification of food production technologies that justifies the attempts of some forecasts in this area. This technology may be named the first generation technology. The technology of food production was used to be limited to hunting and gathering and differed little from the food production in the animal kingdom. Before humans managed to acquire tools to hunt or farm, insects might have been the important portion of their diet. Cave paintings in the Northern Spain dated back about 30000 to 9000 BC depict the collection of edible insects and wild bee nests suggesting for potential entomophagous society [17].

The Old Stone Age (Lower Paleolithic), that is up to 10–8 thousand BC was the period for the fossil man who used stone, wood and bone tools processed with living employment of thereof to differ significantly from other animals (E. Callaway, 2013 [18]; A.C. Guyton, J.E. Hall, 2006 [19]). The first-generation technology provides the energy to approximately 3 million people. Standing on two legs, the human enjoys more rational way to travel as compared to animals running on four legs. Coupled with the with the human body cooling mechanism by sweating, the human being acquired the ability to catch up any hunting animal at long distances (G.A. Harrison, J.M. Tanner, D.R. Pilbeam, P.T. Baker, 1988) [20]. First-generation technologies represent rudiments of second-generation technology that included the food extraction and transportation, more considerable approaches to power supplies saving, in elements of communal pattern in the hunting and gathering area.

Second-generation technologies may be named as reproduction technologies.

Historically, this technology has evolved around 8–3 thousand BC in the New Stone Age (Neolithic Period). Later on, the human being opened up the skills of grinding and drilling of stone tools, spinning and weaving, pottery art. People hunted together with wolves. They kept domesticated animals – cows, sheep, horses. The hunting transferred to its more intense and adjustable phase. At the same time, the gathering activity was developed to cropping and cultivation of useful plants. This technology provides power to approximately 50 million people by the end of the Neolithic Period and for about 3 billion by the year 1960 (J. Armelagos, 2014) [21]. The increasingly growing needs of human beings are mainly met extensively by increasing the area of existence and the number of livestock. The significance of grain culture should be specifically emphasized where people acquired the skills of massive local cultivation and natural conservation of dried grain.

The importance of the grain crop is evidenced by the well-known expression from the 10th satire of the Roman satirical poet Decimus Junius Juvenal (Decimus Junius Juvenalis in Latin, ab. 60-127) "Bread and circuses"! Juvenal used it to describe the policy of statesmen bribing people with money and food and circus performances. Such acts helped them to seize and hold their power in ancient Rome. (http://antique-lit.niv.ru/antique-lit/gilenson-drevnij-rim/yuvenal.htm) [22].

Ordinary Romans ate mostly cereal products – the bread and porridge. As per the Romans, the hunger meant that the grain, the main food reserves, ended manifested in public disaffection and revolts due to the scarcity of grain or cereal crop failures. The bread was used as the manipulating tool to manage political processes not only in ancient Rome [23].

Currently, there is a wide range of grain and pseudo-seeds food on markets, including the wheat, barley, oats, rye, millet, spelt wheat, green grain and corn. There are such grain crops as kamut, the ancient type of wheat used to be mainly cultivated in ancient Egypt. The American rice is largely marketed to be the pre-cooked, dried and purified wheat coarsely or finely grinded. Valuable pseudo-crops, such as amaranth, Quinoa do not refer to grain crops but to plants of genus wormseed. The buckwheat the grain of which resemble the grain crop refers to plants of the buckwheat family (http://ladychef.ru/ingredienty/hleba-i-zrelishh-istoriya-i-raznooobrazie-zlakovyh-kultur) [24].

The main cereal crop is the wheat. China is the main wheat producer in the world. In 2014, the share of China in the world grain crop production reached 17.3%, the volume of production made 126.2 million tons. For 10 years, as compared to 2004, the wheat production in China increased by 37.3% or 34.3 million tons. In the next 10 years the growth of wheat production in China is expected to decline in view of the limited land plot available. By 2024, according to the OECD forecast, it will reach 130.9 million tons that almost matches the level of current indexes. According to the USDA, the wheat crop in China by 2024/2025 will reach 133.1 million tons. Among the wheat-producing countries, Russia is ranked third in the world. In 2014, the wheat production in Russia amounted to 59.7 million tons (8.2% of global production). For the 10 consequent years, the figures increased by 31.4% or 16.6 million tons. In 2015, the wheat production in Russia was over 62 million tons as per the Ministry of Agriculture of the Russian Federation making 63.8 million tons (http://ab-centre.ru/page/proizvodstvo-pshenicy-v-mire-strany-proizvoditeli-pshenicy) [25].

The main factor determining the growth of wheat production in the world was an increase in productivity rather than in acreage. The measures aimed to improve the wheat crop technologies and contribute to higher productivity included the increase in the use of mineral fertilizers. In view to increase the yield results and to hold high level of wheat production in the world, we will need to constantly review the mineral fertilizer dosage used. The challenge is to increase the food yields in future by rational use of fertilizer [26].

As it is well-known, the theory of demographic cycles explores the processes of population change under conditions of limited natural resources.

Raymond Pearl [27] proposed this theory and proved that changes in the number of animal populations (and perhaps humans) are described by the so-called logistic curve.

The logistic curve in Fig. 2 shows that the population grows rapidly in the very beginning with the abundance of resources available and high-consumption rate. Then the growth slows down and the population stabilizes near the asymptote corresponding to the maximum possible volume of complete consumption of natural resources.

The achievement of the maximum possible number of population means that there is a minimum level of consumption at the survival margin where the natural increase is completely eliminated by the starvation death. In fact, this state of "hungry homeostasis" turns out to be unstable, the fluctuations in environmental factors result in "demographic catastrophes", catastrophic hunger or epidemic. The disaster causes a drastic reduction in population followed by the new curl in the new demographic cycle recovered [27, 28].

With regard to changes in the population growth rate in graphs 1 and 2, the availability of demographic cycles in history was proved by Wilhelm Abel in the ‘30s of XX century [29].

Upon the review of data on economic situation in the XII-XIV centuries, V. Abel showed that the population growth fir that period caused the exhaustion of arable land resources; in turn that resulted in food scarcity, increases in grain prices and starvation. Farmers who were unable to get food for their families were forced to cut weekly expenses and went to look for better jobs to larger cities. The urban growth was followed by the craft blooming though the craft itself was not adequate to allow food for the entire surplus population, and the cities were full of unemployed and the poor. Hunger and poverty resulted in riots both in large cities and in villages. In Flanders, such riots were manifested as the social revolution. The French social struggle ended in adoption of absolutism. In the end, the Black Death epidemic that broke under conditions where millions of people were broken by permanent malnutrition resulted in deaths of half the European population. That was the "demographic catastrophe" to end the demographic cycle. Thus, it describes the cycles by R. Pearl that really existed in the past [30].

The second-generation technologies employ elements of the third-generation technology, that is, the technology intensification. The reproduction rate of human beings is rising through breeding more productive animals and growing more efficient plants.

Third-generation technologies may be named as the intensification. The end of the dominance of the second-generation technology can be roughly specified as the middle of the 20th century, when the humankind exhausted all opportunities of extensive growth of food production: the crops suitable for cultivation, the number of animals limited due to the land plot restriction could no longer be increased. It is believed that population will not grow indefinitely and stabilized totaling, as mentioned above, some 10–15 billion people.

Main peculiarities of the third-generation technology, intensification technology, are as follow:

(1) Use of microbiological methods of food production – the efficiency of micro-organisms, algae, fungi is somewhat greater than that of traditional agricultural animals and plants. This is the rule of biology that works to mean that the smaller the body, the less it is effective (Timoshenko L.V., 1999) [31]. It is easy to trace the following patterns: the time to double the cattle biomass is 30–60 days, 20–40 days for pigs, 2–24 days – for chickens, 6–12 days for grass, 2–6 hours for chlorella, 0.3–2 hours for bacteria and yeast. In other words, the pattern may be depicted as 1440:960:576:288:6:2 in hours.

As it already mentioned, a steady increase in population up to 9 billion people was predicted by 2050 that requires an increase in food sources or forage for the existing agro-ecosystems resulting in even greater impact on the environment. The deficiency in agricultural land, water, forest, fisheries and biological resources is already predicted. High quality edible insects contain protein, vitamins and amino acids wholesome for humans. Insects are known for high food conversion ratio, for example, crickets need six times less than cattle, four times less than sheep, or less than half as compared to pigs and broiler chickens to produce the same amount of protein. In addition, they emit fewer greenhouse gases and ammonia than conventional livestock. Insects can be grown on organic waste.

(2) Artificial reduction in trophic food chains (plant – animal – people), food production directly from autotrophic organisms, namely soy milk, cottage cheese, artificial meat, eggs and so forth (J.D. Mauseth, 2008)[32]. In process of feeding, the potential food energy goes to its consumers. When the potential energy is transferred from unit to unit of the food chain, up to 80–90% is lost as the heat. The longer is the trophic chain, the lower is the production of its last link in relation to that of the initial one.

(3) Mass production of genetically modified foods with specific nutritional and medicinal properties.

One of signs of the next food technology generation is the creation of artificial foods. A. N. Nesmeyanov, the Academician of the USSR, the outstanding chemist laid the basis (1962) of the new research trend, namely the synthetic food creation. He specified the pathway (1960–1970) for the synthesis of simple and available compounds (carbohydrates, nitro compounds, aldehydes), amino acids and natural proteins of products to imitate the smell and taste of food [33]. The caviar product named “Iskra” (abbreviated “black artificial granular caviar”, in Russian “ISKRA”) became the first known industrial design of the protein caviar in the USSR. First in the world, the USSR obtained the caviar at the “Chibis” plant constructed in 1960 at the Institute of Elementorganic Compounds (Moscow). The plant capacity – 1.5–2 kg/h of caviar ready for use. The granular caviar produced at the “Chibis” Plant contains the casein with addition of gelatin, dextrin, starch, glycerin and sodium hydroxide. The taste is added with the fish oil and chemical “flavor of glutominate, etc.” [34, 35]).

G. L. Slonimsky, the Doctor of Chemical Sciences who cooperated with A. N. Nesmeyanov in the works of that time stated that: "I flashed with the idea of the caviar molding, so I said I would try to do it. By 1964 we tested our first laboratory samples of the artificial caviar from the skimmed milk. And then, the technology was developed by the Institute by its own resources. Since then, this cheap and delicious product called "Protein Granular Caviar" (based on the casein protein of eggs and other food waste) is manufactured in Moscow and other cities..." [36].

For the first time in the world, the production of the protein caviar was started in the Moscow dock refrigerator. The dairy plant in Myski town in Kuzbass was ranked second in the world in early seventies of the last century (where this industrial technology by Nesmeyanov-Slonimsky was implemented). It was initiated by young leaders of the Kemerovo Institute of Food Science and Technology (KemIFST founded in 1972) supported by the Kemerovo Regional Committee of the CPSU with members who first tasted the caviar. The historical tasting procedure at the meeting of the Regional Party Committee Office was attended by Prof. B. Azarov, the Rector of KemIFST and V. Aret, Ph.D, Vice-Rector of the Research Department. The regional administration authorized to continue the manufacture of this innovative product that required the certain political courage since the production of artificial foodstuff was not acknowledged as the main line of the food programme of the CPSU. Still, sometimes low-expert people spread rumors on production of black caviar from the oil.

Main researches are followed by long-term flow of inventions. For example, ideologically close events are still under development at the institute of the Academician Nesmeyanov.

The range of similar inventions followed first developments at the Nesmeyanov Institute. For example, in 1986, a team of inventors headed by the Academician I. A. Rogov [37] developed the method to manufacture the nutritional protein caviar at the Tbilisi State University. The invention was the use of animal-milk proteins, known as the albumin milk.

Til now, inventors improve various technology aspects using the caviar as the invention by V. A. Gromov in 2003 (V. Gromov, 2003) [38]. The invention will help to create the universal food dye that gives the caviar the color and shade desired.

The next three technology generations can be considered as irrelevant fantasy for evolution. The reason for them lies in reasons other than the increase in human number.

The fourth-generation technology may be called as the nuclear. Signs thereof are as follow:

(1) The development of artificial photosynthesis in similar ways of assimilation of nuclear and other energy.

(2) Integration of food technology and pharmaceutical products aimed at optimizing and providing individualized human body substances vital for activity.

Fifth-generation technology can be called as the biotechnology that will be followed by genetic, chemical, mechanical and information restructuring of plants, animals and humans. Education and social family functions will be fundamentally restructured.

The sixth-generation technology is quite radical and fantastic. It is as follows: Signs thereof are as follow:

(1) Rejection of the protein body as a life carrier, transition to informative electro-magnetic or any other physical field (as per terminology by Vernadsky (2013) [39], that is, the anthroposphere, the final solution to diseases, the beginning and the end of life.

(2) Output of life from the Earth planet to the infinite space and its migration to the speed of light, the problem of the fading sun.

CONCLUSION

The history of mankind is the history of "existence of biopolymer bodies capable of self-replication under the constant exchange of matter and energy with the environment" (as defined by the Academician V. Goldansky (1986) [40]. It will be completed and will go to the history of other intelligent system existence capable of self-replication and non-random impact on the environment.

This optimistic path of evolution may be changed in many possible events, including astrophysical and political ways. For example, a huge meteorite will fall on the Earth destroying the entire life. Or, resulting from the military science development and political conflicts a nuclear war will be broken or humans will be contaminated with incurable diseases.

"We face great environmental challenges: climate change, food production, overpopulation, decimation of other species, epidemic disease, and acidification of oceans. In total, they remind that we live the most dangerous live of the humanity evolution. Nowadays, we dispose of the technology to destroy the planet we live on, but we have not developed the ability to escape it, yet. In a few hundred years, we will possibly establish human colonies amid stars, but right now we live on the one planet and we need to work together to protect it. To do that, we need to break, not build up, barriers within and between nations. If we are to stand a chance of doing that, the global leaders need to acknowledge that they failed and keep on failing. When certain people are authorized to use resources at their hands, we will have to learn to share far more than currently we do" (Stephen Hawking, 2016) [41]. Deep analysis of the problem was given in the work Prosekov A. and Ivanova S. [42].

REFERENCES

1. *World faces 'perfect storm' of problems by 2030, chief scientist to warn*. Available at: https://www.theguardian.com/science/2009/mar/18/perfect-storm-john-beddington-energy-food-climate. (accessed 7 November 2016).

2. Arnold V.I. *Teoriya Katastrof* [Catastrophe Theory]. 4th ed. Moscow: Editorial-URSS Publ., 2004. 128 p.
3. Prigogine I. and Stengers I. *Order out of Chaos: Man's new dialogue with nature*. New York: Bantam Books, 1984. n.p.
4. Von Foerster H., Mora P., and Amiot L. Doomsday: Friday, November 13, AD 2026. *Science*, 1960, vol. 132, no. 3436 (Nov. 4), pp. 1291–1295.
5. Kremer M. Population Growth and Technological Change: on B.C. to 1990. *The Quarterly Journal of Economics*, 1993, vol. 108, no. 3, pp. 681–716. DOI: 10.2307/2118405.
6. US Census Bureau (USCB), "*Total Midyear Population for the World: 1950–2050*", 2008. Available at: http://www.census.gov/ipc/www/idb/worldpop.html. (accessed 09 February 2017).
7. Kapitsa S.P. The phenomenological theory of world population growth. *Advances of Physical Sciences*, 1996, vol. 166, no. 1, pp. 63–80.
8. Verhulst P.F. Recherches Mathématiques sur La Loi D'Accroissement de la Population. *Nouveaux Mémoires de l'Académie Royale des Sciences et Belles-Lettres de Bruxelles*, 1845, vol. 18, art. 1, pp. 1–45.
9. Dublin L.I. and Lotka A.J. On the True Rate of Natural Increase: As Exemplified by the Population of the United States, 1920. *Journal of the American statistical association*, 1925, vol. 20, no. 151, pp. 305–339. DOI: 10.1080/01621459.1925.10503498.
10. Volterra V. Variazone e fluttuazini del numero d'individui in specie animali conviventi. *Mem. Accad. Naz. Lincei*. Ser. 6, 1926. n.p.
11. Haub C. How Many People Have Ever Lived on Earth? *Population Today*, 1995, February, p. 5.
12. *Countrymeters.info.* Available at: http://countrymeters.info/ru/World. (accessed 01 February 2017).
13. Schröder K.-P. and Connon Smith R. Distant future of the Sun and Earth revisited. *Monthly Notices of the Royal Astronomical Society*, 2008, 386, pp. 155–163.
14. Bassham J., Benson A., and Calvin M. The path of carbon in photosynthesis: VIII. The rôle of malic acid. *The Journal of Biological Chemistry*, 1950, no. 185 (2), pp. 781–787.
15. Stayer L. *Biochemistry in 3 volumes*, vol. 2. Wiley, 1985. 312 p.
16. Kormondy E.J. *Concepts of ecology (4th ed.).* New Jersey: Prentice-Hall, 1996. 559 p.
17. Bodenheimer F.S. Why Insects Should Be in Your Diet. *The Scientist*, 27 November 2013, 27, pp. 22–23.
18. Callaway E. Genetic Adam and Eve did not live too far apart in time. *Nature*, 6 august 2013. DOI: 10.1038/nature.2013.13478.
19. Guyton A.C. and Hall J.E. *Textbook of Medical Physiology (11th ed.).* Philadelphia: Elsevier Saunders, 2006. 890 p.
20. Harrison G.A., Tanner J.M., Pilbeam D.R., and Baker P.T. *Human Biology: An introduction to human evolution, variation, growth, and adaptability (3rd ed.).* Oxford: Oxford University Press. 1988. n.p.
21. Armelagos G.J. Brain Evolution, the Determinates of Food Choice, and the Omnivore's Dilemma. *Critical Reviews in Food Science and Nutrition*, 2014, vol. 54, no. 10, pp. 1330–1341. DOI: 10.1080/10408398.2011.635817.
22. Gillenson B.A. Ancient literature. Ancient Rome. Book 2. Available at: http://antique-lit.niv.ru/antique-lit/gilenson-drevnij-rim/index.htm. (accessed 01 February 2017).
23. Hoppen K.T. *Elections, politics and society in Ireland 1832-85*. Oxford, 1984, pp. 90–115.
24. Kremer M. Population Growth and Technological Change: One Million B.C. to 1990. *The Quarterly Journal of Economics*, 1993, vol. 108, no. 3, pp. 681–716. DOI: https://doi.org/10.2307/2118405
25. *International wheat production*. Available at: https://en.wikipedia.org/wiki/International_wheat_production_statistics. (accessed 01 February 2017).
26. Reynolds M.P. (ed.) *Climate change and crop production*. UK, London: CABI, 2010. 292 p.
27. Pearl R. The growth of populations. *The Quarterly Review of Biology*, 1927, vol. 2, pp. 532–548. DOI: 10.1086/394288.
28. Pearl R. and Reed L. On the rate of growth of the population of the United States science 1790 and its mathematical representation. *Proceedings of the National Academy of Sciences*, 1920, vol. 6, pp. 275–288.
29. Abel W. Bevölkerungsgang und Landwirtschaft im ausgehenden Mittelalter im Lichte der Preis- und Lohnbewegung. *Schmollers Jahrbücher*, 1934, Jahrgang, no. 58.
30. Nefedov S.A. The theory of demographic cycles and social evolution of ancient and medieval societies of the East. *East – Oriens*, 2003, no. 3, pp. 5–22.
31. Timoshenko L.V. *Osnovy biotekhnologii* [Basics of Biotechnology]. Tomsk: TPU Press, 1999. 91 p.
32. Mauseth J.D. *Botany: An Introduction to Plant Biology (4 ed.)*. Jones & Bartlett Publishers, 2008. 252 p.
33. Nesmeyanov Alexander Nikolaevich. *Informatsionnaya sistema "Arkhivy RAN"* [Information system "Archives of the Russian Academy of Sciences"]. Available at: http://isaran.ru/?guid=AF893FBC-71D2-050A-FD40-9CA8F4C946C7&q=ru/person (accessed 01 February 2017).
34. Rogovina L.Z. and Slonimskii G.L. Formation, Structure, and Properties of Polymer Gels. *Russian Chemical Reviews*, 1974, vol. 43, no. 6, pp. 503–514. DOI: 10.1070/RC1974v043n06ABEH001821.
35. Belikov V.M., Rogozhin S.V., Slonimskii G.L., Golovnya R.V., and Tolstoguzov V.B. Chemical investigations on artificial and synthetic foods. *Russian Chemical Reviews*, 1969, vol. 38, no. 9, pp. 699–713. DOI: 10.1070/RC1969v038n09ABEH001826.
36. Mdinaradze D., Rogov I.A., Sergeev V.N., et al. *Sposob proizvodstva pishchevoy belkovoy zernistoy ikry* [Way of production of food proteinaceous granular caviar]. Author's certificate SSSR, no. 552738, 1988.

37. *Slonimsky Grigory L'vovich (1915–2004)*. Available at: https://ineos.ac.ru/en/history-famous-scientists/doctors-of-sciences/slonimsky. (accessed 07 February 2017).
38. Gromova V.A. *Sposob prigotovleniya zernistoy ikry ryb* [A method for preparing fish caviar]. Patent RF, no. 2236159, 2003.
39. Vernadskiy V.I. *Sobranie sochineniy v 24 tomakh* [Collected Works in 24 volumes]. Moscow: Nauka Publ., 2013.
40. Gol'danskii V. The emergence of life from the point of view of physics. *Communist*, 1986, no. 1, p. 87–94. (In Russian).
41. Hawking S. *This is the most dangerous time for our planet*. Available at: http://uk.businessinsider.com/ stephen-hawking-this-is-the-most-dangerous-time-for-our-planet-2016-12. (accessed 03 February 2017).
42. Prosekov A.Yu. and Ivanova S.A. Providing food security in the existing tendencies of population growth and political and economic instability in the world. *Foods and Raw Materials*, 2016, vol. 4, no. 2, pp. 201–211. DOI: 10.21179/2308-4057-2016-2-201-211.

Please cite this article in press as: Aret V.A. Use of food resources and development of food production technology. *Foods and Raw Materials*, 2017, vol. 5, no. 1, pp. 4–10. DOI: 10.21179/2308-4057-2017-1-4-10.

FOOD PRODUCTION TECHNOLOGY

INFLUENCE OF THE NEW MULTICOMPONENT BRINE ON THE QUALITY CHARACTERISTICS OF THE BOILED HORSE MEAT PRODUCT

N. I. Gombozhapova, B. A. Bazhenova*, S. Yu. Leskova, T. M. Badmaeva, and A. M. Danilov

East Siberian State University of Technology and Management,
Klyuchevskaya Str. 40v, Ulan-Ude, 670013, Russian Federation

* e-mail: bayanab@mail.ru

Received May 23, 2016; Accepted in revised form September 25, 2016; Published June 29, 2017

Abstract: Currently, as part of import substitution, it is important to effectively use the reserves of animal protein, for example, horse meat, which has dietary properties due to a balanced amino acid and fatty acid composition and high efficiency in the treatment of anemia, hypotrophy and other pathologies. However, ready-made products of meat of adult horses are tough and not succulent; in order to adjust the functional and technological properties of boiled horse meat products, the use of multicomponent brines is promising. A promising ingredient for use in the composition of the stuffing brine is a powdered arabinogalactan, a highly branched polysaccharide, isolated from soft wood. The purpose of the work was to study the possibility of using arabinogalactan in the brine in the technology of whole-muscle boiled horse meat products. The experimental part was carried out in the laboratory of the department "Technology of meat and canned products" of the East-Siberian State University of Technology and Management. The samples of chilled horse meat were tested. These samples were stuffed with a control and experimental brines with a different dose of arabinogalactan with subsequent massaging in a tumbler. In the samples studied, physico-chemical and structural-mechanical characteristics were determined. As a result of the studies, kappa- and iota-carrageenans were selected as ingredients of the stuffing brine with a concentration of 0.8 and 0.2% and the animal protein "Promiat-90" with a concentration of 0.75% of the brine weight basis. The amount of injected arabinogalactan (10%), which provides the necessary density and viscosity of the brine, is experimentally justified. Massaging of salted horse semi-finished products is accompanied by an improvement in their hydrophilic properties, which reach the highest values in 10 hours. The finished experimental product is characterized by better quality and yield (by 6%). Thus, the use of 10% arabinogalactan in a multicomponent brine for horse boiled products makes it possible to improve their functional-technological and taste characteristics.

Keywords: Arabinogalactan, multicomponent brine, horse meat, boiled meat product

DOI 10.21179/2308-4057-2017-1-11-19 *Foods and Raw Materials*, 2017, vol. 5, no. 1, pp. 11–19.

INTRODUCTION

Currently, in accordance with the adopted State Program for the Development of Healthy Nutrition of the Population of the country, one of the main tasks of scientists in the meat industry and meat producers is to provide products not only for everyday demand but also for preventive purposes. At the same time, it is necessary to take into account the specifics of raw materials supply in the meat industry. In the context of import substitution, it is important to use all available animal protein reserves, for example, horse meat as efficiently and effectively as possible.

The horse meat has a pronounced dietary properties due to a well-balanced amino acid and unique fatty acid compositions. It has hypoallergenic properties and high therapeutic efficiency in the treatment of anemia, hypotrophy and other pathologies.

It is known that horse meat has a high content of mineral substances (calcium, phosphorus, iron – more than 20 kinds in all), essential amino acids, vitamins of group A and B. According to the microelement composition, horse meat is close to beef, but contains more iron and copper involved in the process of hematopoiesis, which is a positive factor in the treatment and prevention of anemia, as well as low sodium and many selenium, which strengthens its dietary properties. Horse meat outperforms other types of raw meat by the content of potassium, vitamins A, E, B_1, B_2. A horse is an animal with a unicameral stomach, devoid of the gallbladder, possesses meat that is easily digestible. Horse lipids differ significantly from other types of animal fats in chemical composition and biological value. They are fusible (melting point 28–32°C), rich in fatty acids and

vitamin A valuable for human body, contain little cholesterol. However, the finished products from the meat of adult horses are stiff and not succulent, as the muscle fibers of horse meat are larger in comparison with beef fibers of larger diameter and are characterized by a high content of muscle connective tissue [1–5].

To adjust the functional and technological properties (FTP) of boiled products from horse meat, improve their quality and increase yield, the use of multicomponent salting brines is promising [6, 7].

Boiled delicacies, made from whole-muscle pieces of meat, are becoming increasingly popular on the market. To produce such products in order to achieve a gentler consistency, succulence, better slicing – on the one hand, and obtaining additional profit by increasing the yield of finished products – on the other hand, the multi-component brines are used. Due to the peculiarities of its structure and composition delicacy products from horse meat are practically not represented in the consumer market. Multicomponent brines used for the production of whole-muscle meat products are complex disperse systems and the quality and yield of finished products depend on their physico-chemical properties. Their use contributes to the formation of the necessary technological and consumer properties: taste, flavor, softness and color of the finished product. To achieve this effect, and for the purpose of intensifying the brine treatment process, various mixtures containing sugar, spices, sodium nitrite and food acids, phosphates are used. Traditional methods of injecting brines with a high percentage of injection do not allow the finished product to remain marketable, leading to loss of product mass. These disadvantages can be eliminated by increasing the viscosity of stuffing brines due to various additives.

One of the most promising for use in the composition of stuffing brines is arabinogalactan (AG) – highly branched polysaccharide, contained in large quantities in soft wood (TU 9363-021-39094141-08).

The macromolecule of arabinogalactan from larch wood has a highly branched structure; its main chain consists of galactose units linked by glycosidic bonds β-(1→3), and side chains with bonds β-(1→6) from galactose and arabinose units, from single arabinose units, as well as uronic acids, mainly glucuronic acid. The ratio of galactose and arabinose units is approximately 6 : 1. Moreover, AG is mostly extracted from Siberian larch, in which the percentage of this substance is rather high – up to 35%. The resulting compound is an amorphous yellowish white powder, odorless and tasteless. It dissolves easily in water, both hot and cold, does not dissolve in organic solvents and has an average solubility in diluted alcohol. Fig. 1 shows the formula of arabinogalactan.

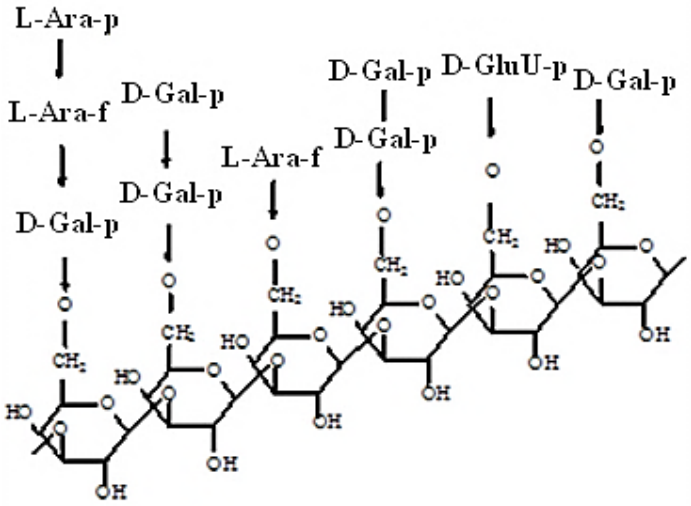


Fig. 1. The formula of arabinogalactan.

In recent years, studies of the biological activity of AG have intensified dramatically [8, 9, 10]. This is facilitated by such properties as high solubility in water, uniquely low viscosity of brines, narrow molecular weight distribution, and also biodegradability.

Arabinogalactan, a water-soluble polysaccharide, is a source of dietary fiber, is characterized by low toxicity and high biological activity (prebiotic, immuno-stimulating, lipid-lowering, gastro- and hepatoprotective). Especially important are its immunomodulating and prebiotic activity, due to which dozens of biologically active additives to human food and feed additives for animals have already been created in the world. In our country these are Fibrolar, Imbalance, Araglin D, Flarabin, Lakbin and a number of others.

Clinical studies have demonstrated not only the prebiotic and immunomodulatory effects of AG, but also a significant reduction in cholesterol in people with hyperlipidemia [11, 12, 13].

Arabinogalactan is registered under the code E409 in the Code of the Expert Committee on Food Additives of the World Health Organization (FAO/WHO) for food products as a stabilizer of emulsions and thickener. In our country, according to

the List approved by the Chief Sanitary Doctor of the Russian Federation, an adequate level of human AG consumption is 10 g/day, and the upper permissible level is 20 g/day. It is approved for use in the food industry as a thickener, stabilizer and gelling agent [11, 14, 15].

Areas of AG consumption in the food industry are largely determined by its physico-chemical properties: solubility in cold water, low viscosity of concentrated solutions, ability to bind fat and retain moisture, resistance to heating up to 130°C. In connection with the foregoing, it can be concluded that AG is a food additive with high biological value and functional properties acceptable for use in food production [16].

In connection with the foregoing, the aim of the work was to study the possibility of using arabinogalactan polysaccharide in multicomponent brines in the technology of whole-muscle boiled horse meat products to improve the quality of the finished product.

OBJECTS AND METHODS OF STUDY

The experimental part was carried out in the laboratory of the department "Technology of meat and canned products" of the East-Siberian State University of Technology and Management.

For the studies, chilled horse of II fatness category was used. The weight of the horse meat samples was 150 ± 10 g. Brine was stuffed into the control and test samples by means of a syringe. Injections were made along and across the muscle fibers of the meat. The test samples were stuffed with multicomponent brine and massaged in a laboratory unit operating as a tumbler (10 rpm) for 12 hours (in the following mode: the first hour of continuous massaging, the following hours: 40 minutes – massaging, 20 minutes – rest). Sampling was conducted every two hours.

Then the samples were subjected to heat treatment: The product was boiled in water at a temperature of 80–85°C for 30 minutes and heat treated with steam (steam temperature 100°C) for 45 minutes. The finished products were cooled to a temperature of 4–6°C.

The brine quality was determined by physicochemical methods: The kinematic viscosity was determined with the VPZH-2 capillary viscometer, the brine density was measured with a densitometer, and the active acidity was measured by a potentiometric method.

To determine the relationship between the duration of massage, the composition of multicomponent brine, and the properties of salted semi-finished product, the water-retaining capacity (WRC) of the semi-finished product was studied by pressing, the structural and mechanical properties were determined with the Warner-Bratzler instrument and the losses in the heat treatment of the finished product were analyzed by the difference in mass before and after boiling.

The quality of the finished product was evaluated in accordance with the indicators established by regulatory documents for whole-muscle products. Organoleptic indicators were determined on a nine-point scale; mass fractions of sodium chloride – in aqueous extract from the product by the Mor method; sodium nitrite – using photometric method by measuring intensity of the color formed in the interaction of nitrite with sulfonamide and N-(1-naphthyl)-ethylenediamine dihydrochloride in protein-free filtrate; protein – by Lowry's method; lipids – by Soxhlet method; total phosphorus – by photometric method, which is based on the reaction of phosphorus with ammonium molybdate in the presence of hydroquinone and sodium sulfite to form a colored compound, the color intensity of which is measured photometrically; residual activity of acid phosphatase - photometrically depending on the intensity of the resulting color, expressed by the mass fraction of phenol, the content of arabinogalactan - by gel permeation chromatography in a glass column with dextran calibration.

For conducting experimental studies, the standard salting brine used in the technology of whole-muscle meat products was taken as the starting material [17]. According to the Technical Regulations of the CU 034/2013, meat producers should use salt-and-nitrite mixtures instead of sodium nitrite in their production, so, in addition to sodium chloride, a salt-and-nitrite mixture Solino 0.5/0.6 was added. Thus, the standard brine included: Sodium salt, saline-nitrite mixture 0.5/0.6 and sucrose. As a control, a standard brine was used with the addition of phosphates and sodium erythorbate. For further studies, the dose of control brine and the amount of salting ingredients according to the FTP were chosen: water-retaining capacity and losses during the heat treatment of the boiled product. Brines were introduced by stuffing in an amount of 20 to 80% of the raw material weight. Samples with 40% brine injection had larger WRC and a smaller amount of losses during heat treatment. The content of salting ingredients (kg) per 100 liters of control brine (with injection in an amount 40 %): Table salt – 4 kg, salting-nitrite mixture – 1.5 kg, sucrose – 1.4 kg, phosphate – 0.5 kg, sodium erythorbate – 0.5 kg.

Currently, in the meat processing industry in the production of whole muscle products carrageenans are used as food hydrocolloids. Different types of carrageenans were added to the experimental samples of brines: kappa carrageenan Bengel 270 and iota-carrageenan MB-150F in an amount of from 0.2 to 1.5% of the brine weight. The control was a basic brine (Table 1).

Table 1. Characteristics of brines with carrageenans

Indicators	Brines								
	Control	Test							
		The dose of carrageenans in brines,%							
		Kappa-carrageenan				Iota-carrageenan			
		0.2	0.5	1.0	1.5	0.2	0.5	1.0	1.5
Density, kg/m^3	1056.0	1056.0	1056.0	1056.0	1057.0	1058.0	1061.0	1064.0	1068.0
pH	6.3	7.2	7.4	7.5	7.7	7.1	7.2	7.5	7.8
Kinematic viscosity, mm^2/sec	1.3892	1.4412	1.5892	1.6082	2.0050	1.8794	3.2564	4.6472	24.0615

RESULTS AND DISCUSSION

At the first stage, the properties of brines were studied. The data given in Table 1 indicate that carrageenans increase density and viscosity of brines, but behave differently. Iota-carrageenan, in contrast to kappa-carrageenan, expands in a cold brine and the brine viscosity increases with increasing its dose from 0.2 to 1.5% by a factor of 1.5–12 as compared to brines containing the same amount of kappa- carrageenan, respectively. Increased viscosity of the brine with iota-carrageenan to a certain extent allows to reduce its losses between injection and massaging. On the other hand, a high viscosity of the brine can lead to clogging of the injector needles.

Kappa-carrageenans expand when heated, providing a high WRC in the finished product. The obtained data show that the dose of carrageenans providing satisfactory parameters for density, viscosity and pH of brines for kappa-carrageenans does not exceed 1%, and iota-carrageenans – 0.5%. In the studied brines, the total content of iota-and kappa-carrageenans was taken in an amount of 1% of the brine weight, with recommended doses of inection into meat products from 0.5 to 2%. Analyzing the experimental data on the kinematic viscosity of brines from the technological point of view, the most acceptable is injection of 0.2% of iota-carrageenan; since the total content of carrageenans is taken in the amount of 1%, the kappa-carrageenan content is 0.8%, thus, the kappa-iota-carrageenan ratio is 4 : 1.

The important structure-forming components used in the technology of production of whole-muscle meat products are protein preparations. Soy and animal proteins are most often used for this purpose.

In connection with the foregoing, soy isolate Supro 595 and animal protein Promiat-90, in concentrations not exceeding the maximum levels of their use in the technology of production of meat products, were injected into brines with carrageenans. The analysis of the data showed that all brines are acceptable in their physicochemical parameters. However, a sample injected with brine, which included a soy isolate, received a relatively low organoleptic evaluation because of the characteristic taste of soy.

Currently, producers of meat products are increasingly using brines with proteins of animal origin, as the demand for products containing soybeans has fallen markedly. On the basis of the physico-chemical indices of the experimental brines and the organoleptic evaluation of the final product, the optimal brine formulation was chosen, including the animal protein and carrageenans (Table 2).

One of the main properties of thickeners of different origin (polysaccharides, proteins) is mutual synergism, when the functional activity of the mixture exceeds the sum of the activities of the components. Against the background of carrageenan, protein preparations significantly reduce product losses during heat treatment, and finished products are less susceptible to the process of syneresis.

At the next stage of the study, the influence of the dose of arabinogalactan on the parameters characterizing the brine quality was studied. Such parameters include kinematic viscosity, density and active acidity of brines. In the experimental brines, AG was added in the amount from 5 to 15% (with increment of 5%). The control was the optimum brine composition shown in Table 2. The experimental data are presented in Table 3.

Table 2. Brine formulations

Ingredients, kg per 100 kg of brine	Control	Optimum brine composition
Table salt	4.00	4.00
Nitrite curing mixture Solino 0.5/0.6	1.50	1.50
Sucrose	1.40	1.40
Phosphate	0.50	0.50
Sodium erythorbate	0.50	0.50
Animal protein	–	0.75
Kappa-carrageenan Bengel 270	–	0.80
Iota-carrageenan MB-150F	–	0.20
Water	92.10	90.35
Total	100.00	100.00

Table 3. Characteristics of multicomponent brines

Indicators	Brines			
	Control	Experimental samples containing arabinogalactan, %		
		5	10	15
Density, kg/m^3	1056.00	1082.00	1094.00	1123.00
Kinematic viscosity, mm^2/s	1.4892	1.9876	2.4932	2.8893
pH	7.04	6.04	5.68	5.28

In the study of brines, it was found that when the amount of injected AG is increased, the density of experimental brines increases insignificantly compared to the control brine. The kinematic viscosity increases with increasing content of AG in the brine, however, is at a level allowing injecting brines by means of stuffing, achieving its rapid distribution in the product.

The active acidity of the brine with increasing the AG injection dose is reduced. This is due to the fact that the active acidity of the pure AG solution is in the range of 4.0 to 4.5. It is known that the area of the most effective action of most of the brine ingredients (pH = 6–7). In this regard, to increase the active acidity of the brine and binding of calcium ions, it was decided to increase the dose of phosphate within the acceptable value to 1.2% [18]. This will increase the moisture-binding ability and softness of meat, stabilize the color, inhibit the oxidation of lipids. These changes in the active acidity of brines with AG at a phosphate content of 1.2% of the brine weight are presented in Table 4.

Table 4 shows that the experiment with 10% arabinogalactan and the phosphate content of 1.2% is the most satisfying to these requirements. Thus, for further study, experimental brine 2 with a 10% AG content was selected.

The compositions of the control and experimental brines are presented in Table 5.

When 40% brine containing 10% AG is added to the unsalted meat, the content of AG in the finished product is about 3 g per 100 g of product, taking into account the loss of loosely bound moisture. Physiologically useful effects were established in humans with consumption of 1.5 to 4.5 grams of AG per day [13]. In accordance with the recommendations of the Expert Committee on Food Additives of the World Health Organization (WHO), a product which contains 3 g of dietary fiber per 100 g is considered a source of dietary fiber.

At the second stage, the relationship between the duration of horse meat massaging in the salting process and the quality indices of the salted semi-finished product was studied.

To study the effect of the composition of a multicomponent brine with 10% AG content and the period of massaging, in the salt semi-finished product, the mass fraction of moisture, the moisture-binding capacity (MBS) and WRC-indicators were measured, which are related to the quality and yield of meat products.

Table 4. Brine active acidity

Samples	Amount of arabinogalactan injected, %	pH of brines with a phosphate content of 1.2%
Control	0	8.28
Experiment	5	7.68
Experiment	10	6.82
Experiment	15	5.94

Table 5. Brine compositions

Ingredients, kg per 100 kg of brine	Brines			
	Control	Experiment brines		
		no. 1	no. 2	no. 3
Table salt	4.00	4.00	4.00	4.00
Nitrite curing mixture Solino 0.5/0.6	1.50	1.50	1.50	1.50
Sugar	1.40	1.40	1.40	1.40
Phosphate	1.20	1.20	1.20	1.20
Sodium erythorbate	0.50	0.50	0.50	0.50
Animal protein Promiat - 90	0.75	0.75	0.75	0.75
Kappa-carrageenan MB-150	–	0.80	0.80	0.80
Iota-carrageenan Bengel 270	–	0.2	0.2	0.2
Arabinogalactan	–	5.00	10.00	15.00
Water	90.65	84.65	79.65	74.65
Total	100.00	100.00	100.00	100.00

The analysis of the obtained data showed that the mass fraction of moisture in the salted semi-finished product increases with the duration of massaging from 2 to 12 hours and 10 hours higher than in the initial measurement by 7–14% both in the control and in the test samples. The results of experimental studies of MBC of a salted semi-finished product are presented in Fig. 2.

The results of experimental studies of the water retention capacity of salted horse meat after heat treatment are shown in Fig. 3.

The data in the figures are presented in relative units, in order to exclude the influence of the raw material properties.

The analysis of the obtained data showed that with increasing duration of massaging MBC and WRC of the control and test samples increase and reach the maximum values during massaging for 10 hours, while the difference between the control and the test samples is 5.8% and 6.3%, respectively. The values of MBC and WRC in the control and test samples correlate in the process of massaging the samples. But in test samples with AG these values are higher in comparison with the control due to the complex carbohydrates contained in arabinogalactan and their branched structure. Reduction of MBC and WRC at a longer massaging can be explained by partial denaturation of proteins.

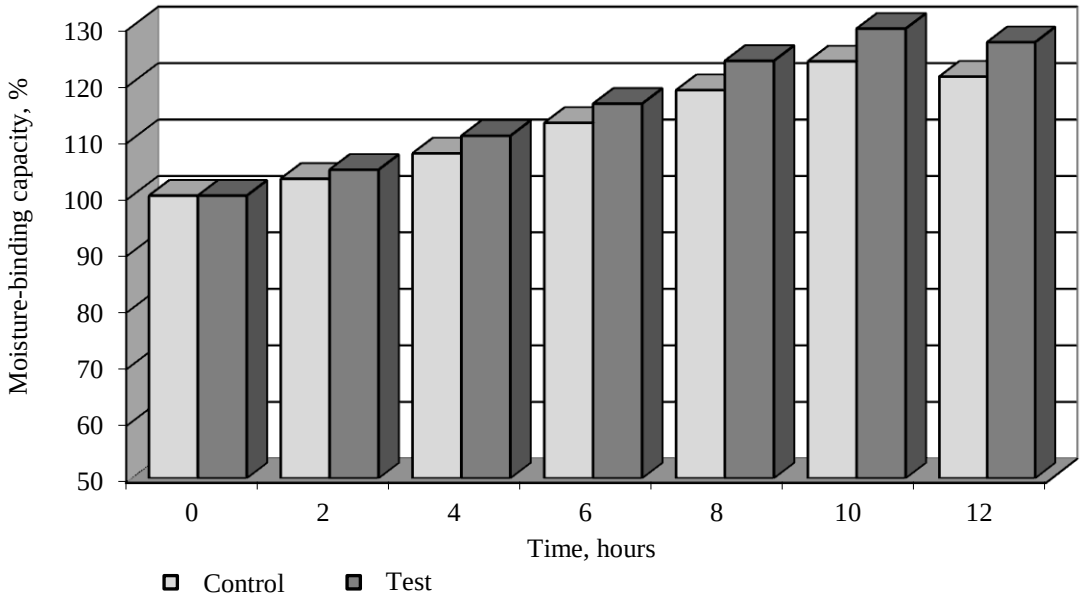


Fig. 2. Dynamics of change in moisture-binding capacity of salted semi-finished product from horse meat.

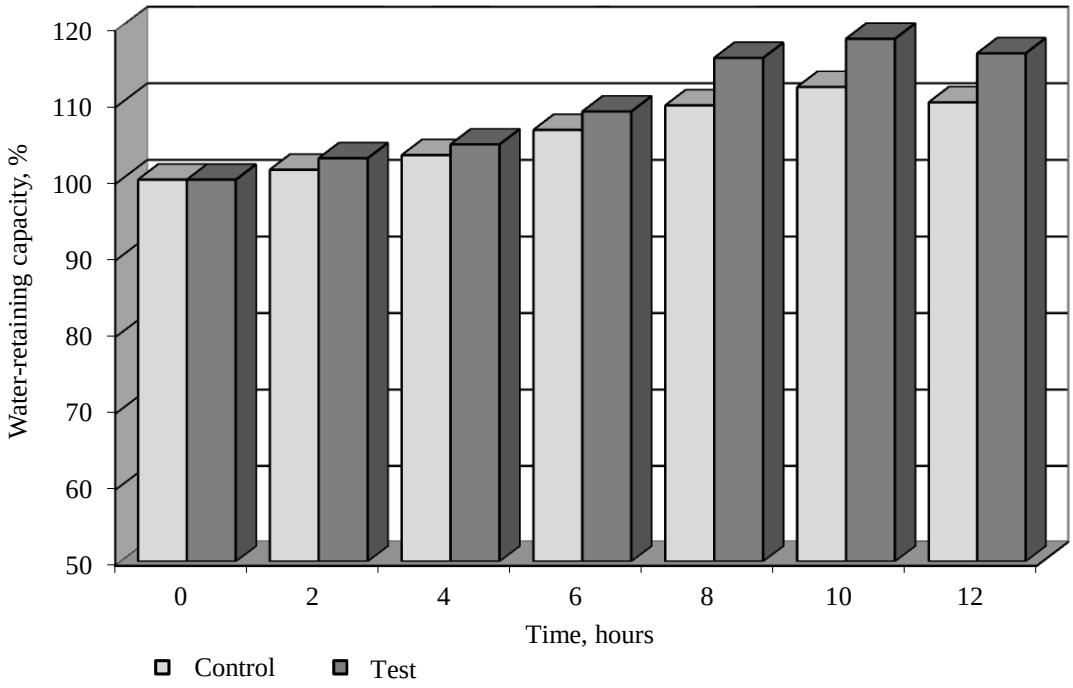


Fig. 3. Dynamics of change in the water-retaining capacity of the finished product.

Based on the FTP of the salted semi-finished product, the duration of mechanical treatment for 10 hours was selected.

The next stage of the study was evaluation of the quality and yield of the finished product. In connection with the task, the quality of the samples was evaluated in accordance with regulatory documents for whole-muscle products. In addition, the FTP and the structural and mechanical properties (SMP) of the control and test samples subjected to massaging for 10 hours were studied (Fig. 4).

An analysis of the results indicates that the best characteristics have the prototype, which has the great plasticity and the less cutting force. The lower the cutting force, the softer the product. The sample has a high WRC and, accordingly, the highest yield after heat treatment – 92%.

The results of study on models allow us to establish the patterns of changes in properties and yield of products when changing recipes, technologies and regimes. The product was boiled in water at a temperature of 80–85°C for 30 minutes and heat treated with steam (steam temperature 100°C) for 45 minutes. The criterion for evaluating the method was the loss during heat treatment. In the course of the conducted studies, it was found out that the losses in cooking with a live steam are lower by 5% than when boiling in water.

The quantitative values of the losses of the finished product during the heat treatment are shown in Table 6.

In the course of the experiment, it was found that after 10 hours of massaging, the losses are reduced in the control sample by 54%, and in the experimental sample by 73%, i.e. the difference between the samples is 19%.

An organoleptic evaluation of the horse meat product with a brine containing 10% AG ("Delicacy horse meat") was carried out on a 9-point scale (Fig. 5).

From the profile record it can be seen that the organoleptic evaluation of the product “Delicacy horse meat” is higher in all indicators, in comparison with the control. Particularly noticeable is the difference in assessment of the consistency, succulency and appearance of the products. In the control sample, the consistency and succulency was evaluated by 6 points, as it was rigid and dry, which correlates with the MBC and the cutting force.

Qualitative parameters of the boiled product “Delicacy horse meat” are presented in Table 7.

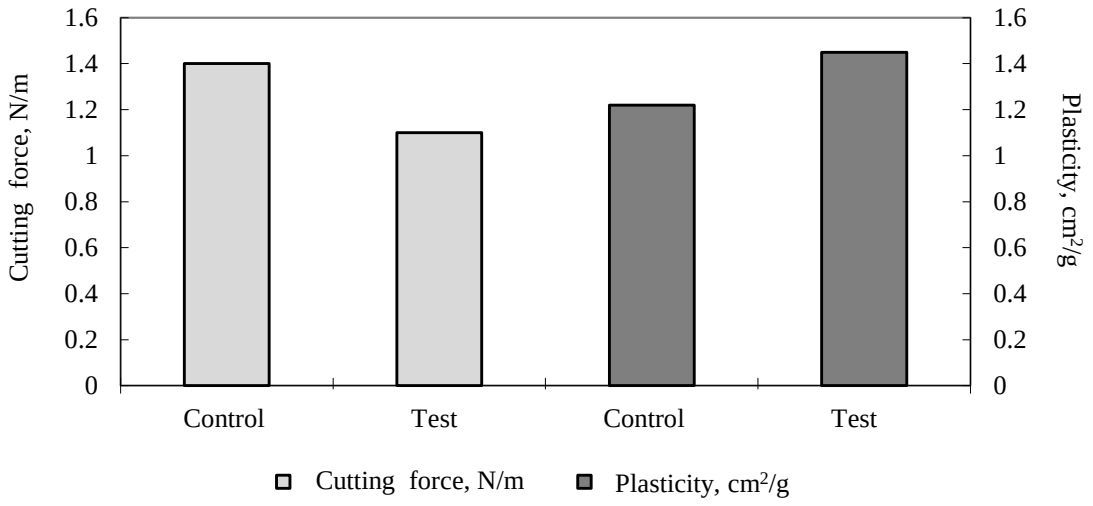


Fig. 4. Structural and mechanical properties of control and test samples.

Table 6. Losses at boiling of salted semi-finished product

Heat treatment losses, %	Duration of massage, hour						
	0	2	4	6	8	10	12
Control	31.9 ± 0.3	23.8 ± 0.6	22.7 ± 0.5	20.1 ± 0.4	17.1 ± 0.7	14.6 ± 0.2	20.3 ± 0.2
Experiment	31.2 ± 0.5	22.8 ± 0.7	18.3 ± 0.5	15.5 ± 0.7	11.2 ± 0.4	8.4 ± 0.4	11.0 ± 0.3

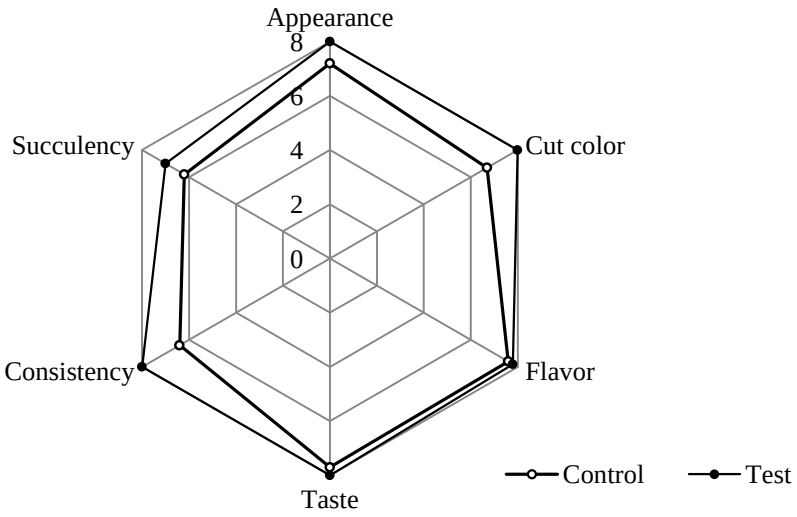


Fig. 5. Profile record of organoleptic indicators of the boiled product “Delicacy horse meat”.

Table 7. Qualitative parameters of the boiled product “Delicacy horse meat”

Indicators	Quality requirements as per GOST 32785-2014. Products of horse meat	Horse meat delicacy
Appearance	The surface is clean, dry with no meat scraps, no fringes, spices and bay leaves	The surface is clean, dry with no meat scraps, no fringes, spices and bay leaves
Shape	Rectangular, oval, cylindrical	Rectangular, oval, cylindrical
Consistence	Elastic	Elastic
Cur color	Uniformly colored muscular tissue from light red to dark red	Uniformly colored muscular tissue from light red to dark red
Taste and flavor	A pleasant taste and flavor	A pleasant taste and flavor
Weight ratio of table salt, %	max. 3.0	2.1 ± 0.2
Weight ratio of sodium nitrite, %	max. 0.005	0.0030 ± 0.0001
Weight ratio of protein, %	min. 14	16.5 ± 0.3
Weight ratio of fat, %	max. 12	4.00 ± 0.06
Weight ratio of total phosphorus in terms of P_2O_5, %	max. 0.8	0.300 ± 0.003
Residual activity of acid phosphatase, %	max. 0.005	0.003
Content of arabinogalactan, g/100 g of product	–	3.0

These parameters indicate the compliance of the boiled product "Delicacy hprse meat" with the requirements of regulatory documents for whole-muscle meat products.

CONCLUSIONS

The use of arabinogalactan in brines provides their density and viscosity; the pH level of such a brine is close to the pH level of the most effective action of the brine ingredients. Massaging the salted semi-finished horse meat is accompanied by an improvement in the functional-technological and structural-mechanical properties of horse meat, which reach their maximum values after 10 hours. The finished experimental product is characterized by better quality and yield (by 6%).

It has been established that the use of arabinogalactan in multicomponent brines for cooked horse meat products allows to improve the taste characteristics of the finished product.

REFERENCES

1. Tuleulov E.T. *Proizvodstvo koniny* [Production of horse-flesh]. Moscow: Agropromizdat Publ., 1986. 281 p.
2. Manyukhin Ya.S., Tchernukha I.M., Kovalyov L.I., et al. The study of horsemeat proteins by use proteomic technologies. *Vse o myase* [All about meat], 2014, no. 3, pp. 20–25. (In Russian).
3. Bouwman F.G., van Ginneken M.M., van der Kolk J.H., et al. Novel markers for tying-up in horses by proteomics analysis of equine muscle biopsies. *Comparative Biochemistry and Physiology - Part D: Genomics and Proteomics*, 2010 Jun, vol. 5, no. 2, pp. 178–183. DOI: 10.1016/j.cbd.2010.03.009.
4. Lorenzo J.M., Sarriés M.V., Tateo A., et al. Carcass characteristics, meat quality and nutritional value of horsemeat: a review. *Meat Science*, 2014, vol. 96, no. 4. pp. 1478–1488. DOI: 10.1016/j.meatsci.2013.12.006.
5. Bazhenova B.A., Badmaeva T.M., and Madagaev F.A. Uluchshenie struktury konskogo myasa [Improving the structure of horse meat]. *Sibirskiy vestnik sel'skokhozyaystvennoy nauki* [Siberian Bulletin of Agricultural Science], 2010, no. 4, pp. 98–102.
6. Kolesnikova I.S., Bazhenova B.A., Badmaeva T.M., Danilov M.B. The influence of multicomponent extruded brine on the quality of boiled-smoked horse meat product. *Vse o myase* [All about meat], 2014, no. 6, pp. 40–43. (In Russian).
7. Gombozhapova N.I., Bryanskaya I.V., and Leskova S. Yu. Brines on the basis of whey for horsemeat products manufacturing. *Myasnaya industriya* [Meat Industry], 2015, no. 6, pp. 18–20. (In Russian).
8. Medvedeva E.N., Neverova N.A., Fedorova T.E., et al. Structural transformations of siberian larch arabinogalactan at mechanochemical treatment and biological properties of products. *Khimija rastitel'nogo syr'ja* [Chemistry of plant raw material], 2009, no. 3, pp. 49–56. (In Russian).
9. Zarubaev V.V., Ostroumova L.A., Medvedeva E.N., et al. Antiviral preparations based on larch wood biologically active substances. *Byulleten' Vostochno-Sibirskogo nauchnogo tsentra Sibirskogo otdeleniya Rossiyskoy akademii meditsinskikh nauk* [Bulletin of the East Siberian Scientific Center SBRAMS], 2010, no. 1, pp. 76–80. (In Russian).
10. Babkin V.A., Malkov Yu.A., Medvedeva E.N., et al. Technology of Obtaining Biologically Active Forage Additives from the Wastes of Larch Biomass Processing. *Khimiya v interesakh ustoychivogo razvitiya* [Chemistry for Sustainable Development], 2015, no. 1, pp. 19–24. (In Russian).
11. Medvedeva E.N., Babkin V.A., and Ostroukhova L.A. Arabinogalaktan listvennitsy – svoystva i perspektivy ispol'zovaniya (obzor) [Larch arabinogalactan - properties and prospects of use (overview)]. *Khimija rastitel'nogo syr'ja* [Chemistry of plant raw material], 2003, no. 1, pp. 27–37. (In Russian).
12. Dubrovina V.I., Medvedeva S.A., Aleksandrova G.P., et al. Immunomoduliruyushchie svoystva arabinogalaktan listvennitsy Sibirskoy [Immunomodulating properties of arabinogalactan of Siberian larch]. *Farmatsiya* [Pharmacy]. 2001, no. 5, pp. 26–27. (In Russian).
13. Milo Ohr L. Dobavki arabinogalaktana ochen' polezny dlya zdorov'ya [Arabinogalactan adds more than health benefits]. *Prepared Foods*, 2001, vol. 170, no. 1, pp. 55.
14. Malkov Yu.A., Medvedeva E.N., and Babkin V.A. *Sposob polucheniya arabinogalaktana* [Method for the preparation of arabinogalactan]. Patent RF, no. 2454429, 2010.
15. Babkin V.A., Nefedova N.A., Medvedeva E.N., et al. Study of physicochemical properties of arabinogalactan of different larch species. *Khimija rastitel'nogo syr'ja* [Chemistry of plant raw material], 2015, no. 2, pp. 29–35. DOI: http://dx.doi.org/10.14258/jcprm.201502557. (In Russian).
16. Gombozhapova N.I., Bryanskaya I.V., Danilov M.B., and Medvedeva E.N. Vliyanie arabinogalaktana na svoystva rassolov dlya delikatesnykh myasoproduktov [Effect of arabinogalactan on the properties of brines for delicacy meat products]. *Izvestia vuzov. Pishevaya tekhnologia* [News institutes of higher Education. Food technology], 2011, vol. 1, no. 1, pp. 152–154. (In Russian).
17. Zharinov A.I., Kuznetsova O.V., and Cherkashina N.A. *Tsel'nomyshechnye i restrukturirovannye myasoprodukty* [Whole muscle and restructured meat products]. Moscow: ITAR-TASS Publ., 1994. 179 p.
18. Efremova A.S. and Zabashta A.G. Osobennosti sostavleniya i ispol'zovaniya rassolov [Features of the preparation and use of brines]. *Myasnye tekhnologii* [Meat technologies], 2009, no. 10, pp. 52–57. (In Russian).

Please cite this article in press as: Gombozhapova N.I., Bazhenova B.A., Leskova S.Yu., Badmaeva T.M., and Danilov A.M. Influence of the new multicomponent brine on the quality characteristics of the boiled horse meat product. *Foods and Raw Materials*, 2017, vol. 5, no. 1, pp. 11–19. DOI: 10.21179/2308-4057-2017-1-11-19.

EFFECTS OF PROPIONIC-ACID BACTERIA AND BIFIDOBACTERIA ON THE QUALITY OF RAW SMOKED SAUSAGES

I. A. Khankhalaeva, I. S. Khamagaeva, and A. P. Nikiforova*

East Siberia State University of Technology and Management,
Klyuchevskaya Str. 40v, Ulan-Ude, 670013, Russian Federation

* e-mail: anna.p.nikiforova@gmail.com

Received July 02, 2016; Accepted in revised form February 06, 2017; Published June 29, 2017

Abstract: Propionic-acid bacteria and bifidobacteria are widely used in food industry. Therefore, it is important to determine their biochemical activity and their aroma producing potential. In this study, the effect of the use of propionibacteria and bifidobacteria as starter cultures on the sensory characteristics of raw smoked sausages has been studied. The sausages were prepared with starter culture consisted of *Propionibacterium shermanii KM-186* and *Bifidobacterium longum B379M* and compared with the sausages with a commercial starter culture Bitec LS-25. The results have shown, that the sausages containing starter culture of propionic-acid and bifidobacteria, obtained better sensory scores, better quality characteristics compared to the sausages made with commercial starter culture. The analysis of volatile compounds has shown, that the addition of starter culture, containing propionic-acid bacteria and bifidobacteria leads to formation of additional compounds, including lactones, phenols, and terpenes. During sensory evaluation, experts noticed the presence of mild creamy note in experimental sample. It can be the result of lactones formation by propionic-acid bacteria and bifidobacteria. In addition, it was shown that the addition of propionic-acid bacteria and bifidobacteria reduces nitrite amount in sausages in several times (11 times approximately compared to commercial starter culture) due to nitroreductase activity of these bacterial strains.

Keywords: Raw smoked sausages, propionic-acid bacteria, bifidobacteria, starter cultures, volatile compounds, flavor, sausages

DOI 10.21179/2308-4057-2017-1-20-29 *Foods and Raw Materials*, 2017, vol. 5, no. 1, pp. 20–29.

INTRODUCTION

The characteristic taste and aroma of fermented sausages originates from the breakdown of carbohydrates, lipids, and proteins through the action of microbial and endogenous meat enzymes [1]. The aroma is a combination of many different non-volatile and volatile compounds. Some originate from added spices, others are metabolic or chemical products derived from carbohydrates, lipids and proteins during the fermentation and drying periods. Microbial growth in the sausage mince, together with the activity of enzymes from the meat and fat, are undoubtedly responsible for many of those components. However, autoxidative reactions initiated by metallo-compounds or other factors may be of great importance as well [2, 3].

Many volatile compounds have been identified in fermented products [4]. The volatile compounds produced during maturation of dry meat products may be of non-enzymatic origin, as during self-oxidation of lipids, or may result from a catalysis. This catalysis is due to endogenous enzymes in the case of non-inoculated products such as dry-cured ham, but depends also on exogenous enzymes in the case of fermented meat products [2].

It is unknown, which processes play the major role in the desirable aroma development of fermented sausages. One of the most studied of processes is the breakdown of triglycerides into free fatty acids, di- and monoglycerides during ripening and the increase of different carbonyl oxidation products like aldehydes and ketones [1].

Lipid oxidation is a reason of formation of the generation of nonbranched aliphatic compounds such as alkanes, alkenes, methyl ketones, aldehydes, alcohols and several furanic cycles. Compounds of low molecular weight form during the fermentation, for example, diacetyl, acetoin, butanediol, acetaldehyde, ethanol, acetic acid etc. [1].

Carbonyl compounds probably have an impact on flavor as they generally have very low sensory threshold values in the ppm to ppb range. Since fatty acids are precursors of carbonyls, lipolytic activity of the microorganisms present in the mince is believed to be of great importance and has been much investigated. However, it is doubtful whether large amounts of free fatty acids are necessary in obtaining the amount of oxidation products demanded for the characteristic sausage flavor, especially when carbonyls may arise from the intact triglycerides as well as from the free fatty acids.

Starter cultures are used in the meat industry to start and propagate the fermentation process, extend the shelf life of the product, improve its hygienic quality

and increase the acceptability of the final product [5]. There are many technologies of meat products, made with the use of starter cultures [6, 7, 8, 9].

Propionic-acid bacteria (PAB), the most abundant flora during ripening of Swiss-type cheeses, are directly involved in the characteristic eye formation and in the production of propionic and acetic acids. Also they play a key role in the formation of cheese flavor [10, 11, 12]. However, they are not widely used in meat industry.

Propionic-acid bacteria grow at low oxygen concentrations (anaerobic to aerotolerant) [13] and their growth is inhibited by high salt-in-moisture (S/M) levels, to an extent dependant on strain type [14, 15, 16]. PAB grow optimally between pH 6 and 7 with a pH maximum for growth at 8.5 and minimum at 4.6 [15, 17]. Cheese pH controls the rate of growth and metabolism of PAB [18] and a higher inocula is required for cheeses with a lower cheese pH [13]. The optimal growth temperature for PAB is 30°C, but growth also occurs between 7 and 45°C as reviewed by Langsrud et al. [15]. Park et al. [7] reported that 16 out of 33 strains of PAB tested grew at 7.2°C and 31 out of 33 grew at 12.8°C. No growth of P. freudenreichii was reported at 2.8°C.

Also dairy PAB have only a few nutritional requirements. Many PAB strains grow in the absence of organic nitrogen sources, in a basal medium containing a carbon and energy source, ammonium, minerals, and 2–4 vitamins (at least pantothenate and biotin are required) [11, 19, 20].

One of the important properties of PAB for use in meat industry is their proteolytic activity. A proteolytic system was found in all the species of dairy Propionibacterium [21]. Searles et al. [22] reported that propionic-acid bacteria, in a medium with acid casein, were able to increase the trichloroacetic-acid (TCA)-soluble nitrogen. Later, El Soda et al. [23] found a "general caseinolytic activity" in three strains of *Propionibacterium freudenreichii* and in one strain of *P. acidipropionici*. Intracellular peptidases have been studied in more details [15, 24, 25] found peptidases able to release proline into the medium. Perez Chaia et al. [26] showed that leucine aminopeptidase and proline iminopeptidase have the good activities in *P. freudenreichii.* This proline iminopeptidase was purified and characterized [27]. El Soda et al. [23] also found prolyl dipeptidyl aminopeptidase activity [21].

Propionic-acid bacteria produce some volatile compounds, which are important for cheese flavor. Thierry et al. [19, 20, 28, 29] studied the formation of these compounds by PAB in cheese. Compounds produced by PAB, which are responsible for flavor of cheese, are acetic, propionic and butanoic acids and 2-methyl and 3-methylbutanal. *P. freudenreichii* for example, produces flavor compounds of varied origins (fermentation, lipolysis, amino acid catabolism). The work of Thierry et al. [28] showed, that various biochemical changes were observed in Raclette cheeses with the addition of *Propionibacterium freudenreichii* compared to the control cheese: the fermentation of lactate to propionate and acetate, a marked enhancement of lipolysis, some modifications of the amino acid profile, the conversion of branched chain amino acid to a variety of aroma compounds, and the increase in other volatile compounds such as esters and ketones.

Bifidobacteria are mainly added to food products, because of their probiotic properties [30, 31, 32, 33]. Bifidobacteria, naturally present in the dominant colonic microbiota, represent up to 25% of the cultivable faecal bacteria in adults and 80% in infants. As probiotic agents, bifidobacteria have been studied for their efficacy in the prevention and treatment of a broad spectrum of animal and/or human gastrointestinal disorders, such as colonic transit disorders, intestinal infections, and colonic adenomas and cancer [32]. Mainly bifidobacteria are used in dairy industry as a component of fermented drinks, but also they are used as a starter culture (in combination with other bacteria) during the production of fermented sausages [31].

According to [34] the use of combined concentrate of propionic-acid bacteria and bifidobacteria has positive effect on sensory profile of dry smoked sausages. New compounds are formed as a result of bacterial action. The content of free fatty acids in the sample with these bacteria is by 20–30% higher than in traditionally produces sausages. It can be result of higher lipase activity of propionic acid bacteria and bifidobacteria. The main difference between the samples was in high amount of lactones in the experimental sample. A weak pleasant creamy tone in the aroma and flavor of the experimental sausage, obtained using propionic acid bacteria and bifidobacteria, probably, the result of presence of lactones in experimental sample.

Considering the above, the effect of propionic-acid bacteria on flavor development of fermented sausages is interesting issue to study. Thus, this work was conducted to investigate the potential benefit from the use of Propionibacteria and Bifidobacteria as starter cultures during the production of raw smoked sausages and their influence on the quality characteristics and chemical composition of sausages. The investigation of the influence of starter culture addition and flavor compounds as well as sensory evaluation, are very interesting objects to study. To determine this effect, sausages with starter culture of propionic-acid and bifidobacteria were compared with sausages with commercial starter culture.

OBJECTS AND METHODS OF STUDY

Manufacture and sampling. The sausages, used in this study, have been produced at the local factory (Republic of Buryatia, Russia). Ingredients of sausages are listed in Table 1. Mean values of results of three experiments were taken.

Raw smoked sausages were produced by using beef, lean pork, pork fat, NaCl, $NaNO_2$, sugar, brandy and spices. On the first step meat was minced, mixed with salt, spices and brandy. On the second step the 5 %-solution of sodium nitrite, brandy, lean pork, pork fat and spices were added. After mincing of meat and mixing, the mixture was divided into two batches: batch A was inoculated with $1cm^3$ of starter culture

containing propionic-acid bacteria and bifidobacteria (LLC Small Commercial Enterprise "Bifivit", Ulan-Ude, Russia) per 100 kg of raw meat, while the commercial starter culture Bitec LS-25 (Frutarom, Germany) was added to batch B was added with a concentration of 0.025%.

Table 1. Composition of raw smoked sausages with starter culture

Materials and ingredients	Percentage share
Basic ingredients	
Beef	35%
Lean pork	35%
Pork fat	30%
Additional ingredients and spices (in kg to 100 kg of basic ingredients)	
NaCl	3.5 kg
$NaNO_2$	0.01 kg (in 5%-solution)
Sugar	0.2 kg
Brandy	0.25 kg
Starter culture	1 cm^3
Black pepper	0.15 kg
Allspice	0.05 kg
Cardamom or Nutmeg	0.05 kg

Experimental starter culture contained strains *Propionibacterium shermanii KM-186* and *Bifidobacterium longum B379M*. Cell counts of each strain were 10 log CFU/cm^3. The starter culture was in the liquid form.

Commercial starter culture Bitec LS-25 contains strains *Staphylococcus carnosus* and *Lactobacillus sakei*. Total cell counts is 1.5 * 10 log CFU/g. The consistency of the starter culture was fine-grained, freeze-dried powder. The producer claims, that the starter culture creates a rapid acidification process and a typical fermentation aroma, accelerates color formation, improves color stability, fat stability and consistency. The strain of lactobacillus contained is highly suited to compete with the spontaneous flora.

The meat mixture was immediately stuffed in natural casings to obtain sausages with an initial weight of approx. 1400-1500 g, a length of approx. 60 cm.

The process of thermal treatment was carried out in termoagregate with automatic control for (3–4) days. On the first day sausages were kept at temperature 24°C, relative humidity 92.3% and air velocity (0.2–0.5) m/s. The temperature was then lowered to (22–20)°C and kept for one day. On the third day sausages were smoked for 4-6 hours, the relative humidity was reduced to 88.3%. Then, on the fourth day smoke intensity was increased, and process was carried out at (20 ± 2)°C, relative humidity (83.3%) and air velocity (0.05–0.1) m/s. The total duration of treatment with smoke was (8–12) hours.

The process of drying was carried out in the same termoagregate at (18 ± 2)°C and relative humidity 82.3% for 1 day. Further drying was carried out at temperature (13 ± 1)°C, relative humidity (77.3%) and air velocity (0.05–0.10) m/s for (17–20) days.

Microbiological analysis. Sausage samples (10 g) were homogenized with 90 ml distilled water. Decimal dilutions were prepared. Microbiological analyses were performed every day during 10 days of ripening.

The numbers of propionic acid bacteria were determined on GMK-1 medium (Biocompas-S, Russia), consisting of corn-milk mixture (30 g), peptone (30 g), lactose (18 g), ascorbic acid (1 g), sodium citrate (12 g), magnesium sulphate (0.24 g), potassium phosphate (monobasic) (4 g), sodium phosphate (dibasic) (2 g), agar (6 g), distilled water (2000 ml). Incubation was performed at 30°C for 5 days.

Bifidobacteria counts were determined using Blaurock medium (Blaurock, 1937) with neomycin (0.2 ml of solution of neomycin was added to 20 ml of medium). For getting of neomycin solution one bottle of neomycin (500000 ME) was dissolved in 50 ml of distilled water. Colonies were counted after incubation at 37°C after 3 days.

Chemical analysis. Analyses of the moisture content, pH, and $NaNO_2$ contents were performed in triplicate. The moisture content of the dry-fermented sausages was determined by dehydration at 103°C to constant weight by the ISO recommended methods (ISO, 1997). The pH was measured using a pH-150M pH meter (Gomel plant of measuring devices, Belarus).

Nitrite amounts were analyzed using spectrophotometric method on KFK-3 (Zagorsk optical and mechanical plant, Russia).

Sensory evaluation. The sensory evaluation was performed by nine trained experts. The experts were asked to evaluate sensory characteristics of the sausages. The sausage samples were sliced (the thickness was approximately 2 mm). Control and experimental batches were numbered and provided to each expert with degustation card. The sensory evaluation was conducted in individual rooms. Six sensory characteristics were evaluated by judges. General appearance, color, aroma, texture, taste, and juiciness were the attributes, evaluated during sensory analysis. The hedonic scale from 1 (extremely poor/ unacceptable) to 9 (extremely acceptable) was used in the study. The mean values of all experts' marks for each characteristic were calculated.

Gas chromatography. To extract volatile substances sausage samples (100 g) were minced, placed into 2-l flask. Content of volatile compounds was determined by gas chromatography (GC) using gas chromatograph Hewlett-Packard 5730 (Hewlett-Packard, USA) equipped with a flame ionization detector and capillary column SPB-1 (50 m * 0.32 mm, 0.25 μm) (Supelco, USA). Chromatographic conditions were as follows: isotherm at 60°C for 5 minutes, then the temperature programming to 250°C. Helium gas velocity through the column was 1.5 ml/ min. The identification of peaks in the sample chromatograms was performed using a system for the processing of chromatographic data Ecokhrom (Russia). The concentration of individual components expressed as μg/ 100 g of product.

Statistical analysis. The data obtained for pH, moisture content, nitrite amounts, volatile compounds,

sensory characteristics was assessed statistically to determine significant differences between products for these parameters. Analyses of each parameter were carried out in triplicate at various sampling times. Mean, standard deviation and standard error were calculated for all quantified variables. An analysis of variance (ANOVA) was carried out. Significance level $P < 0.05$ was used for all data. All the statistical analyses were performed using programs Statistica 6.0 and Microsoft Excel 2010.

RESULTS AND DISCUSSION

Microbiological analysis

The results for analysis of counts of propionic-acid bacteria and bifidobacteria are shown in Fig. 1. In both samples, we can see increasing amount of bacteria during the production process.

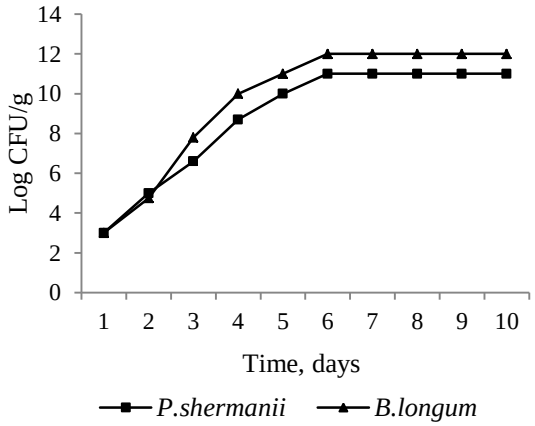


Fig. 1. Changes in growth of propionic-acid and bifidobacteria in raw-smoked sausages.

The initial quantity of probiotic microorganisms was approximately 5 log CFU/g. The quantity of viable cells of bifidobacteria and propionic-acid bacteria has gradually increased starting from second day of manufacturing. After 3 and 4 days the quantities of bifidobacteria were 9 log CFU/g and 10 log CFU/g, the quantities of propionic-acid bacteria were 10–11 log CFU/g. Sausages contained approximately 11–12 log CFU/g bifidobacteria and the same amount propionic-acid after 5 days of manufacturing. This amount of bacteria was stable during the smoking and drying.

The results of research have shown that PAB are resistant to high concentrations of NaCl and low temperatures during salting. The results of the study have shown that propionic acid bacteria and bifidobacteria can survive and grow in meat due to low nutrition requirements of bacteria and their ability to survive at low positive temperatures. This fact makes possible to use these bacteria for production of fermented sausages.

Results of chemical analysis

Results for analysis of pH are shown in Fig. 2. The initial pH of control sample was 6, the pH of sample with starter culture was 5.95, pH values of both samples drastically decreased after 5 days of fermentation. The decrease in sample with experimental starter culture was bigger, than in control sample. The pH values in both samples have slowly increased after (had increased) 10 days of fermentation due to proteolysis of proteins and formation of products of their decomposition. The pH value is close to isoelectric point after 20 days of fermentation.

The moisture content is one of the main characteristics of meat. For raw sausages it is very important. The development of structure of product and overall microflora also depend on the moisture content. In further studies the impact of combined concentrates to moisture content changes in the raw sausage during its production was studied.

The Fig. 3 shows, that water content after 5–10 days in experimental sample is lower, than in control sample. It is related to intensive decreasing of pH value during this period. The loss of water in experimental sample in 15–20 days of manufacture was 24–34%, on the other hand, the loss in control sample 20–30%. The difference in water loss was approximately 4%. After 20 days of manufacture the moisture content in control samples was 27.3%, the same value in control samples was just after 25 days of manufacture.

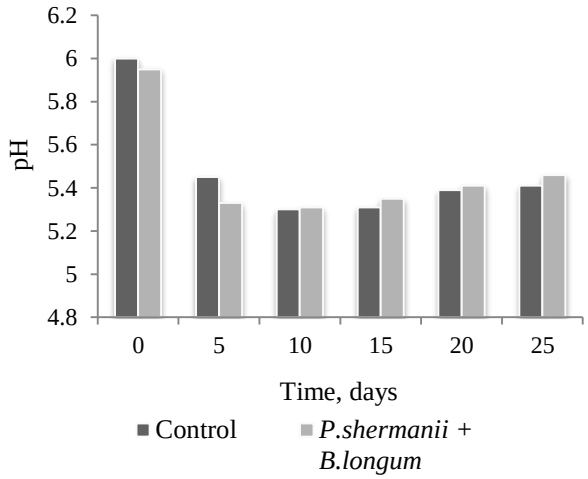


Fig. 2. The changes in pH of raw-smoked sausages added with propionic-acid bacteria and bifidobacteria.

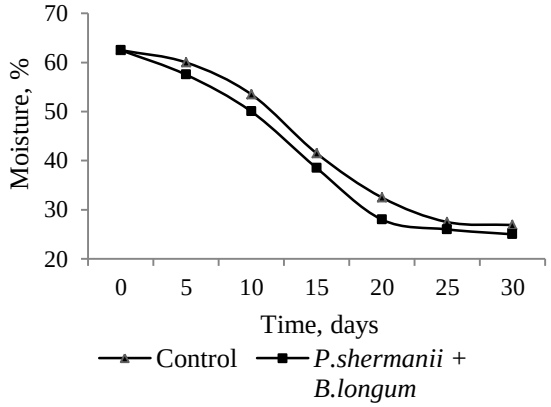


Fig. 3. Effect of the addition of starter cultures of propionic acid bacteria and bifidobacteria on the changes in moisture content.

The main chemical characteristics of control and experimental samples are shown in Table 2. The results show that moisture, protein and ash content were approximately the same in both samples. The difference in $NaNO_2$ content was found between samples. $NaNO_2$ content in experimental sample was 0.00036, and in control sample was 0.0040.

One of the main factors, which form quality of raw-smoked sausages, is pH. When pH values are close to 5.2–5.3, there is swelling of collagen hydrolysis-linking and activation of cellular enzymes, especially cathepsins. At the same value the development of pathogenic and toxicogenic bacteria suppresses. In this regard, the pH value was the main criterion for establishing the dose contributed bacterial concentrates in sausages. Therefore, the different amounts of bacterial concentrate were inoculated in the model samples of minced raw sausages.

It is well known that meat with pH value, which is close to isoelectric point, has the lowest water holding capacity. The lower water holding capacity can accelerate the drying process. In experimental sample pH values were closer to the isoelectric point than in control sample, probably, it is the reason of lower moisture content in this sausage. pH values close to isoelectric point can be a reason of better consistency of the product. The results of the study have shown that the bacterial concentrate of propionic-acid and bifidobacteria can reduce the time of manufacturing process that can have good practical application.

Nitrite has a number of functions in the curing of meat: it is involved in the development of color and odor; it has a preserving and antioxidant effect. Nitrite added in the formulation is reduced to nitric oxide, which interacts with meat pigments (myoglobin) to form nitrosomyoglobin and gives the characteristic cured red meat color. Some authors reported that addition of some propionic-acid bacteria strains can reduce nitrite content in products. According to [35] propionic-acid bacteria have different probiotic properties including reducing nitrates and nitrites with formation of nitrogen monoxide. Nitrate reduction is currently considered to be a key characteristic for the determinative grouping of strains of the Propionibacterium. In work [36] it was proven that strains of *P. acidipropionici*, *P. acnes* and *P. freudenreichii subsp. freudenreichii* are able to reduce nitrate on the yeast extract lactate and yeast extract media. It was found that nitrate reduction was strongly influenced by environmental factors such as oxygen, nitrate concentration, pH, media composition, incubation period and the presence of glucose [36]. As it was reported some strains of genes Propionibacterium can reduce nitrate to nitrite and further to nitrous oxide (N_2O) due to action of enzymes such as nitrate reductase.

Bifidobacteria can also eliminate nitrite by non-enzymic mechanism with generation of nitric oxide [37, 38].

The results of the present research correspond to results of previous research works. The content of $NaNO_2$ in experimental sample (0.00036%) was lower than in control sample (0.0040%) in several times (11 times approximately). It means more complete breakdown of $NaNO_2$ and its transformation to nitrosopigments by bacteria included in starter culture.

We can conclude that the use of combined bacterial concentrate of propionic-acid and bifidobacteria as a starter culture reduces nitrite content and processing time of meat products.

Sensory evaluation

Sensory analysis is one of the most valuable factors in quality evaluation and assessment. It is especially important for evaluation of new products. The sensory profiles of raw smoked sausages are shown in Fig. 4.

Table 2. Characteristics of raw smokes sausages

Sample	Content, %			
	Water	$NaNO_2$	Proteins	Fats
Control	27.0 ± 1.2	0.0040 ± 0.0001	23.3 ± 0.6	43.4 ± 1.4
P.shermanii + B.longum	26.5 ± 1.3	0.00036 ± 0.0001	24.2 ± 0.4	43.9 ± 1.2

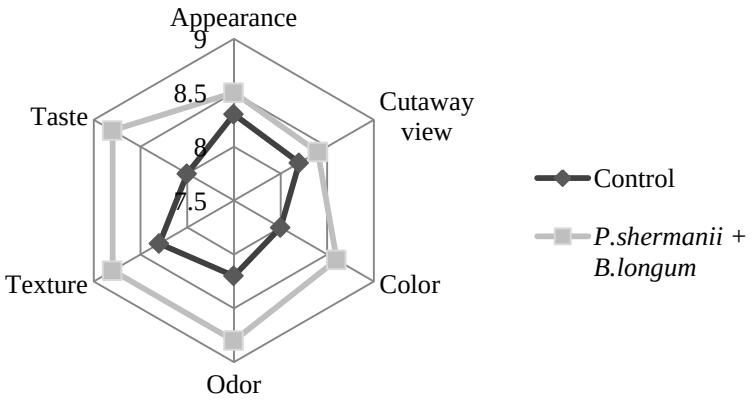


Fig. 4. Sensory profile of raw-smoked sausages.

There were better scores in experimental sample compared to control. Experimental samples had more intensive and pleasant aroma, and mild flavor with a sour milk tone. Consistency of experimental samples was more homogeneous compared to the control. The color characteristics were also different. Sample with propionic-acid and bifidobacteria was dark-red, and it had more uniform color.

The results of sensory analysis have shown that the sample with propionic- acid and bifidobacteria got higher scores in all sensory characteristics. It can be a result of action of starter culture on texture and flavor of products. Thus, the results show positive impact of combined concentrates to organoleptic properties of raw sausages.

Identification of volatile compounds

In the study approximately 140 substances were detected using gas chromatography (GC) and 85 of them were identified. The results from the GC analysis are shown in Table 3. It was found that the main volatile compounds of the sausages are saturated and unsaturated aliphatic aldehydes, alcohols, ketones, lactones, and fatty acids.

All identified compounds were grouped in nine classes including aldehydes, ketones, phenols, esters, terpenes, carbohydrates, alcohols, carboxylic acids, lactones. The content of volatile compounds in raw-cured sausages in percent is shown in Table 4. The most dominant classes of volatiles were Carboxylic acids, Phenols and Aldehydes.

Table 3. *Beginning*. Volatile compounds in fermented sausages

№ of peak	Retention Index	Component name	Concentration, mg/kg	
			Control	*P.shermanii* + *B.longum*
1	545	2-Methylpropanal	0.91	1.29
2	561	2-Methylpropanol	0.68	0.73
3	570	2-Butanone	0.71	0.91
4	579	Diacetyl	0.20	0.20
5	588	2-Butanol	0.43	0.52
6	597	Butanal	0.23	0.23
7	603	Ethyl acetate	0.53	0.57
8	607	2-Methylfuran	0.2	0.05
9	615	2-Butenal	0.21	0.23
10	628	3-Methylbutanal	0.09	0.15
11	639	2-Methylbutanal	1.23	1.47
12	687	Pentanal	0.24	0.27
13	718	2-Pentenal	0.68	0.76
14	760	2-Methylpentanal	0.07	0.12
15	765	Butyric acid	0.12	0.19
16	775	Hexanal	0.11	0.21
17	811	5-Methyl-2-hexanone	0.12	0.12
18	831	Trans-2-hexenal	0.20	0.36
19	866	2-11 anone	0.15	0.17
20	878	Heptanal	0.07	0.08
21	913	5-Methyl-2-heptanone	0.11	0.11
22	926	α -Thujene	–	0.09
23	932	α -Pinene	0.17	0.2
24	933	2-Heptenal	0.15	1.43
25	961	1-Octen-3-ol	1.02	0.71
26	968	Sabinene	0.15	0.60
27	974	β -Pinene	0.08	1.78
28	983	β -Myrcene	0.10	0.66

Table 3. *Continued.* Volatile compounds in fermented sausages

№ of peak	Retention Index	Component name	Concentration, mg/kg	
			Control	*P.shermanii* + *B.longum*
29	999	α -Phellandrene	0.04	0.65
30	1008	3-Carene	0.12	4.69
31	1011	α -Terpinene	0.29	0.58
32	1014	p-Cymene	–	0.70
33	1025	Limonene	0.25	5.81
34	1034	Ocimene	0.55	0.63
35	1052	γ -Terpinene	-	0.92
36	1054	m-Cresol	0.82	0.60
37	1064	Guaiacol	2.4	2.99
38	1084	Nonanal	0.11	0.22
39	1087	Linalool	0.16	0.40
40	1091	Phenylethyl alcohol	–	12.37
41	1127	1,3-Dimethoxybenzene	0.23	1.07
42	1128	2,6-Nonadienal	0.19	–
43	1145	2-Nonenal	0.18	0.15
44	1148	6-Nonenol	0.09	0.13
45	1157	Terpinen-4-ol	0.42	0.31
46	1161	Octanoic acid	0.97	1.19
47	1171	Methylguaiacol	3.07	4.09
48	1178	2,4-Nonadienal	0.14	–
49	1180	Methylchavicol	0.09	0.42
50	1184	Decanal	0.13	0.05
51	1200	Dodecane (internal standard)	5.00	5.00
52	1222	γ -Octalactone	0.26	2.64
53	1257	4-Ethylguaiacol	0.92	0.92
54	1289	Undecanal	0.33	0.56
55	1293	2,4-Decadienal	0.05	0.25
56	1334	Eugenol	0.35	0.52
57	1341	Neryl acetate	0.12	0.50
58	1355	Decanoic acid	4.28	5.05
59	1378	Dodecanal	0.25	0.26
60	1387	β -Elemene	0.04	0.48
61	1400	Tetradecane	0.02	0.15
62	1426	Caryophyllene	0.38	0.79
63	1432	γ -Decalactone	–	7.77
64	1465	δ -Decalactone	0.05	0.46
65	1500	Pentadecane	0.10	0.19
66	1505	β -Selinene	–	0.26
67	1545	Dodecanoic acid	1.24	1.59
68	1559	Germacren D	0.18	0.25

Table 3. *Ending.* Volatile compounds in fermented sausages

№ of peak	Retention Index	Component name	Concentration, mg/kg	
			Control	*P.shermanii* + *B.longum*
69	1588	Tetradecanal	–	0.22
70	1600	Hexadecane	0.12	0.16
71	1661	Bisabolol	0.11	0.14
72	1669	Farnesol	0.15	0.2
73	1682	Pentadecanal	0.46	0.47
74	1700	Heptadecane	0.30	0.42
75	1746	Tetradecanoic acid	4.79	6.05
76	1764	Phthalate	0.16	0.23
77	1777	Hexadecanal	0.09	0.12
78	1800	Octadecane	1.06	6.87
79	1900	Nonadecane	0.16	0.27
80	1924	Hexadecenoic acid	2.06	2.58
81	1948	Hexadecanoic acid	9.03	14.05
82	2000	Eicosane (Hydrocarbon - C20)	1.14	1.62
83	2118	Octadecenoic acid	3.64	2.44
84	2146	Octadecanoic acid	6.79	3.98
85	2175	Octadecadienoic acid	0.50	0.60

Table 4. Percentage of volatile compounds in raw-cured sausages

Samples	Class of compounds, mg/kg								
	Aldehyds	Ketons	Phenols	Esters	Terpenes	Carbohydrates	Alcohols	Carboxylic acids	Lactones
Control	6.06	1.18	6.66	0.53	2.05	5.91	1.49	21.83	0.37
P.shermanii + *B.longum*	9.06	1.40	13.45	0.57	7.25	9.68	14.14	20.43	10.87

Volatile compounds can be separated according to their possible origin. Spices could be responsible for the generation of terpenes and hydrocarbons. Phenols could be the components of smoke fume.

The study was shown that there is significant difference in contents of volatile compounds between sausage samples. Their qualitative compositions are different. Some compounds were found only in experimental samples. For example, α-Thujene, p-Cymene, γ-Terpinene, Phenylethyl alcohol, γ-Decalactone, Tetradecanal, β-Selinene. These results could be related to different activities of starter cultures used in the study.

Carbonyl compounds (aldehydes, ketones etc.) play the main role in formation of aroma profile of meat products. The content of aldehydes in sausage with propionic-acid and bifidobacteria was 30% higher than with control sample. The content of ketones was 17% higher in experimental sample.

In addition, the content of phenols was two times higher in experimental sample than in control. It was stated the high contents of α-Phellandrene, 3-Carene, Methylguaiacol in this sample.

The contents of esters and carboxylic acids were nearly the same in both samples.

It is important to note the difference in terpene content between the sausage samples. The content of terpenes in experimental sample was 3.5-fold higher than in control sample (For example, the content of α-Pinene was 22-fold higher, the content of β-Myrcene

was 6-fold higher, the content of γ-Terpinene was 2-fold higher). α-Pinene has pines odour, β-Myrcene has pleasant smell, γ-Terpinene has lemon odour.

The main difference between the batches was in the content of lactones. It was tenfold higher in experimental sample than in control sample. The contents of δ-Decalactone and γ-Octalactone (both of them have sweet, coconut notes) were 10-fold higher in experimental sample. γ-Decalactone wasn't found in the control sample, but was found in sample with experimental starter culture in concentration 7.77 mg/kg. The odour of γ-Decalactone can be characterized as sweet, fruity-peach and creamy.

It is well known fact that lactones are referred to uronic acids. For example, during fermentation of bifidobacteria D-glucose oxidizes with forming of D-glucuronic acid. The presence of lactones in experimental sample was the reason of mild creamy tone in sausage.

CONCLUSIONS

The study demonstrated that sausages produced with *Propionibacterium shermanii KM-186* and *Bifidobacterium longum B379M* as a starter culture contained several aroma-compounds that were not found in control samples. Also higher contents of terpenes, lactones, alcohols and phenols were found in sausages made with starter culture of propionic-acid bacteria and bifidobacteria compared to control samples. Results of sensory evaluation have shown that the experimental batch had better scores than the control batch. It indicates, that certain aroma compounds plays significant role in the formation of the aroma of raw-smoked sausages.

Thus, the finding of this study was to show that use of *Propionibacterium shermanii KM-186* and *Bifidobacterium longum B379M* as starter cultures has positive influence on sensory characteristics of raw-smoked sausages.

REFERENCES

1. Hui Y.H., Nip W.-K., Rogers R.W., and Young O.A. *Meat Science and Applications*. New York: Marcel Dekker, 2001. n. p.
2. Lücke F.K. Fermented sausages. In: *Wood B.J.B. (ed.) Microbiology of fermented foods*. London: Elsevier Applied Science, 1985, vol. 2, p. 41.
3. Incze K. Raw fermented and dried meat products. *Fleischwirtschaft*, 1992, vol. 72, pp. 58–62.
4. Berdagué J.L., Monteil P., Montel M.C., and Talon R. Effects of Starter Cultures on the Formation of Flavour Compounds in Dry Sausage. *Meat Science*, 1993, vol. 35, no. 3, pp. 275–287. DOI: 10.1016/0309-1740(93)90033-E.
5. Nieto-Lozano J.C., Reguera-Useros J.I., Peláez-Martínez M.C., and Hardisson de la Torre A. Bacteriocinogenic activity from starter cultures used in Spanish meat industry. *Meat Science*, 2002, vol. 62, no. 2, pp. 237–243. DOI: http://doi.org/10.1016/S0309-1740(01)00252-2.
6. Tabanelli G., Coloretti F., Chiavari C., et al. Effects of starter cultures and fermentation climate on the properties of two types of typical Italian dry fermented sausages produced under industrial conditions. *Food Control*, 2012, vol. 26, no. 2, pp. 416–426. DOI: http://doi.org/10.1016/j.foodcont.2012.01.049.
7. Park H.S., Reinbold G.W., Hammond E.G., and Clark W.S. Growth of propionibacteria at low temperatures. *Journal of Dairy Science*, 1967, vol. 50, no. 4, pp. 589–591. DOI: 10.3168/jds.S0022-0302(67)87474-5.
8. Fernández-López J., Viuda-Martos M., Sendra E., et al. Orange fibre as potential functional ingredient for dry-cured-sausage. *European Food Research Technology*, 2007, vol. 226, pp. 1–6. DOI: 10.1007/s00217-006-0501-z.
9. Casquete R., Benito M.J., Martin A., et al. Use of Autochthonous *Pediococcus acidilactici* and *Staphylococcus vitulus* Starter Cultures in the Production of "Chorizo" in 2 Different Traditional Industries. *Food Science*, 2012, vol. 71, pp. 70–79.
10. Dherbecourt J., Maillard M.-B., Catheline D., and Thierry A. Production of branched-chain aroma compounds by *Propionibacterium freudenreichii*: links with the biosynthesis of membrane fatty acids. *Journal of Applied Microbiology*, 2008, vol. 105, pp. 977–985. DOI: 10.1111/j.1365-2672.2008.03830.x.
11. Vorobjeva L.I. *Propionibacteria*. Springer Netherlands Publ., 1999, 281 p. DOI: 10.1007/978-94-017-2803-4.
12. Hettinga D.H. ande Reinbold G.W. The propionic acid bacteria. A review. *Journal of Milk and Food Technology*, 1972, vol. 35, pp. 295–301, pp. 358–372, pp. 436–447.
13. Frohlich-Wyder M.T. and Bachmann H.P. Cheeses with propionic acid fermentation. In: *Fox PF., McSweeney P.L.H., Cogan T.M., and Guinee T.P. (eds). Cheese chemistry, physics and microbiology, vol. 1. General aspects.* London: Elsevier Publ., 2004, pp. 141–156.
14. Boyaval P., Deborde C., Corre C., Blanco C., and Begue E. Stress and osmoprotection in propionibacteria. *Lait*, 1999, vol. 79, pp. 59–69.
15. Langsrud T. and Reinbold G.W. Flavour development and microbiology of Swiss cheese. A review. II Starters, manufacturing process and procedure. *Journal of Milk and Food Technology*, 1973, vol. 11, pp. 531–542.
16. Richoux R., Faivre E., and Kerjean J.R. Effet de la teneur en NaCl sur la fermentation du lactate par *Propionibacterium freudenreichii* dans des minifromages a` pate cuite. *Lait*, 1998, vol. 78, pp. 319–331.
17. Field M.F. and Lichstein H.C. Factors affecting the growth of propionibacteria. *Journal of Bacteriology*, 1957, vol. 73, no. 1, pp. 96–99.
18. Kurtz F.E., Hupfer J.A., Corbin E.A., Hargrove R.F., and Walter H.E. Interrelationships between pH, populations of *Propionibacterium shermanii*, levels of free fatty acids, and the flavour ratings of Swiss cheeses. *Journal of Dairy Science*, 1959, vol. 42, no. 6, pp. 1008–1019. DOI: 10.3168/jds.S0022-0302(59)90684-8.

19. Thierry A., Deutsch M.S., Falentin H., et al. New insights into physiology and metabolism of *Propionibacterium freudenreichii*. *International Journal of Food Microbiology*, 2011, vol. 149, no. 1, pp. 19–27. DOI: http://doi.org/10.1016/j.ijfoodmicro.2011.04.026.
20. Thierry A., Falentin H., Deutsch S.M., and Jan G. *Propionibacterium. spp*. In: *Fuquay J.W., Fox P.F., McSweeney P.L.H. Encyclopedia of Dairy Sciences. 2nd edn.* Academic Press, 2011, pp. 403–411.
21. Dupuis C., Corre C., and Boyaval P. Proteinase activity of dairy *Propionibacterium*. *Applied Microbiology and Biotechnology*, 1995, vol. 42, no. 5, pp. 750–755. DOI: 10.1007/BF00171957.
22. Searles M.A., Argyle P.J., Chandan R.C., and Gordon J.F. Lipolytic and proteolytic activities of lactic cultures. *XXVIII International Dairy Congress*. Australia, Sydney, 1970, vol. 1, p. 111.
23. El-Soda M, Ziada N., and Ezzat N. The intracellular peptidehydrolase system of *Propionibacterium*. *Microbios*., 1992, vol. 72, pp. 65–74.
24. Sahlström S., Espinoza C., Langsrud R., and Sørhaug T. Cell wall membrane and intracellular peptidase activities of *Propionibacterium shermanii*, *Journal of Dairy Science*, 1989, vol. 72, no. 2, pp. 342–350. DOI: https://doi.org/10.3168/jds.S0022-0302(89)79115-3.
25. Langsrud T., Sorhaug T., and Vegarud G.E. Protein degradation and amino acid metabolism by propionibacteria. *Le Lait*, 1975, vol. 75, pp. 325–330.
26. Perez Chaia A., Pesce de Ruiz Hoigado A., and Oliver G. Peptide hydrolases of propionibacteria: effect of pH and temperature. *Journal of Food Protection*, 1990, vol. 53, no. 3, pp. 237–240. DOI: http://dx.doi.org/10.4315/0362-028X-53.3.237.
27. Panon G. Purification and characterization of a proline aminopeptidase from *Propionibacterium shermanii* ATCC 13673. *Lait*, 1990, vol. 70, pp. 439–452.
28. Thierry A., Maillard M.B., Bonnarme P., and Roussel E. The addition of *Propionibacterium freudenreichii* to Raclette cheese induces biochemical changes and enhances flavour development. *Journal of Agricultural and Food Chemistry*, 2005, vol. 53, no. 10, pp. 4157–4165. DOI: 10.1021/jf0481195.
29. Thierry A., Maillard M.B., Hervé C., et al. Varied volatile compounds are produced by *Propionibacterium freudenreichii* in Emmental cheese. *Food Chemistry*, 2004, vol. 87, no. 3, pp. 439–446. DOI: https://doi.org/10.1016/j.foodchem.2003.12.018.
30. Holkoa I., Hraběa J., Šalakováb A., and Radac V. The substitution of a traditional starter culture in mutton fermented sausages by *Lactobacillus acidophilus* and *Bifidobacterium animalis. Meat Science*, 2013, no. 3, vol. 94, pp. 275–279. DOI: https://doi.org/10.1016/j.meatsci.2013.03.005.
31. Rouhi M., Sohrabvandi S., Mortazavian A.M. Probiotic Fermented Sausage: Viability of Probiotic Microorganisms and Sensory Characteristics. *Critical Reviews in Food Science and Nutrition*, 2013, vol. 53, no. 4, pp. 331–348. DOI: http://dx.doi.org/10.1080/10408398.2010.531407.
32. Picard C., Fioramonti J., Francois A., et al. Review article: bifidobacteria as probiotic agents – physiological effects and clinical benefits. *Alimentary Pharmacology & Therapeutics*, 2005, vol. 22, no. 6, pp. 495–512.
33. Ashraf R. and Shah N.P. Immune system stimulation by probiotic microorganisms. *Critical Reviews in Food Science and Nutrition*, 2014, vol. 54, no. 7, pp. 938–956. DOI: http://dx.doi.org/10.1080/10408398.2011.619671.
34. Misharina T.A., Terenina M.B., Krikunova N.I., et al. The influence of starter cultures on the formation of volatile compounds in dry smoked sausages. *Applied Biochemistry and Microbiology*, 2008, vol. 44, no. 5, pp. 545–550. DOI: 10.1134/S0003683808050165.
35. Vorobjeva L.I., Khodjaev E.Yu., and Vorobjeva N.V. Propionic acid bacteria as probiotics. *Microbial Ecology in Health and Disease*, 2008, vol. 20, no. 2, pp.109–112.
36. Swart R., Riedel K.H., and Britz T. Optimized standard conditions for determination of nitrate reduction in propionibacteria. *Lait*, 1998, no. 78, pp. 217–226.
37. Grill J.-P., Crociani J. and Ballongue J. Effect of bifidobacteria on nitrites and nitrosamines. *Letters in Applied Microbiology*, 1995, vol. 20, no. 5, pp. 328–330. DOI: 10.1111/j.1472-765X.1995.tb00456.x.
38. Sobko T., Reinders C.I., Jansson E.A., et al. Gastrointestinal bacteria generate nitric oxide from nitrate and nitrite. *Nitric Oxide Biology and Chemistry*, 2005, vol. 4, pp. 272–278.

Please cite this article in press as: Khankhalaeva I.A., Khamagaeva I.S., and Nikiforova A.P. Effects of propionic-acid bacteria and bifidobacteria on the quality of raw smoked sausages. *Foods and Raw Materials*, 2017, vol. 5, no. 1, pp. 20–29. DOI: 10.21179/2308-4057-2017-1-20-29.

INFLUENCE OF THE WHEY TYPE ON COMPOSITION AND PROPERTIES OF ITS MINERALIZATES

A. G. Khramtsov, A. V. Blinov, A. A. Blinova*, and A. V. Serov

North Caucasus Federal University,
Pushkin Str. 1 Bldg. 1, Stavropol, 355009, Russian Federation

* e-mail: blinov.a@mail.ru

Received April 01, 2017; Accepted in revised form May 24, 2017; Published June 29, 2017

Abstract: Physical and chemical properties of whey mineralizates obtained from unsalted cheese whey, curdy whey and casein whey treated by electrodialysis. The extent of electrodialysis treatment of whey on the structure of its dispersed phase was studied by the photon-correlation spectroscopy method. The considerable effect of electrodialysis treatment on the dispersed structure of whey, on stability of whey proteins that form the basis of the dispersed phase of whey was defined. These variations may significantly affect the organoleptic and technological properties of demineralized whey, its shelf life and biological value. It's been established that the demineralization causes significant changes to the specific electrical conductivity and the active acidity of both whey and whey mineralizates. Their physical and chemical properties were studied with the following methods: potentiometry, conductometry, stalagmometric method, viscometry, refractometry. The elemental and phase composition were studied by a range of advanced methods, such as X-ray phase analysis, scanning electron microscopy, energy dispersive X-ray fluorescent microanalysis, infrared spectroscopy. It's revealed that the main crystalline phases of whey mineralizates are the potassium and sodium chlorides, calcium and magnesium phosphates, calcium sulfate and carbonate. The results of infrared spectroscopy allowed identification of the lactate, citrate, sulfate and phosphate ions in the structure of whey mineralizates. The ultimate composition of whey mineralizates is represented by such chemical elements as *Cl*, *Ca*, *Na*, *Mg*, *K*, *S*, *P*, *O*, *Al*, *Si* and *N*. The correlation between the composition and properties of whey mineralizate and initial milk whey is established.

Keywords: Whey mineralizates, infrared spectroscopy, X-ray phase analysis, scanning electron microscopy, energy-dispersive microanalysis

DOI 10.21179/2308-4057-2017-1-30-40 *Foods and Raw Materials*, 2017, vol. 5, no. 1, pp. 30–40.

INTRODUCTION

Electrodialysis treatment of whey is found to be the most effective method of targeted control of its mineral composition and acidity [1, 2]. It should be noted that the whey electrodialysis does not significantly affect the qualitative and quantitative properties of whey proteins, lactose content, and the content of vitamins in demineralized whey; in the meantime, its technological and organoleptic properties considerably improve [3].

The process of whey electrodialysis desalination or demineralization ends in demineralized whey and salt concentrate, namely, the whey mineralizate. The demineralized whey (especially when dry) is used in food production for children and for special purposes; in confectionery and bakery; for meat products; in pharmaceutical industry, etc. [1–5]. On the other hand, the whey mineralizates have not found the practical use. As shown in works [6, 7], whey mineralizates may be used as the basis for washing and disinfecting agents used in dairy enterprises. In this regard, the study of physical and chemical, surface-active properties and the composition of whey mineralizates, as well as the impact caused by the type of initial whey to such parameters are quite relevant.

OBJECTS AND METHODS OF THE STUDY

The targets of this research are the milk whey and whey mineralizates obtained by electrodialysis of unsalted cheese whey, curdy whey and casein whey. Milk whey was demineralized by the *ED-mini* electrodialysis device (manufactured by *MEGA JSC*, Czech Republic) using *RALEXAMH-PES* anion exchange membranes and *RALEXSMH-PES* cation exchange membranes. Samples were treated under the electrodialysis until 90% demineralization was achieved. Parameters of electrodialysis included the following: voltage $U = 12.5$ V; membrane area – 0.14 m^2; steam of membranes – 10; diluate flow – 70 l/h; temperature $t = 22.0 \pm 2$°C. The volume of experimental whey mineralizates was produced at the International R&D "Electro-and Baromembrane Technologies" Laboratory of MEGAProfiLine LLC (Stavropol Territory, Stavropol).

The composition and properties of milk whey mineralizates were studied by laboratories of the Applied Biotechnology Department of the Institute of Living Systems and of the Department of Nanomaterial Technology of the Institute of Electric Power Engineering, Electronics and Nanotechnologies,

Federal State Autonomous University of Higher Education North-Caucasian Federal University, as well as by the R&D Laboratory "Physical Methods of Research and Analysis" of the Center for Collective Use of Scientific Equipment (Stavropol Territory, Stavropol).

The structure of the milk whey discontinuous phase was assessed by the photon-correlation spectroscopy method at the *Photocor Complex* unit (by Antek-97 LLC, Russia) [8]. The array of spectroscopic data was processed using the *DynaLS* software. The method of conductivity measurements at the EXPERT-002 conductometer [9, 10] was applied to measure the specific conductivity (SC) of milk whey and its mineralizates. The active acidity of whey and mineralized whey was determined by potentiometric method; the density was measured by the hydrometer [11]; the limiting wetting angle was measured by the sessile drop method that is the direct measurement of the angle by the shape of a drop on the solid surface; the surface tension was measured by stalagmometric method [12]; the kinematic viscosity was measured by the glass capillary viscosimeter VPZh-1 (Technocom NPO, Russia) [13]; the refractive index was measured by the refractometer; the titrated acidity of whey mineralizates was determined by titrimetry as per the procedure [14]. The structure of mineralizates the availability of certain vibrations of atomic group bonds was determined by the infrared spectroscopy (IR spectroscopy) using the IR Fourier spectrometer of FSM 1201 model listed with the No. 18895-99 in the National Register of Measuring Equipment of Russia. The phase composition of dry residues of whey mineralizates was evaluated by X-ray phase analysis by the method of powder diffraction at the *PANanytical Empyrean* X-ray diffractometer (manufactured by *PANalytical BV*, the Netherlands) as per the procedure [15]. The elemental composition of whey mineralizate dry residues was investigated using the energy-dispersive (elemental) analysis at the *MIRA-LMH* scanning electron microscope with the element determination system *AZtecEnergy Standart/X-max 20 (standard)* (manufactured by *Tescan*, Czech Republic) [16].

RESULTS AND DISCUSSION

Physical and chemical properties of whey and whey mineralizates were studied at the first stage. The process of milk whey electrodialysis allowed obtaining dependences of specific conductivity (SC) and active acidity of curdy whey, cheese whey, casein whey and whey mineralizates on demineralization level. The results are shown graphically below. Fig. 1 shows the dependence of the specific conductivity of milk whey on the degree of its demineralization.

As shown by the data analysis in Fig. 1, prior to the demineralization process, the initial milk whey had the values of specific conductivity as follow: the largest value obtained for the casein whey with SC = 9.54 ± 0.50 mS/cm, followed by the curdy whey with SC = 7.19 ± 0.55 mS/cm and the lowest value for the cheese whey with SC = 5.17 ± 0.52 mS/cm. The specific conductivity of all the whey samples studied in process of electrodialysis treatment decreased on a straight-line basis. The process of demineralization of milk whey was completed as the specific conductivity value was reached of about 1–1.5 mS/cm that corresponded to 90% of demineralization.

Fig. 2 shows the dependence of specific conductivity of whey mineralizates on the extent of whey demineralization.

Analysis of dependencies shown in Fig. 2 shows that the specific electrical conductivity of whey mineralizates increases as the extent of whey demineralization rises due to ion transition entering the dispersion medium of milk whey and to the salt concentrate influenced by the electromotive force (EMF). Upon completion of electrodialysis treatment, the casein whey mineralizate has the greatest specific conductance (SC) followed by the curdy and cheese whey that correlates with ion concentrations and SC of initial whey.

In parallel with SC measurement, the active acidity (*pH*) was measured for both whey of various types and whey mineralizates. Fig. 3 shows the results of *pH* measurement of milk whey as it is demineralized.

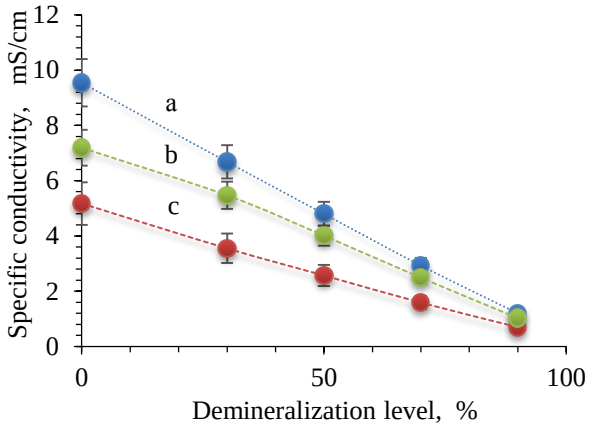


Fig. 1. Dependence of specific conductivity of milk whey on the extent of its demineralization: (a) casein, (b) curdy, (c) cheese.

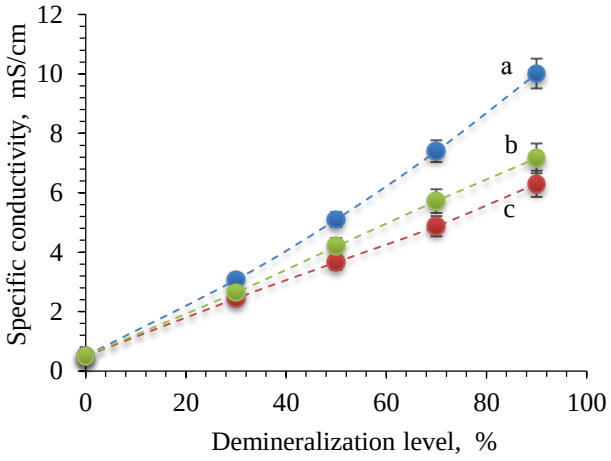


Fig. 2. Dependence of specific conductivity of whey mineralizates on the extent of whey demineralization: (a) casein, (b) curdy, (c) cheese.

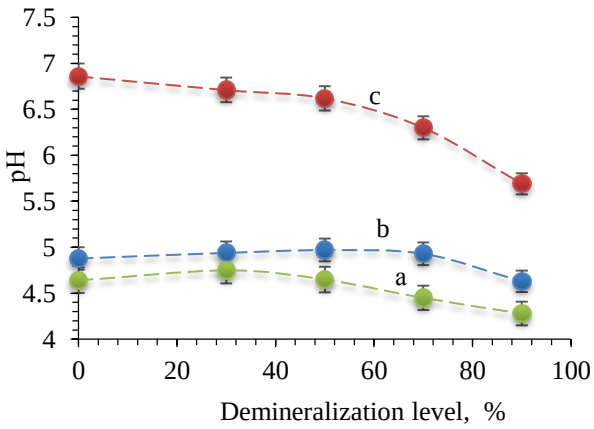


Fig. 3. Dependence of the milk whey active acidity on the extent of its demineralization: (a) casein, (b) curdy, (c) cheese.

As per the analysis of dependencies shown Fig. 3, the active acidity values of tested whey species were as follow prior to demineralization: casein whey $pH = 4.64 \pm 0.11$; curdy whey $pH = 4.88 \pm 0.12$ and cheese whey $pH = 6.86 \pm 0.10$. These active acidity values are well correlated with published data and are associated with processes to obtain these types of milk whey [2, 5]. For example, to produce the casein whey, the protein is coagulated using the hydrochloric acid (pH << 7), adding the *HCl* solution to the source milk until the isoelectric point of casein is reached (pH = 4.6) [17]. When producing curdy whey, the protein coagulation is associated with vital activity of lactic acid bacteria resulting in the large amount of lactic acid which is the weak electrolyte (pH < 7). The production of cheese whey is associated with the use of enzymatic processes that do not have a significant effect on acid-base properties of milk.

By the results of dependencies analysis as shown in Fig. 3, it was found that the active acidity of whey types tested decreases during demineralization. The greatest changes in whey pH are reported at the about 50% demineralization. This is apparently due to the process of water molecule decomposition on the membrane surfaces when this level of demineralization is reached under the effect of electric forces. This results in the release of the certain amount of H^+ protons that determine the value of active acidity of the medium, and as a result, pH decreases. OH^- ions released during the water molecule decomposition have no significant effect on the whey active acidity as they are removed in process of further desalting, which may be related to the process technique due to the selective permeability of membranes used relative to hydroxide ions.

Fig. 4 shows dependences of whey mineralizate active acidity on the extent of whey demineralization. It was found that the process of electrodialysis treatment results in the decrease of mineralizate active acidity of casein and curdy whey due to hydrochloric and lactic acid penetrated therein, respectively.

The active acidity of the cheese whey mineralizate varies insignificantly and is within $6 \le pH \le 7.5$; this is apparently due to the order of ion passing to the mineralizate. It is possible that at the beginning of electrodialysis, the ions with acidic properties pass into the mineralizate to explain the decrease in pH, followed by ions of basic properties. At the end of electrodialysis treatment, the active acidity of mineralizates is within: in acidic area - for casein and curdy mineralizates ($pH = 4.01 \pm 0.21$ and $pH = 5.05 \pm 0.22$, respectively), in the slightly acidic area - for cheese mineralizate ($pH = 5.92 \pm 0.25$).

Data were also obtained on the influence of extent of the whey electrodialysis treatment on the structure of its dispersed phase. The average hydrodynamic radius of particles of the whey dispersed phase was found by the photon correlation spectroscopy. Figure 5 shows the histogram of particle size distribution of the dispersed phase of initial curdy whey sample prior to electrodialysis treatment, distribution histograms of the disperse phase particles for the cheese and casein wheys are similar.

The analysis of results indicates that curdy, cheese and casein whey samples have a single dispersed phase with the average hydrodynamic radius of about 130 ± 50 nm. Quite monodisperse distribution should be noted for the dispersed phase of milk whey by particle sizes.

The distribution histograms of the average hydrodynamic radius of particles of the disperse phase of curdy, cheese and casein whey at 90% demineralization are shown in Fig. 6 a, b, c.

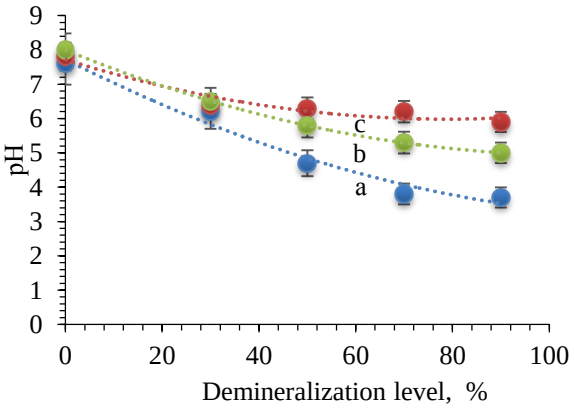


Fig. 4. Dependence of whey mineralizate active acidity on the extent of whey demineralization: (a) casein, (b) curdy, (c) cheese.

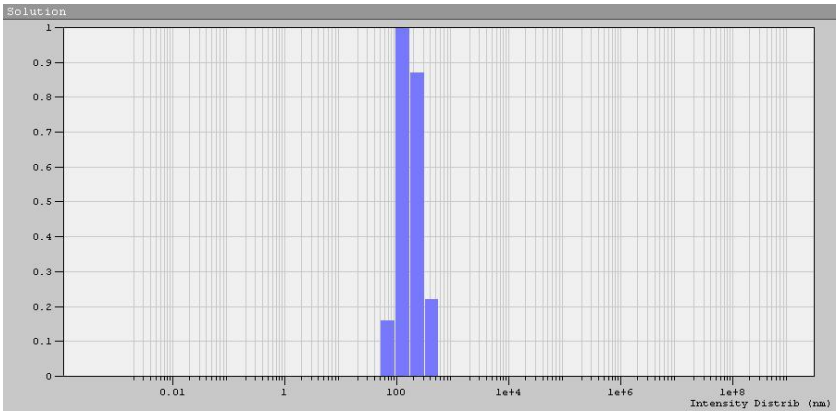
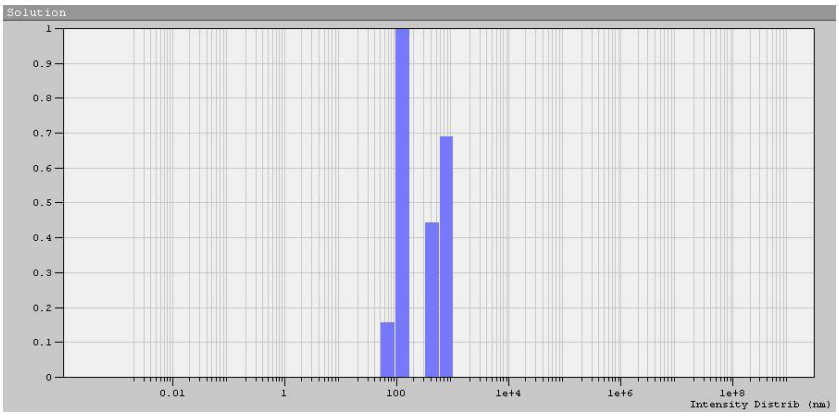
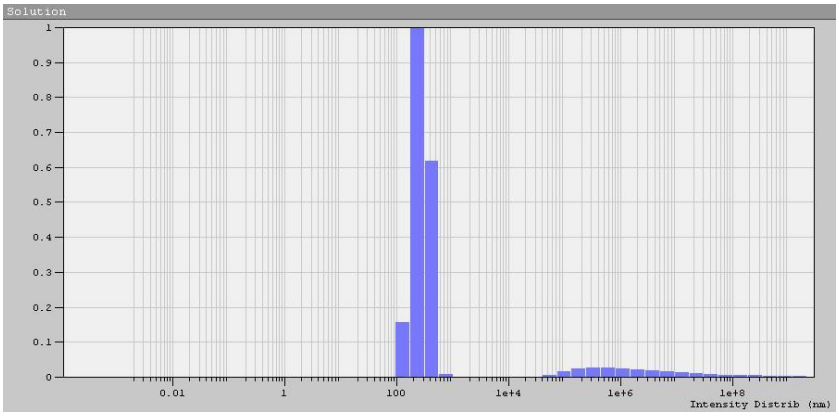


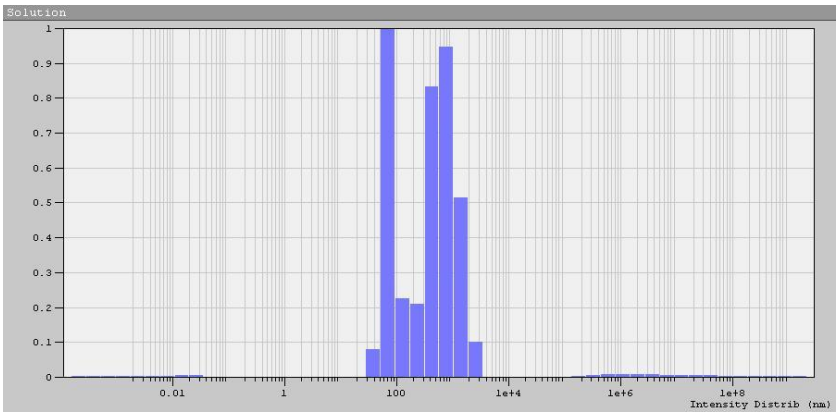
Fig. 5. Histogram of distribution of hydrodynamic radii of particles of the curdy whey disperse phase.



(a)



(b)



(c)

Fig. 6. Distribution histograms of the hydrodynamic radii of particles of the whey dispersed phase at 90% demineralization: (a) curdy, (b) cheese, (c) casein.

As per the analysis of histograms shown in Fig. 6 a, b, c, at 90% demineralization the second fraction occurrence was reported in all three milk whey samples and its content in curdy and casein whey is signify.cant totaling over 50%; the content of the second fraction is about 5% in the cheese whey.

At the second stage of the study, data were obtained on physical and chemical properties of whey mineralizates as shown in Table 1.

The analysis of data shown in Table 1 indicates that values of such physical and chemical properties as density, wetting angle, surface tension, kinematic viscosity and refractive index are similar for all mineralizates tested and do not depend on the origin of raw stock. The active acidity of the medium, specific electrical conductivity and titratable acidity depend on the ionic composition of whey mineralizates and, in turn, they correlate with the ionic composition of the raw stock (curdy, cheese and casein whey).

At the third stage of the study, whey mineralizate samples were dried and tested by IR spectroscopy, X-ray phase analysis and scanning electron microscopy. Fig. 7 shows the IR spectra obtained.

As shown by the IR spectra explanation [18, 19] of dry residues of whey mineralizates, bands are seen in the area of valence vibrations that may be associated with *-OH, -CH* and *-NH* groups forming part of mineralizates [18, 19]; comprising mineralizates; the area of deformation vibrations is represented by bands typical for bonds present in lactate, citrate, sulfate and phosphate ions.

Due to the fact that certain compounds with ionic bonds comrising mineralizates are optically transparent in the IR spectrum area, the X-ray phase analysis was used to identify them and to define their structure. The resulting X-ray diffraction patterns are shown in Fig. 8.

As per the analysis of diffractograms, main phases of curdy, cheese and casein whey mineralizates are the potassium and sodium chlorides, as well as calcium and magnesium phosphates, calcium sulphate and carbonate. Main components of the crystalline phase of whey mineralizates are described in Table 2 [20].

Table 1. Physical and chemical properties of whey mineralizates

Type of initial milk whey	Physical and chemical properties							
	Active acidity of the medium, *pH*	Density, ρ, kg/m^3	Wetting angle, θ, °	Surface tension, σ, mN/m	Titrable acidity, T°	Kinemtic viscosity, β, 10^{-6}·m^2/s	Refractive index, *n*	Specific conductivity, $\varkappa$, mS/cm
Curdy	5.05	1.005	96	76	16	0.904	1.334	7.16
Cheese	5.92	1.004	97	78	14	0.907	1.334	6.30
Casein	4.01	1.006	95	77	19	0.903	1.334	10.01

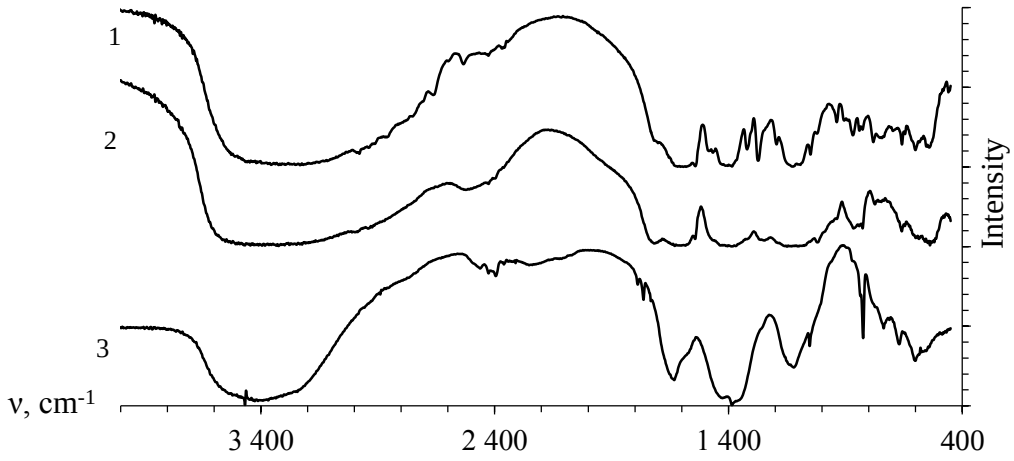


Fig. 7. IR spectra of dry residues of whey mineralizates: (1) cheese whey, (2) curdy whey, (3) casein whey.

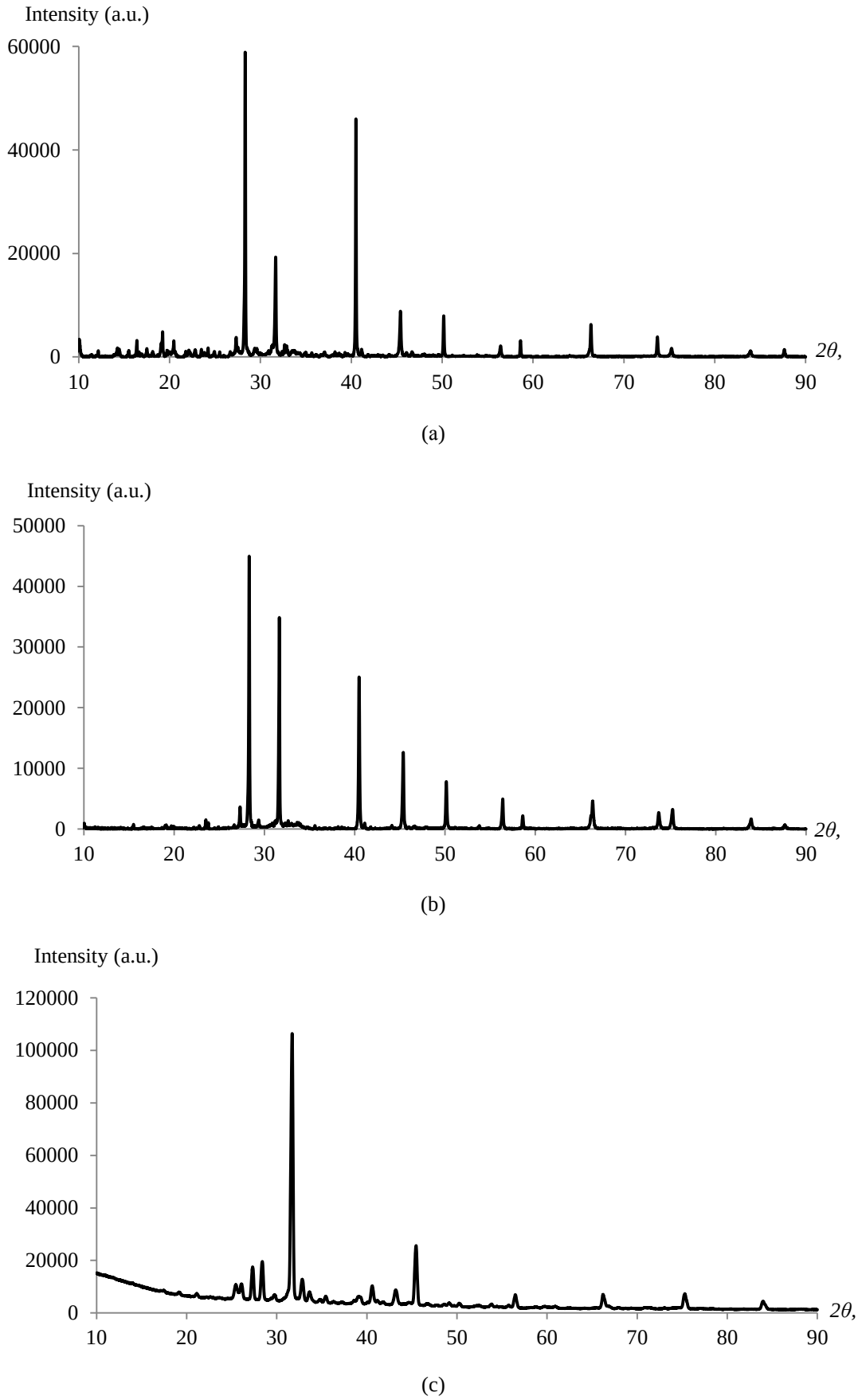


Fig. 8. Diffractograms of dry residues of mineralizates of various whey: (a) cheese whey mineralizate; (b) curdy whey mineralizate; (c) casein whey mineralizate.

Table 2. Description of main components of the whey mineralizate crystalline phase

Compound	Formula	Molecular mass	Type of crystal lattice	Space group	Elementary cell parameters
Potassium chloride	*KCl*	74.5	Cubic	*Fm-3m*	a = b = c (*Å*):6.2917 Alpha = Beta = Gamma (°):90.0000
Sodium chloride	*NaCl*	58.5	Cubic	*Fm-3m*	a = b = c (Å):5.6418 Alpha = Beta = Gamma (°):90.0000
Calcium sulphate	$CaSO_4$	136	Orthorhombic	*Bmmb*	a(Å):6.9920 b(Å):6.9990 c(Å):6.2400 Alpha = Beta = Gamma (°):90.0000
Calcium carbonate	$CaCO_3$	100	Orthorhombic	*Pmcn*	a(Å):4.9653 b(Å):8.0088 c(Å):5.7847 Alpha = Beta = Gamma (°):90.0000
Calcium orthophosphate	$Ca_3(PO_4)_2$	310	Orthorhombic	*R3c*	a (Å):10.3633 b (Å):10.3633 c (Å):37.2581 Alpha (°):90.0000 Beta(°):90.0000 Gamma(°)120.0000
Magnesium orthophosphate	$Mg_3(PO_4)_2$	262	Triclinic	*P-1*	a (Å):8.5120 b(Å):8.9820 c (Å):9.3200 Alpha (°):116.3400 Beta (°):91.5000 Gamma(°):114.4900

Whey mineralizate samples were tested by the scanning electron microscopy at the scanning electron microscope *MIRA-LMH* with the unit structure determination system *AZtecEnergy Standart/X-max 20* (*standard*) by *Tescan* Company. Previously, the whey mineralizate sample elements were studied by the energy-dispersive microanalysis. The *EDX* spectra obtained are shown in Fig. 9.

Mathematical processing of *EDX*-spectra helps to specify components of whey mineralizates as shown in Table 3.

As per the analysis of data shown in Table 3, curdy, cheese and casein whey mineralizates contain such elements as *Cl, Ca, Na, Mg, K, S, P, O, Al, Si* (nitrogen (*N*) is also found in the cheese whey mineralizate). The highest content of *Cl* is found in the casein whey mineralizate due to the hydrochloric acid used to produce it. The content of *Ca* and *P* in mineralizates of curdy and casein whey is several times higher than in that of cheese whey. The reason is as follows: the calcium phosphate in the casein and curdy whey is mainly ionic and is easily removed treated by electrodialysis and easily passes into mineralizates; the calcium phosphate is colloidal in the cheese whey of $pH \approx 7$, so it is hardly removed during electrodialysis. The content of *K, Na, Mg, S* in all milk whey mineralizates is fairly similar. In milk and whey, these elements form the ion-salt balance being not actively involved in colloidal system stabilization; these elements easily transform to mineralizate under the electrodialysis treatment of the milk whey.

It should be noted that it is not feasible to define the percentage of carbon by this method due to specific conditions for sampling, where a thin layer of carbon (5–10 nm) is applied onto the sample surface.

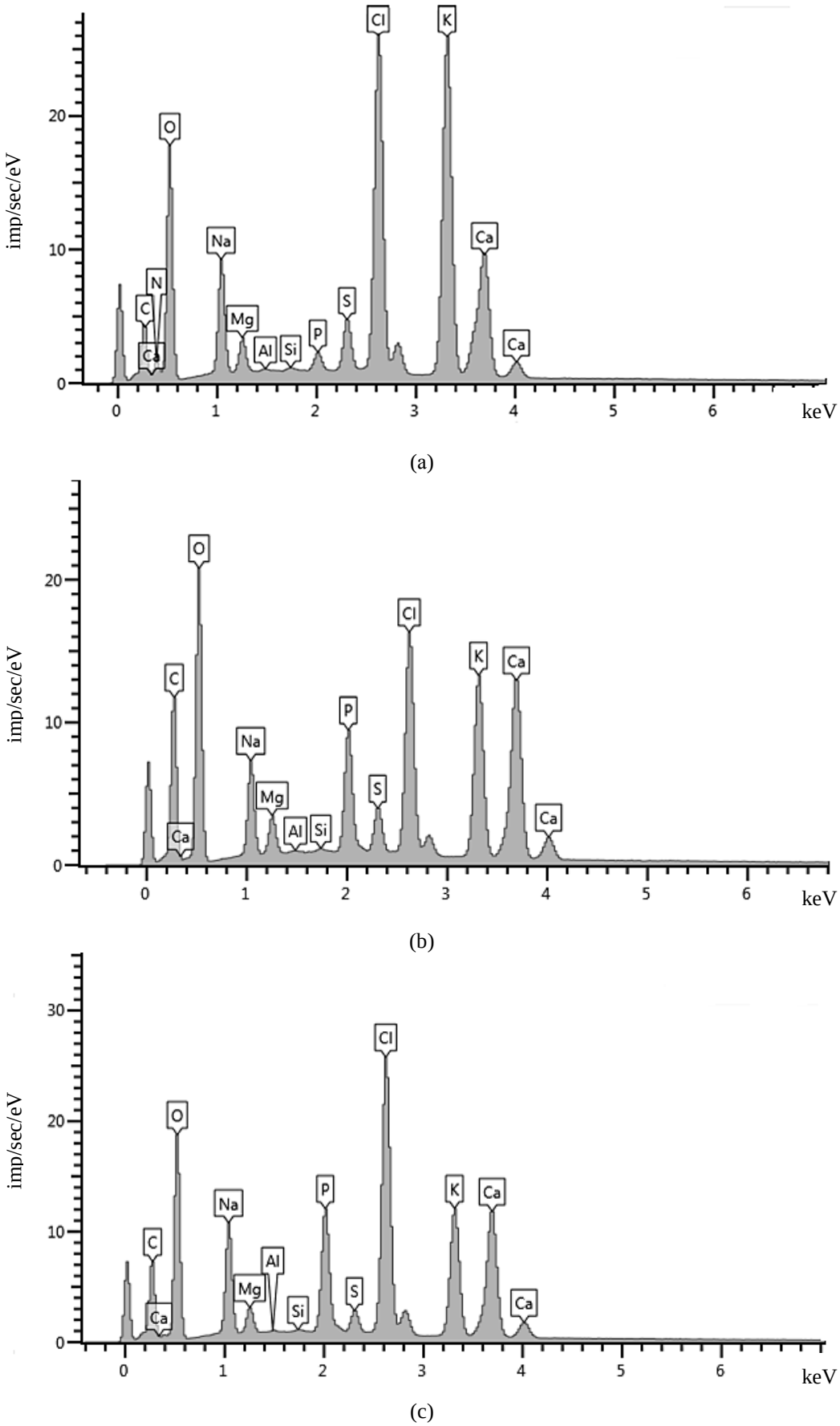


Fig. 9. *EDX*-spectrum of whey mineralizates: (a) cheese whey mineralizate; (b) curdy whey mineralizate; (c) casein whey mineralizate.

Table 3. Unit structure of milk whey mineralizates

Unit	Content of elements in milk whey mineralizates,%		
	casein	curdy	cheese
N	–	–	8.54
O	45.76	51.14	45.01
Na	8.41	6.05	6.20
Mg	1.57	1.87	1.43
Al	0.07	0.07	0.07
Si	0.09	0.10	0.09
P	6.13	4.94	0.64
S	1.20	1.92	1.80
Cl	15.79	10.32	12.99
K	9.92	11.04	11.72
Ca	11.06	12.55	7.52

Figures 10–12 show the test results of dry residues micro-structure of casein, cheese and curdy whey mineralizers obtained by scanning electron microscopy.

As per the analysis of SEM micro-images of whey mineralizate samples as shown in Figures 10–12, the microstructure strongly depends on the origin of the raw material, namely the whey. Polycrystalline formations of quite higher polydispersity are found in all milk whey mineralizates. The crystallite size in the casein whey mineralizate sample is 2 to 200 μm, of cubic shape that is relevant to the structure of potassium and sodium chlorides. Polycrystalline formations sized about 2 to 50 μm comprising of plates ("scales") are found in samples of both cheese and curdy whey mineralizates.

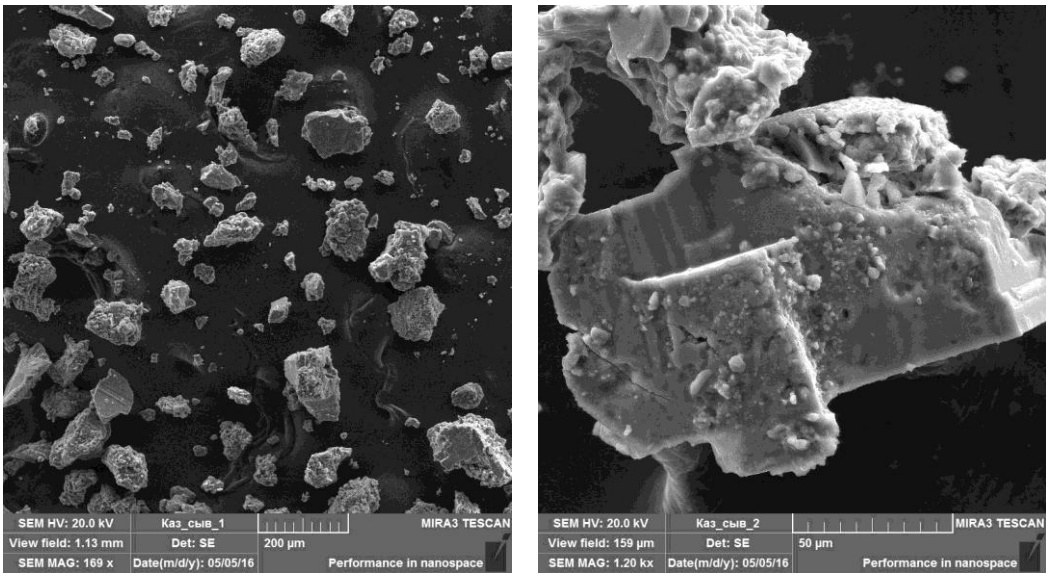


Fig. 10. SEM micro-images of the dry residue of casein whey mineralizate.

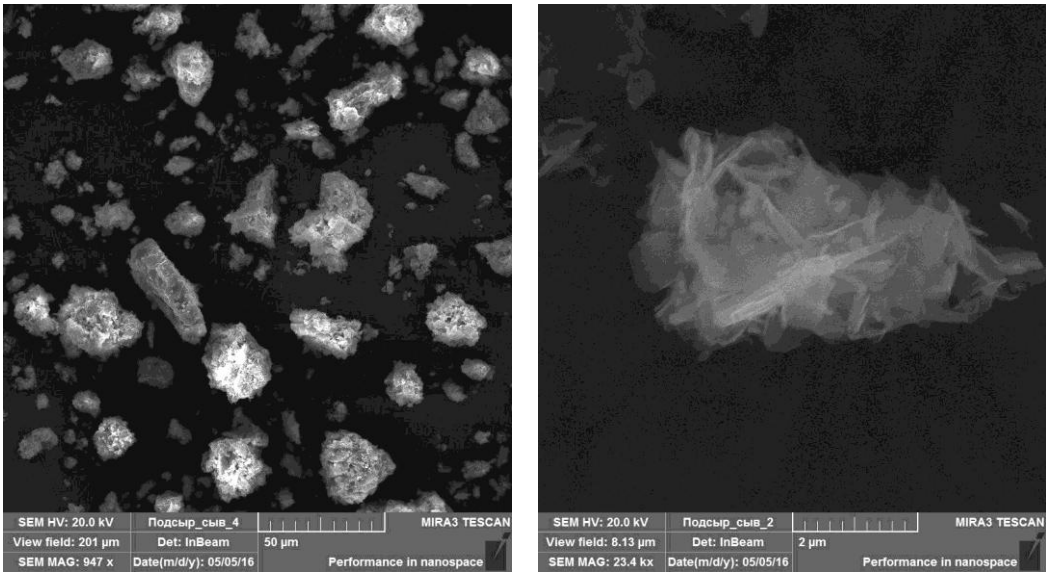


Fig. 11. SEM-micro-images of the dry residue of the cheese whey mineralizate.

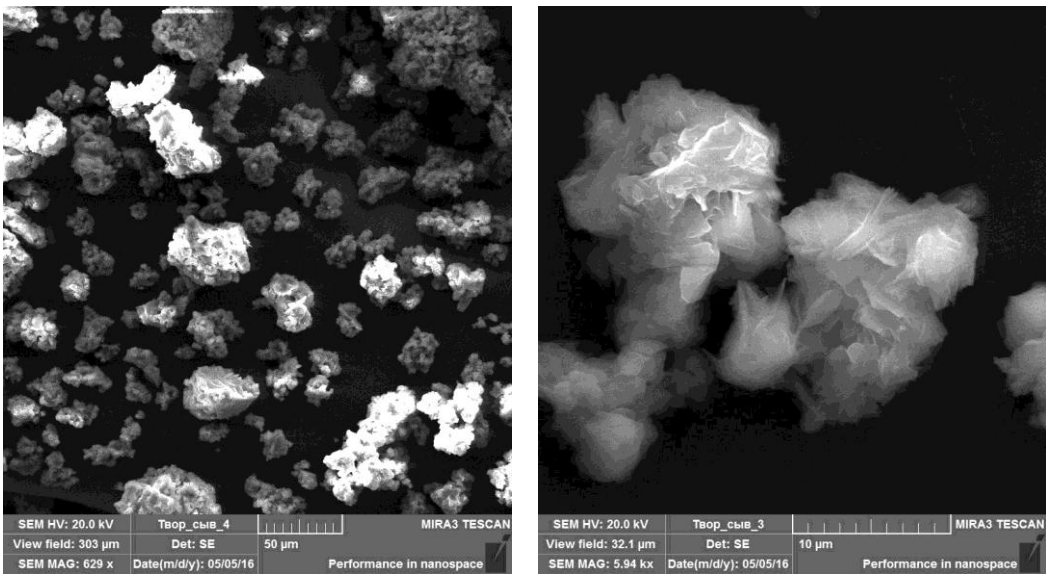


Fig. 12. SEM micro-images of the dry residue of curdy whey mineralizate.

CONCLUSIONS

Resulting from studies above, we may conclude on the considerable impact of electrodialysis treatment on the dispersed composition of milk whey and, consequently, on the stability of whey proteins as the basis of the milk whey dispersed phase. These variations may significantly affect the organoleptic and technological properties of demineralized whey, its shelf life and bioavailability. The study of the impact of nature and ion concentration on the particle consolidation process of the milk whey dispersed phase remains urgent and requires further studies.

We can further conclude that the type of dairy raw material considerably impact the physical and chemical properties and structure of whey mineralizates.

ACKNOWLEDGEMENTS

The work was supported by the Ministry of Education and Science of the Russian Federation (Contract Minobrnauki of Russia № 2017-218-09-162).

REFERENCES

1. Ponomarev A.N., Klyuchnikov A.I, and Polyansky K.K. *Osnovnye napravlenia membrannykh technologiy pri pererabotke molochnoy produktsii* [Main areas of membrane technologies for diary product processing]. Voronezh: Istoki Publ., 2011. 356 p.
2. Donskikh A.N. *Razrabotka alternativnykh technologiy proizvodstva demineralizovannoy tvorozhnoy syvorotki* [Alternative technology development for production of demineralized whey]. Cand. eng. sci. thesis. Stavropol, 2013. 24 p.
3. Avanesova A.V. *Razrabotka technologii varenykh kolbas s ispolzovaniem mineralizata syvorotochnogo* [Technology development of cooked sausage using the whey mineralisate]. Cand. eng. sci. diss. Stavropol, 2011. 216 p.
4. Volodin D.N., Zolotaryova M.S., Topalov V.K., et al. Milk whey processing: conceptual strategy, real technologies, adequate investments, demanded products. *Molochnaya promyshlennost'* [Diary industry], 2015, no. 5, pp. 36–41.
5. Khramtsov A.G. *Fenomen molochnoy syvorotki* [Milk whey phenomenon]. St. Petersburg: Professija Publ., 2012. 803 p.
6. Blinova A.A., Serov A.V., Khramtsov A.V., and Naberezhny D.O. Sravnitelnaya otsenka effektivnosti novogo moyusche-dezinfitsiruyuschego sredstva [Comparative assessment of the new detergent and disinfectant agent performance]. *Materialy IV-ü ezhegodnoy nauchno-prakticheskoy konferentsii «Universitetskaya nauka – regionu»* [Proc. of the IV Ann. Sci. Pract. Conf. "University Science to Regions"]. Stavropol: SKFU Publ., 2016. 278 p.
7. Blinova A.A., Blinov A.V., Serov A.V., et al. Normalnye otkhody pererabotki molochnoy syvorotki – perspektivnaya otsenka dlya sozdaniya moyusche-dezinfitsiruyuschikh rastvorov [Normal wastes of milk whey processing – perspective basis to create detergent and disinfectant solutions]. *Materialy III ezhegodnoy nauchno-prakticheskoy konferentsii posvyaschennoy 85 letiyu Severo-Kavkazskogo Federalnogo Universiteta «Universitetskaya nauka – region»* [Proc. of the III Ann. Sci. Pract. Conf. to honor 85th of the North Caucasus Federal University "University Science to Regions"]. Stavropol, SKFU Publ., 2015. 344 p.
8. *Spektrometr dinamicheskogo and staticheskogo rasseyaniya sveta Photocor Complex* [Photocor Complex Spectrometer of dynamic and static light diffusion]. Available at: http://www.photocor.ru/dlsinstrument (accessed 19 February 2017).
9. *Tekhnicheskie usloviya TU 4215-004-52722949-2002. Analizatory zhidkosti. Konduktometr «Ekspert-002»* [Specifications TU 4215-004-52722949-2002. Liquid scanners. Conductometer "Expert-002"].

10. *Rukovodstvo po ekspluatatsii i metodika proverki «Konduktometry EKSPERT-002»* [Operating manual and verification method "Conductometers EXPERT-002"]. Moscow: EKONIKS-EKSPERT Publ., 2002. 23 p.
11. *GOST 18481-81. Areometry i tsilindry steklyannye. Obshchie tekhnicheskie usloviya* [State Standar 18481-81. Densimeters and glass cylinders. General specifications]. Moscow: Standartinform Publ., 2007. 22 p.
12. Vereshchagin A.L. and Balabanova S.S. *Svoystva rastvorov kolloidnykh poverkhnostno-aktivnykh veshchestv: metodicheskie rekomendatsii po vypolneniyu laboratornykh rabot po kursam «Kolloidnaya khimiya», «Poverkhnostnye yavleniya»* [Properties of colloidal solutions of surface-active substances: guidelines for laboratory procedures for "Colloid Chemistry", "Superficial phenomena"]. Biysk: Polzunov Altai State University of Engineering Publ., 2008. 19 p.
13. *GOST 10028-81. Viskozimetry kapillyarnye steklyannye. Tekhnicheskie usloviya* [State Standar 10028-81. Glass capillary viscosity meters. Specifications]. Moscow: Standartinform Publ., 2015. 15 p.
14. *GOST 3624-92. Moloko i molochnye produkty. Titrimetricheskie metody opredeleniya kislotnosti. Moloko i molochnye produkty. Obshchie metody analiza* [State Standar 3624-92. Milk and dairy products. Titrimetric methods for acidity determination. Milk and dairy products. General test methodsa]. Moscow: Standartinform Publ., 2011. 10 p.
15. Pentin Yu.A. and Vilkov L.V. *Fizicheskie metody issledovaniya v himii* [Physical test methods in chemistry]. Moscow: MIR Publ., 2003. 683 p.
16. Elektronnaya mikroskopiya [Electronic Microscopy]. Available at: http://emicroscope.ru/microscopes/microanaliz/eds (accessed 19 February 2017).
17. Tepel A. *Khimiya i fizika moloka* [Chemistry and physics of milk]. St. Petersburg: Professija Publ., 2012. 832 p.
18. Nakanisi K. *Infrakrasnye spektry i stroenie organicheskikh soedineniy: prakticheskoe rukovodstvo* [IR-spectra and structure of organic compounds: practical guide]. Moscow: MIR Publ., 1962. 220 p.
19. Nakamoto K. *IK-spektry i spektry-KR neorganicheskikh i koordinatsionnykh soedineniy* [IR-spectra and Raman spectra of non-organic and complex compounds]. Moscow: MIR Publ., 1991. 536 p.
20. Lipson G. and Steeple G. *Interpretatsiya poroshkovykh rentgenogramm* [Interpretation of powder X-ray]. Moscow: MIR Publ., 1972. 350 p.

Please cite this article in press as: Khramtsov A.G., Blinov A.V., Blinova A.A., and Serov A.V. Influence of the whey type on composition and properties of its mineralizates. *Foods and Raw Materials*, 2017, vol. 5, no. 1, pp. 30–40. DOI: 10.21179/2308-4057-2017-1-30-40.

IMPACT OF BETALACTOGLOBULIN HYDROLYSATE ON STRUCTURAL AND MECHANICAL PROPERTIES OF ALLERGENIC POTENCY-RESTRICTED YOGURT

A. N. Ponomarev[a], E. I. Melnikova[a], E. V. Bogdanova[a,*], and D. V. Kharitonov[b]

[a] Voronezh State University of Engineering Technologies,
Revolyutsii Ave. 19, Voronezh, 394036, Russian Federation

[b] All-Russia Dairy Research Institute,
Lyusinovskaya Str. 35 Bldg. 7, Moscow, 115093, Russian Federation

* e-mail: ek-v-b@yandex.ru

Received September 13, 2016; Accepted in revised form December 18, 2016; Published June 29, 2017

Abstract: Creation and development of low-allergenic food products in sour-milk drink groups is the urgent trend in dairy industry development. By the results of patent search, one of challenging methods to reduce the dairy product allergenicity has been identified. To produce such products, the method involves using whey protein hydrolysates, in particular, β-lactoglobulin hydrolysate obtained by using enzyme preparations Flavorpro 750MDP and Promod 439L. The research aimed to study normalized milk mixtures fermented with β-lactoglobulin hydrolysate with the resulting changes in the chemical composition, as well as to select starter microorganisms that provide the required stability and structure of the milk coagulum by producing exopolysaccharides. The researches were carried out at the base of several laboratories as follow: The Federal Research Centre "Fundamentals of Biotechnology" of the Russian Academy of Sciences, Christian Hansen LLC, the Voronezh State University of Engineering Technologies and the Federal Research Centre of Nutrition and Biotechnology. This work is based on standard and conventional research methods. Advanced tools and information technologies were used to assess the properties of raw materials, semi-finished products and food products. By the results of studies completed, it was found unreasonable to replace over 20% of whole milk with β-lactoglobulin hydrolysate during normalization, since such replacement resulted in an increase in the mixture acidity and prevented the normal growth and development of Streptococcus thermophilus, the basic exopolysaccharide producer. At the same time, the length of fermentation increased up to 5–6 h as the mass fraction of β-lactoglobulin hydrolysate increased. The viscosity of the resulting coagulum increased due to the reaction of exopolysaccharides with the protein gel mesh and fixation thereof on the surface of protein matrix. The residual antigenicity of the finished product decreased to 48.5% relative to that of sour-milk drinks produced as per traditional technology.

Keywords: Low-allergy yogurt, β-lactoglobulin hydrolysate, starter microorganisms, exopolysaccharides, rheological behavior

DOI 10.21179/2308-4057-2017-1-41-50 *Foods and Raw Materials*, 2017, vol. 5, no. 1, pp. 41–50.

INTRODUCTION

Currently, the sour-milk production, particularly production of beverages, is reported to develop at the rapid rates as compared to other dairy products [1], and to employ greater development challenges. This benefits from price affordability of this food category. In addition, the increase in output and consumption of sour-milk drinks is due to the widespread promotion of healthy food among the population.

These products are reported in the high content of essential amino acids (7–11 times higher than in fresh milk), magnesium salts, phosphorus, calcium, vitamins A, D, E that are involved in the human metabolism [2]. Organic acids and carbon dioxide have a strong stimulating effect on digestive glands, thereby improving the process of digestion and intestinal uptake. Sour-milk products enrich the gastrointestinal tract with lactic acid and other bacteria that can considerably increase the human immune activity, and some of them can also "settle down" in the intestinal tract [3]. These microorganisms are antagonists of pathogenic and opportunistic pathogenic microflora as well as of putrefactive bacteria in the human intestine. The calcium of fermented dairy products is easier digested since it transforms to a soluble state in the acid environment and it partially releases from protein molecules due to protein hydrolysis by starter microorganisms [4].

Currently, the Russian market of fermented drinks offers quite a wide range of products. However, of special importance are the development and integration of technologies to produce hypoallergic and

low-allergenic dairy products with the known reduced residual antigenicity that ensure immunological tolerance.

In our country, the product line of hypoallergic and low-allergenic dairy products is limited to imported dry infant milk mixes [5]. In this sector, the integration of import substitution technologies is of great scientific and practical importance.

As per the data by the International Union of Immunological Societies, the known food-borne allergens in dairy products are the following: caseins, immunoglobulins, β-lactoglobulins, α-lactoalbumins, bovine serum albumin [6]. Hereat, as per the database by IUIS, BiPep, Allergen Online, AllerMatch, β-lactoglobulin is the most allergenic fraction [7, 8]. This is because the β-lactoglobulin is not hydrolyzed during ingestion affected by the pepsin (gastric juice enzyme) unlike other milk proteins. When proteins interact with cells of specific immunity in the human body, IgE and IgG are synthesized to different antigenic determinants of these proteins.

Various technologies are reported to ensure low-allergenic properties of dairy products as follow: isolation of protein substances using specific sorbents, physical effect on protein molecules, protein proteolysis affected by enzyme preparations [9]. It results in conformational transitions in protein molecules causing changes in the structure and digestibility of denatured proteins, as well as the destruction or access restriction to antigenic epitopes [10, 11].

The most challenging approach to reduce the allergenicity of dairy products is the biocatalytic conversion of milk proteins focused on obtaining hydrolysates thereof with specified molecular mass distribution and residual antigenicity. The specificity of proteolytic enzymes with respect to the type of peptide bond is one of the main properties of such systems that allow obtaining food products of various level of protein hydrolysis. The use of enzymatic hydrolysates as a protein component of specialized products is aimed at reducing or eliminating the milk protein allergenicity and concurrent eliminating the risk of the body sensitization. In addition, hydrolysed proteins are reported to have certain physiological effect on the human body resulting from the accelerated indigestion process of short-chain peptides in the intestinal tract as compared with native proteins and amino acids [12].

To obtain the yogurt with the reduced residual antigenicity, we proposed to use β-lactoglobulin hydrolysate developed using enzymatic preparations Flavorpro 750MDP and Promod 439L [13]. It is a source of functional ingredients as follow: protein (3.18%, including the pure protein 1.17%), lactose (4.5%), calcium (84 mg%), phosphor (157 mg%), magnesium (10 mg%), potassium (102 mg%), retinol (0.03 mg%), tocopherol (0.03 mg%), Vitamin C (1.17 mg%), pyridoxine (0.07 mg%), riboflavin (0.14 mg%), thiamine (0.035 mg%), vitamin PP (0.05 mg%) [14]. As components of the β-lactoglobulin hydrolysate, calcium and phosphor are at the ratio best effective for indigestion, where the balanced content of essential aminoacids ensures its high biological value and digestibility. The biofunctional properties studied *in vitro* and *in vivo* proved that resulting from the cheese whey bioconversion, the hydrolysate obtained is described to have the antioxidant, hypolipidemic and hypocholesteremic action.

The specific whey flavor of the hydrolysate may be eliminated by the lactic acid fermentation since lactic acid microorganisms are known for their ability to use certain amino acids and peptides as a source of nitrogen for their metabolic needs. This accelerates the fermentation process and avoids the potential bitter taste of the finished product.

The proportioning of the normalized formula and the β-lactoglobulin hydrolysate was of great importance when developing the formulation since hydrolysis products (peptides, amino acids) are known for their bitterness. Challenging was to ensure a decrease in antigenicity and acceptable organoleptic properties of the sour-milk drink obtained. To this end, the feasibility to introduce various mass fractions of β-lactoglobulin hydrolysate to normalized mixtures was studied (Table 1). The change in the ratio of casein to whey proteins in the normalized formula resulting from β-lactoglobulin hydrolysate available in the formulation may cause a decrease in the ability of the mixture to acid gelation due to different spatial structure of molecules [15].

Monomeric casein components are associated in submicelles resulting from the hydrophobic and weak electrostatic interaction, and also due to the formation of phosphate-calcium bridges. The high content of proline uniformly distributed over the surface of casein micelles prevents the formation of the compact globular structure. The decrease in the surface potential results in reduction of the thickness of micelles hydrated shell and the strength of their intermicellar repulsion. When the isoelectric point is attained, the micelles are associated with gel formation or casein coagulation.

Table 1. Ratio of formulation ingredients in normalized formulas studied

Sample	Milk mix / β-lactoglobulin hydrolysate, %	Mass fraction of β-lactoglobulin hydrolysate, %	Weight ratio, % of total protein, %	Mass fraction of pure protein, %	Ratio casein/serum proteins/peptides + free amino acids	Mass fraction of lactose, %
Control	100/0	0.33	3.2	3.17	88/10/2	4.70
1	90 : 10	0.29	3.2	3.06	80/11/9	4.72
2	80 : 20	0.25	3.2	2.93	73/12/15	4.74
3	70 : 30	0.22	3.2	2.72	65/13/22	4.76

Serum proteins are known for the compact structure of spherical or ellipsoidal shape. Intramolecular disulfide bridges stabilize the folds of the polypeptide chain. Hydrophobic side chains are inside the molecules where polar and electrically charged groups are found on the surface that forms the hydrated shell with the help of hydrogen bonds. Electric charges are uniformly distributed over the surface with low total value thereof. These molecules form the hydrophilic sol that does not precipitate at the isoelectric point, and coagulates when the larger amount of electrolyte is added. Due to that, caseins coagulate at the isoelectric point unlike serum proteins that remain in the serum as dissolved [16].

For sour-milk drinks, the strength of the gel obtained is the quality parameter. It depends on the structure of aggregates formed, including on the strength and location of casein fibers, dimensions of cavities in the gel mesh. Gels with larger cells of the spatial structure are more delicate, too sensitive to physical impact where the presence of large capillaries facilitates the retention of water by these gels. The excess content of denatured β-lactoglobulin bound to κ-casein prevents the heavier association of casein particles during the gel structure formation.

Since β-lactoglobulin hydrolysate added in the course of normalization process results in considerable changes in the ratio of casein/whey proteins/peptides and free amino acids, as well as in an increase in the lactose mass fraction in the mixture, the research aimed at studying the fermentation of normalized mixtures with β-lactoglobulin hydrolysate in view of the ability of starter microorganisms to synthesize exopolysaccharides (EPS) and to participate in the formation of structural and mechanical properties of the finished product. EPSs are known for the certain physiological effect. The availability of these substances increases the time for the consumed product to be ingested in the gastrointestinal tract that may be useful for the short-term colonization of probiotic bacteria.

OBJECTS AND METHODS OF STUDY

Research objects are the normalized formulas with β-lactoglobulin hydrolysate obtained by using enzyme preparations Flavorpro 750MDP and Promod 439L (STO 00426012-005-2014) [11] and the yogurt based on them.

Pilot studies were conducted at the base of The Federal Research Centre "Fundamentals of Biotechnology" of the Russian Academy of Sciences, Christian Hansen LLC, the Voronezh State University of Engineering Technologies and the Federal Research Centre ofNutrition and Biotechnology (Russian Federation).

Research methods are standard and common for research practice, as well as modified, improved and specific implemented by using the advanced equipment and information technologies to assess properties of raw materials, semi-finished products and food products.

To isolate EPSs from the resulting sour-milk coagulum, pronase and sodium azide were used. The enzymatic reaction was blocked by boiling followed by centrifugation to separate germ cells and proteins. EPS was coagulated by adding ethanol and sodium chloride solution at the concentration of 5 mol/dm^3 to the supernatant. Prior to the test, the EPS was dissolved in the distilled water. The EPS concentration in the resulting solution was determined by the colorimetric phenol-acid method [17]. As a standard substance, glucose was used.

The structural and mechanical properties of yogurts were evaluated using the Brookfield RVDV-II + Pro rotary viscometer (USA). The mechanical stress was determined as the function of shear rate. The mechanical shear was established by the time of increase or decrease in the shear rate. The study results were evaluated by the deflection curve used to calculate the apparent (effective) viscosity at different shear rates, as well as hysteresis (cyclic zone between the upper and lower curve).

The impact of the mass fraction of β-lactoglobulin hydrolysate added and the type of starter culture used on the viscosity of the finished product was evaluated upon the fermentation of the normalized mixture for 5–6 hours at the temperature of (40 ± 2)°C [18, 19].

The experimental study results have been processed using the method of mathematical statistics as the data of various experiments were evaluated in triple sequence. Calculations, plotting and description thereof were supported by the Brookfield Rheocalc32 software and Microsoft Office 13 Application for Windows 8. The MathCad 16.0 application software package was used for graphical interpretations and data processing. The results obtained are known for high reproducibility, mutual consistency of test values and the correct statistical processing.

The study results were validated under factory conditions at the PJSC Dairy Plant "Voronezhsky" (Voronezh, Russian Federation).

RESULTS AND DISCUSSION

In compliance with the technical regulations of the Customs Union "On safety of milk and dairy products" TR TS 033/2013, a mixture of strains of *Lactobacillus bulgaricus* and *Streptococcus thermophilus* is used to produce the product line of yogurt [20].

As the strains are added to the normalized milk, they rapidly multiply since the mixture acidity furthers their growth. At the initial stage, they use free amino acids of milk to synthesize proteins and enzymes in the course of their activity the amount of which decreases during the first hours of culturing. Further on, the proteolytic decomposition of milk proteins occurs when exoenzymes of bacterial cells are generated. Concurrently, to obtain the right volume of energy, lactose is fermented by lactic-acid bacterium to form the lactic acid [21]. As they multiply, the lactic acid intensely accumulates, the medium pH decreases and at pH = (4.6–4.7) the milk proceeds to gel formation.

The lactic acid formation determines the process of protein coagulum formation to define the consistency of the finished product. It adds some pleasant and sourish flavor to the yogurt, and its content depends on the composition of the normalized formula, the

composition of the bacterial starter and process parameters. It is known that when mixed cultures of lactic microorganisms are used, the rate of acid formation is higher than separate strains are used [21]. This is due to the fact that resulting from the symbiosis, the cultures known for weak proteolytic activity (for example, *Str. Thermophilus*) are stimulated by cultures with higher activity (*Lbm. Bulgaricus*) that ensures an increase in the overall degree of protein hydrolysis. Therefore, the possibility to use the formula of various starter cultures has been studied to produce the high quality yogurt. When selecting strains of microorganisms the following factors were considered:
– maximum dynamics of acid formation during fermentation in the medium with high content of free amino acids;
– high capacity of starter cultures to synthesize exopolysaccharides that compact the product consistency by binding unbound moisture and slowing the serum separation.

EPSs are the carbohydrates of high molecular weight consisting of repeated residues of monosaccharides. The concentration of EPS found in fermented milk products usually ranges from 50 to 600 mg/dm^3 depending on the culture and fermentation conditions. The amount of EPS is also dependent on the structure of the growth medium, especially the presence of carbon and nitrogen sources [22]. The ability to produce EPSs is common among some lactic bacteria, in particular, in some strains of *S. thermophilus*, *Lb. Bulgaricus* and *Lactococcus lactis subsp. cremoris* that are widely used in production of sour-milk drinks.

The EPS bio-synthesis may be divided in two stages: The first stage is the central carbohydrate metabolism when precursors of nucleotide sugars are formed. On the second stage, nucleotide sugars are combined to form the oligosaccharide repeating unit that polymerizes and is released. These stages are encoded in genes in the EPS gene cluster, for example, in the chromosome of *S. thermophilus*. The production of EPS is unstable, they may break down when cultivating microorganisms. This may result in the loss of plasmids in their cells as a result of mobile genetic element emergence or DNA erasure, as well as of DNA rearrangement [22].

The milk gel containing EPS is the mixture of bio-polymer proteins and EPS along with other components. The properties of this mixture depend on whether the bio-polymers are segregational at certain concentration (thermodynamically incompatible, resulting in aggregation of molecules of the similar type or in phase separation), compatible (coexisting in solution) or associative (capable of complex aggregation) [22, 23]. In this case, their charge is important since it is known that direct interaction can occur between negatively charged EPS and the protein structure only. This makes it possible to obtain the protein coagulum of high gloss and viscosity and of low degree of strength and syneresis.

The reason of syneresis may be the casein particle restructuring in the gel structure and the degree of dissolution of the colloidal calcium phosphate during the coagulum formation. The protein structure compression, as well as the internal pressure of the coagulum and protein sedimentation during storage may also cause the syneresis. This phenomenon results in the reduction in the shelf life of fermented milk products, so it is undesirable for the process cycle.

It is established that the maximum volume of EPSs was produced by cultures fermented by F-DVS YF-LX700 (Fig. 1). This sample of yogurt was known for its high viscosity, low syneresis and higher resistance to stirring. The reduction in serum separation in the finished product is due to resulting EPSs that further bind the protein mesh encasing the serum by its strands. The syneresis prevention is directly proportional to the EPS concentration (the higher is the EPS content, the better is the encapsulation).

All the samples studied may be classified as pseudo-plastic rheological objects described by the Ostwald equation and are known for their coagulation-condensation structure [24]. Their response to the applied deformation varied depending on the shear rate. The presented rheological curves describe the properties of structured systems that characterizes intermolecular interaction between the EPS and the protein coagulum in all fermented drinks. Hereat, the plastic flow of milk gels and disproportionate dependence between the shear rate and internal stress in samples were noted. The transition of tested samples to the state of spreadable flow upon application of the constant load resulted in stabilization of viscosity values of mixtures corresponding to the horizontal section of curves. The tested food systems had stable structures. As the shear rate increased, the viscosity of samples reduced to be explained by the breakdown of the protein coagulum structure. The maximum values of critical shear stress were reported in drinks produced by using starters F-DVS YF-LX700 and F-DVS YoFlex Harmony 1.0 (Fig. 2).

It was found that an increase in the mass fraction of β-lactoglobulin hydrolysate in the normalized mixture resulted in the decrease in the critical shear stress of yogurt samples (Fig. 3). An inverse relationship between the viscosity and stability of the resulting milk gel was reported. The concept of stability includes the values of elastic and viscous modulus, depends on the length of load application and is the qualitative parameter of organoleptic yogurts properties.

Studies have been conducted to change rheological properties of yogurt samples produced by using fermentation starters F-DVS YF-LX700 and the control sample (*Str. thermophilus* and *Lbm. delbrueckii subsp. bulgaricus*) upon the destruction (loading) and subsequent reconstitution (unloading) of the structure (Fig. 4). During the stress phase in sour-milk drinks, the reversible structural decomposition occurred resulting in the decrease in the sample viscosity. During the phase of discharge, the structure of tested samples partially reconstituted.

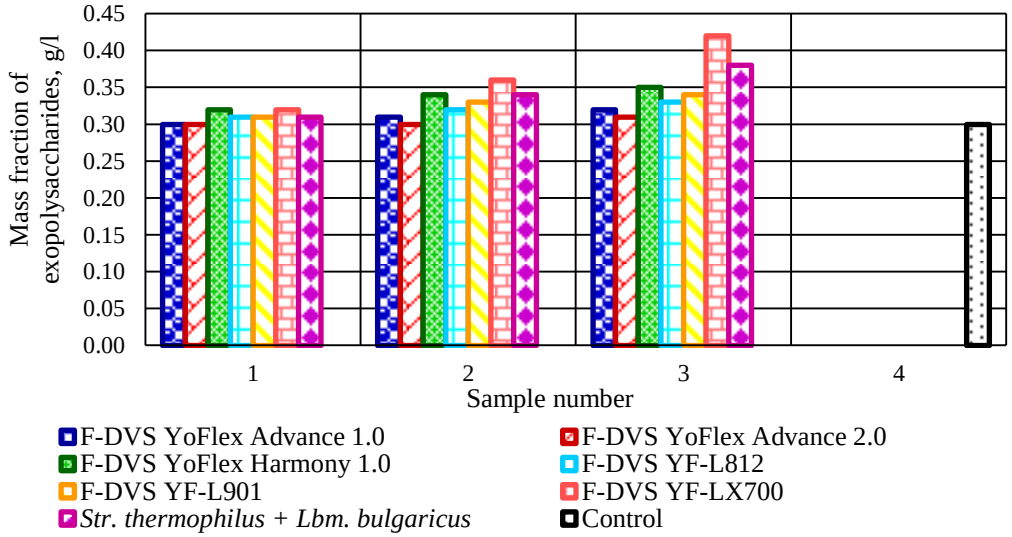


Fig. 1. Content of EPS in yogurt samples.

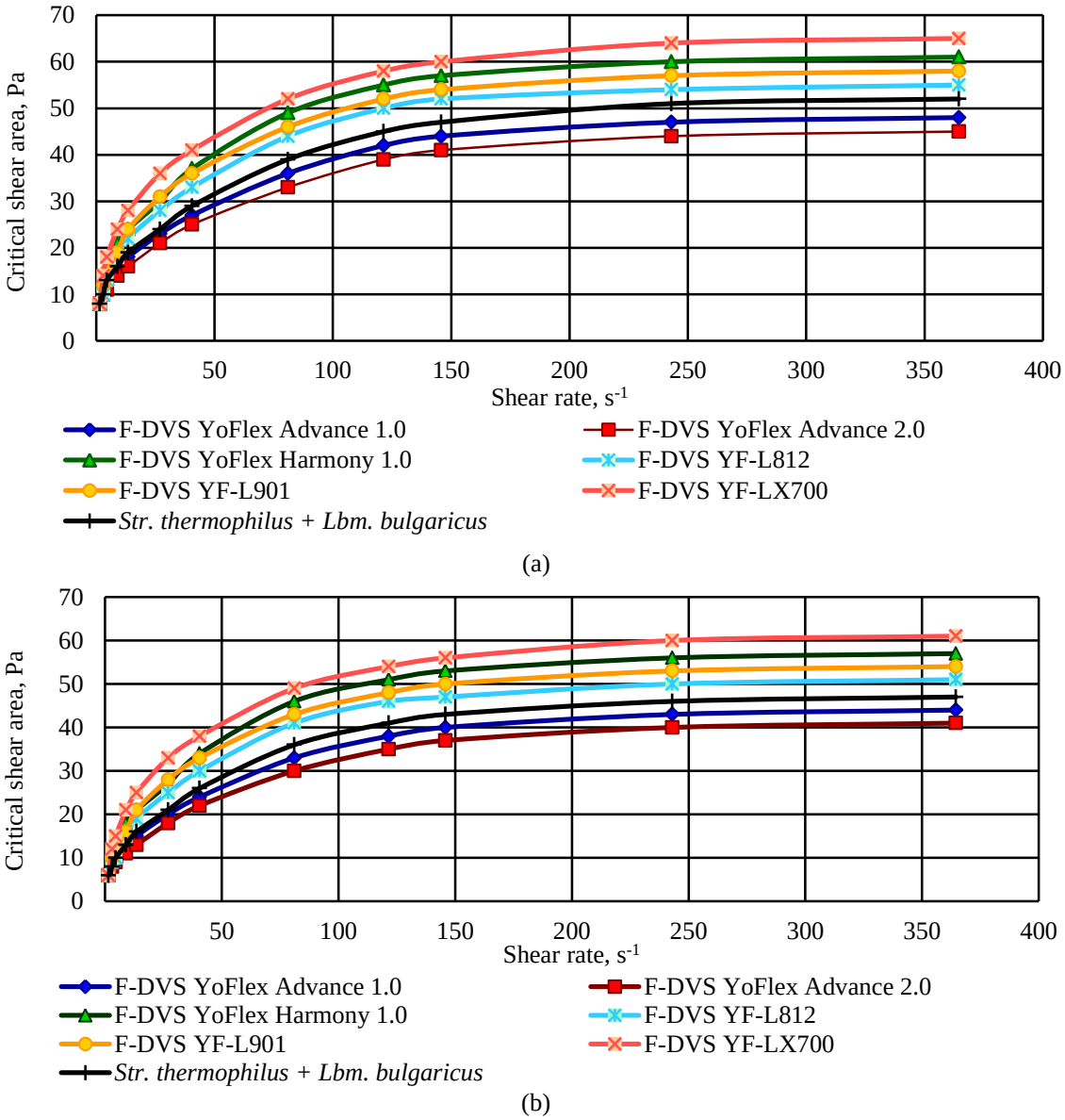
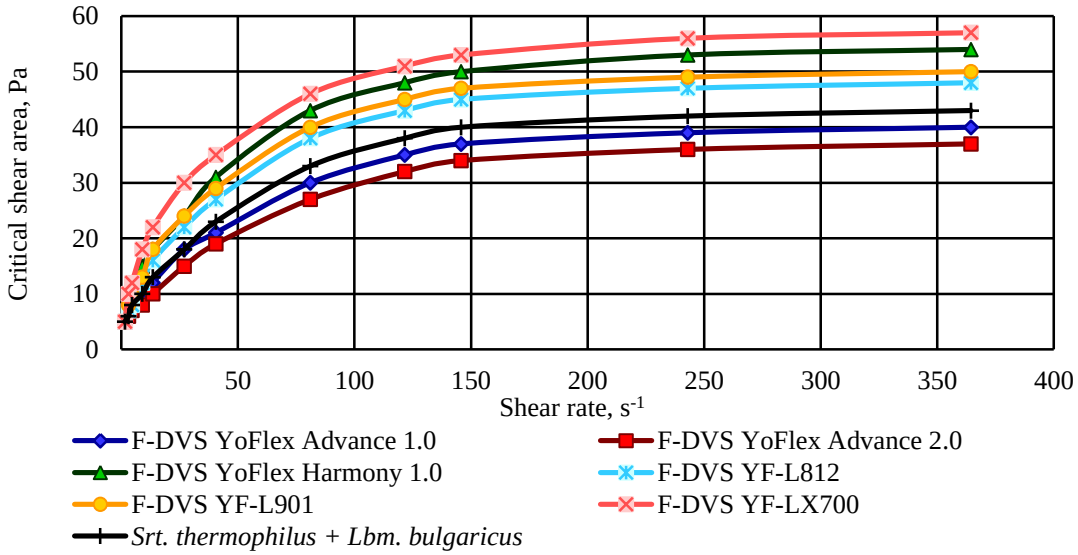
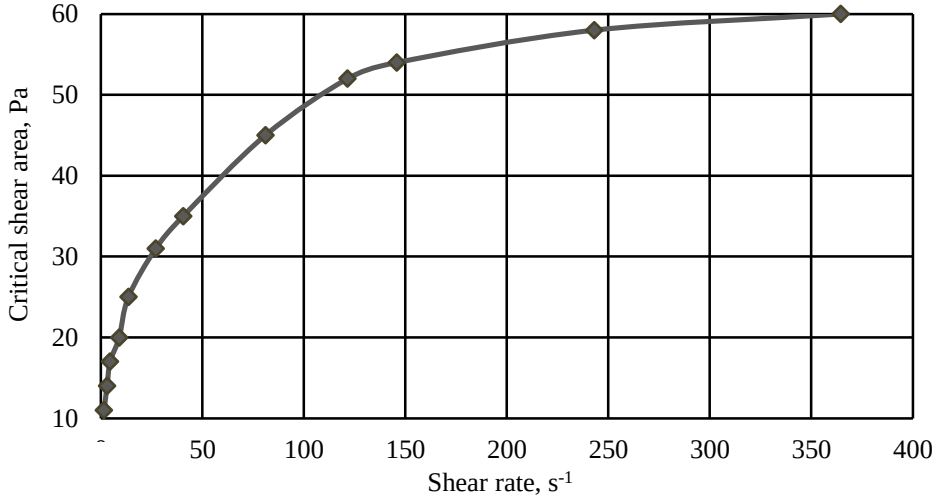


Fig. 2. *Beginning.* Graphic expression of the dependence of critical shear stress on the shear rate of yogurt samples: (a) no. 1; (b) no. 2; (c) no. 3; (d) of control sample.



(c)



(d)

Fig. 2. *Ending.* Graphic expression of the dependence of critical shear stress on the shear rate of yogurt samples: (a) no. 1; (b) no. 2; (c) no. 3; (d) of control sample.

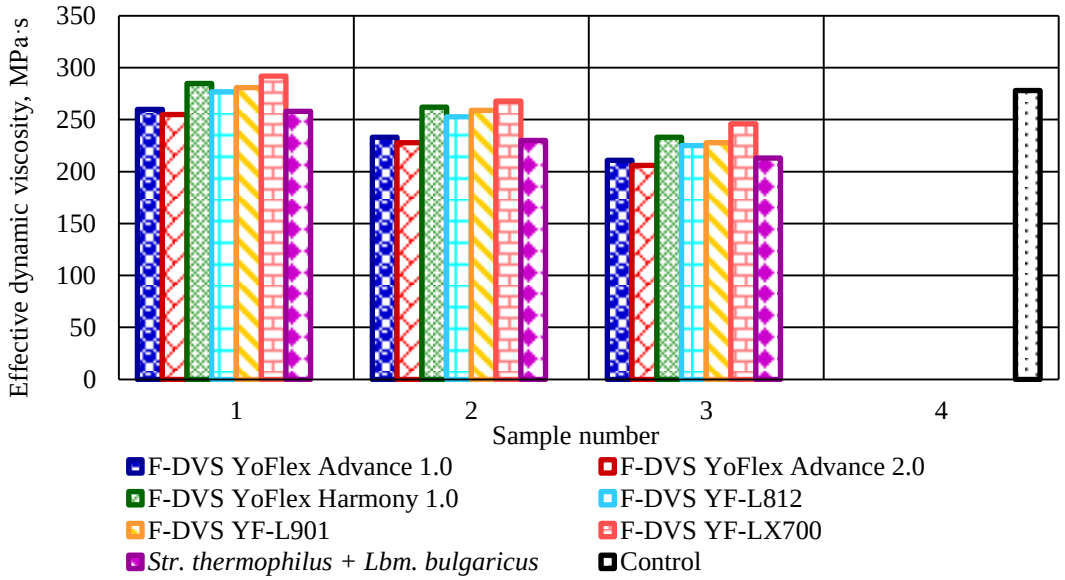


Fig. 3. Effective dynamic viscosity of yogurt samples (at the share rate of 300 s^{-1}).

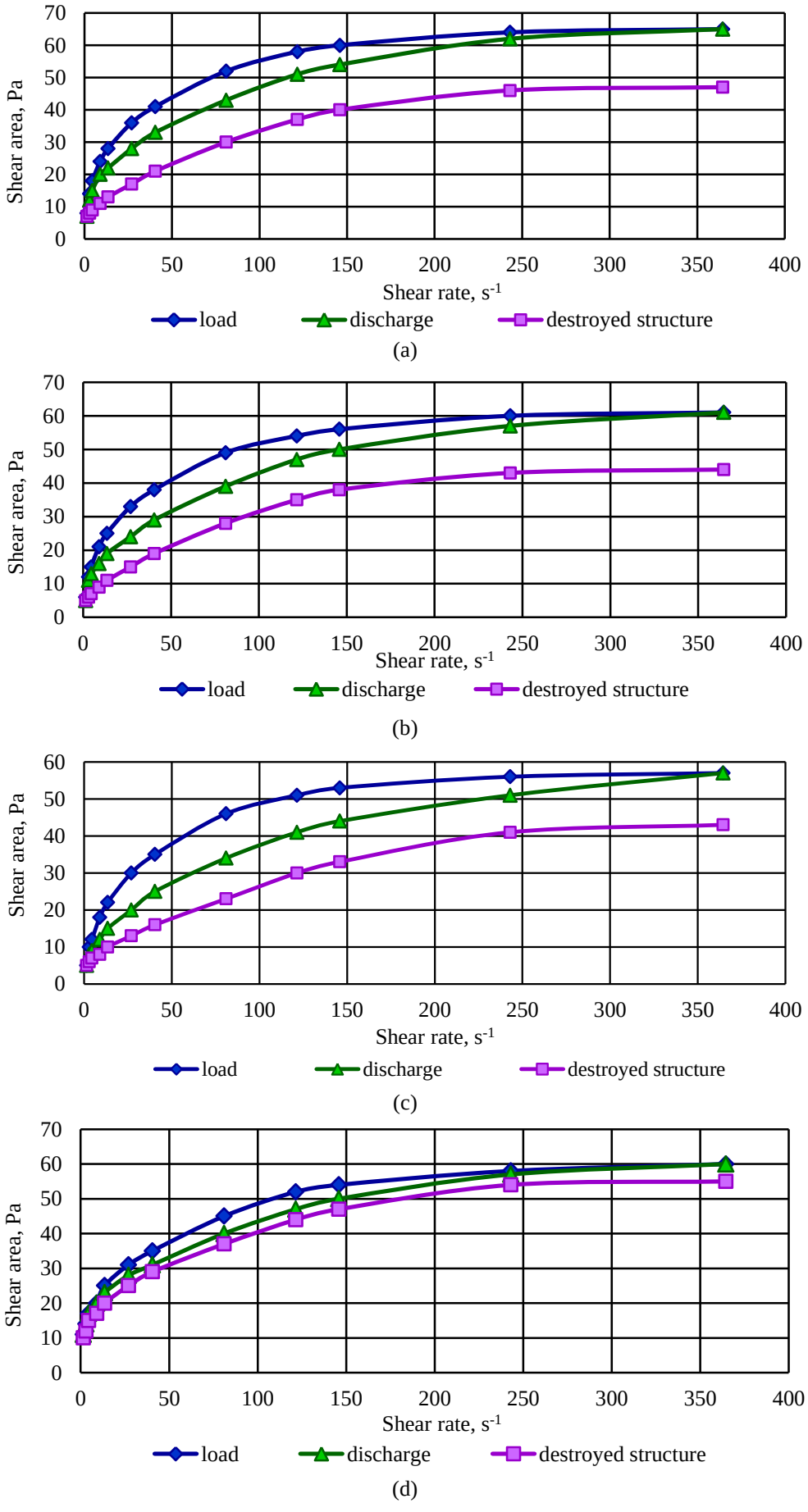


Fig. 4. Graphic expression of the dependence of critical shear stress on the shear rate of yogurt samples: (a) no. 1; (b) no. 2; (c) no. 3; (d) of control sample.

The area of the hysteresis loop (as a percentage of area under the upper curve) is not a direct physical parameter of viscosity. However, the high level of hysteresis in yogurts containing EPS means that these products are less able to reconstruct the structure upon the failure by shear. The structure of the sour-milk drink partially breaks down in the rheometer and in the mouth when having meal. Thus, in case of shear, EPS are likely to be redistributed into large clusters into the intermediate continuous phase and surrounded by acidified casein helium particles obtained by breaking the initial gel. As a result of thermodynamic incompatibility between the casein and EPS, the intermediate phase slows the protein fragment reassociation. Therefore, yogurts containing EPS are reported to have a higher level of hysteresis with respect to the product obtained by using the traditional technology.

Thus, it is established that an increase in the mass fraction of β-lactoglobulin hydrolysate, and accordingly, in the mass fraction of free amino acids in the normalized mixture will promote an increase in the rate of starter microorganism growth. This is due to the fact that a larger number of amino acids are required for the life of lactic bacteria and the thermophilic streptococcus is known to have the maximum need for this growth factor [21].

However, by the results of studies completed, it was found unreasonable to replace over 20% of whole milk with β-lactoglobulin hydrolysate during normalization, since such replacement resulted in an increase in the mixture acidity and prevented the normal growth and development of *Streptococcus thermophilus*, the basic exopolysaccharide producer. This may be explained by that the optimum of enzyme action triggered by the yogurt ferment varies within pH = (5.7–6.0), and at pH below 5.0 their activity reduces for 50% [21]. At the same time, the length of fermentation increased up to 5–6 h as the mass fraction of β-lactoglobulin hydrolysate increased. The viscosity of the resulting coagulum increased due to the reaction of exopolysaccharides with the protein gel mesh and fixation thereof on the surface of protein matrix.

Based on researches conducted, the component formulation for the low-allergenic yogurt was developed providing for 20% replacement of the normalized milk mixture with β-lactoglobulin hydrolysate, elimination of the stabilizer as compared with the control sample and the reduction of the residual antigenicity of the finished product to 48.5% relative to the sour-milk drinks produced by standard technology.

To validate low-allergenic properties of the yogurt obtained, its clinical and physiological properties were evaluated at the Allergology Department of the Federal Research Centre of Nutrition and Biotechnology. By the results of clinical chemical and immunological studies it has been established that the content of high-molecular protein structures does not exceed 57.5% of the total protein-peptide material, and not more than 44.4% of peptide-amino acid structures of the molecular masses less than 11.3 kDa.

Daily consumption of the yogurt obtained for 14 days by patients with known alimentary allergy did not result in changes in the level of serum concentration of total protein and circulating IgG and IgE antibodies specific for β-lactoglobulin. When the test product was added to the patients' diet, there was no statistically significant changes in the serum concentration of TBA-reactive products, as well as changes in the anion-exchange capacity of blood serum of patients relative to the peroxyl radical. This indicates that the lipid peroxidation is prohibited due to the high concentration of peptides with antioxidant properties in the finished product.

In compliance with the report by Federal Research Centre of Nutrition and Biotechnology, the sour-milk drink obtained was classified as the dietary (preventive) food product for children over 3 years of age with the known alimentary allergy to milk proteins.

The physical and chemical and microbiological properties of the finished product met requirements of TR TS No. 027/2012 "On safety of certain types of specialized food products, including dietary health food and dietary preventive nutrition", and TR TS No. 033/2013 "On safety of milk and dairy products". The low-allergenic yogurt was reported to have the mass fraction of physiologically functional ingredients, including vitamins, so it may be classified as the food of the functional product group.

Based on the study of microbiological, physical and chemical properties of the developed sour-milk drink during its storage, it has been established that its shelf life is no longer than 14 days at the temperature of 4 ± 2°C and the relative humidity of not more than 83%.

To produce the new sour-milk drink, the standard scheme was taken as the basis that specifies the use of additional operations to obtain the β-lactoglobulin hydrolysate. Due to application of commercially available equipment, the presented process scheme does not complicate the production process.

This process scheme is adapted to the HACCP system: the temperature, time intervals of temperature influence and residual antigenicity were taken as critical control points using the "decision tree" method. The application of this scheme in the technological process will ensure high quality, reduction of residual antigenicity, sanitary and hygienic safety, biological value and stability of properties of the finished product.

The technical documentation (TU 9222-512-00419785-13 “Lactic food products for dietary preventive nutrition”) was developed and approved, and the state registration certificate was obtained for the yogurt with the reduced allergenicity.

ACKNOWLEDGEMENTS

The researches were conducted as part of the Target Program of the Ministry of Education and Science of the Russian Federation “Research and Development in Priority Development Fields of Science and Technology Sector of Russia for 2007–2013”, State Contract no. 12.527.11.0008.

REFERENCES

1. Timush L.G. and Yusova O.V. *Sostoyanie rossiyskogo rynka kislomolochnykh produktov na konets 2015 goda* [The state of the Russian market of fermented milk products by the end of 2015]. *NOVAINFO.RU*, 2016, vol. 2, no. 40, pp. 69–77. Available at: http://novainfo.ru/article/4272. (accessed 27.06.2016).
2. Surzhik A.V., Kon' I.Ya., and Safronova A.I. Sovremennye predstavleniya o svoystvakh i pishchevoy tsennosti kislomolochnykh produktov i ikh ispol'zovanii v pitanii detey [Modern ideas on properties and nutritional value of fermented milk products and their use in children's nutrition]. *Voprosy detskoy dietologii* [Children's Dietology Issues], 2007, no. 5, pp. 54–58.
3. Belda-Ferre P., Alcaraz L.D., Cabrera-Rubio R., et al. The oral metagenome in health and disease. *The ISME Journal*, 2012 Jan., vol. 6(1), pp. 46–56. DOI: 10.1038/ismej.2011.85.
4. Borovik T.E., Ladodo K.S., Zakharova I.N., et al. Sour milk foodstuff in infants diet. *Voprosy Sovremennoi Pediatrii* [Current pediatrics], 2014, vol. 13, no. 1, pp. 89–95. DOI: http://dx.doi.org/10.15690/vsp.v13i1.916. (In Russian).
5. Rynok detskikh molochnykh smesey [Market of infant formula]. *Molochnaya sfera* [Diary Sector], 2014, no. 3(50), pp. 24–29.
6. Golovach T.N., Kurchenko V.P., and Survilo L.I. Antigennye svoystva nativnykh i termoobrabotannykh syvorotochnykh belkov i ikh fermentativnykh chastichnykh gidrolizatov [Antigenic properties of native and heat-treated whey proteins and their enzymatic partial hydrolysates]. *Trudy Belorusskogo gosudarstvennogo universiteta* [Scientific works of the Belarusian State University], 2011, vol. 6, part 1, pp. 209–223.
7. Antipova T.A., Felik S.V., Kuznetsov V.V., et al. Fermented milks with reduced allergenity for children. *Molochnaya promyshlennost'* [Diary Industry], 2013, no. 7, pp. 64–65.
8. Golovach T.N., Chervyakovsky E.M., and Kurchenko V.P. *Fiziko-khimicheskaya i immunokhimicheskaya kharakteristika chastichnogo gidrolizata syvorotochnykh belkov* [Physicochemical and immunochemical characteristics of partial hydrolyzate of whey proteins]. *Pishchevaya promyshlennost': nauka i tekhnologii* [Food Industry: Science and Technologies], 2011, no. 1, p. 28.
9. López-Fandiño R. Functional Improvement of Milk Whey Proteins Induced by High Hydrostatic Pressure. *Critical Reviews in Food Science and Nutrition*, 2006, vol. 46, no. 4, pp. 351–363. DOI: 10.1080/10408690590957278.
10. von Berg A., Filipiak-Pittroff B., Krämer U., et al. Allergies in high-risk schoolchildren after early intervention with cow's milk protein hydrolysates: 10-year results from the German Infant Nutritional Intervention (GINI) study. *Journal of Allergy and Clinical Immunology*, 2013, vol. 131, no. 6, pp. 1565–1573. DOI: 10.1016/j.jaci.2013.01.006.
11. von Berg A., Filipiak-Pittroff B., Schulz H., et al. Allergic manifestation 15 years after early intervention with hydrolyzed formulas – the GINI Study. *Allergy*, 2016, vol. 71, no. 2, pp. 210–219. DOI: 10.1111/all.12790.
12. Purohit D.H., Hassan A.N., Bhatia E., et al. Rheological, sensorial, and chemopreventive properties of milk fermented with exopolysaccharide-producing lactic cultures. *Journal of Dairy Science*, 2009, vol. 92, no. 3, pp. 847–856. DOI: https://doi.org/10.3168/jds.2008-1256.
13. Ponomareva N.V., Mel'nikova E.I., and Bogdanova E.V. Bioconversion of milk proteins aimed at reducing of their residual antigenicity. *Biotechnology in Russia*, 2015, no. 1, pp. 70–74.
14. Ponomareva N.V. and Melnikova E.I. Composition and properties of the hydrolyzate of the p-lactoglobulin with reduced residual antigenicity. *Molochnaya promyshlennost'* [Diary Industry], 2015, no. 8, pp. 46–47. (In Russian).
15. Chatterjee A., Kanawjia S.K., and Khetra Y. Properties of sweetened Indian yogurt (mishti dohi) as affected by added tryptic whey protein hydrolysate. *Journal of Food Science and Technology*, 2016, vol. 53, no. 1, pp. 824–831. DOI: 10.1007/s13197-015-1768-5.
16. Smirnova I.A., Gralevskaya I.V., Shtrigul V.K., and Smirnov D.A. Investigation of various ways of milk coagulation for the purpose of milk protein microparticles formation. *Food Processing: Techniques and Technology*, 2012, no. 3(26), pp. 112–120. (In Russian).
17. Cui S.W. and Brunner Y. *Food carbohydrate chemistry, physical properties and applications. Chapter 2. Understanding carbohydrate*. CRC Press, Taylor &Fracis Group, 2005. 432 p.
18. Losev A.N., Melnikova E.I., and Stanislavskaya E.B. Fermented milk drink with microparticulate of whey protein. *Pishchevaya promyshlennost'* [Food processing industry], 2015, no. 12, pp. 36–38. (In Russian).
19. Golubeva L.V., Dolmatova O.I., Gubanova A.A., and Grebenkina A.G. Studying the process of syneresis of fermented drinks. *Pishchevaya promyshlennost'* [Food processing industry], 2015, no. 4, pp. 42–43. (In Russian).
20. *TR TS 033/2013. Tekhnicheskiy reglament Tamozhennogo soyuza «O bezopasnosti moloka i molochnoy produktsii», 9 oktyabrya 2013 goda № 67* [TR TS 033/2013. Technical Regulation of the Customs Union "On safety of milk and diary products", dd. Oct. 9, 2013 No. 67]. Kazan', 2013. 192 p.
21. Chramostová J., Mošnová R., Lisová I., Pešek E., et al. Influence of cultivation conditions on the growth of *Lactobacillus acidophilus*, *Bifidobacterium* sp. and *Streptococcus thermophilus*, and on the production of organic acids in fermented milks. *Czech Journal of Food Sciences*, 2014, vol. 32, no. 5, pp. 422–429.

22. Gentès M.-C., St-Gelais D., and Turgeon S.L. Gel formation and rheological properties of fermented milk with in situ exopolysaccharide production by lactic acid bacteria. *Dairy Science & Technology*, *EDP sciences/Springer*, 2011, vol. 91, no. 5, pp. 645–661. DOI: 10.1007/s13594-011-0039-0.
23. Feldmane J., Semjonovs P., and Ciprovica I. Potential of exopolysaccharides in yoghurt production. *International Journal of Biological, Biomolecular, Agricultural, Food and Biotechnological Engineering*, 2013, vol. 7, no. 8, pp. 767–770.
24. Melnikova E.I., Stanislavskaya E.B., and Korotkov E.G. Preparation and use of whey proteinmicroparticulate in synbiotic drink technology. *Foods and Raw Materials*, 2015, vol. 3, no. 2, pp. 96–104. DOI: 10.12737/13125.

Please cite this article in press as: Ponomarev A.N., Melnikova E.I., Bogdanova E.V., and Kharitonov D.V. Impact of betalactoglobulin hydrolysate on structural and mechanical properties of allergenic potency-restricted yogurt. *Foods and Raw Materials*, 2017, vol. 5, no. 1, pp. 41–50. DOI: 10.21179/2308-4057-2017-1-41-50.

FORMATION AND STUDY OF SYMBIOTIC CONSORTIUM OF LACTOBACILLI TO RECEIVE A DIRECT APPLICATION STARTER

S. A. Sukhikh[a,*], V. Yu. Krumlikov[a], A. O. Evsukova[b], and L. K. Asyakina[a]

[a] Kemerovo Institute of Food Science and Technology (University), Stroiteley blvd. 47, Kemerovo, 650056, Russian Federation

[b] All-Russia Scientific Research Institute of Technology of Canning, Shkol'naya Str. 78, Moscow region, Vidnoe, 142703, Russian Federation

* e-mail: stas-asp@mail.ru

Received April 10, 2017; Accepted in revised form May 30, 2017; Published June 29, 2017

Abstract: One of the ways of formation of innovative products is the design of new types of direct application starters on the basis of viable microorganisms for their further use in the dairy industry. The purpose of the study was the isolation of lactobacilli activators of lactic fermentation made of national Kazakh drinks (ayran, koumiss, chegen and kurunga) for the formation of symbiotic consortium to receive a direct application starter. The authors have isolated and studied the following strains of microorganisms: *Lactobacillus delbrueckii subsp. bulgaricus*, *Lactobacillus acidophilus*, *Streptococcus thermophiles*, *Lactococcus lactis subsp. lactis*, *Lactococcus lactis subsp. lactis biovar diacetilactis*, *Lactobacillus paracasei*, *Lactobacillus fermentum*, *Pediococcus damnosus*, *Pediococcus acidilactici*, *Lactobacillus gallinarum*. Cultural, morphological and physiological and biochemical properties have been studied, the antibiotic resistance, antagonistic activity and biocompatibility of the isolated microorganisms have been determined. It has been established that the isolated microorganisms have a stick-like shape of 0.6 x 3.5 to 6.0 x 0.7 microns in size characteristic of the sort *Lactobacillus bacteria*, and are Gram-positive and nonspore-forming. Mobility was only observed in the strains *Lactococcus lactis subsp. lactis biovar diacetilactis*, *Pediococcus damnosus* and *Pediococcus acidilactici*. The strains differed considerably from each other by the consumption of other carbohydrates, however all the studied strains ferment ribose, D-galactose, D-glucose, D-fructose, D-mannose, N-acetyl-glucosamin, amygdalin, aesculin, salicin, cellobiose, maltose, lactose, D-sucrose which is characteristic of the representatives of the sort *Lactobacillus*. All the studied strains are sensitive to the effect of β-laktam antibiotics except *Streptococcus thermophilus*. The analysis of biocompatibility has shown that full compatibility is only characteristic of four strains – *Lactobacillus gallinarum* (kurunga), *Streptococcus thermophilus* (koumiss), *Lactococcus lactis subsp. lactis* (ayran) and *Pediococcus damnosus* (chegen). To create a symbiotic consortium such strains of microorganisms as *Lactobacillus gallinarum, Streptococcus thermophilus, Lactococcus lactis subsp. lactis and Pediococcus damnosus* and optimum conditions of cultivation have been chosen. The maximum growth of microorganisms has been noted in the following culture medium: proteose-peptone – 5.00; meat extract – 10.00; yeast extract – 5.00; glucose – 20.00; Tween-80 – 1.00; ammonium citrate – 1.00; manganese sulfate – 0.05; sodium hydrophosphate – 1.00; agar-agar – 15.00; methyl rosaniline – 0.0002; casein hydrolyzate – 12.50; papain digest of soy flour 2.50; sodium chloride – 3.00; sodium citrate – 0.50; sodium sulfite – 0.20; L-cystine – 0.05; sodium azide – 0.10; potassium phosphate dibasic – 0.50; ammonium citrate dibasic – 0.80.

Keywords: Consortium of microorganisms, lactobacilli, dairy products, microorganism isolation, direct application starter, antagonistic properties, antibiotic resistance, identification of microorganisms, symbiotic systems

DOI 10.21179/2308-4057-2017-1-51-62 *Foods and Raw Materials*, 2017, vol. 5, no. 1, pp. 51–62.

INTRODUCTION

The problems of production and consumption of dairy products become more and more relevant and increasingly dependent on the general tendencies of development of the world food market [1]. Changes in the development of dairy business which are already determined by the processes of globalization of the world economy, the changes of the social food patterns of the population which are reflected in the structure of agrofood markets, the growth of level of information and technical support, the deterioration in the ecological situation and the achievements of world science in the field [1, 2] can already be observed in practice.

According to experts, only 8-12% of the health of a nation depend on the health system while the percentage of influence on the health of social and economic conditions and mode of living is 52–55%, at the same time one of the main components is the food factor [3, 4].

Improper feeding is the frequent reason of the development of malfunction of a lot of organs and

systems. It is possible to influence metabolism and the adaptive and compensatory abilities of an organism by changing feeding habits. Now the developments of healthy food products that meet the evidence-based recommendations about the balanced diet of the population [4] are being performed. The main orientation of these studies is the improvement of metabolism and the increase in the immune properties of an organism by the correction of the protein, fat and carbohydrate component of the product.

Sour-milk products make a sizable group of healthy food products. The useful properties of sour-milk products are, first of all, that they improve metabolism, stimulate the exudation of gastrointestinal juice and are the source of highly digestible calcium. The presence of the microorganisms in their structure capable to survive in intestines and to supress putrefactive microflora provides the inhibition of putrefactive processes and the termination of formation of poisonous proteolysis products flowing into human blood [5, 6].

Starters are pure cultures or the mix of pure cultures of the lactic bacteria added into milk to obtain high-quality sour-milk products by means of lactic and spirit fermentation.

Starters consisting of different strains and often of different types and sorts of microorganisms, as well, are applied to produce sour-milk products [7]. It allows to improve the starter resistant to adverse effects [8].

Starters are usually prepared on the basis of monocultures or of the mechanical mix of several strains. The most often applied lactobacilli which are the causative agents of lactic fermentation are: *Lactobacillus delbrueckii*, *Lactobacillus acidophilus*, *Lactobacillus bulgaricus, Lactobacillus ptantarum*., *Lactobacillus brevis* and *Lactobacillus helveticus* [9, 10].

However such starter cultures are often insufficiently effective. The abstract concepts allow to believe that it is preferable to use symbiotic cultures of microorganisms. The elaboration of combined direct starters is due to a new approach – the creation of the artificial symbiotic systems that have a wide range of necessary characteristics [11].

In this regard, the development of the evidence-based approaches based on the study of physiological and biochemical and industrially valuable properties of lactic microorganisms of various groups is relevant when making combined starters of direct application with a high activity.

The purpose of the work is the formation and study of symbiotic consortium of lactobacilli to obtain a direct application starter.

OBJECTS AND METHODS OF STUDY

The strains of microorganisms isolated from national Kazakh drinks became the object of scientific research:

– ayran in accordance with GOST 31702-2013 [12];

– koumiss in accordance with GOST R 52974-2008 [13];

– chegen (imported);

– kurunga in accordance with GOST 10382-85 [14].

The isolation of microorganisms from national Kazakh drinks was performed as follows: 1 ml of each of sour-milk drinks (ayran, kurunga, koumiss and chegen) was taken, culture media were added and plates and test tubes were incubated statically at a temperature of 37°C in a carbon dioxide medium for 1–5 days.

For primary isolation a lactic medium – sterile skim milk; MRS broth, brain heart infusion broth; milk agar – milk with agar of 3% in the ratio of 1 : 1; fish peptone agar and MRS agar were used.

Exhaustive sowings with the use of plates were performed from the test tubes with the visible growth of microorganisms (turbidity or the presence of a dairy clot) and from the combined lawns. The isolated microorganisms were cultivated on the agarized media (fish peptone agar, MRS agar and milk agar), cloned to pure cultures and their genetic identification and the analysis of antimicrobic properties were performed.

The study of phenotypical and morphological properties of microorganisms was performed in a dense medium – MRS agar, g/l: bacto-peptone – 10.0; meat extract – 10.0; yeast extract – 5.0; glucose – 20.0; Tween – 1.0; ammonium citrate – 2.0; sodium acetate – 5.0; sodium hydrophosphate – 2.0; magnesium sulphate 7-water – 0.1; manganese sulfate 5-water – 0.05; agar – 20.0.

In the course of study the diameter of colonies, color, their form, consistence, structure, surface and edge pattern were determined.

The main method to study the morphology of bacteria is the microscopy of the fixed stained medicines. The microscopic examination was performed with the use of the biological microscope Axio Scope A1 ("Carl Zeiss", Germany). The determination of sizes of cells of the studied cultures of microorganisms was performed with the use of an ocular ruler and an object micrometer.

The differentiation of bacteria by the biochemical properties of their cellular wall was performed according to Gram with the use of a set for Gram staining ("Lab-Biomed", Moscow). The essence of the method is that the cellular wall of Gram-positive bacteria tightly fixes gentian violet, does not become colourless after using ethanol and therefore does not perceive additional dye (fuchsin). Gentian violet is easily washed away by ethanol from the cell in Gram-negative microbes, and they are stained by additional dye.

The staining of bacteria spores was performed according to Schäffer-Fulton. The essence of the method is the combined effect of concentrated solution of ethyl green dye and temperature on the low-permeable spore exine with the further decoloration of cytoplasm of a vegetative cell and its contrast finishing dyeing using safranin. Spores are stained in green and cells in red during the microscopic examination.

The existence of flagella is established by the study of cultures for vagility in "the crushed drop" medicines.

The determination of physiological and biochemical properties of strains of microorganisms was performed with the use of microtests – the API-50

test systems (Promix, Russia) or the indicator paper systems which are a set of plastic holes with indicators.

The antibiotic resistance of the considered lactic bacteria was analyzed by means of a set of the disks impregnated with different types of antibiotics. The antibiotic disks were plated on a dense culture medium sowed by the culture of the studied strain and were cultivated for a day at a temperature of 37°C. Then the diameter of inhibition zone around the disks was measured.

The antagonistic activity was studied with the use of the following test strains: *Escherichia coli* B-6954, *Bacillus fastidiosus* B-5651, *Pseudomonas fluorescens* B-3502, *Pseudomonas aeruginosa* ATCC 9027, *Leuconostoc mesenteroides* B-8404, *Candida albicans* ATCC 885-653 and *Staphylococcus aureus* ATCC 25923 based on a dense culture medium using a diffusive method. In this regard, the test strain was plated on an agarized culture medium (fish peptone agar) in the form of lawn and the lawn at the same time was covered with the paper discs impregnated with lactobacillus metabolites (10 µl per disc). A disk with the MRS medium was used as a control sample, and disks with the antibiotics ciprofloxacin and gentamycin from a standard set were used as comparison medicines. The plates were incubated at 37°C for 24 hours. The results were taken into account by the presence and size (in mm) of the transparent zone of non-growth of microorganisms around the disc.

The study of biocompatibility of microorganisms was performed using the method of co-culture on a dense MRS culture medium. The diurnal culture grown up on a liquid culture medium and standardized according to the standard of turbidity was put on the surface of dense culture medium in the form of a bacteriological loop with a diameter of 3 mm. A drop of other tested culture which covered approximately half of the first drop when spreading was put on the surface of the same medium with the same volume after the absorption of the drop, having receded 1–2 mm from its edge.

In the superimposed part the cultures develop with a mutual presence (co-culture) competing with each other. After drying of the second drop the plate with crops was turned upside down and incubated at 28–32°C in the air medium. Each experiment was made with two repetitions, changing the position of cultures (to exclude the influence of sequence of stratification of drops of cultures on the nature of growth in the co-culture zone). The drops of the same culture layered on each other according to the technique described above were the control sample.

The account of results was performed in 24 and 48 h after the beginning of incubation. With the growth inhibition of one of the studied cultures the relations between them were considered as antagonistic, and the cultures themselves were assigned to the category of bioincompatible ones. The cultures were considered biocompatible in case of revelation of full merge of spots or an increase in the growth of the studied strains in the co-culture zone (mutualism, synergysm and satellism). If one of the cultures goes upward in the co-culture zone suppressing the growth of the second culture irrespective of the sequence of their application, such a variant was regarded as poor antagonism. The existence of a distinct oppression (growth inhibition) zone of one culture along the periphery of stain of the other tested culture was regarded as a sign of high antagonism.

The choice of optimum composition of culture medium for the cultivation of consortium of microorganisms was performed by means of variation of the ratio of components and the assessment of viability of consortium of microorganisms. The cultivation was performed at a temperature of 37.0 ± 2.0^{o}C, with the active acidity of 6.8 ± 0.2 and duration of 24 h.

RESULTS AND DISCUSSION

Table 1 provides the pure cultures of microorganisms isolated from dairy drinks.

The morphological properties of microorganisms are studied in stained medicines for the purpose of their differentiation, analyzing their geometry, size, Gram staining, the existence of spores, capsules and flagella [15]. The shape and size of bacteria are influenced by the composition of culture medium and the cultural variability of microorganisms [16].

Table 2 provides the results of study of cultural and morphological properties of the isolated strains of microorganisms.

Table 1. Results of isolation of microorganisms from national Kazakh sour-milk drinks

№	Name of the microorganism	Source of isolation
1	*Lactobacillus delbrueckii subsp. bulgaricus*	Koumiss, ayran
2	*Lactobacillus acidophilus*	Koumiss
3	*Streptococcus thermophilus*	Koumiss, ayran
4	*Lactococcus lactis subsp. lactis*	Ayran
5	*Lactococcus lactis subsp. Lactis biovar diacetilactis*	Ayran
6	*Lactobacillus paracasei*	Chegen
7	*Lactobacillus fermentum*	Chegen
8	*Pediococcus damnosus*	Chegen
9	*Pediococcus acidilactici*	Chegen
10	*Lactobacillus gallinarum*	Kurunga

ISSN 2310-9599. Foods and Raw Materials, 2017, vol. 5, no. 1

Table 2. Characteristic of the cultural and morphological properties of the strains of microorganisms isolated from national Kazakh sour-milk drinks

Parameters	Name of the microbial strain									
	Lactobacillus delbrueckii subsp. bulgaricus	*Lactobacillus acidophilus*	*Streptococcus thermophilus*	*Lactococcus lactis subsp. lactis*	*Lactococcus lactis subsp. lactis biovar diacetilactis*	*Lactobacillus paracasei*	*Lactobacillus fermentum*	*Pediococcus damnosus*	*Pediococcus acidilactici*	*Lactobacillus gallinarum*
Spore formation	–	–	–	–	–	–	–	–	–	–
Vagility	–	–	–	–	+	–	–	+	+	–
Size of bacteria (microns)	0.6 x 3.5	0.9 x 5.3	0.7 x 1.0	0.7 x 4.3	0.6 x 1.0	0.9 x 2.6	0.9 x 1.0	0.8 x 1.0	0.6 x 1.0	6.0 x 0.7
Shape	stick-like	stick-like	spherical	stick-like	spherical	stick-like	stick-like	spherical	spheri cal	stick-like
Edge pattern	fringed	wave-shaped	straight	fringed	straight	wave-shaped	wave-shaped	straight	straight	indistinct
Profile	flat	flat	convex	convex	convex	flat	convex	convex	convex	convex
Surface	smooth	rough	smooth	smooth	rough	smooth	rough	rough	rough	smooth
Color	creamy white	white	white	skin-colored	white	creamy white	skin-colored	skin-colored	skin-colored	grayish
Structure	homogeneous	homogeneous	homogeneo us	homogeneous	homogeneous	homogeneous	homogeneous	homogeneous	homogeneous	homogeneous
Consistence	dense	soft	soft	soft	soft	dense	dense	soft	soft	soft
Transparence	mat	mat	non-transparent	mat	non-transparent	mat	mat	non-transparent	non-transparent	mat
Gram-color staining	+	+	+	+	+	+	+	+	+	+

The results of studies of cultural and morphological properties of the microorganisms isolated from national Kazakh sour-milk drinks testify that the strains *Lactobacillus delbrueckii subsp. bulgaricus*, *Lactobacillus acidophilus*, *Lactococcus lactis subsp. lactisbiovar diacetilactis*, *Lactobacillus paracasei*, *Lactobacillus fermentum* and *Lactobacillus gallinarum* have a stick-like shape from 0.6 x 3.5 to 6.0 x 0.7 microns in size characteristic of bacteria of the sort *Lactobacillus*. The microorganisms are Gram-positive, nonspore-forming, vagility is only observed in the strains *Lactococcus lactis subsp. Lactis biovar diacetilactis*, *Pediococcus damnosus* and *Pediococcus acidilactici*.

Bacteria have a homogeneous structure soft in consistence. The consistence of colonies is only dense in *Lactobacillus delbrueckii subsp. bulgaricus*, *Lactobacillus paracasei* and *Lactobacillus fermentum*. The colonies of the studied microorganisms *Lactobacillus delbrueckii subsp. bulgaricus*, *Lactobacillus acidophilus*, *Lactococcus lactis subsp. lactis*, *Lactobacillus paracasei*, *Lactobacillus fermentum* and *Lactobacillus gallinarum* are mat, and the colonies of the strains *Streptococcus thermophilus*, *Lactococcus lactis subsp. lactis biovar diacetilactis*, *Pediococcus damnosus* and *Pediococcus acidilactici* are non-transparent.

The profile of colonies is various, too, thus, a flat profile of colonies was observed during the study in *Lactobacillus delbrueckii subsp. bulgaricus*, *Lactobacillus acidophilus* and *Lactobacillus paracasei*, and a convex profile of colonies in *Streptococcus thermophilus*, *Lactococcus lactis subsp. lactis*, *Lactococcus lactis subsp. lactis biovar diacetilactis*, *Lactobacillus fermentum*, *Pediococcusdamnosus* and *Pediococcus acidilactici*. At the same time the edge pattern in *Lactobacillus delbrueckii subsp. bulgaricus* and *Lactococcus lactis subsp. lactis* is fringed, and it is straight in *Streptococcus thermophilus*. *Lactobacillus gallinarum* is characterized by an indistinct edge of the colony while the edge pattern of the colony in *Lactobacillus acidophilus*, *Lactobacillus paracasei* and *Lactobacillus fermentum* is wave-shaped.

The smooth surface of the colony is observed in five strains of microorganisms (*Lactobacillus delbrueckii subsp. bulgaricus*, *Streptococcus thermophilus*, *Lactococcus lactis subsp. lactis* and *Lactobacillus paracasei* and *Lactobacillus gallinarum*), and it is rough in the others. According to the results of the study, the color of the studied microorganisms varies from white to skin and grayish. The color of the colony in *Lactobacillus gallinarum* is grayish, and the skin color is observed in the strains *Lactococcus lactis subsp. lactis* and *Lactobacillus fermentum*. Colonies of white color are formed by the microorganisms of *Lactobacillus acidophilus* and *Streptococcus thermophilus*.

For the purpose of deeper identification of bacteria a microscopic examination was performed using the inverted microscope AxioVert.A1 (Carl Zeiss, Germany). In the course of microscopic examination the size of particles, the area and number of colonies were determined, besides, photographing of the studied samples the results of which are presented in Fig. 1 was performed.

Then, the physiological and biochemical properties of the strains of microorganisms isolated from national Kazakh sour-milk drinks were studied. The identification of microorganisms only by cultural and morphological features is difficult due to the simplicity of geometry of microorganisms and the same structure of eukaryotic cell [17]. Besides, the physiological and biochemical properties allow to judge about the fitness of microorganisms to various external and internal factors of the environment and to increase the biomass of cultural cells to the maximum.

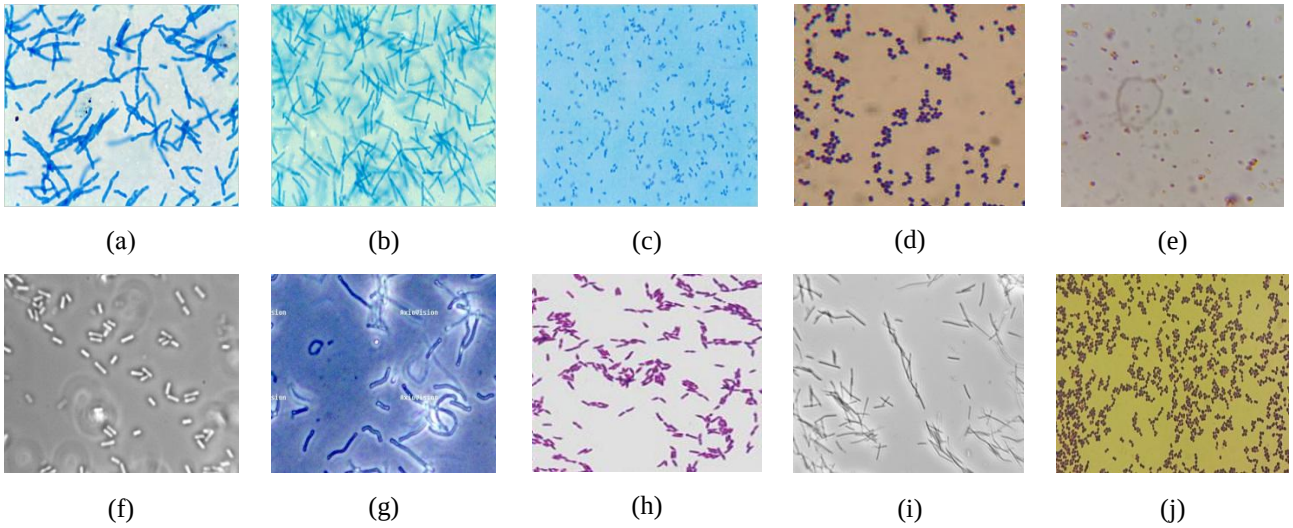


Fig. 1. Micrographs of native dabs of the strains of microorganisms isolated from the national Kazakh sour-milk drinks: (a) *Lactobacillus delbrueckii subsp. bulgaricus*; (b) *Lactobacillus acidophilus*; (c) *Streptococcus thermophilus*; (d) *Lactococcus lactis subsp. lactis biovar diacetilactis*; (e) *Pediococcus damnosus*; (f) *Lactobacillus fermentum;* (g) *Lactobacillus gallinarum*; (h) *Lactococcus lactis subsp. lactis*; (i) *Lactobacillus paracasei;* (j) *Pediococcus acidilactici.*

It is known that microorganisms differ from each other in biochemical properties – the ability to metabolize nutrients, antibiotic substances, various oxygen-containing organic compounds, such as carbohydrates, sugar, alcohols and organic acids, to synthesize enzymes, proteins, amino acids and vitamins [18].

The study of physiological and biochemical properties of bacteria allows to divide them by means of special culture media, to reveal their pertaining to a species and to divide them by strain. It is relevant for pure cultures, lactic and other kinds of bacteria used in the food industry [19].

Using the culture conditions and the composition of the medium, it is possible to determine the distinctive features of a microorganism used in taxonomy, the ecological niche and to find out a possibility of its use to solve practical tasks [17]. At last, the control of growth of cultures is the basis of biotechnological processes. All this emphasizes the importance of study of nature of growth and nutritious requirements of bacterial cultures. Table 3 provides the results of study of the physiological and biochemical properties of the strains isolated from national Kazakh sour-milk drinks.

The methods of study of physiological and biochemical strains of the microorganisms isolated from national Kazakh sour-milk drinks come down to the use of the microtests or the indicator paper systems which are a set of plastic holes with indicators. Some microorganisms can be identified by the ability to form stained compounds [20, 21].

The analysis of data of Table 3 allows to draw a conclusion that all the studied strains ferment ribose, D-galactose, D-glucose, D-fructose, D-mannose, N-acetyl-glucosamin, amygdalin, aesculin, salicin, cellobiose, maltose, lactose and D-sucrose which is characteristic of the representatives of the sort *Lactobacillus*. Strains considerably differ from each other in the consumption of other carbohydrates.

The research of antibiotic resistance of the strains of microorganisms isolated from national Kazakh sour-milk drinks is an important component in the course of complex study of microorganisms. A lot of microorganisms show resistance to the effect of antibiotics for several reasons. First, the resistance to the effect of antibiotic emerges with a change of genome as a result of multiple or single mutations. The acquired resistance descends further from one microorganism to another. As a result, a new population of the microorganisms resistant to the effect of antibiotics emerges. Thus, there is a selection of bacterial cells. Secondly, microorganisms are capable to adapt in adverse conditions, in particular to the effect of antibiotic substances. As a result, the replacement of the metabolitic links of a microorganism, the natural course of which is broken by an antibiotic, with other metabolitic reactions resistant to the effect of the medicine occurs. Thirdly, microorganisms are capable to provide the synthesis of the substances destroying an antibiotic molecule in adverse conditions [22, 23].

Table 4 provides the results of the studies of antibiotic resistance of the strains of microorganisms isolated from national Kazakh sour-milk drinks.

The analysis of the empirical data provided in Table 4 testifies that bacterial cells are sensitive to the effect of the antibiotics that inhibit protein synthesis: laevomycetin, tetracycline and doxycycline (the diameter of the zone of inhibition is at the level from 18.4 to 34.0 mm) and are to a lower degree sensitive to the effect of the aminoglycoside antibiotic substances that impede both protein synthesis and the processes of replication of a cell genome. Neomycin, sizomicin, kanamycin and streptomycin belong to such antibiotics (the width of zone of inhibition is at the level from 0 to 10.5 mm) [24].

These data confirm the belonging of the considered microorganisms to the group of Gram-positive bacteria. Besides, the results presented in Table 4 testify that all the studied strains are sensitive to the effect of β-lactam antibiotics which inhibit the synthesis of a cellular wall (ampicillin), except *Streptococcus thermophilus*.

The study of antagonistic properties of the strains of microorganisms isolated from national Kazakh sour-milk drinks is an important component of scientific research of the process of development of technology of a direct application starter as the antagonistic properties of microorganisms are the mechanism of functioning of microbiocenoses. In case of antagonism, some microorganisms oppress the development of other species, and sometimes they completely destroy it. The antagonistic properties are very widespread among microorganisms. Various populations of microorganisms have developed these or those methods of fight against their competitors. The antagonistic properties may consist in very fast reproduction, at the same time the microorganisms that grow fast push out and slow down the other microorganisms. And they can also relate to the synthesis of specific and nonspecific metabolites which can be formed not only during the cultivation of monocultures, but also in the presence of heterogeneous cultures. At the same time, co-culture provides the amplification of antagonistic properties of bacteria [25]. A method of co-culture on dense culture media was used to define the antagonistic activity of the strains of microorganisms isolated from national Kazakh sour-milk drinks. In the course of work, antagonistic properties of the strains of microorganisms isolated from national Kazakh sour-milk drinks using a diffusive method on a solid culture medium with the use of the following test strains were studied: *Escherichia coli* B-6954, *Bacillus fastidiosus* B-5651, *Pseudomonas fluorescens* B-3502, *Pseudomonas aeruginosa* ATCC 9027, *Leuconostoc mesenteroides* B-8404, *Candida albicans* ATCC 885-653 and *Staphylococcus aureus* ATCC 25923. Table 5 provides the results of the studies of antagonistic properties of the strains of microorganisms isolated from national Kazakh sour-milk drinks.

Table 3. Distinctive physiological and biochemical features of the strains isolated from sour-milk Kazakh products

Name of the substratum	Name of the microbial strain									
	Lactobacillus delbrueckii subsp. bulgaricus	*Lactobacillus paracasei*	*Lactobacillus acidophilus*	*Lactobacillus fermentum*	*Lactococcus lactis subsp. lactis*	*Lactococcus lactis subsp. lactis biovar diacetilactis*	*Pediococcus damnosus*	*Streptococcus thermophilu*	*Pediococcus acidilactici*	*Lactobacillus gallinarum*
Control	–	–	–	–	–	–	–	–	–	–
Glycerin	+	+	+	+	+	+	+	–	–	–
Erythritol	–	–	–	+	–	–	–	–	–	–
D-arabinose	–	–	–	–	–	–	+	+	+	–
L-arabinose	–	+	+	+	+	–	–	+	+	–
D-ribose	+	+	+	+	–	+	–	+	+	+
D-xylose	–	+	–	–	–	–	+	–	–	+
L-xylose	–	–	–	–	–	–	–	–	–	–
D-adonitol	+	–	–	–	–	+	+	–	–	–
Methyl-βD-xylopyranoside	–	–	+	–	–	–	+	–	–	+
D-galactose	+	–	–	–	–	+	–	+	+	+
D-glucose	+	+	–	+	+	+	+	+	+	+
D-fructose	+	+	+	+	–	+	–	–	–	+
D-mannose	+	+	+	+	+	+	+	+	+	+
L-sorbose	–	–	–	–	–	–	–	–	–	–
L-rhamnose	–	–	–	–	–	–	–	–	–	–
Dulcitol	–	–	–	–	–	–	–	–	–	–
Inosite	+	–	–	–	–	+	+	–	–	–
D-mannite	+	+	–	+	–	+	+	+	+	–
D-sorbite	–	+	+	+	–	–	–	–	–	–
Methyl-αD-mannopyranoside	+	–	–	–	–	+	+	–	–	–
Methyl-αD-glucopyranoside	+	+	+	–	+	+	+	+	–	–
N-acetylglucosamin	+	+	+	+	–	+	+	+	+	+
Amygdalin	+	+	+	+	+	+	+	+	–	+
Arbutin	+	+	+	+	+	+	–	+	+	–
Aesculin	+	+	+	+	+	+	+	+	–	+
Salicin	+	+	+	+	+	+	+	+	+	+
D-cellobiose	+	+	+	+	+	+	+	+	–	+
D-maltose	+	+	–	+	+	+	+	+	+	+
D-lactose	+	–	–	–	–	+	–	+	+	+
D-melibiose	+	–	–	–	–	+		–	–	–
D-sucrose	+	+	+	+	+	+	+	+	+	+
D-trehalose	+	+	+	+	+	+	–	–	–	–
Inulin	–	–	+	–	–	–	–	–	–	–
D-melezitose	+	–	–	–	–	+	+	–	–	–
D-raffinose	+	+	+	+	+	+	+	+	–	+
Starch	+	+	+	+	–	+	+	–	–	+
Glycogen	+	+	+	+	–	+	–	–	–	–
Xylitol	–	–	–	–	–	–	–	–	–	+
Gentiobiose	+	+	+	+	+	+	–	+	+	+
D-turanose	+	–	+	–	–	+	+	–	–	–
D-lyxose	–	–	–	–	–	–	+	–	–	–
D-tagatose	–	–	–	–	+	–	–	–	–	–
D-fucose	–	–	–	–	–	–	–	+	+	–
L-fucose	+	+	–	–	–	+	+	–	–	+
D-arabitol	–	–	–	–	–	–	+	–	–	–
L-arabitol	–	–	–	–	–	–	–	–	–	–

Designations: "+" is a positive result; "–" is a negative result.

Table 4. Antibiotic resistance of the strains isolated from sour-milk Kazakh products

Antibiotic	Name of the microbial strain									
	Lactobacillus delbrueckii subsp. bulgaricus	*Lactobacillus paracasei*	*Lactobacillus acidophilus*	*Lactobacillus fermentum*	*Lactococcus lactis subsp. lactis*	*Lactococcus lactis subsp. lactis biovar diacetilactis*	*Pediococcus damnosus*	*Streptococcus thermophilu*	*Pediococcus acidilactici*	*Lactobacillus gallinarum*
Ampicillin	32.0 ± ± 1.9	33.2 ± ± 1.9	19.5 ± ± 1.2	26.5 ± ± 1.6	35.6 ± ± 1.8	29.9 ± ± 1.5	32.2 ± ± 1.6	21.6 ± ± 1.3	0	19.8 ± ± 1.2
Benzylpeni cillin	20.7 ± ± 1.2	18.7 ± ± 1.1	22.5 ± ± 1.3	19.0 ± ± 1.1	17.4 ± ± 1.0	18.5 ± ± 1.1	17.9 ± ± 1.0	22.6 ± ± 1.3	0	24.3 ± ± 1.4
Doxycycline	18.4 ± ± 1.2	22.3 ± ± 1.3	34.0 ± ± 2.0	31.5 ± ± 1.9	0	0	17.6 ± ± 1.0	31.9 ± ± 1.9	35.7 ± ± 2.1	0
Kanamycin	5.0 ± ± 0.3	3.0 ± ± 0.2	0	0	15.6 ± ± 0.8	0	0	0	0	0
Carbeni cillin	14.5 ± ± 0.8	12.4 ± ± 0.7	16.7 ± ± 0.9	13.0 ± ± 0.7	8.6 ± ± 0.5	11.2 ± ± 0.6	18.9 ± ± 1.1	12.3 ± ± 0.7	15.8 ± ± 0.9	9.3 ± ± 0.5
Chloromy-cetin	32.0 ± ± 1.9	28.7 ± ± 1.7	26.4 ± ± 1.5	30.6 ± ± 1.8	37.0 ± ± 1.9	32.0 ± ± 1.6	28.4 ± ± 1.7	31.6 ± ± 1.8	27.8 ± ± 1.4	28.9 ± ± 1.7
Methicillin	15.6 ± ± 0.9	13.5 ± ± 0.8	22.3 ± ± 1.3	21.0 ± ± 1.2	14.5 ± ± 0.8	28.9 ± ± 1.7	12.6 ± ± 0.7	0	0	14.9 ± ± 0.1
Neomycin	7.0 ± ± 0.4	6.0 ± ± 0.3	0	5.0 ± ± 0.3	2.0 ± ± 0.1	0	6.3 ± ± 0.3	0	0	3.4 ± ± 0.2
Oxacilline	9.5 ± ± 0.5	10.7 ± ± 0.6	16.0 ± ± 0.9	14.0 ± ± 0.8	28.5 ± ± 1.4	25.6 ± ± 1.3	8.3 ± ± 0.5	13.2 ± ± 0.8	0	26.8 ± ± 1.6
Oleandomy cin	27.5 ± ± 1.6	22.6 ± ± 1.3	15.4 ± 0.9	24.0 ± ± 1.4	26.9 ± ± 1.6	23.6 ± ± 1.4	22.7 ± ± 1.3	15.8 ± ± 0.5	19.7 ± ± 0.5	24.8 ± 1.6
Ristomycin	11.7 ± ± 0.7	8.5 ± ± 0.5	7.0 ± ± 0.4	9.0 ± ± 0.5	12. 1± ± 0.7	6.8 ± ± 0.4	7.2 ± ± 0.4	7.0 ± ± 0.2	9.2 ± ± 0.2	7.3 ± ± 0.4
Sizomicin	0	0	0	3.0 ± ± 0.1	0	0	0	0	0	2.0 ± ± 0.1
Streptomy cin	2.0 ± ± 0.1	4.5 ± ± 0.2	10.5 ± ± 0.6	6.0 ± ± 0.2	0	9.8 ± ± 0.6	3.6 ± ± 0.2	0	0	2.8 ± ± 0.1
Tetracycline	24.0 ± ± 1.4	26.7 ± ± 1.6	32.0 ± ± 1.9	27.6 ± ± 1.6	0	24.5 ± ± 1.2	19.8 ± ± 1.1	0	34.2 ± ± 1.7	22.7 ± ± 1.3
Cefalexin	32.0 ± ± 1.9	25.0 ± ± 1.5	19.6 ± ± 1.1	21.4 ± ± 1.3	0	0	18.2 ± ± 1.1	21.5 ± ± 1.4	32.9 ± ± 1.6	33.8 ± ± 1.7

Table 5. Antagonistic properties of the strains of microorganisms isolated from national Kazakh sour-milk drinks

Name of the strain	Name of the strain									
	Lactobacillus delbrueckii subsp. bulgaricus	*Lactococcus lactis subsp. lactis*	*Lactobacillus paracasei*	*Pediococcus acidilactici*	*Lactobacillus acidophilus*	*Lactobacillus fermentum*	*Lactococcus lactis subsp. lactis biovar*	*Pediococcus damnosus*	*Streptococcus thermophilus*	*Lactobacillus gallinarum*
Escherichia coli B-6954	0	0	0	0	0	0	0	9	0	9
Bacillus fastidiosus B-5651	7	9	10	7	0	0	0	3	0	8
Pseudomonas fluorescens B-3502	0	6	0	0	0	0	0	0	0	8
Pseudomonas aeruginosa ATCC 9027	8	0	0	0	0	0	0	0	0	0
Leuconostoc mesenteroides B-8404	0	3	1	0	0	0	0	6	0	3
Candida albicans ATCC 885-653	0	3	0	0	0	0	0	3	0	0
Staphylococcus aureus ATCC 25923	0	8	0	7	0	0	0	2	0	6

The analysis of empirical data on the study of antagonistic properties of the strains of microorganisms isolated from national Kazakh sour-milk drinks presented in Table 5 testifies that such natural strains as *Escherichia coli* B-6954, *Bacillus fastidiosus* B-5651, *Pseudomonas fluorescens* B-3502, *Pseudomonas aeruginosa* ATCC 9027, *Leuconostoc mesenteroides* B-8404, *Candida albicans* ATCC 885-653 and *Staphylococcus aureus* ATCC 25923 turned out to be the most sensitive to metabolites of lactic bacteria. Such strains as *Lactobacillus delbrueckii subsp. bulgaricus, Lactococcuslactis subsp. lactis, Pediococcus acidilactici, Lactobacillus paracasei, Pediococcus damnosus and Lactobacillus gallinarum* show the highest antagonistic activity. Thus, for example, the microorganism strain *Lactobacillus delbrueckii subsp. bulgaricus* has an adverse effect on the strains *Bacillus fastidiosus* B-5651 and *Pseudomonas aeruginosa* ATCC 9027; the strain *Lactococcus lactis subsp. lactis* has an adverse effect on the strains *Bacillus fastidiosus* B-5651, *Pseudomonas fluorescens* B-3502, *Leuconostoc mesenteroides* B-8404, *Candida albicans* ATCC 885-653 and *Staphylococcus aureus* ATCC 25923; the strain *Lactobacillus paracasei* shows antimicrobic properties against *Bacillus fastidiosus* B-5651 and *Leuconostoc mesenteroides* B-8404; the strain *Pediococcus acidilactici* has an adverse effect on *Bacillus fastidiosus* B-5651 and *Staphylococcus aureus* ATCC 25923; the microorganism strain *Pediococcus damnosus* shows antimicrobic properties against *Escherichia coli* B-6954, *Bacillus fastidiosus* B-5651, *Leuconostoc mesenteroides* B-8404, *Candida albicans* ATCC 885-653 and *Staphylococcus aureus* ATCC 25923; the microorganism strain *Lactobacillus gallinarum* shows antimicrobic properties against *Escherichia coli* B-6954, *Bacillus fastidiosus* B-5651, *Pseudomonas fluorescens* B-3502, *Leuconostoc mesenteroides* B-8404 and *Staphylococcus aureus* ATCC 25923.

When determining biocompatibility the isolated strains are subdivided into four categories: biocompatible strains, bioincompatible strains, strains with weak antagonism and strains that have a high antagonistic effect. Table 6 provides the results of the study.

Interpreting the results of the study presented in Table 6, we draw a conclusion that full compatibility is only characteristic of four strains – *Lactobacillus gallinarum (kurunga), Streptococcus thermophilus (koumiss), Lactococcus lactis subsp. lactis (ayran) and Pediococcus damnosus (chegen).*

Thus, it was established during the study that of ten strains of microorganisms isolated from national Kazakh sour-milk drinks the most suitable for further studying for the purpose of development of technology of a direct application starter are the microorganisms isolated from kurunga – *Lactobacillus gallinarum*, koumiss – *Streptococcus thermophilus*, ayran – *Lactococcus lactis subsp. lactis* and chegen – *Pediococcus damnosus*.

Table 7 provides the compositions of culture media.

Table 6. Biocompatibility of the strains of microorganisms isolated from national Kazakh sour-milk drinks

Name of the strain	Name of the strain									
	Lactobacillus delbrueckii subsp. bulgaricus	*Lactococcus lactis subsp. lactis*	*Lactobacillus paracasei*	*Pediococcus acidilactici*	*Lactobacillus acidophilus*	*Lactobacillus fermentum*	*Lactococcus lactis subsp. lactis biovar*	*Pediococcus damnosus*	*Streptococcus thermophilus*	*Lactobacillus gallinarum*
Lactobacillus delbrueckii subsp. bulgaricus		+	+	–	+	±	–	+	+	+
Lactococcus lactis subsp. lactis	+		+	–	±	±	–	+	±	+
Lactobacillus paracasei	+	+		–	±	+	–	±	+	+
Pediococcus acidilactici	±	+	–			+	+	+	+	±
Lactobacillus acidophilus	+	±	+	±		+	+	+	+	+
Lactobacillus fermentum	±	+	+	+			+	+	±	+
Lactococcus lactis subsp. lactis biovar	+	+	+	–	±	–		±	+	+
Pediococcus damnosus	–	+	–	±	–	–	+		+	+
Streptococcus thermophilus	–	+	–	–	±	–	+	±		+
Lactobacillus gallinarum	–	+	±	–	±	±	+	+	±	

Notes. "+" stands for biocompatible strains; "–" stands for incompatible strains; "±" stands for partially compatible strains

Table 7. Variants of culture media for the cultivation of consortium of microorganisms

Name of the component	Number of the culture medium depending on the content of components, g/l			
	1	2	3	4
proteose-peptone	10	5	15	–
meat extract	15	10	8	–
yeast extract	10	5	8	5
glucose	15	20	5	20
Tween-80	1	1	1	1
ammonium citrate	2	1	2	1
sodium acetate	5	–	2.5	5
magnesium sulfate	0.1	–	–	0.1
manganic sulfate	0.05	0.05	–	0.05
sodium hydrophosphate	0.5	1.0	1.5	2.0
agar-agar	12.0	15.0	15.0	14.0
methyl rosaniline	0.0001	0.0002	0.0001	–
casein hydrolysate	15.0	12.5	20.0	8.0
papain digest of soy flour	5.0	2.5	–	5.0
sodium chloride	4.0	3.0	1.0	1.0
sodium citrate	0.5	0.5	–	1.0
sodium sulphite	0.1	0.2	0.1	0.2
L-cystine	0.1	0.05	–	0.2
potassium phosphate dibasic	1.5	0.5	–	2.0
sodium azide	0.05	0.1	0.1	0.2
ammonium citrate dibasic	1.2	0.8	1.0	2.0
sodium acetate	5.0	–	1.0	2.5

The analysis of results of the choice of optimum composition of culture medium for the cultivation of symbiotic consortium of the microorganisms provided in Fig. 1 testifies that the maximum viability and activity of the microorganisms which are part of consortium is observed when it is cultivated on culture medium No. 2. The concentration of microorganisms amounts to 28.3 CFU/g after 24 h of cultivation on culture medium No. 2 $\cdot 10^6$ which is 15% higher than the concentration of the microorganisms grown up on culture medium No. 3 and is 32% higher than the concentration of the microorganisms grown up on culture medium No. 4 under equal conditions.

Fig. 2 provides the results of selection of composition of culture medium for the cultivation of consortium of microorganisms.

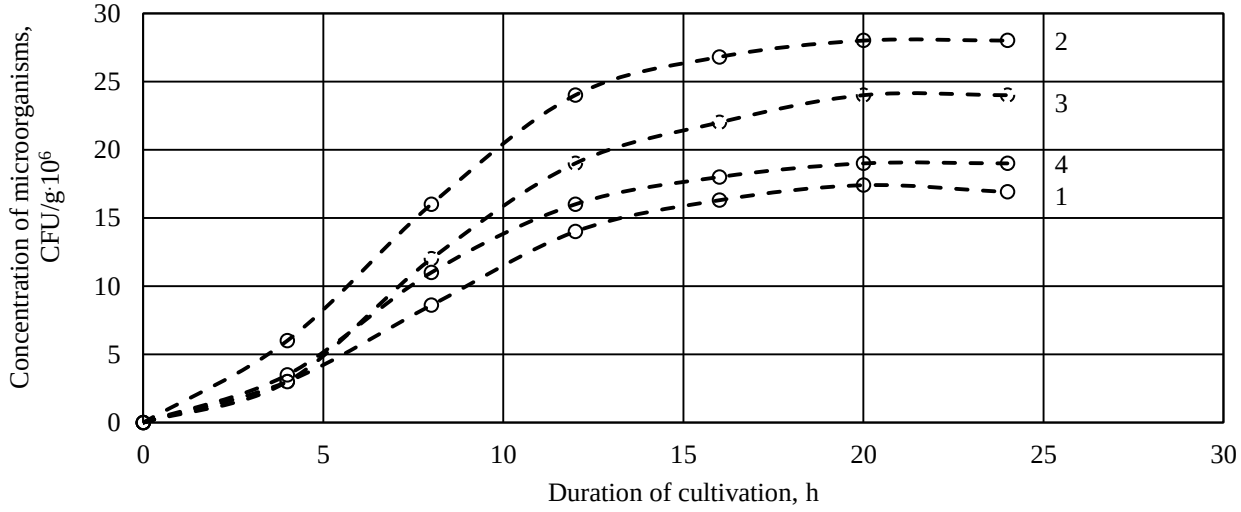


Fig. 2. Influence of composition of culture medium on the viability and activity of symbiotic consortium: (1) culture medium No. 1; (2) culture medium No. 2; (3) culture medium No. 3; (4) culture medium No. 4.

CONCLUSIONS

(1) Such strains of lactobacilli as *Lactobacillus delbrueckii subsp. bulgaricus*, *Lactobacillus acidophilus*, *Streptococcus thermophiles*, *Lactococcus lactis subsp. lactis*, *Lactococcus lactis subsp. lactis biovar diacetilactis*, *Lactobacillus paracasei*, *Lactobacillus fermentum*, *Pediococcus damnosus*, *Pediococcus acidilactici* and *Lactobacillus gallinarum* have been isolated from national sour-milk food products: chegen, ayran, koumiss, kurunga.

(2) Cultural, morphological, physiological and biochemical properties have been studied, antibiotic resistance, antagonistic activity and biocompatibility of the microorganisms isolated from national Kazakh drinks have been determined. It has been established that the isolated microorganisms have a stick-like shape of 0.6 x 3.5 to 6.0 x 0.7 microns in size characteristic of bacteria of the sort *Lactobacillus* and are Gram-positive and nonspore-forming. It has been shown that strains considerably differ from each other in the consumption of other carbohydrates. It has been established that all the studied strains are sensitive to the effect of β-lactam antibiotics which inhibit the synthesis of cellular wall (ampicillin), except *Streptococcus thermophilus*. The analysis of biocompatibility has shown that full compatibility is only characteristic of four strains – *Lactobacillus gallinarum (kurunga), Streptococcus thermophilus (koumiss), Lactococcus lactis subsp. lactis (ayran) and Pediococcus damnosus (chegen).*

(3) Such strains of microorganisms as *Lactobacillus gallinarum, Streptococcus thermophilus, Lactococcus lactis subsp. lactis and Pediococcus damnosus* have been chosen to form a symbiotic consortium.

(4) Optimum conditions of cultivation of symbiotic consortium of microorganisms have been selected. It has been established that the growth of microorganisms is the maximum when the composition of culture medium is the following: proteose-peptone – 5.00; meat extract – 10.00; yeast extract – 5.00; glucose – 20.00; Tween-80 – 1.00; ammonium citrate – 1.00; manganese sulfate – 0.05; sodium hydrophosphate – 1.00; agar-agar – 15.00; methyl rosaniline – 0.0002; casein hydrolyzate – 12.50; papain digest of soy flour 2.50; sodium chloride – 3.00; sodium citrate – 0.50; sodium sulfite – 0.20; L-cystine – 0.05; sodium azide – 0.10; potassium phosphate dibasic – 0.50; ammonium citrate dibasic – 0.80.

REFERENCES

1. Özer B.H. and Kirmaci H.A. Functional milks and dairy beverages. *International Journal of Dairy Technology*, 2010, vol. 63, no. 1, pp. 1–15. DOI: 10.1111/j.1471-0307.2009.00547.x.
2. Astakhova L., Babich O., Prosekov A., et al. Short chain fatty acids (SCFA) reprogram gene expression in human malignant epithelial and lymphoid cells. *PLoS ONE*, 2016, vol. 11, no. 7, e0154102. DOI: 10.1371/journal.pone.0154102.
3. Zimina M.I., Sukhih S.A., Babich O.O., Noskova S.Yu., Abrashina A.A., and Prosekov A.Yu. Investigating antibiotic activity of the genus Bacillus strains and properties of their bacteriocins in order to develop next-generation pharmaceuticals. *Foods and Raw Materials*, 2016, vol. 4, no.2, pp. 95–100. DOI: 10.21179/2308-4057-2016-2-92-100.
4. Michaelidou A. and Steijns J. Nutritional and technological aspects of minor bioactive components in milk and whey: Growth factors, vitamins and nucleotides. *International Dairy Journal*, 2006, vol. 16, no. 11, pp. 1421–1426. DOI: 10.1016/j.idairyj.2006.06.018.
5. Side C. *Food Product Development: Based on Experience*. Iowa, Blackwell publishing company, 2008. 199 p.
6. Surkov I.V., Prosekov A.Yu., Ermolaeva E.O., et al. Evaluation and preventing measures of technological risk of food technology. *Modern Applied Science*, 2015, no. 4, pp. 45–52. DOI: http://dx.doi.org/10.5539/mas.v9n4p45.
7. Novoselova M.V. and Prosekov A.Yu. Technological options for the production of lactoferrin. *Food and Raw Materials*, 2016, vol. 4, no. 1, pp. 90–101. DOI: 10.21179/2308-4057-2016-1-90-101.
8. Kinsella J.E. and Morr C.V. Milk proteins: Physicochemical and functional properties. *CRC Critical Reviews in Food Science and Nutrition*, 1984, vol. 21, no. 3, pp. 197–220. DOI: http://dx.doi.org/10.1080/10408398409527401.
9. Dyshlyuk L., Babich O., Belova D., and Prosekov A. Comparative analysis of physical and chemical properties of biodegradable edible films of various compositions. *Journal of food process engineering*, 2017, vol. 40, n/a, e12331. DOI: 10.1111/jfpe.12331.
10. Jakubczak A. and Stachetska M. Health benefits resulting from probiotic bacteria consumption. *Adv. Agrycultyral Science*, 2011, no. 14, pp. 53–63.
11. Juszczyk S. The rational managing rule and the way of improving the effectiveness of milk production. *Zagadn. Ekon. roln.*, 2007, no. 3, pp. 56–71.
12. Korhonen H. and Pihlanto A. Bioactive peptides: Production and functionality. *International Dairy Journal*, 2006, vol. 16, no. 9, pp. 946–956. DOI: https://doi.org/10.1016/j.idairyj.2005.10.012.
13. Prosekov A.Yu. and Ivanova S.A. Providing food security in the existing tendencies of population growth and political and economic instability in the world. *Foods and Raw Materials*, 2016, vol. 4, no. 2, pp. 201–211. DOI: 10.21179/2308-4057-2016-2-201-211.
14. Zamberlin S., Dolencic S.I., Kelava N., and Samarzija D. Probiotic bacterium Lactobacillus rhamnosus: Benefical and a dverse effects on human health. *Milchwissenschaft*, 2012, no. 1, pp. 30–33.
15. Gorska S., Grycko P., Rybka J., et al. Exopolysaccharides of lactic acid bacteria: structure and biosynthesis. *PostepyHig Med Dosw*, 2007, vol. 61, pp. 805–818.

16. *GOST 31702-2013. Ayran. Tekhnicheskie usloviya* [State Standard 31702-2013. Ayran. Technical conditions]. Moscow: Standards Publ., 2014. 17 p.
17. *GOST R 52974-2008. Kumys. Tekhnicheskie usloviya* [State Standard R 52974-2008. Kumis. Technical conditions]. Moscow: Standards Publ., 2010. 15 p.
18. *GOST 10382-85. Konservy molochnye. Produkty kislomolochnye sukhie. Tekhnicheskie usloviya* (State Standard 10382-85. Canned milk. Sour-milk products dry. Technical conditions]. Moscow: Publishing House of Standards, 1987. 25 p.
19. Prosekov A.Yu. and Ostroumov L.A. Innovation management biotechnology of starter cultures. *Food Processing: Techniques and Technology*, 2016, vol. 43, no. 4, pp. 64–69. (In Russian).
20. Robinson R.K. (ed.) *Dairy Microbiology Handbook. The Microbiology of Milk and Milk Products*. USA: John Wiley & Sons, 2002. 765 p.
21. Shishin M.V. and Prosekov A.Yu. Investigation of morphological and antimicrobial properties of intestinal tract microorganisms. *Food Processing: Techniques and Technology*, 2015, vol. 39, no. 4, pp. 131–137. (In Russian).
22. Lewisi M.J. Microbiological issues associated with heat treated milks. *J. Soc. Dairy Technol*., 2002, no. 3, pp. 121–125.
23. Ludikhuyze L., Claeys W., and Hendrickx M. Combined Pressure—temperature Inactivation of Alkaline Phosphatase in Bovine Milk: A Kinetic Study. *Journal of Food Science*, 2000, vol. 65, no. l, pp. 155–160. DOI: 10.1111/j.1365-2621.2000.tb15972.x.
24. Morris G. and Harding S. Polysaccharides, Microbial. *Applied Microbiology: Industrial*, 2009, pp. 482–494.
25. Akalin A.S. and Una G. The influence of milk supplementarion on the microbiological stability and textural characteristics of fermented milk. *Milchwissenschaft*, 2010, no. 3, pp. 291–294.

Please cite this article in press as: Sukhikh S.A., Krumlikov V.Yu., Evsukova A.O., and Asyakina L.K. Formation and study of symbiotic consortium of lactobacilli to receive a direct application starter. *Foods and Raw Materials*, 2017, vol. 5, no. 1, pp. 51–62. DOI: 10.21179/2308-4057-2017-1-51-62.

ISSN 2310-9599. Foods and Raw Materials, 2017, vol. 5, no. 1

GRAPE POMACE EXTRACT AND PEAR IN SNACK PRODUCTION TECHNOLOGY

D. F. Valiulina*, N. V. Makarova, and I. A. Kustova

Samara State Technical University,
Molodogvardeyskaya Str. 244, Samara, 443100, Russian Federation

* e-mail: dinara-bakieva@mail.ru

Received April 21, 2016; Accepted in revised form September 10, 2016; Published June 29, 2017

Abstract: The article is devoted to the study of the influence of process parameters for the production of pear snacks with the addition of grape extract secondary raw materials on the chemical composition and antioxidant activity of the resulting product. This paper describes the selection of the most optimum conditions for production of high quality, competitive product with the highest antioxidants activity. The object of the study were temperature, time of soaking pear slices in the extract, drying process. Analysis on the content of total amount of phenolic compounds the content of Gallic acid, flavonoids and tannins content of catechin, anthocyanin content cyanidin-3-glycoside, antiradical capacity using the free radical DPPH method (2,2-diphenyl-1-picrylhydrazyl), antioxidative activity by the method of ABTS (2,2'-settlement Azino-bis(3-ethylbenzothiazoline-6-sulfonic acid), which restores the force by the method of FRAP (ferric reducing antioxidant power), antioxidant activity in linoleic acid system. The obtained results are vivid enough and allow us to conclude that the best way to obtain high-quality resulting product out of pear fruit crop is freeze-drying, and the shelf life of an opened package in no longer than 38 hours. This study was financially supported by the Ministry of Education and Science of the Russian Federation within the basic part of the government task number 2014/199 FSBEI HPE Samara State Technical University by the project «Creating Scientific Methodology of Developing Formulation and Technologies of Food Products Fighting Oxidant Stress in Human's Body» code 974.

Keywords: Pears, snack, antioxidant activity, extract, grape, freeze drying

DOI 10.21179/2308-4057-2017-1-63-72 *Foods and Raw Materials*, 2017, vol. 5, no. 1, pp. 63–72.

INTRODUCTION

Pear is one of the major crops and is highly valued for its taste and technological qualities of the fruit. [1] Pear fruits are characterized by medical and nutritional value. They contain sugar, acids, tannins, mineral nutrients, vitamins, pectin substances. Especially pear fruits are valuable for containing such an important substance for the human organism as chlorogenic acid, and arbutin. There is more chlorogenic acid in pear fruit than in apples, and its amount depending on the class is of 30–70 mg%. It has healing properties for liver diseases [2].

Shelf life of pears is small, so raw fruit processing is becoming an important area of food industry. One of the main stages which determines the quality of the manufactured product is the selection of technological modes. The mode is called optimal when the product is produced with the best rates and efficiency of the process is the highest.

The aim of this work is the development of pear snack production technology with addition of an extract [3] of the secondary raw grape materials. In addition, we studied the effect of technological parameters on physical and chemical [4] and antioxidant rates [5] of the finished product. To develop the technology of obtaining a functional food item - pear snacks – some research was conducted on the effect of pear slices thickness, a mass fraction of extract for soaking pear slices, temperature of soaking pear slices in the extract, drying technology, technological modes of drying on the organoleptic, physical and chemical, structural and mechanical rates of finished products.

OBJECTS AND METHODS OF STUDY

Chemicals and reagents. Folin-Ciocalteu reagent in sodium carbonate, gallic acid, catechin, ABTS (2,2'-azino-bis (3-ethylbenzthiazoline-6-sulfonic acid) were purchased from Fluka (Germany). DPPH (2,2-diphenyl-1-picrylhydrazyl), Tween 40, hydrogen peroxide, sodium nitrite, aluminum chloride, thiobarbituric acid, trichloroacetic acid were purchased from Sigma-Aldrich Chem. mp. (USA).

Fruit collection. The grapes and pears collected on the territory of the Russian Federation at the enterprise wineries in the city of Samara in 2014.

Determination of total phenols. Total phenolic content of methanolic fruit extracts was assessed using a modified version of the Folin–Ciocalteu assay [6]. Gallic acid was used as a standard and the aqueous gallic acid solution (200 mg l 1) was diluted with distilled water to give appropriate concentrations for a

standard curve. For the analysis, 100 ll of methanolic fruit extract or gallic acid standard, 100 ll of methanol, 100 ll of Folin–Ciocalteu reagent and 700 ll of Na_2CO_3 were added into 1.5 ml micro-centrifuge tube. The samples were vortexed immediately and the tubes were incubated in the dark for 20 min at room temperature. After incubation all samples were centrifuged at 13,000 rpm for 3 min. The absorbance of the supernatant was then measured at 735 nm in 1 ml plastic cuvettes using evolution 200 Series spectrophotometer. The results were expressed in mg gallic acid equivalent/100 g dry weight.

Determination of total flavonoids. The flavonoid content of the methanolic extracts was measured using a assay [7]. A known volume (0.5 ml) of the extract or standard solution of quercetin was added to a 10 ml volumetric flask. Distilled water was added to make a volume of 5 ml. At zero time, 0.3 ml of 5% w/v $NaNO_2$ was added to the flask. After 5 min, 0.6 ml of 10% w/v $AlCl_3$ was added and after 6 min, 2 ml of 1 M NaOH was added to the mixture followed by the addition of 2.1 ml distilled water. Absorbance was read at 350 nm against the blank (water) and flavonoid content was expressed as mg quercetin equivalents in 100 g of fresh material.

Determination of the anthocyanin profile. The concept of determining the amount of anthocyanin present in a material by measuring the change in absorbance at 2 different pH values (3.4 and 2.0) [8]. Researchers have proposed using the pH values of 1.0 and 4.5 (2–5). Monomeric anthocyanins undergo a reversible structural transformation as a function of pH (colored oxonium form at pH 1.0 and colorless hemiketal form at pH 4.5. Thus, the difference in absorbance at the vismax (520 nm) of the pigment is proportional to the concentration of pigment. Degraded anthocyanins in the polymeric form are resistant to color change with change in pH. Therefore, polymerized anthocyanin pigments are not measured by this method because they absorb both at pH 4.5 and 1.0.

Determination of condensed tannins. In presence of concentrated H_2SO_4, condensed tanins were transformed by the reaction with vanillin to anthocyanidols [9]. 50 l of the methanolic seed extract appropriately dilute was mixed with 3 ml of 4% methanol vanillin solution and 1.5 ml of H_2SO_4 . After 15 min, the absorbance was measured at 500 nm. Condensed tannin contents of seeds (three replicates per treatment) were expressed as mg catechin equivalents (CE) per gram of dry weight through the calibration curve with catechin. The calibration curve range was 50–600 mg ml^{-1}.

DPPH radical scavenging activity. The scavenging activity of samples was measured in accordance with the method [10]. The method was based on the reduction of methanolic DPPH in the presence of a hydrogen-donating antioxidant. DPPH solution was an intense violet colour and showed an absorption band at 515 nm. Adsorption and colour lowered when DPPH was reduced by an antioxidant compound. The remaining DPPH corresponded inversely to the radical-scavenging activity of the antioxidant. DPPH (2 mg) was dissolved in 54 ml of MeOH. Aliquots of investigated extract (50, 100, 200, 300, 500 and 1000 lg) were dissolved in 2 ml of MeOH. Then 1.0 ml of each solution was added to 2.0 ml of DPPH solution at room temperature. The absorbance at 515 nm was measured against a blank (2 ml MeOH in 2.0 ml of DPPH solution) using evolution 200 Series spectrophotometer. The results were expressed as percent-age of reduction of the initial DPPH adsorption by test samples:

% of reduction of the initial DPPH adsorption = ADPPH(t)_Asample (t)/ADPPH (t) _ 100,
ADPPH(t) is absorbance of DPPH at time t and
Asample (t) is absorbance of sample at t the same time.

FRAP assay. The FRAP assay was carried [11]. The FRAP solution was freshly prepared on the day of use, by mixing acetate buffer (pH 3.6), ferric chloride solution (20 mM) and TPTZ solution (10 mM TPTZ in 40 mM HCl) in a proportion of 10 : 1 : 1, respectively. Following this the FRAP solution was heated, while protected from light, until it had reached a temperature of 37 LC. Appropriate dilutions of methanolic fruit extracts were prepared. One hundred microlitres of the diluted sample extract (or for blank 100 ll methanol and for Trolox standard curves 100 ll Trolox of appropriate concentration) and 900 ll of FRAP solution were added into a micro-centrifuge tubes. The tubes were vortexed and left at 37 LC for exactly 40 min, and the absorbance was measured at 593 nm. The Trolox standard curves were used to calculate the antioxidant activity of the samples in relation to Trolox and were expressed as mg Trolox equivalent/100 g dry weight sample (mg TE 100 g 1 DW).

ABTS free radical decolorization assay. The total antioxidant capacity assay conducted using evolution 200 Series spectrophotometer. The procedure was based on a method [12] with some modification. ABTS + was generated by reacting ABTS (7.4 mM) with potassium persulphate (2.6 mM). The solution was diluted to obtain an absorbance of 1.4 units at 414 nm (molar extinction coefficient E = 3.6_104 mol_1 l cm_1, Forni, Morla-Arellano, Packer, & Willison 1986) with 50 mM glycine-HCl buffer (pH 4.5) before use. Three millilitres of the solution were added to 20–80 ml of AA, trolox, hydroquinone, pyrogallol and fruit extracts separately. The changes in absorbance at 414 nm were recorded at 1, 3, 6, 10, 20, 30, 40, 60 and 90 min after mixing and until the absorbance reached a plateau. The antioxidant capacities, obtained by comparing the absorbance change at 414 nm in a test reaction mixture containing extract of fruit with that containing AA, were expressed as mg of AA equivalents per 100 g of homogenate (AEAC).

Determination of Antioxidant Activity in a Linoleic Acid System. The total antioxidant activity of FEHP was carried out by use of a linoleic acid system [13]. The linoleic acid emulsion was prepared by mixing 0.2804 g of linoleic acid, 0.2804 g of Tween 20 as emulsifier, and 50 mL of phosphate buffer (0.2 M, pH 7.0), and then the mixture was homogenized. A 0.5 mL ethanol solution of different

concentration of FEHP (50–500 íg/mL) was mixed with linoleic acid emulsion (2.5 mL, 0.2 M, pH 7.0) and phosphate buffer (2 mL, 0.2 M, pH 7.0). The reaction mixture was incubated at 37°C in the dark to accelerate the peroxidation process. The levels of peroxidation were determined according to the thiocyanate method by sequentially adding ethanol (5 mL, 75%), ammonium thiocyanate (0.1 mL, 30%), sample solution (0.1 mL), and ferrous chloride (0.1 mL, 20 mM in 3.5% HCl). After the mixture was left for 3 min, the peroxide value was determined by reading the absorbance at 500 nm on a spectrophotometer.

RESULTS AND DISCUSSION

Based on the example of soaking pear slices in grape extract the dependence of physical and chemical and antioxidant properties of snacks on mass fraction of the added extract was revealed. Four samples of the product with a mass fraction of the extract of 20, 40, 60 and 80% of the feedstock mass were prepared.

Comparative analysis has shown (Table 1) that with increasing concentrations of grapes pomace extract, chemical composition rates increase. Thus, comparing the concentration of 20 and 80% we can observe that there is a 4 times increase in flavonoid (110 and 437 mg of catechin / 100 grams of feedstock, respectively), and the anthocyanins and tannins increase almost by 10 times.

Studying the rates in Fig. 1, we can also see an increase in the restoring force rates and the antioxidant capacity of pear snack with the addition of grapes pomace extract compared with the feedstock. Thus comparing the feedstock with pear snack soaked in 80% extract the restoring force rates and antioxidant capacity are increased by 6 times.

After analyzing the data of Fig. 2, in terms of anti-radical activity rate E_{C50} (extract concentration required to bind 50% of free radicals DPPH) the feedstock does not show any anti-radical activity. The greatest antiradical activity was shown by pear slices soaked in 80% extract (E_{C50} = 94 mg / ml).

Thus, it can be concluded that soaking pear slices in the extract of different concentrations leads to an increase of the chemical composition and antioxidant properties as compared with the feedstock.

Table 1. The change of pear snack chemical composition with the addition of extract with different concentration

Extract %	Total content of phenols, mg of gallic acid/ 100 g of material	Total content of flavonoids, mg of catechine/ 100 g of material	Total content of anthocyanins, mg of cyanidin-3- glycoside/ 100 g of material	Total content of tannins, mg of catechine/ 100 g of material
0	118	47	Absent	0.12
20	110	31	3.18	0.12
40	189	136	4.23	0.16
60	224	189	25.24	0.88
80	437	314	31.6	1.02

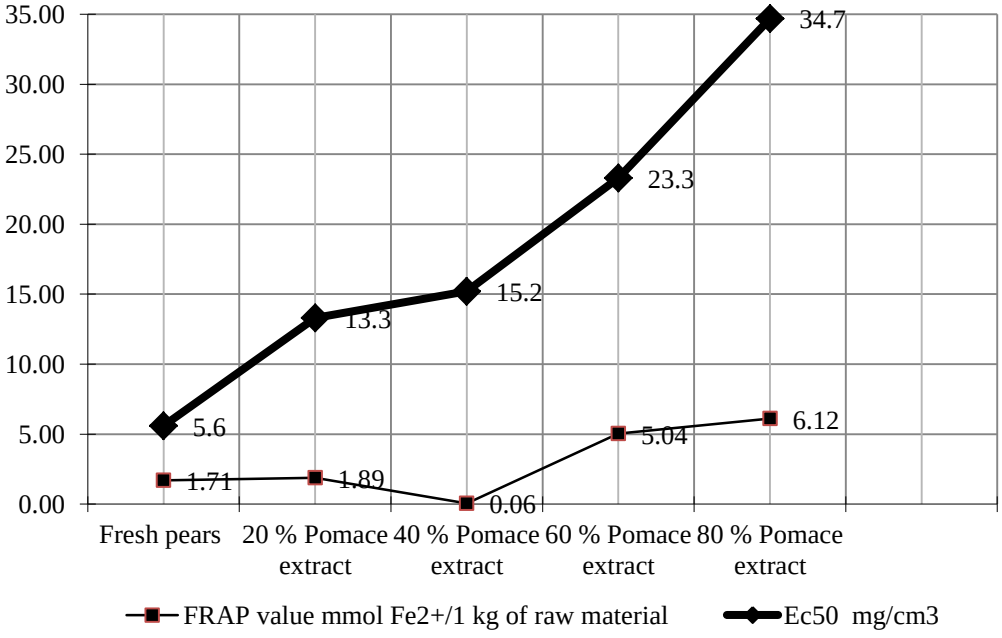


Fig. 1. Study of restoring force and antioxidant activity.

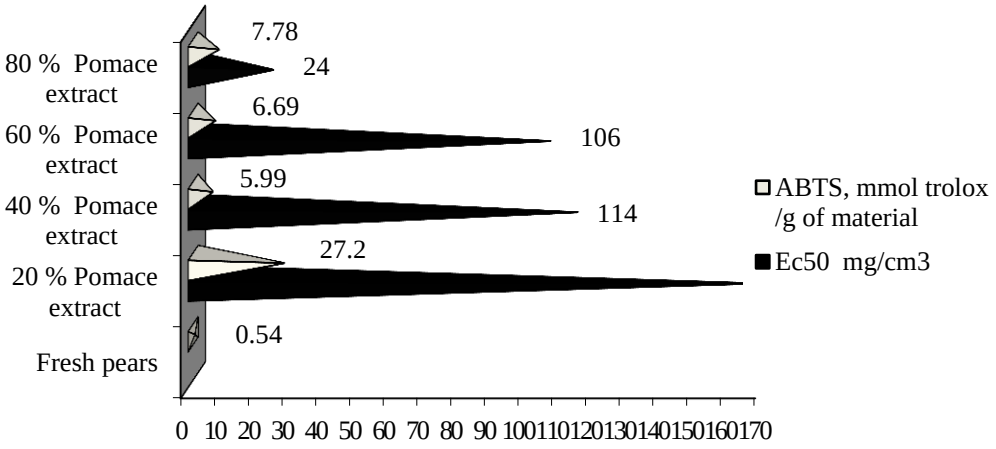


Fig. 2. Study of antioxidant activity.

The analysis of the data in the Table 2 allows to conclude that with the increasing temperature of pear samples soaked in 80% extract, chemical composition rates increase.

As seen in Fig. 3, the highest concentration of E_{C50}, and consequently, the lowest activity against trapping radicals found in pears soaked in extracts at 5°C. Pears soaked in room temperature extract and 35°C extract have lower values of the active concentration, hence higher antiradical activity. By the ability to capture radicals ABTS, all the temperatures of soaking pear slices in grape pomace extract are about the same level.

In the analysis of the Fig. 4 we can notice that pear samples soaked in the extract at 35°C have the greatest restoring force, the pear samples soaked in the extract at room temperature differ slightly. The ability of pears to inhibit the oxidation of linoleic acid in model system, is characterized as the antioxidant activity. The highest antioxidant activity is shown in pear samples soaked in room temperature extract. In case of heating the extract pears showed the least antioxidant activity compared to other monitored temperatures.

The room temperature of 20–22°C was chosen from all the monitored temperatures, because in terms of chemical composition and antioxidant properties it is slightly different from the temperature of 35°C. In addition, the use of room temperature will allow to reduce extra energy usage.

There is some specific interest in measuring the mass fraction of soluble solids in the processed pear slices, both before and after heat treatment (Fig. 5).

Table 2. The Change of chemical composition of pear snacks

Parametres	Total content of phenols, mg of gallic acid/ 100 g of material	Total content of flavonoids, mg of catechine/ 100 g of material	Total content of anthocyanins, mg of cyanidin-3- glycoside/ 100 g of material	Total content of tannins, mg of catechine/ 100 g of material
5ºC	191	186	57.77	1.22
20ºC	425	302	61.29	4.06
35ºC	432	312	62.79	4.54

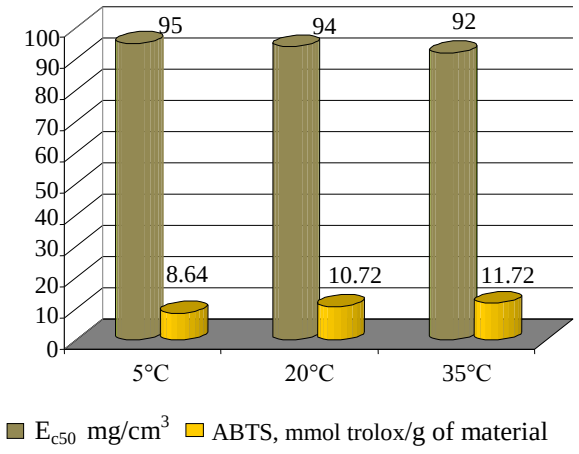


Fig. 3. Study of antioxidant properties.

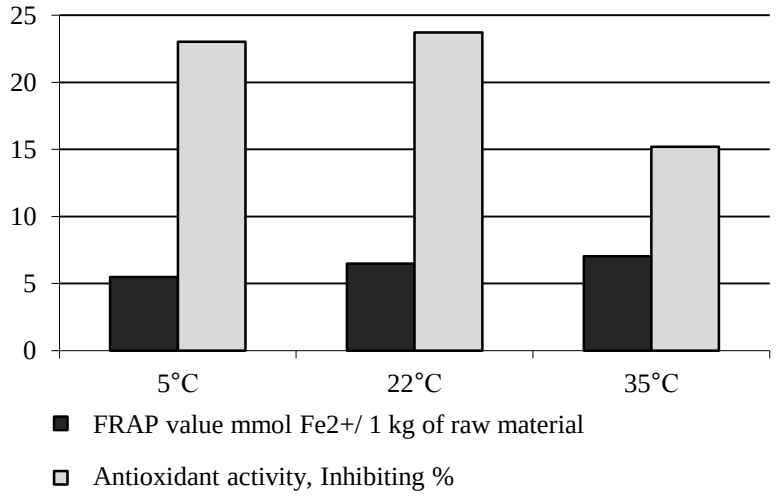


Fig. 4. Study of the restoring force and antioxidant activity.

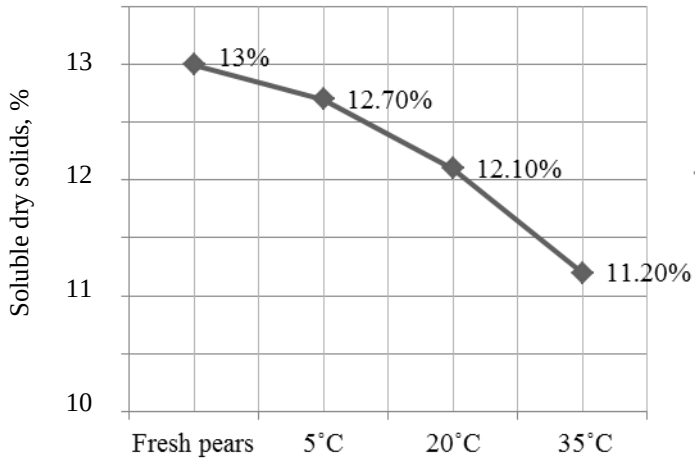


Fig. 5. Mass fraction of soluble solids.

Fig. 5 shows the average data on the change of the mass fraction of soluble solids in fresh pears and pears soaked in the extract at different temperatures. Sliced pear fruits were kept in grapes pomace extract for one hour at 5°C, 25°C and 35°C. As a result of the work the direct dependence of the loss of soluble solids from the extract temperature was observed. During the data processing the loss of the mass fraction of soluble solids in the leaching and the removal of air contained in the intercellular tissue spaces of pear slices was revealed. On average, after treatment, the samples lost by 1 to 2% solids.

For obtaining the final product - pear snacks – three kinds of drying were researched: convective at 70°C, IR drying at 70°C, freeze-drying.

Table 3 shows that the highest content of phenolic compounds (458 mg of gallic acid / 100 g of feedstock) and flavonoids (317 mg of catechin / 100 g of feed-stock) is had by pear snacks dried in freeze-drying. This type of drying preserves the greatest amount of anthocyanins (63.8 / 100 grams of feedstock) and tannins (2.52 mg of catechin / 100 grams of feedstock). It should also be noted that the heat treatment of pear snack is inferior to freeze drying on the total content of phenolic compounds, flavonoids, anthocyanins and tannins.

According to the Fig. 6 data it can be concluded that the highest antiradical activity, characterized by the lowest concentration of the extract (EC50) necessary for the binding of free radicals 50% 2,2-diphenyl-1-picrylhydrazyl (DPPH), is shown in freeze-dried pear snacks.

The highest antioxidant activity (15.1%) and the restoring force (15.1 mmol Fe2 + / 1 kg IP) belongs to pear snacks which are also freeze-dried (Fig. 7). Low antioxidant activity (10.2%) and the restoring force (7.38 mmol Fe_{2+} / 1 kg IP) are observed in snacks dried using IR method.

Practically all kinds of heat treatment decrease the antioxidant capacity of snacks. This is explained by the following: not only the phenolic substances, flavonoids, but also vitamins C, A, E, the enzyme system of the cell possess the antioxidant activity in plant cells as well. When heated these antioxidants are apparently destroyed and there is antioxidant activity inherent in the phenolic antioxidant complex left.

Table 3. Study of chemical composition of final product dried in different ways

Drying type	Total content of phenols, mg of gallic acid/ 100 g of material	Total content of flavonoids, mg of catechine/ 100 g of material	Total content of anthocyanins, mg of cyanidin-3- glycoside/ 100 g of material	Total content of tannins, mg of catechine/ 100 g of material
IR	211	251	Absent	2.40
Convective	314	285	24.57	1.54
Freeze	458	317	63.80	2.52

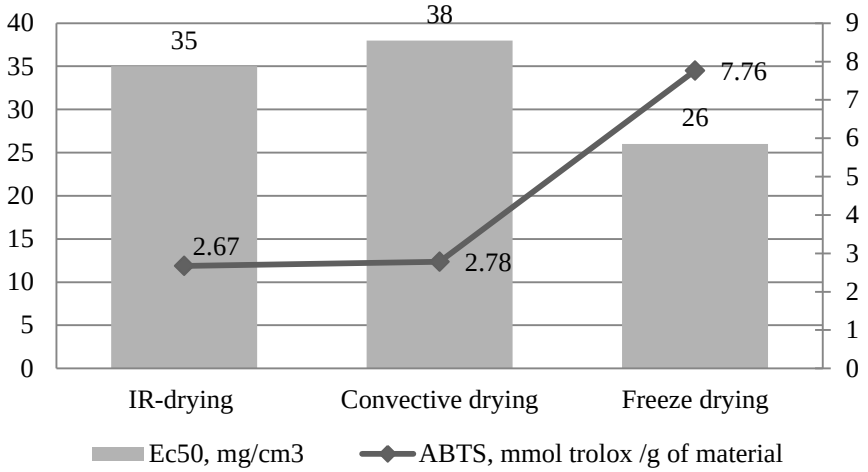


Fig. 6. Study of antioxidant activity of the final product.

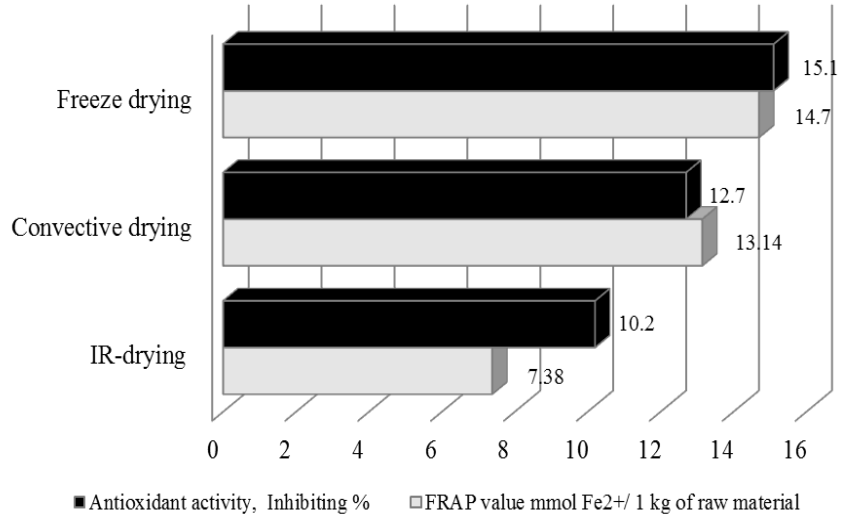


Fig. 7. Study o restoring force and antioxidant activity of the finished product.

During the convective snack drying method initially drying process is sufficiently effective. However, as the product of dehydration and the consequent decrease in its heat- and mass-providing characteristics, an increasing share of thermal energy does not flow inside the dried products [14]. The energy output of the process is grows, drying time increases, there are local overheating of the product, which is reflected in the quality of the finished snack.

In terms of convective heating the product is heated up primarily due to heat-and-moisture providing which is determined by thermal diffusion of moisture. Because of the small thermal conductivity capacity at 70°C drying flows for long enough, even with a small sample thickness, moisture evaporation is slow, which is to be explained by increased content of strongly bound moisture as well.

Using a vacuum freeze drying allows to reduce the process duration in 2–3 times, to improve structural and rheological characteristics as well as to achieve a water activity rate that ensures microbiological stability of the product, organoleptic characteristics typical of dry products.

In this connection, the possibility of using freeze drying, resulting in the process which is the inverse of condensation has been studied. Thus the fluid is displaced by a completely different method, which contributes to a higher quality and, of course, useful products. First, the product undergoes a deep freeze, and then the moisture is "dried" out of it under the pressure.

The research resulted in development of the technology for snack production including the following operations: acceptance of raw materials, cleaning, inspection, seed chamber removal, cutting, soaking, freeze-drying, re-inspection, pre-packing, packing (Fig. 8).

These pear snacks dried with three different methods were analyzed on organoleptic and biochemical parameters. Fig. 9 shows comparative data of physical-chemical rates of fruit snacks prepared by freeze, convective and IR drying methods.

The content of moisture mass fraction in fruit snacks, prepared by convective drying method is 4.7 ± 0.1%, at snacks dried by IR-method it is 4.6 ± 0.1%, while for chips prepared by freeze method I is about 4.8 ± 0.1 %. The average content of titratable acids in fruit snacks, prepared by convective drying and IR methods is 2.3 ± 0.1%, for the snacks prepared by freeze method is 2.4 ± 0.1%. The content of reducing substances in the fruit snack prepared by convection, freeze and IR drying methods range from 27.3 to 27.9%.

So the pear snacks tasting with the addition of grape pomace extract obtained by convective, infrared, and freeze-drying, received the following tasting evaluation (Fig. 10).

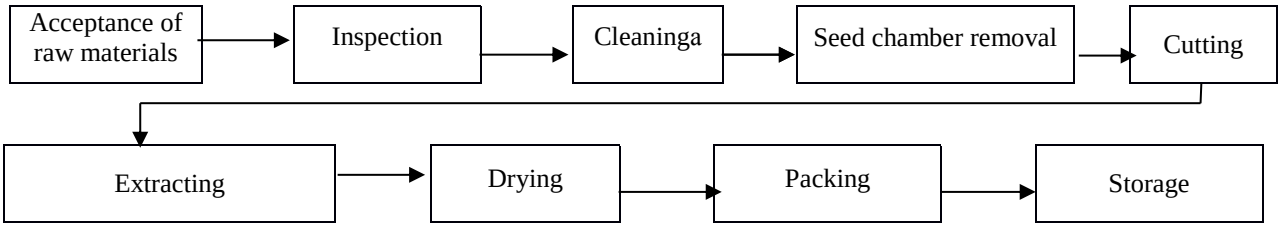


Fig. 8. Flow chart.

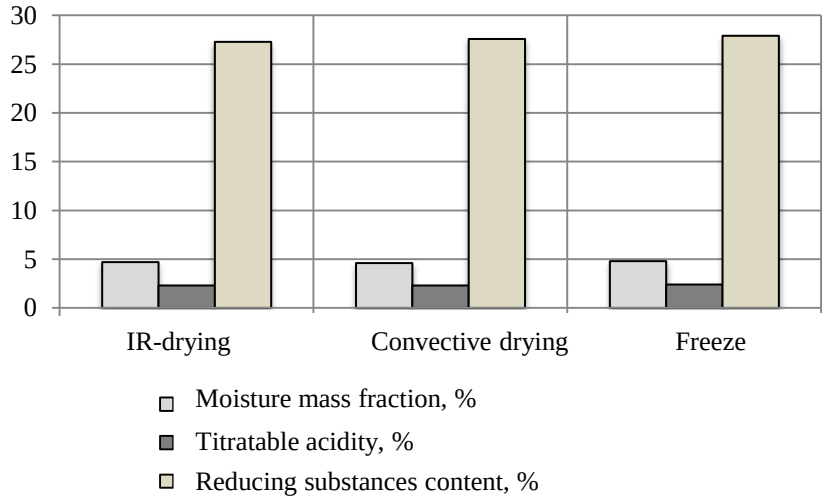


Fig. 9. Comparative analysis of physical-chemical rates of fruit snacks prepared by convective, freeze and IR drying methods.

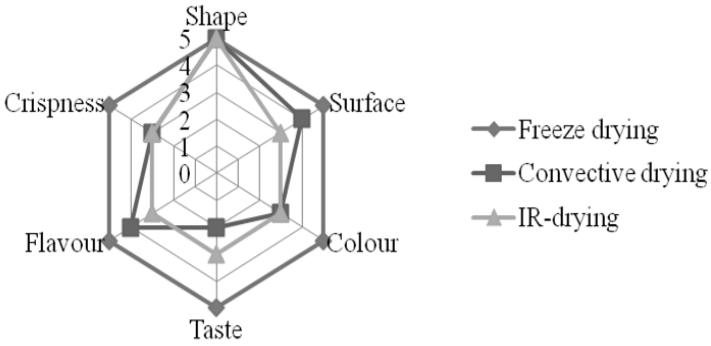


Fig. 10. Tasting evaluation of pear samples with the addition of grape pomace extract dried by different drying methods.

Analyzing the tasting evaluation data corresponding to the high quality of the final product, it must be concluded that the freeze drying method id the most advantageous one in the production of pear snacks with the addition of grape pomace extract, a freeze drying method.

Microbiological spoilage of food is determined by huge variety of bacteria, molds and yeasts. Safety of the studied pear snacks was evaluated by 3 factors (Table 4):

(1) The number of mesophilic aerobic and facultative anaerobic microorganisms QMAFAnM - a criterion which at 30°C for 48–72 hours allows to reveal all groups of microorganisms growing in certain environments. The identification of QMAFAnM was carried out according to All Union State Standard 10444.15-94 (23).

(2) The number of coliform bacteria (All Union State Standard 31747-2012) (34 ells).

(3) Mold and yeast were determined according to All Union State Standard P 10444.12 (36 ells).

Tests were conducted in an accredited testing laboratory of Hygiene and Epidemiology Centre in the Samara region.

Based on the data available, it can be concluded that the microbiological rates of pear snacks with high antioxidant properties prepared by freeze-drying, fully meet the requirements of TR CU 021/2011 "On food safety".

The shelf life of food - is one of the most important indicators, which depends on many factors: the quality of the raw material used, sanitary conditions of production, technology, equipment, storage and packaging conditions.

During the storage, studies of physical and chemical rates and antioxidant properties of natural pear snacks and snacks with grape pomace extract added were carried out. Experimental snack samples were packaged in foil and paper bags, laminated with heat-sealable materials approved for use by the institutions of Russian Federal Service for Consumer Rights Protection and Human Welfare, and providing the quality of product safety during storage and transportation. Storaged packaged snacks were evaluated in terms of shelf life, physical, chemical, organoleptic rates and content of the antioxidant activity with a period of 3 months. Recommended storage time during freeze-drying method is 12 months with a relative humidity of 60% and a temperature of 23˚C.

The results of physical and chemical rates are showed in Table 5.

Based on data in Table 5 we can conclude that by the study of physical and chemical parameters of snacks with higher antioxidant properties during 12 months' storage, the content of moisture mass fraction, acidity and reducing substances vary within established norms.

Studies of the content of antioxidant activity in pear snacks with enhanced antioxidant properties showed that during the storage rates have not changed unlike those of natural snacks (Table 6).

Study of Table 6 allows to conclude, that the grape pomace extract has a prolonging effect on the antioxidant properties of the final product during the storage.

The freshly collected samples were also analyzed for the duration of storage on the content of moisture mass fraction in accordance with All Union State Standard 5900-73 "Food concentrates. Methods for determination of moisture " (24) with a time period of 3 hours.

Table 4. Microbiological rates of snacks with antioxidant hyperactivity

Rates, measurement unit	Allowable levels	Actual Value	Normative Documents on Testing Methods
Total microbial number, KOE/g	Not more than 1×103	Less than 1.0×101	All Union State Standard 10444.15-94
Coliform, g	Is not allowed in 1.0	Not found в 1.0	All Union State Standard 31747-2012
Mold, KOE/g	Not more than 50	Less than 10	All Union State Standard 10444.12
Yeast, KOE/g	Not more than 50	Less than 10	All Union State Standard 10444.12

Table 5. Physical and chemical rates of pear snacks during the storage

Rates	Object	
	Fresh snacks	After 12 months' storage
Moisture Mass fraction, %	4.8 ± 0.3	4.9 ± 0.3
Titratable acidity, % calculated as Apple acidity	2.4 ± 0.1	2.3 ± 0.1
Content of soluble solids, %	27.9 ± 0.4	27.5 ± 0.4

Table 6. Study of chemical composition and antioxidant activity of pear snacks during the storage

Products of long-term storage	Total content of phenols, mg of gallic acid/ 100 g of material	Total content of flavonoids, mg of catechine/ 100 g of material	E_{c50} mg/cm^3	FRAP value mmol Fe2+/ 1 kg of raw material	Antioxidant activity, Inhibiting %
Pear snacks					
3 months' storage	116.3	46.3	169.3	1.73	4.6
6 months' storage	112.7	43.4	174.8	1.67	4.1
9 months' storage	109.3	40.1	190.4	1.23	4.1
12 months' storage	87.6	39.7	198.7	1.14	3.8
Pear snacks with higher antioxidant properties					
3 months' storage	457.3	317.1	26.0	14.4	14.9
6 months' storage	457.1	316.8	26.2	14.3	14.8
9 months' storage	456.7	316.6	26.2	13.1	14.1
12 months' storage	456.4	315.8	26.6	13.2	13.4

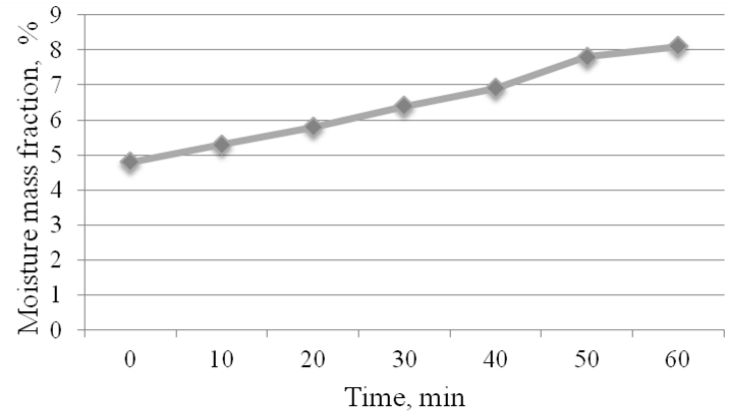


Fig. 11. Change of moisture mass fraction in final product without package.

It was found that in case of an opened package during the time crunch indicator decreases (Fig. 11), thus it is not recommended to store the opened package for more than 38 hours. The critical moisture content is 8%, as at higher humidity of the product development of microorganisms occurs.

The obtained results are quite illustrative and allow us to conclude that freeze-drying is the best way to produce a high quality final product of fruit crops of pears.

ACKNOWLEDGEMENTS

This study was financially supported by the Ministry of Education and Science of the Russian Federation within the basic part of the government task number 2014/199 Samara State Technical University on the project Creation of a scientific methodology for developing formulations and technologies of food products to control oxidative stress in humans code 974.

REFERENCES

1. Sedov E.N. *Selektsiya i sortiment yabloni dlya tsentral'nykh regionov Rossii* [Selection and apple crops for the central regions of Russia]. Orel: All-Russian Research Institute of Fruit Crop Breeding Publ., 2005. 311 p.
2. Shobinger U. *Fruktovye i ovoshchnye soki: nauchnye osnovy i tekhnologii* [Fruit and vegetable juices: scientific basis and technologies]. St. Petersburg: Professija Publ., 2004. 640 p.
3. Kulkarni S., DeSantos F.A., Kattamuri S., et al. Effect of grape seed extract on oxidative, color and sensory stability of a pre-cooked, frozen, re-heated beef sausage model system. *Meat Scienc*e, 2011, vol. 88, no. 1, pp. 139–144. DOI: https://doi.org/10.1016/j.meatsci.2010.12.014.
4. Guendez R., Kallithraka S., Makris D.P., and Kefalas P. Determination of low molecular weight polyphenolic constituents in grape *(Vitis uinifera sp.)* seed extracts: Correlation with antiradical activity. *Food Chemistry*, 2005, vol. 89, no. 1, pp. 1–9. DOI: https://doi.org/10.1016/j.foodchem.2004.02.010.
5. Sun T., Powers J.R., and Tang J. Evaluation of the antioxidant activity of asparagus, broccoli and their juices. *Food Chemistry*, 2007, vol. 105, no. 1, pp. 101–106.

6. Rockenbach I.I., Rodrigues E., Gonzaga L.V., et al. Phenolic compunds content and antioxidant activity in pomace from selected red grapes (*Vitis vinifera L.* and *Vitis Labrusca L.*) widely produced in Brazil. *Food Chemistry*, 2011, vol. 127, no. 1, pp. 174–179. DOI: https://doi.org/10.1016/j.foodchem.2010.12.137.
7. Škerget M., Kotnik P., Hadolin M., et al. Phenols, proanthocyanidins, flavones and flavonols in some plant materials and their antioxidant activities. *Food Chemistry*, 2005, vol. 89, no. 1, pp. 191–198. DOI: https://doi.org/10.1016/j.foodchem.2004.02.025.
8. Harbourne N., Jacquier J.C., Morgan D.J., and Lyng J.G. Determination of the degradation kinetics of anthocyanins in a model juice system using isothermal and non-isothermal methods. *Food Chemistry*, 2008, vol. 111, no. 2, pp. 204–208. DOI: https://doi.org/10.1016/j.foodchem.2008.03.023.
9. Crespy A. Tannins de pepins de raisin: possibilites de stabilization de la couleur, de protection contre l'oxydation et d'amelioration de la tenue en boushe sur vins rouges et roses. *Rev. fr. Oenol.*, 2002, vol. 195, pp. 23–27.
10. Rufino M.S.M., Fernandes F.A.N., Alves R.E., and de Brito E.S. Free radical-scavenging behaviour of some north-east Brazilian fruits in a DPPHradical dot system. *Food Chemistry*, 2009, vol. 114, no. 4, pp. 693–695. DOI: https://doi.org/10.1016/j.foodchem.2008.09.098.
11. Nilsson J., Stegmark R., and Åkesson B. Total antioxidant capacity in different pea (*Pisum sativum*) varieties after blanching and freezing. *Food Chemistry*, 2004, vol. 86, no. 4, pp. 501–507. DOI: 10.1016/j.foodchem.2003.09.002.
12. Arts Mariken J.T.J, Dallinga J Sebastiaan, Voss Hans-Peter, et al. A new approach to assess the total antioxidant capacity using the TEAC assay. *Food Chemistry*, 2004, vol. 88, no. 4, pp. 567–570. DOI: https://doi.org/10.1016/j.foodchem.2004.02.008.
13. Li Y., Jiang B., Zhang T., et al. Antioxidant and free radical-scavenging activities of chickpea protein hydrolysate (CPH). *Food Chemistry*, 2008, vol. 106, no. 2, pp. 444–450. DOI: https://doi.org/10.1016/j.foodchem.2007.04.067.
14. Korotkiy I.A. Analysis of the energy efficiency of the fast freezing of blackcurrant berries. *Foods and Raw Materials*, 2014, vol. 2, no. 2, pp. 3–14. DOI: 10.12737/5454.

Please cite this article in press as: Valiulina D.F., Makarova N.V., and Kustova I.A. Grape pomace extract and pear in snack production technology. *Foods and Raw Materials*, 2017, vol. 5, no. 1, pp. 63–72. DOI: 10.21179/2308-4057-2017-1-63-72.

ISSN 2310-9599. Foods and Raw Materials, 2017, vol. 5, no. 1

OPTIMIZATION OF TECHNOLOGICAL PARAMETERS OF PREPARATION OF DOUGH FOR RUSKS OF HIGH NUTRITION VALUE

A. A. Zhuravlev[a], S. I. Lukina[b,*], E. I. Ponomareva[b], and K. E. Roslyakova[b]

[a] Military Educational and Scientific Centre of the Air Force
N.E. Zhukovsky and Y.A. Gagarin Air Force Academy,
Starykh Bolshevikov Str. 54A, Voronezh, 394064, Russian Federation

[b] Voronezh State University of Engineering Technologies,
Revolyutsii Ave. 19, Voronezh, 394036, Russian Federation

* e-mail: lukina.si@yandex.ru

Received March 14, 2017; Accepted in revised form May 24, 2017; Published June 29, 2017

Abstract: The work has been performed on the basis of Department of technology of baking, confectionery, macaroni and grain processing productions of Voronezh State University of Engineering Technologies. The urgent line of development of the baking industry is the development of new formulations and resource-saving technologies of dry bread products of high nutrition value and functional orientation. The application of flour made of wholemeal wheat instead of high-quality wheat flour is perspective to realize it. An important condition to obtain consistently high-quality products and increase production efficiency is the establishment of optimum technological parameters of preparation of dough. Mathematical methods of planning of experiment are applied to study the interaction of the major technological factors influencing the process of preparation and the quality of dry bread products. The following are chosen as the major factors: the dosage of flour made of wholemeal wheat and the humidity of dough. The main indicator of quality of rusks characterizing their swelling capacity in water – the swelling capacity coefficient – was the output parameter. The optimization of parameters of preparation of dough for rusks was performed using experimental and statistical methods. As a result of the performed experiment a mathematical model in the form of regression equation which adequately describes the studied process has been developed. The statistical processing of experimental data has been performed according to Student, Kokhren and Fischer criteria (with the confidential probability of 0.95). The mathematical and graphic interpretation of regression equation have allowed to determine previously the optimum area of factorial space in which the highest value of output parameter is reached. The optimization of technological parameters of preparation of dough in the value of swelling capacity coefficient of rusks was performed using the method of Lagrange multipliers. Rational values of factors have been determined: the dosage of flour made of wholemeal wheat is 99.82%, the humidity of dough is 40.86%. Their choice has been validated by a series of parallel experiments which has shown sufficient convergence of results with the average square error of no more than 0.67%. On the basis of the obtained data a formulation and a way of production of rusks of high nutrition value "Crackling delicacy" has been developed.

Keywords: Flour made of wholemeal wheat, rusks, swelling capacity coefficient, central composite rotatable uniform planning, optimization

DOI 10.21179/2308-4057-2017-1-73-80 *Foods and Raw Materials*, 2017, vol. 5, no. 1, pp. 73–80.

INTRODUCTION

The technologies of ecologically safe resource-saving production and processing of agricultural raw materials and food products play a fundamental role in the social and economic development of the state. The implementation of programs for the creation of waste-free and low-waste complex technologies is based on the modern scientific achievements and their practical realization. One of the effective measures is the introduction of innovative technology of processing of wheat grain into flour made of wholemeal wheat and its use in baking production. Such a technology will allow to increase the quality and nutrition value of production, to reduce its prime cost, to intensify the technological process, will provide an opportunity for the enterprise to react more flexibly to market conditions. Thanks to the application of disintegration-wave method of crushing, flour made of wholemeal wheat is characterized by a 100% output, high dispersion (on average, 38–40 microns) and a high nutrition value. It preserves all the components of grain having a high potential in the content of protein and irreplaceable amino acids, food fibers, vitamins and mineral substances. The expediency of application of flour made of wholemeal wheat in the production of bakery products of wide range, including that for dietetic and preventive nutrition has been established by the performed researches. The regular use of

products made of this flour provides the activation of human's own microflora, the improvement of digestion processes and an increase in the accessibility of other products [1, 2].

One of the types of bakery products is rich rusks – the products with low humidity, a high nutritional value and a long period of storage allowing their use in remote regions of the country. Dry bread products are very popular with all the age groups of the population. According to Rosstat [the Federal State Statistics Service], the volume of their production in Russia steadily increases for the last 5 years, the annual gain averages 3–4%. In this regard, the development of new formulations and technologies of dry bread products of high nutrition value and functional orientation is urgent. At the same time, an important condition to obtain consistently high-quality products and increase production efficiency is the establishment of optimum technological parameters of preparation of dough.

The purpose of work was the study of interaction of the major technological factors influencing the process of preparation and the quality of dry bread products, the search of their optimum values with the use of methods of mathematical modeling.

STUDY OBJECTS AND METHODS

The objects of the study were dry bread products. Children's rusks developed in accordance with GOST 8494-96 have been taken as a basis. The dough for test specimens was prepared in the accelerated way, at the same time they replaced high-grade wheat flour by flour made of wholemeal wheat, butter – by mustard, the mass of sugar was reduced by 1/3, the mass of yeast was increased by 0.6 kg, they also added whey in the amount of 15 kg per 100 kg of flour according to the formulation. The duration of dough fermentation was 90 min. to the acidity of 4.0–4.5 degrees. The fermented dough was subjected to cutting and proving for 50 min. and baking for 15 min. at a temperature of 210–220°C. The baked dry bread plates were held at a temperature of 18–20°C for 10 h, further on their cutting in chunks and the drying of rusks for 15 min. at 180^{o} were performed.

Methods of mathematical planning of experiment – central composite rotatabel uniform planning – have been used in the work. The processing of experimental data consisted in the check of reproducibility of experiments (Kokhren Criterion), the calculation of coefficients of regression equation and the check of their statistical importance (Student Criterion), the establishment of adequacy of the obtained regression equation (Fischer Criterion) [3, 4].

The following are chosen as the major factors: x_1 is the dosage of flour made of wholemeal wheat (wheat germ oil), % to the total mass of flour; x_2 is the humidity of dough, % (Table 1). The main indicator of quality of rusks characterizing their swelling capacity in water – the swelling capacity coefficient – was used as the output parameter y. The swelling capacity of specimens was determined according to the technique provided in GOST 8494-96, the swelling capacity coefficient was calculated proceeding from an increase in the mass of each specimen after its swelling.

Table 1. Planning characteristics

Planning conditions	Values of factors	
	Dosage of wheat germ oil x_1, %	The humidity of dough x_2, %
Basic level (0)	75.00	41.0
Variability range	17.73	1.0
Upper level (+1)	92.73	42.0
Lower level (–1)	57.27	40.0
High "star" point (+1.41)	100.0	42.4
Low "star" point (–1.41)	50.00	39.6

The choice of intervals of change of factors was caused by the technical characteristics and quality of the finished products. The addition of wheat germ oil in the amount of less than 50% is inefficient as it does not has a considerable impact on the nutrition value of products. The increase in dough humidity by more than 42.0% provides a decrease in its viscosity and dilution. The semi-finished product with the dough humidity of less than 39.0% has a high viscosity and "abrupt" consistence which complicates its formation and affects the formation of properties of semi-finished products in the course of fermentation, proving and baking.

The optimization of technological parameters of preparation of dough for rusks of high nutrition value was performed using the methods of mathematical statistics and differential calculus.

RESULTS AND DISCUSSION

The first stage of work consisted in the identification of parameters of the mathematical model which adequately describes the dependence of output parameter on the studied factors. For these purposes the complete factorial experiment of type 2^2 according to the planning matrix given in Table 2 has experimentally been made (Experiments 1–4). Each experiment was implemented with two-time replication. Taking into account a possible future transition to second order planning, 5 parallel experiments have been implemented at the center point of the design (Experiments 9–13). To exclude the influence of uncontrollable parameters on the results of experiment the randomization of experiments with the application of the table of random numbers was used. Table 2 provides the arithmetic averages of response function according to the results of two parallel experiments.

Table 2. Planning matrix and results of the experiment

Experiment No.	Code values of factors		Natural values of factors		Response function
	X_1	X_2	x_1, %	x_2, %	y, c.u.
1	+1	+1	92.73	42.0	5.1
2	+1	–1	92.73	40.0	5.5
3	–1	+1	57.27	42.0	4.1
4	–1	–1	57.27	40.0	5.0
5	+1.41	0	100.0	41.0	5.8
6	0	+1.41	75.0	42.4	4.0
7	–1.41	0	50.0	41.0	4.7
8	0	–1.41	75.0	39.6	5.0
9	0	0	75.0	41.0	4.6
10	0	0	75.0	41.0	5.0
11	0	0	75.0	41.0	4.7
12	0	0	75.0	41.0	4.8
13	0	0	75.0	41.0	4.9

The application of complete factorial experiment provides the opportunity to calculate the estimates of regression coefficients and to develop a first order equation. It is known [3] that the intercept b_0 of regression equation is the estimate of process output at the center point of experiment which is mixed with the total estimate of quadratic effects of all factors. If the quadratic terms are significant, the predicted results of experiments at the center point of the design of experiment will considerably differ from their experimental values, as well. The parallel experiments at the center point of the design of experiment allow, without even starting the calculation of all (except b_0) estimates of coefficients of the equation, to judge about the possibility of description of the studied dependence using a first order equation without the inclusion of quadratic terms in it.

In this regard, values of the intercept b_0, arithmetic mean values of response function $\bar{y}_0$ at the center point of experiment, the estimation of difference dispersion $S^2(\bar{y}_0 - b_0)$ and the confidential error of difference ε (Table 3) have been calculated.

Table 3. Results of calculation of confidence error

Parameter	Value
Intercept b_0	4.93
Arithmetic average value of response function at the center point of the experiment $\bar{y}_0$	4.8
Difference-based variance estimate $S^2(\bar{y}_0 - b_0)$	$1.3 \cdot 10^{-3}$
Difference $\lvert\bar{y}_0 - b_0\rvert$	0.13
Confidence error of difference ε	0.078

The confidence error of difference ε has been estimated according to the formula

$$\varepsilon = t_{кр} \cdot \sqrt{S^2(\bar{y}_0 - b_0)}, \quad (1)$$

where t_{kp} is the critical value of Student criterion (t_{kp} = 2.16) with the accepted confidential probability of 0.95 and the number of degrees of freedom of 13.

The fulfillment of the condition $\varepsilon < \lvert\bar{y}_0 - b_0\rvert$ follows from the results of Table 3. It allows to recognize with the accepted confidential probability of 0.95 the distinction between $\bar{y}_0$ and b_0 essential, and to consider the linear regression equation obtained using the results of complete factorial experiment an unsatisfactory mathematical description. In this regard, a decision on the transition to second order planning allowing to obtain the adequate mathematical description due to the inclusion of estimates of quadratic effects of factors in it has been made.

For this purpose, the experiments at the "star" points (Table 2, Experiments 5–8) were added to the planning matrix. The choice of value of "star" leverage ± of 1.41 is caused by the need of obtaining a uniform rotatabel design providing the obtaining of the same value of dispersion and the prediction for any point within the studied area. The experiments at the "star" points were realized with two-time replication, as well. Table 2 provides the arithmetic averages of response function according to the results of two parallel experiments.

The statistical processing of results of uniform rotatabel planning consisted in the calculation of estimates of coefficients of regression equation, the check of their importance, the estimation of reproducibility of experiments and the establishment of adequacy of the obtained regression equation [3, 5]. Statistical Student, Kokhren and Fischer criteria (with the confidential probability of 0.95) have been used for this purpose.

As a result of statistical processing of results of planning of experiment (Table 2) a regression equation which adequately describes the dependence of swelling

capacity coefficient of rusks y on the studied factors has been obtained:

$$y = 4.8 + 0.39X_1 - 0.35X_2 + 0.15X_1X_2 + \\ +0.23X_1^2 - 0.14X_2^2, \quad (2)$$

where X_i is the code values of the factors related to the natural values x_i with the ratios:

$$X_1 = \frac{x_1 - 75}{17.73}; \quad X_2 = \frac{x_2 - 41}{1}. \quad (3)$$

The second stage consisted in the interpretation of the regression equation (2). The mathematical description obtained using the results of rotatabel planning provides the information on the response surface, however, the interpretation of equation in the form of (2) is complicated. In this regard, to establish the type of surface and reduce the equation to the accepted form we will use the means of analytical geometry [6].

For this purpose we will present the regression equation (2) in the form of the general second order surface equation:

$$a_{11}x^2 + a_{22}y^2 + a_{33}z^2 + 2a_{12}xy + 2a_{13}xz + \\ + 2a_{23}yz + 2a_1x + 2a_2y + 2a_3z + a_0 = 0, \quad (4)$$

where a_0 and a_{ii} are the coefficients of the equation of surface of the second order; x, y and z are the variables which correspond to the factors X_1 and X_2 and the response function y.

Comparing the regression equation (2) with the general surface equation (4), we determine the coefficients a_0 and a_{ii} (Table 4). Orthogonal invariants of the quadratic function (4) provide the information on the configuration of surface of the second order which is described by the equation (2):

– the determinant δ of a matrix of quadratic form

$$\delta = \begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{12} & a_{22} & a_{23} \\ a_{13} & a_{23} & a_{33} \end{vmatrix} = \begin{vmatrix} 0.23 & 0.075 & 0 \\ 0.075 & -0.14 & 0 \\ 0 & 0 & 0 \end{vmatrix} = 0,$$

– the determinant δ of a matrix of quadratic function

$$\Delta = \begin{vmatrix} a_{11} & a_{12} & a_{13} & a_1 \\ a_{12} & a_{22} & a_{23} & a_2 \\ a_{13} & a_{23} & a_{33} & a_3 \\ a_1 & a_2 & a_3 & a_0 \end{vmatrix} = \begin{vmatrix} 0.23 & 0.075 & 0 & 0.195 \\ 0.075 & -0.14 & 0 & -0.175 \\ 0 & 0 & 0 & -0,5 \\ 0.195 & -0.175 & -0.5 & 4.8 \end{vmatrix} = 0.00946,$$

– the trace τ_1 of the matrix (the sum of diagonal elements of the matrix A)

$$\tau_1 = a_{11} + a_{22} + a_{33} = 0.23 + (-0.14) + 0 = 0.09,$$

– the sum τ_2 of the main minors of the second order of the matrix

$$\tau_2 = \begin{vmatrix} a_{11} & a_{12} \\ a_{12} & a_{22} \end{vmatrix} + \begin{vmatrix} a_{11} & a_{13} \\ a_{13} & a_{33} \end{vmatrix} + \begin{vmatrix} a_{22} & a_{23} \\ a_{23} & a_{33} \end{vmatrix} = \\ = \begin{vmatrix} 0.23 & 0.075 \\ 0.075 & -0.14 \end{vmatrix} + \begin{vmatrix} 0.23 & 0 \\ 0 & 0 \end{vmatrix} + \begin{vmatrix} -0.14 & 0 \\ 0 & 0 \end{vmatrix} = -0.03783.$$

As $\delta = 0$ and $\Delta > 0$ are the determinants, the response surface described by the equation (2) has the form of a hyperbolic paraboloid.

The reduction of a square regression equation of the type (2) to the accepted form consists in the transition from the initial coordinate axes X_1 and X_2 to the new axes Z_1 and Z_2. At the same time the beginning of coordinates should be transferred to a new point of factorial space, and the new coordinate axes Z_1 and Z_2 should be turned by a certain angle of φ of the initial axes X_1 and X_2.

Proceeding from the necessary condition of existence of the function extremum y

$$\begin{cases} \frac{\partial y}{\partial X_1} = 0.39 + 0.15X_2 + 0.46X_1 = 0, \\ \frac{\partial y}{\partial X_2} = -0.35 + 0.15X_1 - 0.28X_2 = 0, \end{cases}$$

we define the coordinates $X_{1s} = -0.37$ and $X_{2s} = -1.45$ of the stationary point (the center of response surface) which contains the extremum of function (2). The insertion of coordinates of the stationary point in the equation (2) provides the value of response function at the center point of the surface $y_s = 4.98$.

Solving the second order characteristic equation

$$\begin{vmatrix} (b_{11} - B) & \frac{1}{2}b_{12} \\ \frac{1}{2}b_{21} & (b_{22} - B) \end{vmatrix} = \\ = B^2 - (b_{11} + b_{22})B + (b_{11}b_{22} - 0,25b_{12}^2) = 0,$$

we define the coefficients of the accepted form $B_{11} = 0.25$ and $B_{22} = -0.15$.

Table 4. Values of coefficients of the general equation of surface of the second order (5)

Coefficient	a_{11}	a_{22}	a_{33}	a_{12}	a_{13}	a_{23}	a_1	a_2	a_3	a_0
Value	0.23	–0.14	0	0.075	0	0	0.195	–0.175	–0.5	4.8

Thus, the regression equation (2) after canonical transformations has the form

$$y = 4.98 + 0.25Z_1^2 - 0.15Z_2^2. \quad (5)$$

The angle of rotation of the new coordinate axes Z_1 and Z_2 of the initial axes X_1 and X_2 is

$$\varphi = \frac{1}{2}\text{arctg}\frac{b_{12}}{b_{11} - b_{22}} = 10.9\,°.$$

Taking into account the parameters of the canonical transformation the relation between the coordinates X_i and the new Z_i has the form:

$$X_1 = (Z_1 + X_{1s})\cos\phi - (Z_2 + X_{2s})\sin\phi = 0.982Z_1 - 0.19Z_2 - 0.087,$$
$$X_2 = (Z_1 + X_{1s})\sin\phi + (Z_2 + X_{2s})\cos\phi = 0.19Z_1 + 0.982Z_2 - 1.494.$$

Fig. 1 provides the graphic interpretation of the regression equation (2) in the form of response surface. It is visible that the surface described by the equation (2) the accepted form of which is presented in the form of (5) has the form of a hyperbolic paraboloid with a special central point (the minimax point). In the line of one of the accepted axes there is the minimum and in the line of other axis there is the maximum.

More detailed information on the configuration of response surface is provided by its two-dimensional sections. Fig. 2 provides flat sections of response surface. It is visible that the sections of hyperbolic paraboloid made by the coordinate planes $y = h$ (where h is an arbitrary constant) have the form of hyperboles. With $h < 4.98$ the half-hyperboles are extended along the accepted axis Z_2, and with $h > 4.98$ the half-hyperboles are extended along the accepted axis Z_1.

Fig. 2 also presents a two-dimensional section of the area of experiment in the form of a circle with a radius of $R = 1.41$ the center of which coincides with the center point of the experiment.

The analysis of two-dimensional sections of response surface allows to determine previously the optimum area of factorial space in which the highest value of output parameter y is reached. Such a mode (see Fig. 2) obviously corresponds to the vicinities of the right "star" point (according to Table 1 for dosages of wheat germ oil x_1 = 100% and the humidity of dough x_2 = 41%).

These results are determined by the influence of flour made of wholemeal wheat and the humidity of dough on the formation of properties of semi-finished products and indicators of quality of finished products. It has been revealed that with an increase in the dosage of flour made of wholemeal wheat and a decrease in the humidity of dough the swelling capacity coefficient of rusks increases. Its highest value has been noted when adding the maximum amount of wheat germ oil and humidity of dough at the center point of the design (Fig. 2). The existence of considerable amounts of peripheral parts of grain (food fibers) with a high water absorbing ability in such flour is determinative. The mass of water retained by 1 g of flour made of wholemeal wheat is 1.27 g compared to 0.85 g for high-grade wheat flour.

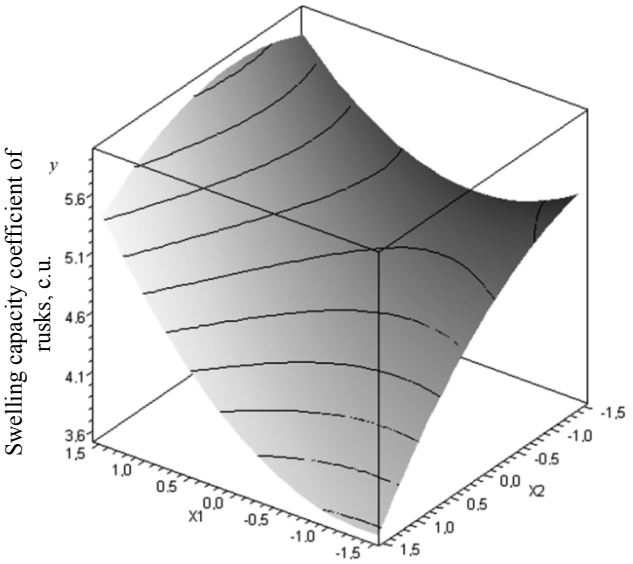


Fig. 1. General view of the response surface y.

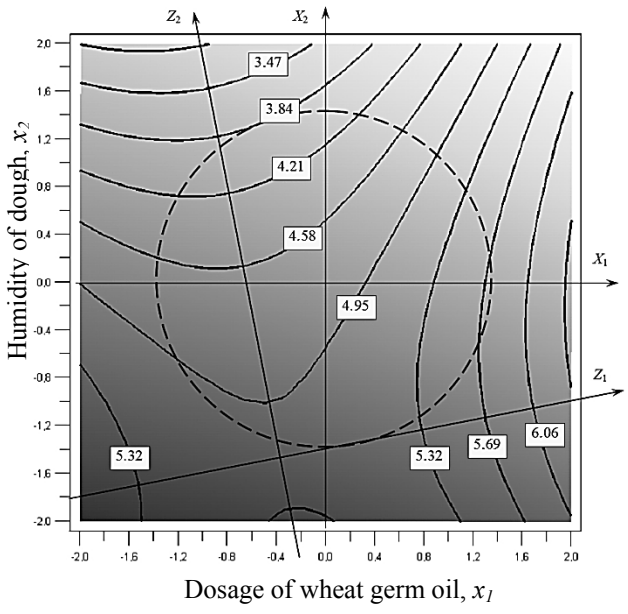


Fig. 2. Flat sections of response surface.

The third stage consisted in the optimization of dough formulation in the value of swelling capacity coefficient of rusks y.

We will formulate the problem of optimization of technological parameters of preparation of dough for rusks of high nutrition value as follows. It is necessary

to determine such values of the variables X_1 and X_2 which provide the maximum value of the swelling capacity coefficient $y = y(X_1, X_2)$. At the same time the values of the variables X_1 and X_2 are also to be in the area of experiment the borders of which are determined by the values of factors at the "star" points.

We will present the specified restriction imposed on the variables X_1 and X_2 in the form of constraint equation

$$\varphi(X_1, X_2) = X_1^2 + X_2^2 = R^2, \quad (6)$$

which is a sphere in the factorial space with a radius of R the center of which is at the center point of the experiment.

Thus, we have a problem of conditional optimization:

$$\begin{cases} y(X_1, X_2) = 4.8 + 0.39X_1 - 0.35X_2 + 0.15X_1X_2 + 0.23X_1^2 - 0.14X_2^2 \to \max \\ \phi(X_1, X_2) = X_1^2 + X_2^2 = R^2. \end{cases} \quad (7)$$

We will solve the problem of conditional optimization using the method of Lagrange multipliers [7] which allows to reduce the problem of conditional extremum to an unconditional problem of search of function extremum.

For this purpose we will generate a Lagrange auxiliary function $F(X_1, X_2, \lambda)$ which is the sum of the equation $y(X_1, X_2)$ and the restriction $\varphi(X_1, X_2)$ multiplied by an uncertain Lagrange multiplier λ:

$$F(X_1, X_2, \lambda) = 4.8 + 0.39X_1 - 0.35X_2 + 0.15X_1X_2 + 0.23X_1^2 - 0.14X_2^2 + \lambda(X_1^2 + X_2^2 - R^2). \quad (8)$$

A necessary condition of unconditional extremum of Lagrange function $F(X_1, X_2, \lambda)$ is the equality of differential derivatives of function (8) to zero by all the independent variables X_1, X_2 and an uncertain multiplier λ:

$$\begin{cases} \frac{\partial F(X_1, X_2, \lambda)}{\partial X_1} = 0.39 + 0.15X_2 + 0.46X_1 + 2\lambda X_1 = 0 \\ \frac{\partial F(X_1, X_2, \lambda)}{\partial X_2} = -0.35 + 0.15X_1 - 0.28X_2 + 2\lambda X_2 = 0. \\ \frac{\partial F(X_1, X_2, \lambda)}{\partial \lambda} = X_1^2 + X_2^2 - R^2 = 0 \end{cases} \quad (9)$$

To solve the system of equations (9) it is necessary to assign the values of the radius R in the range from 0 to 1.41. However, as it follows from Fig. 2, the conditional extremum of coefficient of swelling of rusks $y = y(X_1, X_2)$ is reached under the condition $R = 1.41$. In this regard the problem of optimization is considered in future for the case $R = 1.41$.

Solving the system (9) referring the variables X_1, X_2 and the Lagrange multiplier λ, we obtain the values λ^* and coordinates of stationary points of factorial space X_1^* and X_2^* at which the conditional extremum of function is reached (2) (Table 5). It is not difficult to see that the coordinates of each extreme point satisfy the constraint equation (6).

The condition (9) is a necessary condition for the existence of Lagrange function extremum (8), but not a sufficient one. To check the sufficient condition for the existence of the found extrema and the establishment of their character we will use a matrix

$$H = \begin{pmatrix} 0 & \frac{\partial \varphi}{\partial X_1} & \frac{\partial \varphi}{\partial X_2} \\ \frac{\partial \varphi}{\partial X_1} & \frac{\partial^2 F}{\partial X_1^2} & \frac{\partial^2 F}{\partial X_1 \partial X_2} \\ \frac{\partial \varphi}{\partial X_2} & \frac{\partial^2 F}{\partial X_2 \partial X_1} & \frac{\partial^2 F}{\partial X_2^2} \end{pmatrix}, \quad (10)$$

which is generated using the differential derivatives $\frac{\partial \varphi}{\partial X_i}$ of the constraint equation (6) and the Hessian matrix $\begin{pmatrix} \frac{\partial^2 F}{\partial X_1^2} & \frac{\partial^2 F}{\partial X_1 \partial X_2} \\ \frac{\partial^2 F}{\partial X_2 \partial X_1} & \frac{\partial^2 F}{\partial X_2^2} \end{pmatrix}$.

Table 5. Results of optimization

Point No.	X_1^*	X_2^*	λ^*	det$H$	Constraint extremum functions	y, c.u.
1	–0.55	1.30	0.31	–8.57	min	3.86
2	–0.44	–1.34	–0.016	–2.12	min	4.98
3	–0.99	–1.0	–0.11	2.18	max	5.0
4	1.40	–0.14	–0.36	7.62	max	5.82

Inserting all the differential derivatives in the matrix (10), we will generate its determinant

$$\det H = \begin{vmatrix} 0 & 2X_1 & 2X_2 \\ 2X_1 & (0.46+2\lambda) & 0.15 \\ 2X_2 & 0.15 & (-0.28+2\lambda) \end{vmatrix}. \quad (11)$$

For each found stationary point with the coordinates (X_1^*, X_2^*, λ^*) we calculate the value of determinant of the matrix H (Table 5) using the formula (11). It is visible that the matrix H is negatively certain for the first two stationary points (since $\det H < 0$), therefore, for these points, the second order differential of the Lagrange function $d^2F > 0$ and, thus, these points are the points of conditional minimum. For other stationary points, the matrix H is positively certain, the second order differential of the Lagrange function $d^2F < 0$, therefore, the required stationary points are the points of conditional maximum. The values of optimization parameter y at the established stationary points of factorial space are calculated using the equation 2 and are presented in Table 5.

The results of optimization are in full accordance with the configuration of response surface. Thus, the first two stationary points with the coordinates (–0.55; 1.3) and (–0.44; –1.34) respectively are located on the descending half-hyperbole paraboloids (see Fig. 2). Therefore, the specified points are classified as the points of conditional minimum of the optimization parameter (2) (see Table. 5). Two remained points the coordinates of which are equal to (–0.99;–1.0) and (1.40;–0.14) respectively, are located on the ascending half-hyperbole paraboloids (see Fig. 2) and are classified as the points of the conditional maximum.

Thus, proceeding from the formulated condition of optimization (7), the parameters of doughing $X_1^* = 1.4$ and $X_2^* = -0.14$ those which provide the obtaining of rusks with the maximum value of swelling capacity coefficient, $y = 5.82$ c.u., should be considered as rational ones.

The transition from code values of factors to natural ones taking into account the characteristics of planning (see Table 1) allows to obtain rational values of dosage of wheat germ oil x_1 = 99.82% and humidity of dough x_2 = 40.86%.

The fourth stage consisted in the estimation of reliability and degree of accuracy of the obtained value of optimization criterion.

Dispersion of prediction of the value of optimization parameter [3]

$$S^2(y) = S_{b_0}^2 + S_{b_i}^2 R^2 + S_{b_{ii}}^2 R^4 + 2\,\mathrm{cov}_{b_0 b_{ii}} R^2, \quad (12)$$

where $S_{b_0}^2$, $S_{b_i}^2$ and $S_{b_{ii}}^2$ are the dispersions when determining the regression coefficients b_0, b_i and b_{ii} respectively; $\mathrm{cov}_{b_0 b_{ii}}$ is covariance; R is the radius of the sphere with a point of the optimum values of factors $X_1^* = 1.4$ and $X_2^* = -0.14$ ($R = 1.41$).

Dispersions when determining regression coefficients are related to residual dispersion and constants of dispersion matrix by the known ratios. Error of prediction of value of optimization criterion

$$\delta = t_{кр}\sqrt{S^2(y)}, \quad (13)$$

where t_{kp} is the critical value of Student criterion (t_{kp} = 2.37 with the significance value p = 5% and the number of degrees of freedom f = 7).

Table 6 provides the results of calculations of dispersion of prediction $S^2(y)$ of the optimization parameter and its confidential interval $y \pm \delta$ (with the confidential probability of 0.95).

The objectivity of determination of rational values of parameters of preparation of dough is confirmed by the results of parallel experiments that show sufficient convergence of results. The average square error did not exceed 0.67%.

CONCLUSION

On the basis of the obtained data a formulation and a way of production of rusks of high nutrition value "Crackling delicacy" has been developed. As for the organoleptic and physical and chemical indicators of quality, the products do not concede the traditional ones, and as for the content of protein, food fibers, mineral substances and vitamins they considerably surpass them (Table 7). Technical documentation (TU 9110-394-02068108-2017) has been developed for the enriched product.

Table 6. Optimum modes. Results of determination of confidential interval

Parameter	Value
Optimum value of criterion of optimization, c.u.	5.82
Dispersion S^2 (ŷ)	0.08
Prediction error δ , c.u.	0.67
Confidential interval $y \pm \delta$, c.u.	5.82 ± 0.67

Table 7. Characteristics of nutrition value of dry bread products

Name of the indicator	Daily rate for the adult (according to TR TS 022/2011)	Children's rusks (control)		Rusks "Crackling delicacy"	
		Contents in 100 g of the product	Degree of satisfaction of daily requirement, %	Contents in 100 g of the product	Degree of satisfaction of daily requirement, %
Proteins, g	75	9.6	13	11.9	16
Fats, g	83	2.9	3	4.6	6
Carbohydrates, g	365	74.9	21	63.1	17
Food fibers, g	30	3.1	10	9.8	33
Potassium, mg	3500	108	3	307	9
Calcium, mg	1000	16	2	55	6
Phosphorus, mg	800	76	9	336	42
Magnesium, mg	400	14	4	98	25
Iron, mg	14	1.3	9	4.2	30
Vitamin B_1, mg	1.4	0.14	10	0.40	28
Vitamin B_2, mg	1.6	0.02	1	0.13	8
Vitamin PP, mg	18	1.05	6	4.80	27
Vitamin E, mg	10	0.85	9	3.88	39
Caloric value, kcal / kJ	2500/10467	364/1524	15	341/1428	14

REFERENCES

1. Magomedov G.O. and Ponomareva E.I. *Nauchnye i prakticheskie osnovy tekhnologii sbivnykh funktsional'nykh khlebobulochnykh izdeliy* [Scientific and practical bases of technology of whipped functional bakery products]. Voronezh: VSTU Publ., 2010. 248 p.
2. Ponomareva E.I., Lukina S.I., Odintsova A.V., and Zubkova E.V. Primenenie muki iz tsel'nosmolotogo zerna pshenitsy i pryanostey v proizvodstve akhloridnogo khleba [Use of flour from wholemeal wheat and spices in the production of non-chloride bread]. *Khleboprodukty* [Bakery products], 2016, no. 8, pp. 40–41.
3. Grachev Yu.P. and Plaksin Yu.M. *Matematicheskie metody planirovaniya eksperimenta* [Mathematical methods of planning of experiments]. Moscow: DeLi Print Publ., 2005. 296 p.
4. Magomedov G.O., Lukina S.I., Zhuravlev A.A., and Israilova Kh.A Optimisation of the recipe formula of a bisquit with the use of experimentally-statistical approach. *Storage and processing of farm products*, 2011, no. 8, pp. 38–42. (In Russian).
5. Myers R.N., Montgomery D.C., and Anderson-Cook C.M. *Response Surface Methodology: Process and Product Optimization Using Designed Experiments*. Wiley (Wiley Series in Probability and Statistics), 2009. 680 p.
6. Kanatnikov A.N. and Krishchenko A.P. *Analiticheskaya geometriya* [Analytical geometry]. Moscow: MSTU of N.E. Bauman Publ., 2000. 388 p. Available at: http://bookree.org/reader?file=475658&pg=1 (accessed 31 March 2017).
7. Tsirlin A.M. *Metody optimizatsii dlya inzhenerov: monografiya* [Methods of optimization for engineers: monograph]. Moscow–Berlin: Direkt-Media Publ., 2015. 214 p.

Please cite this article in press as: Zhuravlev A.A., Lukina S.I., Ponomareva E.I., and Roslyakova K.E. Optimization of technological parameters of preparation of dough for rusks of high nutrition value. *Foods and Raw Materials*, 2017, vol. 5, no. 1, pp. 73–80. DOI: 10.21179/2308-4057-2017-1-73-80.

INNOVATIVE ENCAPSULATION TECHNOLOGY OF FOOD SYSTEMS USING A BY-PRODUCT OF DAIRY PRODUCTION

R. A. Zhuravlev[a], M. Yu. Tamova[a,*], N. A. Bugayets[a], V. M. Poznyakovskiy[b], and N. D. Penov[c]

[a] Kuban State Technological University,
Moskovskaya Str. 2, Krasnodar, 350072, Russian Federation

[b] South Ural State University (National Research University),
Lenin Ave. 76, Chelyabinsk, 454080, Russian Federation

[c] University of Food Technologies,
Maritsa Blvd. 26, Plovdiv, 4000, Bulgaria

* e-mail: tamova_maya@mail.ru

Received December 07, 2016; Accepted in revised form February 23, 2017; Published June 29, 2017

Abstract: Currently, promising innovative direction in the food production technology is the use of techniques of "molecular gastronomy", allowing to modify the consumer properties of traditional foods. One of the techniques of this direction is the technology of "spherification" – the process of encapsulation of various food masses (sauces, juices, extracts, etc.). This technology will allow not only to use it as a tool of innovative management in the restaurant business, but also to expand the field of application of encapsulation in connection with the use of structure-forming agents of domestic production and by-products of the dairy industry. The purpose of the study was to investigate the influence of various factors on the process of encapsulation of food masses: generation of alginate shell when using curd whey as a capsule-forming medium. Methods of instrumental analysis are used in the work. Determination of the qualitative composition and identification of the test ingredients for encapsulation was carried out by IR-Fourier spectrometry. Capsules were prepared by axially feeding into the curd whey of sodium alginate solutions through a device for producing encapsulated products with a fixed size of the nozzle outlets. The results of determining the qualitative composition of the binary system "sodium alginate – curd whey" presumably indicate the complexation of polymers present in the system. It was found that in order to obtain a capsule shape close to a roundly regular one, the concentration of sodium alginate in the encapsulated solution should be between 0.8% and 1.2%. With an increase in the outlet diameter, and also with an increase in the concentration of the structure-forming agent in the encapsulated solution, an increase in the diameter of capsules was observed. The diameter of capsules obtained under the given conditions ranged from 3.7 to 5.7 mm. Generalization of the experiment results served as the basis for developing the technology of encapsulated food products based on the "spherification" method by diffusion of the cross-linking ion (Ca^{2+}) from an external reservoir (curd whey) into a capsular liquid containing sodium alginate. Process conditions for the production of encapsulated food products with specified consumer properties have been established.

Keywords: Capsulation, sodium alginate, milk whey, calcium alginate

DOI 10.21179/2308-4057-2017-1-81-89 *Foods and Raw Materials*, 2017, vol. 5, no. 1, pp. 81–89.

INTRODUCTION

One of the innovative directions in the technology of catering production is the use of "molecular gastronomy" techniques, based on scientific knowledge of the properties of food products and the possibility of modifying their consumer properties [1].

With the advent of "molecular gastronomy," the technological properties of little-known hydrocolloids became more applicable for catering producers, which influenced the expansion of their use in the development of innovative food products [2, 3]. One of the methods of this direction is encapsulation of various food masses (sauces, juices, extracts, etc.).

In the food industry, the use of encapsulation technology is due to a variety of reasons. This method is an effective tool for delivering biologically active molecules (antioxidants, minerals, vitamins, phytosterols, polyunsaturated fatty acids, etc.) and living cells (probiotics) into food [4–6].

Encapsulation is the process of incorporating one material into a shell made of another material to produce particles ranging in size from several nanometers to several millimeters, in other words, immobilizing solid, liquid or gaseous substances into capsules that release the contents at a controlled rate for a predetermined period of time under certain

environment conditions. The substance that is encapsulated is called the active substance, or the main product, or internal phase. The material into which the main product is enclosed is called a shell, a membrane, a wall, an outer phase, or a matrix [7–11].

The following substances are used as membrane material for encapsulation: Hydrogels (agar-agar, k-carrageenan, alginates, chitosan, cellulose, etc.), proteins (collagen, gelatin, chicken egg whites, fibrin, etc.), synthetic polymers (polyacrylamide, polyvinyl alcohol, polyethylene glycol methacrylate, polyisocyanates, polyurethane, etc.), etc. Based on the desired characteristics of the finished capsules, it is possible to select a particular substance for encapsulation [12–14].

Alginates are one of the most preferred ingredients for use in encapsulation technology. They are widely distributed in nature as a structural component of brown algae [15]. The safety of alginic acid and its ammonium, calcium, potassium and sodium salts was established by the Joint Expert Committee on Food Additives (JECFA) in 1992 [16].

Alginates are a family of unbranched binary copolymers formed by the residues of β-D-mannuronic acid (M) and α-L-guluronic acid (D), connected by a (1→4)-bond, which vary greatly in composition and sequence. The composition and structure of the sequence may vary depending on the season and growth conditions, as well as the part of the plant from which the structure-forming agent was obtained. The distribution of monomer residues of these acids along the polymer chain has a block character and forms three types of blocks:

– Homopolymer blocks of monotonic sequences of β-D-mannuronic acid residues (M-blocks);

– Homopolymer blocks of monotonic sequences of α-L-hyaluronic acid residues (H-blocks);

– Heteropolymer blocks with alternation of residues of both acids (M-H-blocks).

Such a structure of polymer molecules leads to formation of crystallinity zones in H-blocks, amorphous regions (flexibility zones) in M-blocks and areas with intermediate rigidity in heteropolymer M-H-blocks [17, 18].

Alginic acid salts are classified as high molecular weight water-soluble compounds used in the food industry as a structure-forming agent [19].

Alginates are thermostable compounds. The viscous properties of alginate remain in a wide range of temperatures. The viscosity of alginate solutions decreases by approximately 12% with temperature increase by every 5.6°C. These changes are reversible, solutions acquire initial viscosity upon cooling again. However, as a result of high thermal effects (above 95°C), destruction of the alginate molecule and the weakening of the van der Waals cohesion forces in the dispersion medium occur, which leads to a complete loss of aggregative gel stability, combination of colloidal particles in large aggregates, and formation of a dense precipitate, coagulate [20, 21].

Alginates have an important ability to bind ions, which is the basis of their gel-forming properties. The affinity of alginates for alkaline earth metals increases in the following order: $Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}$. This unique property of alginates distinguishes them from other polyanions. The only polyanion resembling alginates from this point of view is pectic/pectinic acid, whose affinity follows the scheme Mg < Ca, Sr < Ba [22]. In the absence of a bivalent cation (Ca^{2+}, Mg^{2+}), alginates only increase the viscosity of the solutions in proportion to the concentration of the structure-forming agent. However, when a multivalent cation is added, especially calcium and at a low pH (≤ 4), a gel is formed. The molecules in this case will be crosslinked by polyvalent ions (the "egg box" model). As the acidity of the solution decreases, the charge of dispersed particles decreases, and the forces of attraction begin to predominate over the repulsive forces. The residues of guluronic acid form a curved conformation, which ensures effective binding of cations (Fig. 1) [23, 24].

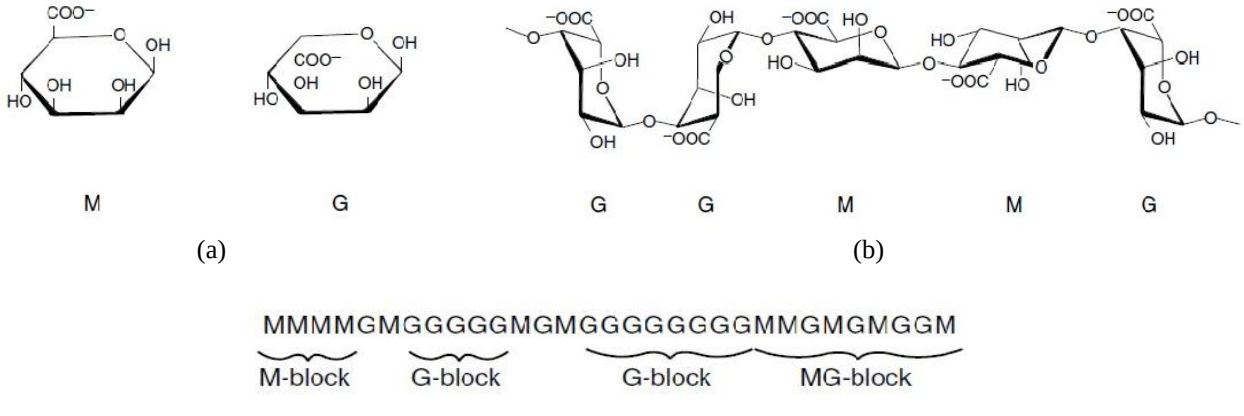


Fig. 1. Structural characteristics of alginates: (a) M: β-D-mannuronate, G: α-L-guluronate; (b) chain conformations; (c) block distribution.

In solving problems associated with gelation of sodium alginate, the determining property is the ability to regulate the introduction of cross-linking ions. This control can be carried out using two basic methods of preparing an alginate gel: method of diffusion and method of internal gel formation. The first method is characterized by diffusion of a cross-linking ion from the external reservoir into the alginate solution. Internal gel formation (sometimes called gelling in the block (*in situ*) differs from the previous method in that Ca^{2+} ions release from an inert calcium source in an alginate solution in a controllable way. Controlled release is usually achieved by changing pH level and/or by a limited source solubility of the calcium salt [25].

Ferran Adrià, chef at the El Bulli restaurant, became the pioneer of encapsulation technology in public catering, using the ability of alginate solutions to form gels by adding Ca^{2+} ions to them. In gastronomic circles, this method was termed "spherification" [26, 27]. The spherification technology consists in applying the diffusion method. The essence of the method consists in the interaction of sodium alginate with a bivalent cation, for example, a calcium ion or other polyvalent metal (zinc, aluminum, copper), to form a gel. Diffusion formation of the gel structure is characterized by a high gel formation rate, and this high-speed curing is used as a method of immobilizing and restructuring food products. Each drop of the alginate solution forms one granule of gel with the inclusion of the active agent. The spatial grid of the gel is formed by the interaction of calcium ions with carboxyl groups and additionally stabilized by coordination links between calcium ions and hydroxyl groups, hyaluronic acid residues (Fig. 2) [22].

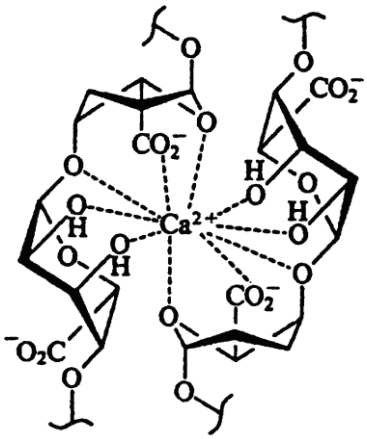


Fig. 2. Formation of a polysaccharide intermolecular complex with calcium ions.

A feature of the diffusion gel formation process is that the resulting gel is characterized by an inhomogeneous distribution of alginate with its high concentration on the surface, which gradually decreases towards the center of the gel. This phenomenon is explained by the fact that during the diffusion process a gelation zone is formed, which moves from the surface to the center of the gel. The alginate activity in this zone is zero, and the alginate molecule diffuses from the internal, unstructured part of the system, passing into the gel, into the zone of zero activity [28, 29].

This process of formation of alginate gels is used to produce spheres of small size with a dense shell and a liquid center. The product obtained in this way has the texture and appearance of natural fish caviar, and at the same time it has a different flavor and taste [30].

For the implementation of the spherification technology, a solution is prepared based on sodium alginate and liquid filler with projected taste. Introduction of the encapsulated mixture is carried out by axial dropping into a prepared solution containing calcium ions, and an instantaneous formation of a spherical shell around the encapsulated substance takes place. One of the striking examples of the use of this technique in the restaurant El Bulli is the production of spherical green "olives", which are served on a special spoon [30].

In the original procedure for the implementation of the spherification method, the concentration of alginate in the encapsulated solution is from 0.6 to 4%, the content of calcium chloride in the forming solution varies from 0.05 to 1.5 mole. Thus, it is possible to obtain spherical capsules with a diameter of 0.2 to 5 mm depending on the instrumentation used (pipette, syringe, oscillating nozzle, spray nozzle, coaxial air flow, electric field, etc.) and viscoelastic characteristics of the encapsulated solution of sodium alginate [5].

In studying this encapsulation technology, scientists have found that the rate of gel formation of sodium alginate solutions is the highest when using calcium chloride as a calcium-containing component. Compositions based on gluconate or calcium lactate have the least gel-forming ability. Alginate capsules formed by keeping them in a solution of calcium chloride acquire the maximum strength characteristics after 100 seconds of droplet retention in the forming solution, while in order to achieve such characteristics, capsules in a calcium lactate solution require a holding time of 500 seconds, calcium gluconate – of 3000 seconds.

Based on the application of the Tate law, a model was developed to predict the shape and size of alginate granules in the range from 2.9 to 3.25 mm produced by the drop method [31].

An alternative to "suppliers" of calcium ions (calcium chloride, lactate and gluconate) is a milk whey, which is a by-product of cheese production, or casein, and is not widely used for commercial purposes, and often simply recyclable.

Milk whey is close to natural cow milk in its composition [32] and is rich in physiologically valuable whey proteins, water-soluble vitamins and lactose. There are two types of milk whey: curd (sour) and cheese (sweet).

The choice of curd whey as a calcium-containing component with the application of encapsulation technology by the method of spherification is due to the high content of calcium in it as compared with the cheese whey [33]. Inclusion of curd whey in the composition of the shell increases the nutritional value of a capsule, and its application in the production of

encapsulated food products seems to be a promising direction.

The purpose of the study was to review the process of the formation of sodium alginate when using by-products of dairy production as a calcium-containing component for encapsulation of food masses.

OBJECTS AND METHODS OF STUDY

Sodium alginate (TU 15-544-83 "Sodium alginate food") and curd whey (GOST R 53438-2009 "Dairy whey. Specifications") were used as the objects of the study.

For the preparation of binary systems "sodium alginate – curd whey", a sample of sodium alginate was injected into the curd whey solution, dispersed at a temperature of 20 to 22°C for 60 minutes with a magnetic stirrer. The resulting solution was dried in a Vac Modul vacuum module, with a vacuum pump VP1, for VD 53 to a moisture mass fraction in the sample of 15%.

To prepare model solutions to be encapsulated, a sample of sodium alginate was dispersed in a mixture of curd whey and water taken at a ratio of 50 : 50 at a temperature of 20 to 22°C for 3–4 minutes on a magnetic stirrer. The resulting solution was placed in a refrigerated cabinet at a temperature of from 2 to 6°C for degassing the solution for 3 hours.

Capsules were produced by axial feeding into the curd whey of sodium alginate solutions through the device for producing encapsulated products [Patent RF 156197] with a fixed size of nozzle outlets. Injection of drops of the extrusion mixture in the form of a sodium alginate solution into the forming medium – curd whey – was carried out at a ratio of 1 : 10. Spheres were obtained differing in their structural and mechanical characteristics and dimensional parameters, due to the diffuse structure formation occurring over time. To maintain a constant amount of Ca^{2+} ions in the whey, its solution was constantly freshened. The finished capsule cores were washed with distilled water and dried on filter paper. The experimental setup layout is shown in Fig. 3.

Determination of the qualitative composition and identification of dry powders taken as the objects of the study was carried out by IR-Fourier spectrometry with an Agilent Cary 660 spectrometer.

Spectra were interpreted using literature data [34].

To determine the dimensional characteristics of the resulting capsules, a XSP 10-640x microscope with a MOV-1-16x screw micro-eyepiece with a measurement scale with measurement limits from 0 mm to 8 mm was used.

The capsule shape factor was determined by the formula [35]:

$$K_f = \pi \cdot \left(\frac{a}{b} + \frac{b}{a} \right), \quad (1)$$

where a and b are semiaxes of the ellipse, mm.

The minimum possible value K_f has the circle ($K_f = 2\pi$).

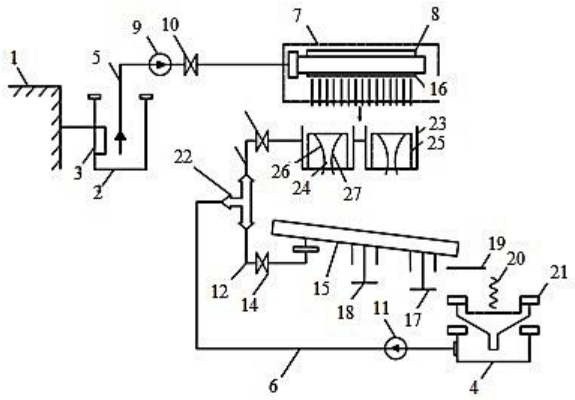


Fig. 3. Diagram of the device for producing encapsulated products: 1 – housing; 2 – vessel for the capsule filler substance; 3 – viscometer; 4 – storage tank for circulating solution; 5,6 – pipeline; 7 – encapsulation unit; 8 – capsulating head; 9 – pump; 10 – valve; 11 – pump; 12, 13 – pipeline; 14 – valve; 15 – conveying trough; 16 – nozzles; 17 – screw; 18 – adjusting screw; 19 – cone-shaped chute; 20 – pipeline; 21 – mesh tray; 22 – valve; 23 – intake vessels; 24 – gap; 25 – forming shape-generating vessels; 26, 27 – parabolic shape planes.

RESULTS AND DISCUSSION

The analysis of the patent information literature and comparative characteristic of the physico-chemical properties of sodium alginate and curd whey composition allowed to formulate the main scientific approaches to the development of encapsulation technology for food systems.

For the scientific substantiation of the use of alginates as a membrane-building material, it is necessary to establish the effect of certain process factors on the characteristics of the gels formed. The most important factors are:

– Concentration of alginate;

– Interaction of calcium ions of curd whey with carboxyl groups of sodium alginate and the ratio between gel-forming and gel-non-forming ions;

– Presence of complexing agents (phosphates, citrate, EDTA, GDL, acids).

In determining the qualitative composition and identifying the ingredients used in the encapsulation technology, the IR spectra of the study objects were obtained: curd whey, sodium alginate and binary system "sodium alginate – curd whey".

The presence of a broad absorption band in the 3600-3100 cm^{-1} region was established in the IR spectra of the curd whey sample, which indicates the presence of valence vibrations of hydroxyl groups (OH) and amino groups (NH) in the molecule (Fig. 4). The presence of absorption bands of 1650 cm^{-1} and 1550 cm^{-1} is due to valence vibrations of the C=O bond and to plane deformation vibrations of the NH bond. Thus, it is confirmed that a protein group is present in the analyte.

The IR spectrum of a sodium alginate sample coincides with the spectrum of a known ingredient recorded in the instrument library (Fig. 5). In the test sample in the 3500–3000 cm^{-1} region, absorption bands

due to stretching vibrations of hydroxyl group are observed, in the region of 2800–3000 cm^{-1}, there are bands of valence vibrations of CH groups, in the region of 1000–1100 cm^{-1}, there are vibration bands of pyranose cycles, absorption bands at 1650–1550 cm^{-1} are typical for the ionized carboxyl groups of which hydrogen ions are replaced by sodium, which in turn when adding whey will be presumably substituted for the calcium ion, due to the greater reactivity of the latter.

To confirm this assumption on the interaction of study objects, a spectrum of the binary system "sodium alginate – curd whey" was obtained. The presence of absorption bands in the 1950–2150 cm^{-1} region indicates the presence of $C=N^{+}=N$ valence bonds (Fig. 6), and the valence vibrations of hydroxyl groups (OH) and amino groups (NH) in the composition under study (Table 1). This fact presumably indicates the complexation of polymers present in the system.

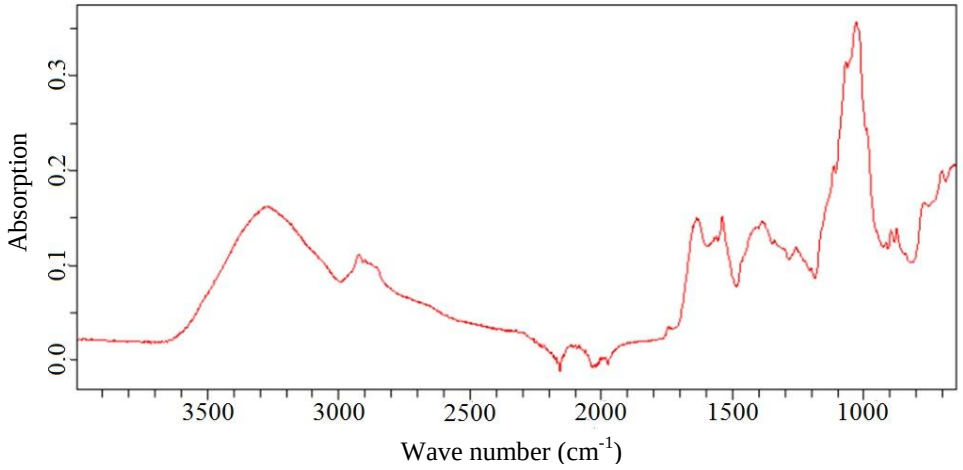


Fig. 4. IR spectra of a curd whey sample.

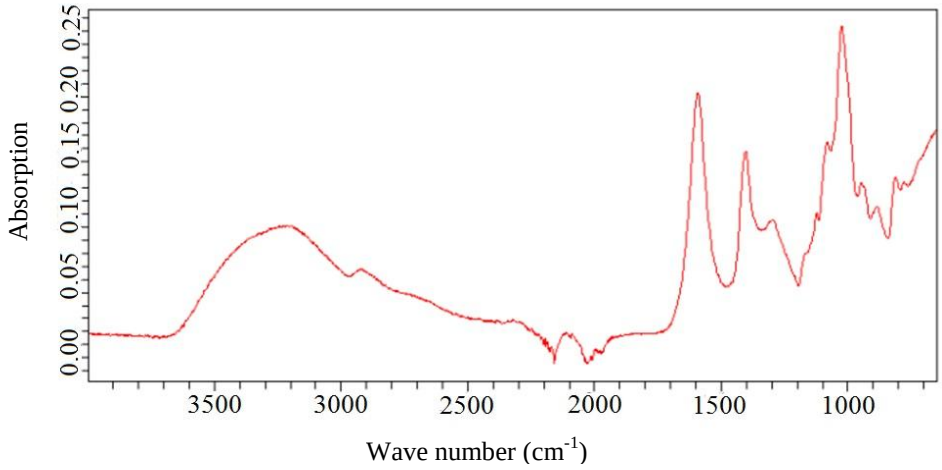


Fig. 5. IR spectra of a sodium alginate sample.

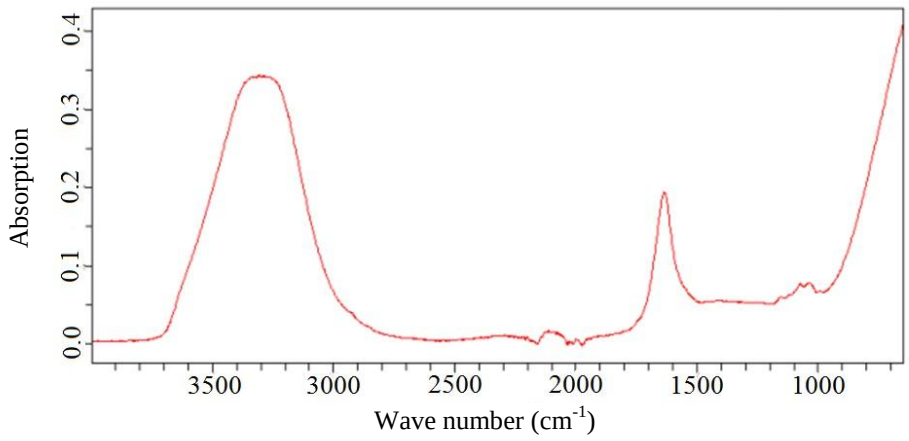


Fig. 6. IR spectra of a binary system sample based on decalcified curd whey and sodium alginate.

Table 1. Assignment of absorption bands in IR spectra of curd whey and sodium alginate before and after interaction

Wave number, cm^{-1}			Bands assignment
sodium alginate	curd whey	"sodium alginate-curd whey"	
1000–1100	–	1000–1100	Vibration bands of pyranose cycles
1260	–	–	Flat deformation vibrations of OH groups in structures
1380	–	–	Scissor vibrations of OH groups, CH_2
1550–1650	1600–1650	1550–1700	Presence of valence vibrations of the C=O bond and plane deformation vibrations of the NH bond
–	–	1950–2050	Presence of $C=N^+=N$ valence bonds
2800–3000	2800–3050	–	Bands of valence vibrations of CH groups
3000–3500	3050–3600	3000–3600	Presence of valence vibrations of hydroxyl groups (OH) and amino groups (NH) in the molecule

To predict the shape and size of the alginate capsules, the influence of various process parameters was studied through a two-factor experiment, planned with the help of Box-Hunter's rotational second-order plans.

As considered factors, presumably having an effect on the diameter of the capsules, the following were accepted: mass fraction of sodium alginate in the encapsulated solution in the range from 0.6 to 1.4% (factor X_1), the outlet diameter is from 1 mm to 5 mm (factor X_2) (Table 2).

The results obtained during the experiment and data processing is presented in Table 3.

As a result of the regression-correlation analysis, an array of data was obtained reflecting the general regression equation showing the relationship between the diameter of the finished capsules and encapsulation parameters under consideration: outlet diameter, mass fraction of sodium alginate

$$Y = 0.225+5.938\cdot X_1+0{,}313\cdot X_2 - -3.281\cdot X_1^2-0.081\cdot X_2^2+0.625\cdot X_1\cdot X_2, \quad (2)$$

The obtained results allow to draw a conclusion that, according to the degree of influence on the diameter of the finished capsules, the factors considered can be arranged in descending order: concentration of sodium alginate injected–outlet diameter (Fig. 7).

Table 2. Values of factors in natural and non-dimensional scales

Name of factors	Possible values				
	–1.414	–1	0	+1	+1.414
X_1 – amount of sodium alginate injected, %	0.6	0.7	1.0	1.3	1.4
X_2 – outlet diameter, mm	1.0	1.6	3.0	4.4	5.0

Table 3. Experiment results

Experiment No.	Varied process parameters		Y value is the capsule diameter, mm
	X_1 – amount of sodium alginate injected, %	X_2 – outlet diameter, mm	
1	0.8	1.6	4.2
2	1.2	1.6	4.5
3	0.8	4.4	4.6
4	1.2	4.4	5.4
5	1.4	3.0	4.9
6	0.6	3.0	4.0
7	1.0	5.0	5.7
8	1.0	1.0	3.7
9	1.0	3.0	5.0
10	1.0	3.0	5.0
11	1.0	3.0	5.0
12	1.0	3.0	5.0

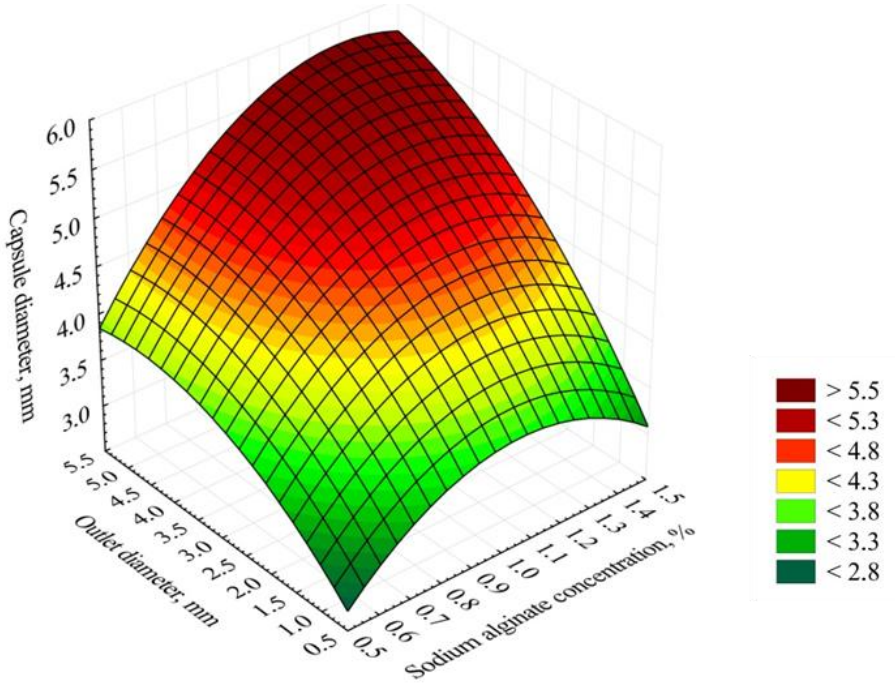


Fig. 7. Dependence of the capsule diameter on process parameters.

Preparation of the desired capsule shape (sphere) with the optimum ratio of the shell thickness to the diameter of the contents is mainly dependent on the viscosity of the encapsulated solution. It is determined that in order to obtain a capsule shape approximating to a roundly regular one, the necessary concentration of sodium alginate in the encapsulated solution should be from 0.8 to 1.2%. As the concentration of the structure-forming agent and, consequently, viscosity of the encapsulated system increases, the shape of the capsules differs from the spherical and approaches it to the elliptical. Reducing concentration of structure-forming agent below the optimal value leads to an increase in the residence time of the capsules in the forming solution, as well as to deformation during their extraction from the curd whey solution.

An increase in the diameter of the capsules is observed with an increase in the concentration of the structure-forming agent in the encapsulated solution and with an increase in the outlet diameter. The diameter of the resulting capsules under given conditions varies from 3.7 to 5.7 mm. At a low concentration of sodium alginate, the axial feed of the solution to the curd whey is not easily implemented, which leads to impossibility of controlling consumption of the filler material of the capsules. This pattern is also observed with an increase in the outlet diameter.

Generalization of the experiment results served as the basis for developing the technology of encapsulated food products by the method of "spherification" based on the gelling of sodium alginate with the calcium-containing component – curd whey.

The encapsulation technology involves extrusion of a capsule mixture containing 1% sodium alginate by axial feeding into a forming solution (curd whey) through a 3-mm diameter outlet (Table 4). In this way, spherical capsules of round-regular shape with a diameter of 5 mm and high organoleptic parameters are obtained.

The proposed technology is tested in production conditions, a sweet dish is prepared: a lemon starch drink, containing a capsular side dish based on raspberry juice and tarragon extract.

Implementation of the developed technology in the food industry will expand the range of innovative culinary products that will increase the competitiveness of industry enterprises.

ACKNOWLEDGEMENTS

The work was carried out within the framework of the contract No. 8260GU/2015 with the Federal State Budget Institution "Foundation for Assistance to Small Innovative Enterprises in Science and Technology" under the UMNIK program and with the financial support of the Russian Humanitarian Scientific Foundation, project No. 15-16-23034 (a).

Table 4. Process parameters of production of capsular side dish by the "spherification" method

Process stage and process mode	Process mode value
1 Preparation of the liquid to be spherified	
1.1 Neutralization of curd whey (to pH ≥ 4.2) amount of acidity regulator, %	1.5
1.2 Dissolution of sodium alginate	
concentration, %	1
volume of decalcified curd whey, %	67.5
volume of encapsulated ingredient, %	30
structure-forming agent expanding, min	40
1.3 Mixing of prepared components	
mixing type	manual/auto
time, sec	30
2. Solution degassing	
cooling, °C	4 ± 2
time, min	30
3. Preparation of the forming solution	
curd whey thermostating	
time, min	30
temperature, °C	20–22
4. Encapsulation	
ratio of the encapsulated mixture to the forming solution, g/g	1 : 10
dynamic viscosity of the encapsulated solution, cP	280–1000
outlet diameter, mm	3
capsule diameter, mm	5
capsule residence time in the forming solution, sec	120
5. Spheres washing	
capsule-water ratio, g/g	1 : 4
time, sec	30
6. Capsule drying	until moisture removal from the surface

REFERENCES

1. Vilgis T.A. and Frenzel R. *Molekularkiiche - das Kochbuch*. Wiesbaden: Auflage, 2007. 208 p.
2. Vilgis T.A. Hydrocolloids between soft matter and taste: Culinary polymer physics. *International Journal of Gastronomy and Food Science*, 2012, vol. 1, no. 1, pp. 46–53. DOI: 10.1016/j.ijgfs.2011.11.012.
3. Adria F., Soler J., and Adria A. *El Bulli 2003–2004*. Stuttgart: Hampp Velag, 2006. 656 p.
4. de Vos P., Faas M.M., Spasojevic M., and Sikkema J. Review: Encapsulation for preservation of functionality and targeted delivery of bioactive food components. *International Dairy Journal*, 2010, vol. 20, no. 4, pp. 292–302. DOI: 10.1016/j.idairyj.2009.11.008.
5. Gaonkar A.G., Vasisht N., Khare A.R. and Sobel R. *Microencapsulatuion in the Food Industry: A Practical Implementation Guide.* New York: Academic Press, 2014. 590 p. DOI: 10.1016/B978-0-12-404568-2.00045-5.
6. Milanovic J., et al. Microencapsulation of Flavors in Carnauba Wax. *Sensors*, 2010, no. 10, pp. 901–912. DOI: 10.3390/s100100901.
7. Zuidam N.J. and Nedovic V.A. (eds.) Encapsulation Technologies for Active Food Ingredients and Food Processing. New York: Springer-Verlag, 2010, 400 p. DOI 10.1007/978-1-4419-1008-0.
8. Fang Z. and Bhandari B. Encapsulation of polyphenols – a review. *Trends in Food Science & Technology*, 2010, vol. 21, no. 10, pp. 510–523. DOI: 10.1016/j.tifs.2010.08.003.
9. Desai K.G.H. and Park H.J. Recent developments in microencapsulation of food ingredients. *Drying Technology*, 2005, no. 23, pp. 1361–1394. DOI: 10.1081/DRT-200063478.
10. Nedovich V., Kalusevic A., Manojlovic V., et al. An overview of encapsulation technologies for food applications. *Procedia Food Science*, 2011, vol. 1, pp. 1806–1815.
11. Voloshin Y., Belaya I., and Krämer R. *The encapsulation phenomenon*. Basel: Springer International Publ., 2016. 1518 p. DOI: 10/1007/978-3-319-27738-7.
12. Bugayets N.A., Tamova M.Yu., Borovskaya L.V., and Mironova O.P. Issledovanie termodinamicheskikh svoystv belkovo-polisakharidnoy sistemy metodom differentsiruyushchey kalorimetrii [Study of the thermodynamic properties of the protein-polysaccharide system by the method of differentiating calorimetry]. *Izvestia vuzov. Pishevaya tekhnologia* [News institutes of higher Education. Food technology], 2003, no. 5–6, pp. 112–113.
13. Bugayets N.A., Tamova M.Yu., Prudnikova S.M., and Dzhioev T.E. Issledovanie mezhmolekulyarnogo vzaimodeystviya v belkovo-polisakharidnykh sistemakh metodom yadernoy magnitnoy relaksatsii [Study of

intermolecular interactions in protein-polysaccharide systems by nuclear magnetic relaxation]. *Izvestia vuzov. Pishevaya tekhnologia* [News institutes of higher Education. Food technology], 2004, no. 4, pp. 54–57.
14. Bugayets N.A., Tamova M.Yu., and Bugayets I.A. Vliyanie pH sredy na strukturno-reologicheskie svoystva rastvorov strukturoobrazovateley polisakharidnoy i belkovoy prirody [Effect of pH medium on structural and rheological properties of polysaccharide and protein nature structure forming solutions]. *Izvestia vuzov. Pishevaya tekhnologia* [News institutes of higher Education. Food technology], 2012, no. 2, pp. 15–18.
15. Kamaruddin M.A., Yusoff M.S., and Aziz H.A. Preparation and Characterization of Alginate Beads by Drop Weight. *International Journal of Technology*, 2014, vol. 5, no. 2, pp. 121–132. DOI: 10.14716/ijtech.v5i2.409.
16. Mabeau S. and Fleurence J. Seaweed in food products: biochemical and nutritional aspects. *Trends in Food Science & Technology*, 1993, no. 4, pp. 103–107. DOI: 10.1016/0924-2244(93)90091-N.
17. Hunt N.C. and Grover L.M. Cell encapsulation using biopolymer gels for regenerative medicine. *Biotechnology Letters*, 2010, vol. 32, no. 6, pp.733–742. DOI: 10.1007/s10529-010-0221-0.
18. Stephen A.M., Phillips O.G., and Williams P.A. *Food Polysaccharides and Their Applications Second Edition*. NW: Taylor & Francis Group, 2006. 712 p.
19. Silva C.M. Alginate microspheres prepared by internal gelation: development and effect on insulin stability. *International Journal of Pharmaceutics*, 2006, vol. 311, no. 1–2, pp. 1–10. DOI: 10.1016/j.ijpharm.2005.10.050.
20. Phillips G.O. and Williams P.A. (eds.) *Handbook of Hydrocolloids*. London: Woodhead Publishing, 2009. 948 p.
21. Kaplan D.L. *Biopolymers from Renewable Resources*. Berlin-New York: Springer-Verlag, 1998. 420 p. DOI 10.1007/978-3-662-03680-8.
22. Hamilton R. and Todoli V. (eds.) *Food for Thought: Thought for Food*. Barselona-New York: Actar, 2009. 343 p.
23. Lee P. and Rogers M.A. Effect of calcium source and exposure-time on basic caviar spherification using sodium alginate. *International Journal of Gastronomy and Food Science*. 2011, vol. 1, no. 2, pp. 96–100. DOI: 10.1016/j.ijgfs.2013.06.003.
24. Martinsen A., Skjaak-Braek G., and Smidsroed O. Alginate as immobilization material: I. Correlation between chemical and physical properties of alginate gel beads. *Biotechnology and Bioengineering*, 1989, vol. 33, no. 1, pp. 79–89. DOI: 10.1002/bit.260330111.
25. Nussinovitch A. (ed) *Polymer Macro- and Micro-Gel Beads: Fundamentals and Applications*. New York: Springer Science+Business Media, 2010. 303 p. DOI: 10.1007/978-1-4419-6618-6.
26. Burke R., This H., and Kelly A.L. Molecular Gastronomy: An Introduction. *Reference Module in Food Science*. 2016. DOI: 10.1016/B978-0-08-100596-5.03384-9.
27. Adria F., Soler J., and Adria A. *El Bulli 1998-2002*. London: Ecco, 2005. 496 p.
28. Draget K.I. and Taylor C. Chemical, physical and biological properties of alginates and their biomedical implications. *Food Hydrocolloids*, 2011, vol. 25, pp. 251–256. DOI: 10.1016/j.foodhyd.2009.10.007.
29. Phillips G.O. and Williams P.A. (eds.) Handbook of hydrocolloids Boca Raton [etc.]: CRC Press ; Cambridge : Woodhead Publishing Limited, 1997 (cop.) (Russ.ed.: Kochetkova A.A. and Sarafanova L.A. *Spravochnik po gidrokolloidam.* St. Petersburg: GIORD Publ., 2006. 536 p.).
30. Adria F., Soler J., and Adria A. *A Day at El Bulli: An insight into the ideas, methods and creativity of Ferran Adria*. London: Phaidon Press Ltd., 2008. 632 p.
31. Lee P. and Rogers M.A. Effect of calcium source and exposure-time on basic caviar spherification using sodium alginate. *International Journal of Gastronomy and Food Science*, 2011, vol. 1, no. 2, pp. 96–100. DOI: 10.1016/j.ijgfs.2013.06.003.
32. Augustin M.A. and Oliver C.M. Use of Milk Proteins for Encapsulation of Food Ingredients. *Microencapsulation in the Food Industry. A Practical Implementation Guide*, 2014, Chapter 19, pp. 211–226.
33. Park Young W., and Haenlein George F.W. (eds.) *Milk and dairy products in human nutrition*. Rome: FAO, 2013. 376 p. DOI: 10.1002/9781118534168.ch1.
34. Nakanishi K. *Infrakrasnye spektry i stroenie organicheskikh soedineniy: Prakticheskoe rukovodstvo* [Infrared spectra and the structure of organic compounds: A practical guide]. Moscow: Mir Publ., 1965. 216 p.
35. Fetisova M.A. and Volodin S.S. *Koeffitsient formy kak geometricheskaya kharakteristika* [Shape factor as a geometric characteristic]. *Molodoy uchenyy* [Young Scientist], 2011, no. 5, pp. 105–108.

Please cite this article in press as: Zhuravlev R.A., Tamova M.Yu., Bugayets N.A., Poznyakovskiy V.M., and Penov N.D. Innovative encapsulation technology of food systems using a by-product of dairy production. *Foods and Raw Materials*, 2017, vol. 5, no. 1, pp. 81–89. DOI: 10.21179/2308-4057-2017-1-81-89.

BIOTECHNOLOGY

ANALYSIS OF INFLUENCE OF BIOHUMUS ON THE BASIS OF CONSORTIUM OF EFFECTIVE MICROORGANISMS ON THE PRODUCTIVITY OF WINTER WHEAT

A. I. Piskaeva[a],*, O. O. Babich[b], V. F. Dolganyuk[a], and S. Yu. Garmashov[a]

[a] Kemerovo Institute of Food Science and Technology (University),
Stroiteley blvd. 47, Kemerovo, 650056, Russian Federation

[b] Kemerovo State University,
Krasnaya Str. 6, Kemerovo, 650043, Russian Federation

* e-mail: a_piskaeva@mail.ru

Received February 02, 2017; Accepted in revised form April 10, 2017; Published June 29, 2017

Abstract: The article considers the problem of recycling of poultry waste, in particular, feather-downy waste and chicken dung. Traditional ways of poultry waste disposal have been shown and their shortcomings have been described. The main advantages of use of bioprocessing methods to implement the process of waste conversion with the formation of effective products – biohumus – have been determined. Biofertilizers or biohumus is a modern innovative means applied not only for the purpose of an increase in productivity, but also for land recultivation and resuscitation. The authors have studied the biohumus obtained by means of processing of mixture of feather-downy waste and dung in the ratio of 8 : 2 with the application of the biological product containing the consortium of decomposer microorganisms: *Bacillus pumilus AL16, Microbacterium terregens AC1180, Aeromonas sp. B5376, Arthrobacter globiformis AC1529, Streptomyces olivocinereus AC1169 and Acinetobacter sp. B390.* An assessment of efficiency of application of various rates of the developed biohumus for winter wheat crops has been made. It is shown that the application of a comparison sample - the organic mineral fertilizer "Universal'noe" (the expense is 150 g/m^2) and the use of the developed biohumus (the expense is 150 g/m^2) provided an increase in its growth, compared with the control sample of the wheat "'Skipetr", by 12 and 15 cm (the stem elongation stage), by 15 and 18 cm (the earing stage), by 21 and 30 cm (the milk stage) and by 19 and 30 cm (the firm ripe stage) respectively. The above values for the grade Zimushka were within the similar limits: an increase in its growth, compared with the control sample, by 17 and 18 cm (the stem elongation stage), by 19 and 21 cm (the earing stage) and by 19 and 31 cm (the milk stage and the firm ripe stage) respectively.An increase in the productivity of grades of the winter wheat "Skipetr" and "Zimushka" by 1.5 times (1.25 ± 0.25 t/hectare) has been established during the application of the obtained biohumus with the rate of 150 g/m^2. The results of studies of change of fractional composition of grain proteins testify that the application of biohumus provides an increase in gluten fractions of winter wheat grains. An assessment of economic efficiency has been performed, it has been established that the highest rates of profitability refer to the variant with the application of the developed biohumus (the expense is 150 g/m^2) – 63.2%, the lowest rates are 39.2% in the control sample.

Keywords: Biohumus, poultry waste, effective microorganisms, waste bioconversion, microbial utilization, biological product, productivity of wheat, biofertilizer

DOI 10.21179/2308-4057-2017-1-90-99 *Foods and Raw Materials*, 2017, vol. 5, no. 1, pp. 90–99.

INTRODUCTION

Recycling of waste and by-products in the branches of food and processing industry provides a number of environmental problems in the sphere of ensuring the sustainable development and protection of the environment [1–3].

Feather-downy waste in the form of by-product is formed in high quantities during commercial poultry processing and, in the chemical relation, is native keratin [2]. The high mechanical stability, hardness and a large number of disulfide bonds of native keratin makes it resistant to the degradation caused by proteolytic enzymes, such as pepsin, trypsin and papain [3, 4, 6]. Due to the high content of nitrogen the accumulation of the formed waste by their storage, burial or burning provides not only the destruction of surface soils, but also considerable losses of biological resources, such as proteins and enzymes [5].

The traditional way of dung removal is burning. However, it is not expedient either from the ecological, or the economic point of view [7]. One of problems of dung utilization by means of burning is a high exit of

CO_2. Taking into account the pollution caused by the use and change of properties of the used lands, about 9% of evolutions of CO_2 [8] fall to the share of poultry-farming sector in the structure of human activity.

The foremost scientists in the field of ecology have proved that poultry waste burning is pernicious for the planet and mankind. It is stated in a report of the UN that poultry farming is the main source of pollution of water and soil – it provides the formation of more greenhouse gases, than that produced by cars, the intensive poultry farming provides the degradation of soils, the pollution of reservoirs and air [9–11].

The simplest of the existing technologies of utilization of mixtures of feather-downy raw materials and dung is composting. Vast free areas remote from settlements are needed to organize it in the open air. The process lasts from 3 to 6 months and demands periodic turning of heaps for the homogenization of mixture and the activization of activity of microbes [11–15].

The classical technology has been recently supplemented with a lot of modifications. For example, composting with the use of steam-gas plants or enzymatic composting where the speed of process increases several times [16].

In recent years the ways of dung utilization with the use of coprophages (larvae of *Musca domestika S.*, specially grown earthworms *Eisenia*) have become popular. For example, a unique way of dung processing with the use of house fly larvae has been worked out in the All-Russian Research Institute of Livestock [17, 18]. During the growth of fly larvae the dung mass turns into a slightly damp friable mass with a slight smell [19, 20]. The final product of processing with the use of this way is the fertilizer which is capable to increase considerably the quality and productivity of soil [21–23]. Vermiculture is quite popular in the Western European countries where people have got used to using the line of earthworms *Eisenia foetida*, or "Red Californian hybrid" [24]. In Russia people use the following hybrids of Red Californian worm: Obninsk, Obolensk, Vladimir and Morevka hybrids [25]. However the method of dung utilization with the use of fly larvae and lines of hybrid earthworms has essential shortcomings: the complexity of maintenance of necessary parameters of temperature and humidity of egg laying and the cultivation of larvae and lines of worms [21–23]; the difficult design of recycling units (the existence of flap doors, a lot of feeders, the complex system of motion of trays along the racks) [26]; the complexity of production organization in the territory of Russia, considering rather low average winter temperatures [27, 28]; the considerable losses of organic substance in the final products: the increased speed of their mineralization and, as a result, the high losses of nitrogen and the formation of a large amount of ammonia [29]; the discrepancy of the final products to the requirements for the physical and chemical composition presented in the Technical specifications of the Russian Federation No. 94991, some international standards and agrochemical indicators [17].

Thus, the technologies of worm composting and the use of fly larvae, even considering all their advantages, are favorable for small farms or for use for one's own needs [25, 28, 29]. The searches of alternative technologies of efficient recycling of waste of the poultry-farming complex have provided the development of biotechnologies, i.e. the use of systems (consortia) of effective microorganisms (EM) capable to process in the course of their activity the organic and inorganic substances, which are part of waste, into efficient final products – fertilizers [8, 31].

In other words, EM provide quick composting – the biological oxidation of organic substrata which provide the enzymatic hydrolysis of keratin – the structural protein of a feather [32].

The activity of effective microorganisms determining the duration and depth of process of biotransformation [32, 33] is the basis of the vast majority of bioconversion technologies. The biological products, biostimulators or the obtained products – bio-fertilizers (biocomposts) applied in the similar technologies are communities of selected microorganisms, or contain a specific strain of microorganisms of a certain type [17, 33].

The application of biological products for organic waste processing allows to correspond to the latest requirements of production of organic fertilizers of livestock waste [31, 33]. Namely, the preservation of its biological potential, the exclusion of a possibility of presence of pathogenic microorganisms, the elimination of an unpleasant smell and the decrease in the risk of incidence of workers at the enterprises of agrarian and industrial complex [32].

Obtaining biofertilizers on the basis of a chicken feather has drawn attention of research scientists [34] since long ago. Feather meal is cheap and easily available source of nitrogen (15% of N) and can be used as an effective biofertilizer with high biogenous properties.

Biotechnologies are the development and expansion of set of processing methods the roots of which appeared [1] thousands years ago. The application of biotechnologies in agriculture, for example, the application of growth enhancing hydrolyzates of proteins is the perspective trend of development of branch and can effectively be applied in the production of fertilizers [9, 29].

The microbial degradation of feather-downy waste is an alternative to the existing technologies of production of nitrogen fertilizers. There are bacteria capable to use feather-downy waste as the main organic substratum and a source of carbon, nitrogen, sulfur and energy [32, 35]. Indolyl-3-acetic acid is the main growth regulator which increases the availability of nutrients for plants, and also provides the growth of roots [33–36].

The degraded product obtained on the basis of feather waste can become an abundant source of the corresponding amount of tryptophane which is the basis of synthesis of indoleacetic acid [1, 36]. The poultry waste biohumus is the product with a low prime cost and a high efficiency that has a number of advantages in comparison with the existing analogs, in

particular, the pathogenic microflora which is a special problem during efficient waste recycling is completely absent in the biohumus [21, 34, 37, 39].

At the present time, one of the urgent issues is meeting the need of the population for food, and first of all it includes grain and bakery products. Based on this fact, as for efficiency, winter wheat is considered to be potential grain crops. Due to a long vegetative period it is capable to use most fully the solar energy, the nutrients contained in soil and moisture during the autumn and spring period [36–38].

The application of high rates of mineral, in particular, nitrogen fertilizersto receive heavy crops of winter wheat grains when sowing them after the late removed predecessors, which is not always justified from the economic and ecological point of view [2].

Thus, the application of new biological fertilizers is an alternative to the new chemical fertilizers that need to be thoroughly checked [40–44].

OBJECTS AND METHODS OF STUDY

At the previous stage of studies a biological product on the basis of consortium of decomposer microorganisms was developed: *Bacillus pumilus AL16, Microbacterium terregens AC1180, Aeromonas sp. B5376, Arthrobacter globiformis AC1529, Streptomyces olivocinereus AC1169 and Acinetobacter sp. B390.* The assessment of the compliance obtained with the application of a biological product, biohumus, with the requirements of regulatory documents for fertilizers of livestock and poultry waste, in particular, the compliance with the sanitary and microbiological and veterinary and sanitary indicators of the obtained biohumus has shown that the optimum time of bioconversion is the term of 14 days. The studies were performed with the substrata with the contents of feather-downy waste and dung of 8 : 2 respectively as this ratio is considered as optimum. As a comparison, samples of raw mixtures of waste were used as the control ones [41].

Field studies of influence of the biohumus obtained from the mixture of poultry wastes on the harvest and quality indicators of winter wheat were performed in 2014–2015 to set the standards of application of biohumus.

The released frost-resistant grades of the winter wheat "Skipetr" and "Zimushka" which steadily provide with heavy crops are chosen as the test crops to assess the efficiency of the developed biohumus.

All the grades of winter wheat impose high requirements for soil properties: high fertility, structure, with the enough content of nutrients, such as nitrogen, phosphorus and potassium. The acidity of soil solution must not exceed the indicator of 7.5, therefore, the medium must be alkalescent or acidic.

Chernozems are considered to be the best soils for winter wheat. They have enormous soil and humus horizons and contain a significant amount of humus (from 8 to 12%).

The agrotechnology standard for the area of studies. The tests were carried out on chernozem soils of the land plots of the Leninsk-Kuznetsky district of the Kemerovo region (Russia). According to the mechanical and agrochemical analyses, this type of chernozem is referred to the soils, heavy in mechanical composition, because of the high content of physical clay (the fraction of 0.01 mm) – up to 72% and bad agrophysical properties – low air and water permeability [39]. The predecessor of crops is the corn prepared as silage.

The studied grades of winter wheat were sown in narrow rows with the sowing rate of 6.0 million of viable seeds per hectare (~ 260 kg/hectare). The experiment was performed on the plots of 50 m^2. The experiment was made with a triple frequency.

Design of the experiment. Fig. 1 provides the design of experiment of the study of influence of various rates of biohumus on the grades of winter wheat.

Proceeding from the analysis of laboratory results the design of experiment consists of the following stages: the biohumus obtained at the first stage of studies is applied for the plots with a crop of winter wheat with the following rates: 1 – the developed biohumus (the expense is 100 g/m^2); 2 – the developed biohumus (the expense is 150 g/m^2); 3 – the developed biohumus (the expense is 200 g/m^2). The following was used as a comparison: 4 – the organic mineral fertilizer "Universal'noe" (the expense according to the instruction is 150 g/m^2); 5 – the control (without the application of biohumus).

Determination of protein and protein fractions in grains. The protein in the grain obtained according to the design of the experiment was determined in accordance with GOST 10846-91 "Grain and products of its processing. Method for determination of protein" with the use of Kjeldahl flask. The protein fractions of grain were determined using the method of gel penetrating planar chromatography (GPPC).

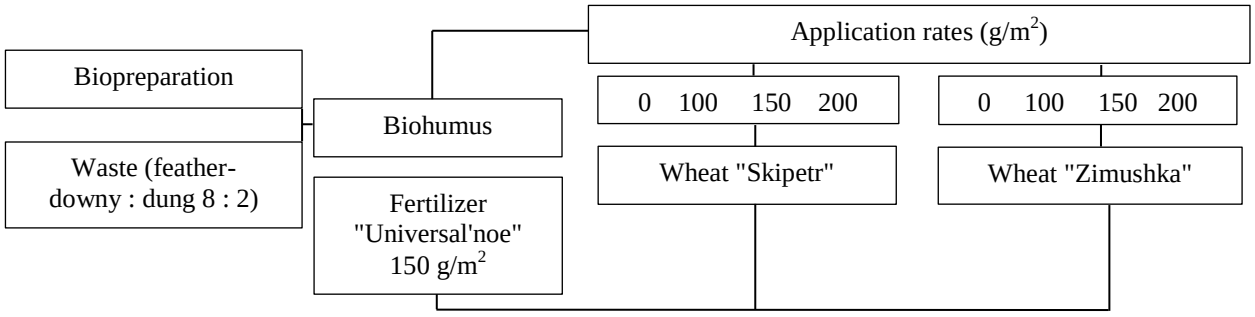


Fig. 1. Design of the experiment.

RESULTS AND DISCUSSION

Table 1 provides the results of a study of determination of the optimum norm of application of the developed biohumus for winter wheat of the grades "Skipetr" and "Zimushka".

According to the data presented in Table 1, the application of the organic mineral fertilizer "Universal'noe" (the expense is 150 g/m^2) and the use of the developed biohumus (the expense is 150 g/m^2) provided an increase in its growth, compared with the control sample of the wheat "Skipetr", by 12 and 15 cm (the stem elongation stage), by 15 and 18 cm (the earing stage), by 21 and 30 cm (the milk stage) and by 19 and 30 cm (the firm ripe stage) respectively.

The use of these biohumus variants has provided the best indicators, both for the grade "Skipetr", and for the wheat of the grade "Zimushka". The above values for the grade "Zimushka" were within the similar limits: an increase in its growth, compared with the control sample, by 17 and 18 cm (the stem elongation stage), by 19 and 21 cm (the earing stage) and by 19 and 31 cm (the milk stage and the firm ripe stage) respectively.

The results provided in the experiment in the study and analysis of dynamics of accumulation of dry weight when applying the developed biohumus and the organic mineral fertilizer "Universal'noe" were unequal. Thus, at the stem elongation stage the largest amount of dry weight is noted in the samples with the application of the organic mineral fertilizer "Universal'noe" (the expense is 150 g/m^2) and with the use of the developed biohumus (the expense is 150 g/m^2). The maximum gain at the earing stage was noted in the sample with the application of the developed biohumus (the expense is 150 g/m^2), and was 340 g per 100 plants (the grade "Zimushka").

The dry biomass in the control sample (without the use of biohumus) and in the variant with the application of the developed biohumus (the expense is 200 g/m^2) is nearly 1.5–2.0 times lower than that in the variant with the application of the developed biohumus (the expense is 150 g/m^2). This regularity in the dynamics of dry biomass is characteristic of the milk stage and the firm ripe stage.

The maximum gain in the noted phases is also in the variants with the application of the developed biohumus (the expense is 150 g/m^2) and the organic mineral fertilizer "Universal'noe".

It is known that the volumes of future harvest are characterized by two basic indicators – the density of productive plant stand and the mass of grain of one ear. These components are the generalizing characteristics of a harvest of winter wheat grains of any grade. Table 2 presents the results of calculation of the above-mentioned indicators during the application of biohumus.

Table 1. Dynamics of the growth (cm) and the accumulation of dry biomass (g/100 sol.) of winter wheat of the grades "Skipetr" and "Zimushka" in the plants depending on the rates of the applied biohumus or fertilizers (the average for 2014–2015)"

Variant of experiment	Growth dynamics (cm) / dry biomass accumulation (g/100 sol.)			
	Stem elongation stage	Earing	Milk stage	Complete ripeness
"Skipetr"				
Developed biohumus (the expense is 100 kg/m^2)	75/143	78/181	95/245	94/245
Developed biohumus (the expense is 150 g/m^2)	88/155	91/225	110/336	110/328
Developed biohumus (the expense is 200 g/m^2)	87/133	89/167	99/267	99/273
Organic mineral fertilizer "Universal'noe" (the expense is 150 g/m^2)	85/133	88/170	101/289	99/289
Control (without the application of biohumus)	73/80	73/133	80/135	80/135
"Zimushka"				
Developed biohumus (the expense is 100 kg/m^2)	79/143	82/183	99/257	99/257
Developed biohumus (the expense is 150 g/m^2)	92/157	96/228	115/340	115/332
Developed biohumus (the expense is 200 g/m^2)	90/136	94/170	103/277	103/277
Organic mineral fertilizer "Universal'noe" (the expense is 150 g/m^2)	91/137	94/170	103/297	103/297
Control (without the application of biohumus)	74/83	75/135	84/142	84/142

Table 2. Influence of various rates of biohumus on the indicators of structure of a harvest of winter wheat of the grades "Skipetr" and "Zimushka" (the average for 2014–2015)

Variant of experiment	Tilling capacity		Ear length, cm	Quantity of cones per ear, pcs	Quantity of grains per ear, pcs
	total	productive			
"Skipetr"					
Developed biohumus (the expense is 100 kg/m^2)	486.0	300.0	5.6	11.0	24.0
Developed biohumus (the expense is 150 g/m^2)	566.0	307.0	6.2	13.5	28.0
Developed biohumus (the expense is 200 g/m^2)	474.0	266.0	5.0	10.5	24.0
Organic mineral fertilizer "Universal'noe" (the expense is 150 g/m^2)	562.0	303.0	6.1	13.8	26.0
Control (without the application of biohumus)	332.0	280.0	4.6	10.1	16.0
"Zimushka"					
Developed biohumus (the expense is 100 kg/m^2)	493.0	305.0	5.9	12.0	25.0
Developed biohumus (the expense is 150 g/m^2)	575.0	312.0	6.6	14.0	29.0
Developed biohumus (the expense is 200 g/m^2)	555,.0	299.0	6.1	13.7	26.5
Organic mineral fertilizer "Universal'noe" (the expense is 150 g/m^2)	570.0	308.0	6.5	14.0	27.0
Control (without the application of biohumus)	337.0	284.0	4.9	10.6	15.9

The highest tilling capacity is shown in the variants of experiments with the application of the developed biohumus (the rate is 150 g/m^2) of the grade "Skipetr" (the total is 566.0 pieces/m, the productive capacity is 307.0 pieces/m); of the grade "Zimushka" (575.0 and 312.0 pieces/m respectively) and of the organic mineral fertilizer "Universal'noe" (the expense is 150 g/m^2), of the grade "Skipetr" (the total is 562.0 pieces/m, the productive capacity is 303.0 pieces/m) and of the grade "Zimushka" (570.0 and 308.0 pieces/m respectively).

Thus, proceeding from the data presented in Tables 1 and 2 it is possible to draw a conclusion that biohumus has a positive effect on the indicators of harvest of the grades of winter wheat "Skipetr" and "Zimushka" under conditions of the Kemerovo region.

Fig. 2 presents the photo of result of use of biohumus for a crop of winter wheat of the grade "Skipetr" in comparison with the control sample (without the use of fertilizers).

As a result of the studies it has been established that the developed biohumus with the application rate of 150 g/m^2 has the highest positive effect.

The application of biohumus allows to increase the quality indicators of composition of a wheat harvest (Table 3).

(a) (b)

Fig. 2. Photo of wheat of the grade "Skipetr": (a) Control (without processing); (b) Processing using biohumus with the rate of 150 g/m^2.

Table 3. Change of productivity and quality indicators of winter wheat grains caused by the use of biohumus, t/hectare (the average for 2014–2015)

Variant of experiment	Productivity, t/hectare	Increase, ±t/hectare	Thousand grain weight, g	Grain unit, g/l	Protein, %	Starch, %	Ash, %
"Skipetr"							
Developed biohumus (the expense is 100 kg/m^2)	4.15	0.89	40.00	770.00	14.15	68.54	1.70
Developed biohumus (the expense is 150 g/m^2)	4.63	1.25	44.00	783.00	15.02	67.00	1.63
Developed biohumus (the expense is 200 g/m^2)	4.13	0.92	41.00	772.06	14.25	63.34	1.54
Organic mineral fertilizer "Universal'noe" (the expense is 150 g/m^2)	4.23	1.12	44.00	783.00	14.76	68.55	1.73
Control (without the application of biohumus)	3.18	–	39.00	758.00	13.20	63.70	1.94
"Zimushka"							
Developed biohumus (the expense is 100 kg/m^2)	4.33	1.05	42.00	784.00	14.56	70.70	1.90
Developed biohumus (the expense is 150 g/m^2)	4.42	1.15	45.00	789.00	15.10	71.54	1.62
Developed biohumus (the expense is 200 g/m^2)	4.13	1.13	43.00	786.00	14.58	70.79	1.70
Organic mineral fertilizer "Universal'noe" (the expense is 150 g/m^2)	4.53	1.11	44.00	787.00	15.00	69.03	1.69
Control (without the application of biohumus)	3.17	–	41.00	769.00	14.32	66.64	2.01

The positive effect on the indicator of productivity depending on the use of biohumus, as for the grade "Skipetr", was 0.89, 1.25, 0.92 and 1.12 t/hectare relating to the control samples, and 1.05, 1.15, 1.13 and 1.11 t/hectare for the grade "Zimushka".

The high weight of 1000 grains characterizes one of the main components of high productivity of wheat winter grains.

A significant amount of authors studied the dependence of productivity and quality indicators of winter wheat grains on the weight of 1000 grains [43–46]. The analysis of results of studies in these works shows that the weight of 1000 grains of the grades of winter wheat studied by the authors changes depending on the features of the grade, the conditions of cultivation of winter wheat seeds and the climatic and weather characteristics of the area.

The studied variants of biohumus with various application rates considerably differ concerning this indicator – the difference in the weight of 1000 grains is on average 5 g. The highest weight of 1000 wheat grains was in the experiment variant where the developed biohumus with the application rate of 150 g/m^2 – 44 g and the organic mineral fertilizer "Universal'noe" (the expense is 150 g/m^2) – 44 g, as well, for the grade "Skipetr" and 45 and 44 g for the grade "Zimushka", respectively, were used.

Confirming the data submitted in the studies [42–47], we draw a conclusion that the change of weight of 1000 grains depending on experiment variants is characterized by the biological features of a grade of winter wheat and the environmental conditions, however the relative fineness of grain remains.

In the made experiments the grain variants obtained with the application of biohumus had an unequal unit the indicator of which fluctuated within 758–783 g/l for the grade "Skipetr" and a high grain unit was noted in the grade "Zimushka' – within 769–789 g/l. On average, the experiment variants with the application of the developed biohumus with the rate of 150 g/m^2 and the organic mineral fertilizer "Universal'noe" (the expense is 150 g/m^2) have the highest indicators of unit for the grade "Skipetr" and "Zimushka".Thus, as a result of the studies a considerable positive influence of the developed biohumus on the productivity of wheat grades "Skipetr" and "Zimushka" with the application rate of 150 g/m^2 has been established.

Table 4 presents the results of determination of protein in the grains of the grades "Skipetr" and "Zimushka" depending on the rates of the applied biohumus.

According to the data presented in Table 4 the application of all rates of the developed biohumus and also the use of the organic mineral fertilizer "Universal'noe" for the crop of winter wheat provides an increase in biosynthesis processes and consequently the growth of percentage of protein in grains.

Table 4. Change of protein content in winter wheat grains caused by the use of biohumus, % (over a period of 2014–2015)

Variant	Years of studies		Years of studies	
	2014	2015	2014	2015
	"Skipetr"		"Zimushka"	
Developed biohumus (the expense is 100 kg/m^2)	10.95	12.84	12.24	13.27
Developed biohumus (the expense is 150 g/m^2)	11.77	14.25	13.09	14.45
Developed biohumus (the expense is 200 g/m^2)	11.52	12.37	13.05	14.23
Organic mineral fertilizer "Universal'noe" (the expense is 150 g/m^2)	11.52	11.91	13.15	14.01
Control (without the application of biohumus)	10.78	10.86	11.35	11.43

On average, the percent of protein in the grains of the grade "Skipetr" with the application of the developed biohumus increased by 1.87%, and by 1.11% for the grade "Zimushka" over a period of 2014 and 2015. The use of the organic mineral fertilizer "Universal'noe" has provided an increase in protein by 0.39 and 1.36% respectively.

Presumably, the application of biohumus accelerates the exchange of nitrogenous substances, thus, starting the process of nitrogen reduction.

According to the results of the studies of protein fractions of winter wheat grains, the use of the developed biohumus for the grades "Skipetr" and "Zimushka" changes the ratio of protein fractions. The data are presented in Table 5.

In winter wheat grains of the grade "Skipetr" there is an increase in protein fractions under the influence of medicines: albumines – by 0.2–1.5 mg/g. The similar concerned the other fractions as well. The prolamine fraction in the variant with the use of the developed biohumus with the application rate of 150 g/m^2 exceeds the control sample by 3.34 mg/g relating to the grade "Skipetr", and by 3.90 mg/g relating to the grade "Zimushka". In general, the results of the studies of change of fractional composition of grain proteins testify that the application of biohumus provides an increase in gluten fractions.

The work provides the assessment of production expenses of cultivation of wheat grades (using an example of the grade "Skipetr") depending on the rate of application of biohumus (Table 6).

Table 5. Change of fractional composition of protein of winter wheat grains depending on the rates of the applied fertilizers, mg/kg (the average for 2014–2015)

Variant	Albumins	Globulins	Prolamins	Glutelins	Total protein
"Skipetr"					
Developed biohumus (the expense is 100 kg/m^2)	9.17	26.53	54.12	33.91	123.73
Developed biohumus (the expense is 150 g/m^2)	9.85	27.12	55.99	34.90	127.86
Developed biohumus (the expense is 200 g/m^2)	9.12	26.17	53.56	33.69	122.51
Organic mineral fertilizer "Universal'noe" (the expense is 150 g/m^2)	9.54	27.04	54.89	33.72	125.19
Control (without the application of biohumus)	8.83	26.17	52.65	32.64	120.29
"Zimushka"					
Developed biohumus (the expense is 100 kg/m^2)	9.78	29.13	54.09	33.01	126.01
Developed biohumus (the expense is 150 g/m^2)	10.39	28.45	57.79	38.13	134.76
Developed biohumus (the expense is 200 g/m^2)	10.19	28.41	57.61	36.89	133.10
Organic mineral fertilizer "Universal'noe" (the expense is 150 g/m^2)	9.98	29.29	54.59	35.23	129.09
Control (without the application of biohumus)	9.63	27.64	53.89	33.55	124.71

Table 6. Economic efficiency of cultivation of winter wheat depending on the rate of application of biohumus (using an example of the grade "Skipetr")

Parameter	Variant				
	Control	Biohumus (the expense is 100 kg/m^2)	Biohumus (the expense is 150 g/m^2)	Biohumus (the expense is 200 g/m^2)	Organic mineral fertilizer "Universal'noe" (the expense is 150 g/m^2)
Productivity, t/hectare	2.97	3.96	4.43	4.22	4.15
Production costs, rub/hectare	21790	29220	33010	32040	32360
Cost per unit of output, rub/hectare	15230	18990	20180	19930	19440
Product unit cost, rub/centner	510.3	445.3	423.8	435.6	437.8
Product sales profit, rub/hectare	5990	11020	12760	12410	12170
Level of profitability, %	39.3	58.0	63.2	62.2	62.6

The analysis of economic efficiency has shown that the largest investments are required during the cultivation of wheat with use of the organic and mineral fertilizer "Universal'noe" – 32360 rub/hectare and the smallest in the variant without the application of biohumus or any other fertilizers – the control variant – 21790 rub/hectare. However, in view of various productivity of grains of wheat which changes depending on the influence of various rates of biohumus, the product unit cost considerably changes and is within the limits of 423.8 (biohumus, the expense is 150 g/m^2) – 510.3 rub/centner (control). The variant with the use of the developed biohumus (the expense is 150 g/m^2) has the highest level of profitability – 63.2%, the control sample has the smallest level – 39.2%.

Thus, at the level of profitability of 63.2% it is necessary to grow up winter wheat of the grade "Skipetr" with the use of biohumus with the application rate of 150 g/m^{2}on chernozem soils of the land plots of the Kemerovo region for receiving heavy grain crops (4.4–4.7 t/hectare) with high quality indicators.

ACKNOWLEDGEMENTS

The research was supported by Russian President scholarships for studies abroad 2014/15. (Order No. 304 of 10.04.2014 of the Ministry of Education and Science of Russia, Order No. 558 of 03.06.2015 of the Ministry of Education and Science of Russia).

REFERENCES

1. Russ W. and Meyer-Pittroff R. Utilizing waste products from the food production and processing industries. *Critical Reviews in Food Science and Nutrition*, 2004, vol. 44, no. 2, pp. 57–62. DOI: 10.1080/10408690490263783.
2. Tiwary E. and Gupta R. Medium optimization for a novel 58 kDa dimeric keratinase from *Bacillus licheniformis ER-15*; biochemical characterization and application in feather degradation and dehairing of hides. *Bioresource Technology*, 2010, vol. 101, no. 15, pp. 6103–6110. DOI: 10.1016/j.biortech.2010.02.090.
3. Tsavkelova E., Oeser B., and Oren-Young L. Identification and functional characterization of indole-3-acetamide mediated IAA biosynthesis in plant associated *Fusarium* species. *Fungal Genetics and Biology*, 2012, vol. 49, no. 1, pp. 48–57. DOI: 10.1016/j.fgb.2011.10.005.
4. Kim J.M., Lim W.J., and Suh H.J. Feather degrading *Bacillus* species from poultry waste. *Process Biochemistry*, 2001, vol. 37, no. 3, pp. 287–291. DOI: 10.1016/S0032-9592(01)00206-0.
5. Lasekan A., Abu Bakar F., and Hashim D. Potential of chicken by-products as sources of useful biological resources. *Waste Management*, 2013, vol. 33, no. 3, pp. 552–556. DOI: 10.1016/j.wasman.2012.08.001.
6. Lateef A., Oloke J.K., and Gueguim Kana E.B. Keratinolytic activities of a new feather- degrading isolate of *Bacillus cereus* LAU 08 isolated from Nigerian soil. *International Biodeterioration & Biodegradation*, 2010, vol. 64, no. 2, pp. 162–165. DOI: 10.1016/j.ibiod.2009.12.007.
7. Chen S. and Carroll D.L. Synthesis and Characterization of Truncated Triangular Silver Nanoplates. *Nano letters*, 2002, vol. 2, no. 9, pp. 1003–1007. DOI: 10.1021/nl025674h.
8. Kovalev N.G. Biokonversiya otkhodov zhivotnovodstva [Bioconversion of livestock wastes]. *Vestnik Rossiyskoy akademii sel'skokhozyaystvennykh nauk* [Bulletin of the Russian Academy of Agricultural Sciences], 2003, no. 2, pp. 28–30.
9. Kuz'mina L. N. Poluchenie nanochastits serebra metodom khimicheskogo vosstanovleniya [Possibility of receiving nanoparticles of silver by a method of chemical restoration]. *Zhurnal Rossiyskogo khimicheskogo obshchestva im. D. Mendeleeva* [The Journal of Russian Chemical Society (called by the name of D. Mendeleev)], 2007, no. 8, pp. 7–12.

10. Piskaeva A.I., Dyshlyuk L.S., Sidorin Yu.Yu., and Zimina M.I. Analysis and Selection of the Ion Concentrations and the Cluster of Silver for Micro-organisms-Destructors *Bacillus fastidiosus*, *Lactobacillus sp*., *Microbacterium terregens*. *Khranenie i pererabotka sel'khozsyr'ya* [Storage and processing of farm products], 2014, no. 9, pp. 53–55.
11. Cheng Xu. Innovative approach to utilizing agro-organic wastes and Chi-nese ecological agriculture. *Transactions from the Chinese Society of Agricultural Engineering*, 2002, vol. 5, pp. 1–6.
12. Morones J.R., Elechiguerra J.L., Camacho A., et al. The bactericidal effect of silver nanoparticles. *Nanotechnology*, 2005, vol. 16, no. 10, pp. 2346−2353.
13. Piskaeva A.I., Sidorin Yu.Yu., and Prosekov A.Yu. Comparative Analysis of the Activity of Silver Nanoparticles against Native Microflora from Poultry Processing Plants Wastes. *Nano Hybrids and Composites, 2017*, vol. 13, pp. 176–183. DOI: 10.4028/www.scientific.net/NHC.13.176.
14. Meng C., Li-Ying, Jian-Tao Han, et al. Preparation and Study of Polyacryamide-Stabilized Silver N Panoparticles through a One-Pot Process. *Journal of Fudan Universiry*, 2006, vol. 17 (45), pp. 34–38.
15. Prosekov A.Yu., Babich O.O., and Bespomestnykh K.V. Identification of industrially important lactic acid bacteria in foodstuffs. *Foods and Raw Materials*, 2013, vol. 1, no. 2, pp. 42–45. DOI: 10.12737/2053.
16. Bryant M.P. Microbial methane production theoretical aspects. *Journal of Animal Science*, 1978, vol. 48, no. 1, pp. 193–201. DOI: 10.2527/jas1979.481193x.
17. Ernst L.K., Malenko A.G., and Shapira V.A. Otsenka organicheskogo udobreniya, poluchennogo putem biologicheskoy pererabotki lichinkami komnatnoy mukhi nativnogo svinogo navoza [Assessment of the organic fertilizer received by biological processing of native pork manure by larvae of a room fly]. *Byulleten' VNII udobreniy i agropochvovedenie* [Bulletin of the All-Russian Research Institute of fertilizers and agrology], 2001, no. 14, pp. 188–189.
18. Ernst L.K., Zlochevskiy F.K., and Erastov G.S. Pererabotka otkhodov zhivotnovodstva i ptitsevodstva [Processing of livestock and poultry farming waste]. *Zhivotnovodstvo Rossii* [Livestock production in Russia], 2004, no. 5, pp. 23–24.
19. Fisinin V.I. *Promyshlennoe ptitsevodstvo* [Industrial poultry farming]. Sergiyev Posad, 2010. 599 p.
20. Peregudov S.V. and Shilova E.Yu. Vozmozhnost' povysheniya plodorodiya pochv s pomoshch'yu organomineral'nykh smesey na osnove otkhodov sakharnogo proizvodstva [Possibility of increase in fertility of soils with the help the organic mineral mitures on the basis of waste of sugar production]. *Plodorodie* [Fertility], 2011, no. 2, pp. 35–43.
21. Piskaeva A.I., Sidorin Yu.Yu., Dyshlyuk L.S., Zhumaev Yu.V., and Prosekov A.Yu. Research on the influence of silver clusters on decomposer microorganisms and *E. Coli* bacteria. *Foods and Raw Materials*, 2014, vol. 2, no. 1, pp. 62–66. DOI: 10.12737/413.
22. Elin E.N. Novyy vid biogumusa i ego ispol'zovanie [New type of biohumus and its use]. *Kartofel' i ovoshchi* [Potatoes and vegetables], 2002, no. 6, pp. 25.
23. Arkhipchenko N.A. and Orlova O.V. Perspektivy ispol'zovaniya mikrobnoy ekotekhnologii dlya pererabotki otkhodov ptitseferm [The prospects of using microbial ecotechnology for processing of poultry wastes]. *Doklady Rossiyskoy akademii sel'skokhozyaystvennykh nauk* [Proceedings of the Russian Academy of Agricultural Sciences], 2011, no. 6, pp. 30–32.
24. *Metodicheskie rekomendatsii po proektirovaniyu sistem udaleniya, obrabotki, obezzarazhivaniya, khraneniya i utilizatsii navoza i pometa* [Methodical recommendations for the technological designing of the systems of removal, treatment, disinfecting, storage and utilization of manure and dung]. Moscow: Gipronisel'khoz Publ., 2010. 59 p.
25. Wang, C.L., Li D.F., Lu W.Q., Wang Y.N., and Lai C.N. Influence of cultivating conditions on the alpha-galactosidase biosynthesis from a novel strain of *Penicillium* sp. in solid-state fermentation. *Letters in Applied Microbiology*, 2004, vol. 39, no. 4, pp. 369–375. DOI: 10.1111/j.1472-765X.2004.01594.x.
26. Ivanov V.F., Kolupaev B.I., and Okhotnikov S.I. Ispol'zovanie netraditsionnykh substratov v vermiproizvodstve [Use of nonconventional substrata in earthworm production]. *Khimiya v sel'skom khozyaystve* [Agricultural chemistry], 2004, no. 4, pp. 10–11.
27. Prosekov A.Yu. and Ivanova S.A. Providing food security in the existing tendencies of population growth and political and economic instability in the world. *Foods and Raw Materials*, 2016, vol. 4, no. 2, pp. 201–211. DOI: 10.21179/2308-4057-2016-2-201-211.
28. Denisov A.V. Mobil'nye izmel'chiteli: pererabotka biomassy [Mobile grinders: biomass processing]. *Tverdye bytovye otkhody* [Municipal solid waste], 2011, no. 3, pp. 33–34.
29. Kalinina O.Yu. Sravnenie svoystv kompostov i vermikompostov, poluchennykh iz organicheskikh otkhodov [Comparison of properties of the composts and vermicomposts received from organic waste]. *Materialy po izucheniyu russkikh pochv* [Materials on the study of Russian soils], 1999, no. 1, pp. 78–72.
30. Dyshlyuk L., Babich O., Belova D., and Prosekov A. Comparative analysis of physical and chemical properties of biodegradable edible films of various compositions. *Journal of food process engineering*, 2017, vol. 40, n/a, e12331. DOI: 10.1111/jfpe.12331.
31. Lysenko V.P. Perspektivnaya tekhnologiya pererabotki pometa [Promising Technologies of Manure Processing]. *Ptitsevodstvo* [Poultry farming], 2011, no. 1, pp. 52–55.
32. Cooperband L.R. Composting: Art and Science of Organic Waste Conver-sion to a Valuable Soil Resource. *Laboratory Medicine*, 2000, vol. 31, pp. 283–290.

33. Elzey S. and Grassian V.H. Agglomeration, isolation and dissolution of commercially manu-factured silver nanoparticles in aqueous environments. *Journal of Nanoparticle Research*, 2010, vol. 12, no. 5, pp. 1945−1958. DOI: 10.1007/s11051-009-9783-y.
34. Prosekov A.Yu. and Mudrikova O.V. Neobkhodimost" formirovaniya znaniy o printsipakh i vozmozhnostyakh biotekhnologii [The necessity of forming knowledge about the principles and opportunities of biotechnology]. *Mezhdunarodnyy zhurnal eksperimental'nogo obrazovaniya* [International Journal of Experimental Education], 2011, no. 7, p. 75. Available at: http://www.expeducation.ru/ru/article/view?id=2008 (accessed 08 January 2017).
35. Lin X., et al. Hydrolysis of Feather Keratin by Immobilized Keratinase. *Applied and Environmental Microbiology*, 1996, vol. 62, no. 11, pp. 4273–4275.
36. Vessey J.K. Plant growth promoting rhizobacteria as biofertilizers. *Plant and Soil*, 2003, vol. 255, no. 2, pp. 571–586. DOI: 10.1023/A:1026037216893.
37. Daguzhieva Z.Sh. and Mamsirov N.I. Nekotorye elementy tekhnologii vozdelyvaniya i zashchita posevov ozimoy pshenitsy v Adygee [Some elements of technology of cultivation and protection of winter wheat crops in Adyghea]. *Novye tekhnologii* [New technologies], 2015, no. 3, pp. 92–96.
38. Piskaeva A.I. and Prosekov A.Yu. Optimizatsiya parametrov kul'tivirovaniya konsortsiuma mikroorganizmov-destruktorov keratina v biotekhnologicheskikh tselyakh [Optimization of Cultivation Parameters of the Microbial Consortium for Recycling of Feather Wastes into Fertilizer]. *Izvestiya Irkutskogo gosudarstvennogo universiteta* [The Bulletin of Irkutsk State University. Series «Biology, Ecology»], 2016, no. 16, pp. 53–61.
39. Shakhov A.V. *Organizatsionno-ekonomicheskie osnovy realizatsii bioenergeticheskogo potentsiala agrarnogo proizvodstva* [Organizational and economic bases of realization of bioenergy potential of agrarian production]. Dr. econ. sci. thesis. Moscow, 2011. 42 p.
40. Zhang D., Jianyou D., Jiaoai W., et al. Regulating effect of nitrogen application rate on different quali-ty types of wheat yield, quality and flag leaf photosynthesis. *Plant Nutr. Fert. Sci.*, 2007, vol. 13, no. 4, pp. 535–542.
41. Zhongzhi C., Guangcai Z., Jiaguo Z., et al. Effects of nitrogen fertigation rate on protein components in grains and processing quality of different wheat varieties. *Agric. Sci. Technol*., 2012, vol. 13, no. 2, pp. 370–374.
42. Zong-Bin M., Shu-Ping X., Xin-Ming M., et al. Advances in regulating effects of appling nitrogen on wheat quality. *Journal of Henan Agricultural University*, 2011, vol. 41, pp. 117–122.
43. Zimina M.I., Sukhih S.A., Babich O.O., Noskova S.Yu., Abrashina A.A., and Prosekov A.Yu. Investigating antibiotic activity of the genus Bacillus strains and properties of their bacteriocins in order to develop next-generation pharmaceuticals. *Foods and Raw Materials*, 2016, vol. 4, no.2, pp. 95–100. DOI: 10.21179/2308-4057-2016-2-92-100.
44. Shishin M.V. and Prosekov A.Yu. Investigation of morphological and antimicrobial properties of intestinal tract microorganisms. *Food Processing: Techniques and Technology*, 2015, vol. 39, no. 4, pp. 131–137. (In Russian).
45. Prosekov A.Yu. and Ostroumov L.A. Innovation management biotechnology of starter cultures. *Food Processing: Techniques and Technology*, 2016, vol. 43, no. 4, pp. 64–69. (In Russian).
46. Astakhova L., Babich O., Prosekov A., et al. Short chain fatty acids (SCFA) reprogram gene expression in human malignant epithelial and lymphoid cells. *PLoS ONE*, 2016, vol. 11, no. 7, e0154102. DOI: 10.1371/journal.pone.0154102.

Please cite this article in press as: Piskaeva A.I., Babich O.O., Dolganyuk V.F., and Garmashov S.Yu. Analysis of influence of biohumus on the basis of consortium of effective microorganisms on the productivity of winter wheat. *Foods and Raw Materials*, 2017, vol. 5, no. 1, pp. 90–99. DOI: 10.21179/2308-4057-2017-1-90-99.

ANTIBACTERIAL EFFECT OF COLLOIDAL SOLUTIONS OF SILVER NANOPARTICLES ON MICROORGANISMS OF CEREAL CROPS

O. A. Suvorov[a], S. Yu. Volozhaninova[a,*], G. V. Balandin[b], Yu. V. Frolova[a], A. E. Kozlovskaya[a], E. N. Fokina[a], and N. V. Labutina[a]

[a] Moscow State University of Food Production,
Volokolamskoe Highway 11, Moscow, 125080, Russian Federation

[b] ResFood,
1st Varshavsky Passage 1A, Moscow, 115201, Russian Federation

* e-mail: volozhaninova@mail.ru

Received November 11, 2016; Accepted in revised form January 30, 2017; Published June 29, 2017

Abstract: Due to the growing problem of decrease in the quality and biological safety of food raw materials and the food obtained from it, the increase in the measures for grain improvement as one of the main vegetable resources of food productions is a necessary condition in the modern food industry. A perspectively new way of providing biosafety of grain raw materials is the use of silver nanoparticles. The present work provides data on the inhibiting influence of silver colloidal solutions on the bacterial composition of microflora of the most demanded grain crops of wheat and rye. Various antimicrobial efficiency of influence of the chosen colloidal solutions "Adzhenta colloidal silver" and "Colloidal silver concentrate KND-S-K" within 24 and 144 hours after the processing of grain crops has been shown. Various influence of experimentally chosen concentrations of solutions of silver nanoparticles of 0.1 g/dm^3 and 0.075 g/dm^3 on the number of viable cells of grain bacteria has been described. An approximate mechanism of effect of colloidal solutions of silver nanoparticles on the bacterial cells of microorganisms has been stated. A negative role of bacterium *Bacillus subtilis* in grain production has specially been noted. Their identification in grain crops has been performed and measures for effective destruction of them in grain by means of silver nanoparticles have been proposed. The current data can be used for providing biological safety of grain and an effective solution of the problems on its processing for the purpose of manufacturing of quality products.

Keywords: Silver nanoparticles; food production; grain biosafety; *Bacillus subtilis*

DOI 10.21179/2308-4057-2017-1-100-107 *Foods and Raw Materials*, 2017, vol. 5, no. 1, pp. 100–107.

INTRODUCTION

Nanodimensional structures of silver metals are a perspectively new type of materials used in scientific research due to their versatile application in various areas [1, 2].

In comparison with other metals, silver has strongly marked bactericidal and fungicide characteristics. Besides, the use of silver in the form of nanoparticles has allowed to manipulate its size and properties at the nanolevel which resulted in an increase in the antimicrobial potential. As with a decrease in the size of particles the specific phase interface increases and the area of contact of silver with bacteria considerably extends. Thus, it is confirmed that the bactericidal effect of silver nanoparticles depends on their sizes. And even after long processing, the ability of microorganisms to develop resistance to nanosilver [3] hasn't been observed.

The value of silver nanoparticles (SNP) in the food industry – the technologies of application of colloidal systems in the following developments – should specially be noted:

– the manufacturing of packing materials covered with a nanofilm with bactericidal and fungicide properties;
– the use of biodegradable nanosensors to control the temperature and humidity of foodstuffs;
– the addition of emulsion nanosystems in food to increase nutrient availability;
– the development of chelate nanocompounds for more effective delivery of nutrients to cells without a change of color and taste of food;
– receiving nanodisperse amplifiers of taste and aroma;
– the production of nanodimensional powders that make it easier to digest nutrients;
– the use of the nanoparticles capable to take up and remove selectively food contaminants, for example, mycotoxins;
– the development of the antimicrobic nanocomponents providing control for the development of infectious agents of food infections;
– the creation of nanosensors for the identification of vegetable and animal pathogens;

– the use of fluorescent nanoparticles with attached antibodies for the determination of chemicals or food pathogens [4, 5, 6].

Studies in the scope of SNP as an antimicrobial agent when developing antibacterial means against a number of bacteria and filamentous fungi are of great interest in the food industry [7, 8].

It is due, first of all, to the growing problem of a decrease in the quality and biological safety of foodstuffs at all stages of production and storage as a result of high adaptive ability of pathogenic microorganisms to the changing conditions of the environment [9, 10].

Special vigilance is caused, in particular, by practical lack of application of effective and eco-friendly measures for the improvement of grain production. Grain is provided quite well with the nutrients which are a favorable environment for the development of microorganisms under certain conditions. The significant amount of microorganisms negatively influence grain under certain favorable conditions, in other words, they reduce the content of solids in it, provide its pollution, and also poison it with toxic waste products. The contamination of grain by depredators and diseases is revealed during its further processing in the food industry. In this regard, the negative processes in the flour-grinding and baking industries are a serious threat to human health, provide a further decrease in the quality of bakery products. The contamination of grain by infectious agents of the mushroom and bacterial etiology occurs annually to some extent and though the level of contamination is corrected by a number of edaphoclimatic and anthropogenous factors, the harvest shortage can make in some cases up to 30% with a simultaneous decrease in the technological and baking qualities of grain [10, 11].

An important role in the decrease in the harvest and quality indicators of grain and its derivative products, in particular bread, is played by the infectious agents of bacterioses – sporous bacteria of *Bacillus mesentericus vulgatus Flügge* and *Bacillus subtilis* and other species of this genus [12, 13].

According to the most widespread systematics of phytopathogenic bacteria [14] based on the signs of existence or lack of flagella, Gram staining of colonies and their pigmentation, the genus *Bacillus* which is a part of the *Bacillaceae* family is presented by the most harmful types.

After cooling of bread, in case of low acidity and the temperature above 25°C, the sporous forms of infectious agent begin to develop causing chemical changes in the newly-baked bread. Under the influence of the active amylases emitted by the bacteria in bread the quantity of dextrines which provide the mucilagination of the crumb, loss of its structure and the formation of emptiness increases. Under the influence of proteolytic enzymes of bacteria disintegration products of proteins that give a pungent specific smell to bread are formed. Such bread is not suitable for consumption, nor as animal forage either.

A different degree of contamination by bacteria spores is noted on wheat and corn grain, in soft and hard wheat flour, in bran and other products which are raw materials for bread and bakery products [15, 16, 17].

All the above allows to establish the fact of a huge damage sporous bacteria and other phytopathogenic microorganisms may cause to the food market of the country. The infectious agents of bacterial etiology are wide-spread and have a high level of injuriousness which, along with the decrease in productivity, consists of the contamination of wheat grain providing loss of technological and baking properties in the latter.

Due to this, the main purpose of this work is the study of influence of various concentrations containing silver nanoparticles on the viability of bacterial microbiota of seeds of some grain crops.

OBJECTS AND METHODS OF STUDY

To study the contamination of grain crops, seeds of *Irgin* summer wheat (*Triticum aestivum L.*) and *Krone* winter rye (*Secale cereale*) were used as the objects. The quantitative and qualitative composition of bacterial microflora of grain was studied using the method of electronic microscopy.

To inhibit the processes of microbiological spoilage of grain crops the SNP colloidal solutions "Adzhenta colloidal silver" (the manufacturer is LLC "KorolevFarm", Russia) and the colloidal solution of silver nanoparticles KND-S-K (Scientific and Production Enterprise LLC "Sentoza Faktoring NP", Russia) were used.

Using the method of dynamic laser light scattering dispersion and distribution was studied by the sizes of nanoparticles in the studied colloidal solutions. The test specimens with the volume of 0.7–3.0 ml were placed in the ditch of the device and measurements were taken at a temperature of 23 ± 1°C using the laser particle size analyzer Nanotrac – the modification of Zetatrac ("Microtrac Inc.", the USA) – by means of the Microtrac FLEX software.

The studied SNP colloidal solutions, using the method of dilution by distilled water, brought up to the use rates of 0.075 and 0.1 g/dm^3 which had experimentally been selected taking into account the compliance to normative documents in the tolerant (transferable) content of silver in drinking water (WHO, SanPiN) [18, 19]. Seeds of wheat and rye were processed using the obtained solutions. For this purpose 50 g of seeds and the calculated dose of preparative form of silver colloidal solution taking into account the concentrations of nanoparticles were put into a 150 ml flask. The flask with seeds was stirred up for 2–3 minutes before the full distribution of the preparation on the surface of seeds. Then the processed grain was left for 2 hours after which the test specimens of the studied samples were selected and put into sterile ware in the aseptic conditions excluding the microbial contamination of raw materials and total of bacteria using the method of washed out crops with the dilution degree of 1 : 100 per meat-and-peptone agar (MPA) with the subsequent cultivation at the temperature of 30 ± 1°C for 24–48 hours was determined.

To study the influence of SNP on the bacterial microbiota of grain crops in detail the analysis of contamination of samples was also performed in 24 and 144 hours after processing. The choice of temporary intervals is justified, among other things, by the features of development of microflora of grain crops (by the antagonistic effect of some microorganisms on others).

To study the qualitative composition of microflora, microscopic preparations (fixed dabs painted according to Gram - to study bacterial morphology) were made of the colonies of the microorganisms differing from each other in cultural properties.

The spore-forming bacteria of the genus *Bacillus* were determined using the technique described in GOST ISO 21871 [20]. Initially, inoculation, first, of a liquid enriched medium (tryptone soy polymixil broth (TSPB) with the established volume of initial sample of suspension of 10 ml in the pasteurized washouts from the samples at the rate of 1 : 100 was consistently performed. The duration of incubation was 48 h at a temperature of 30°C. Then, a transfer to a solid nutrient medium (PEMBA) and incubation for 18–48 h at 37°C for the further analysis of Petri dishes to check the presence of the colonies which, according to the characteristics, can correspond to presumptive *Bacillus* bacteria was performed. Microbiological medium from HiMedia Laboratories, India, Merck Ltd., SRL Pvt., Ltd., Mumbai were used to perform the studies.

RESULTS AND DISCUSSION

According to TR TS 021/2011 certain complexes of microorganisms of grain crops (Table 1) [21] are normalized.

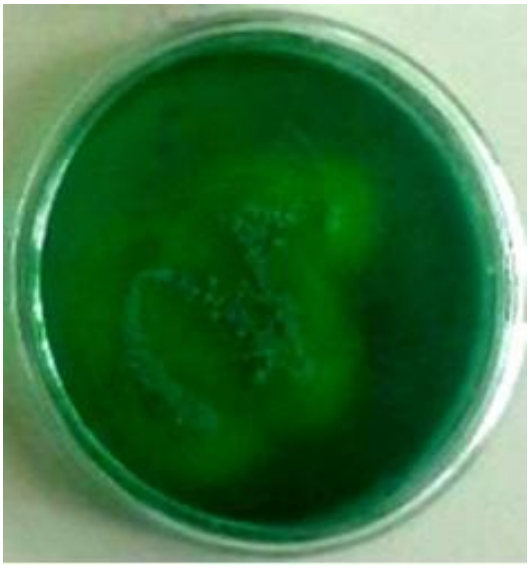
The determination of content of microorganisms of the studied grain has shown compliance with the normalized indicators, except the indicator of the total plate count. According to the obtained data, the indicator was 9.0×10^3 CFU/g and 7.0×10^3 CFU/g for wheat and rye respectively with the norm of 5.0×10^3 CFU/g.

When studying the qualitative composition of microbiota of wheat and rye seeds it has been established that the bacterial complex is presented by: Gram-negative bacteria *Erwinia herbicola*, *Escherichia coli* and *Pseudomonas fluorescens* and Gram-positive spore-forming bacteria of the genus *Bacillus* (presumably *Bacillus subtilis*), *Clostridium perfringens* and gram-positive cocci.

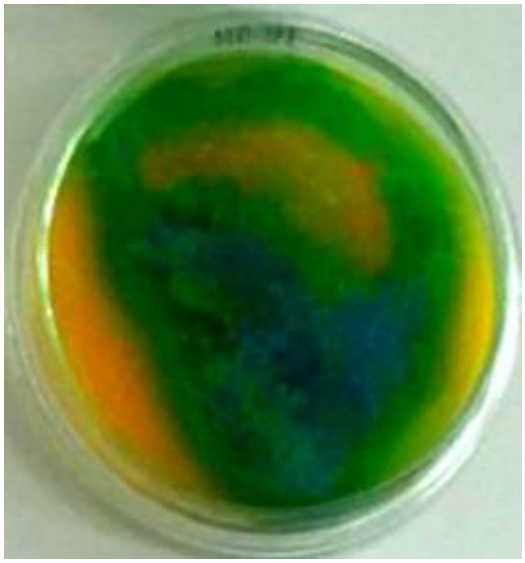
The results of the experiments according to the method [20] of identification of bacteria of the genus *Bacillus* in the composition of microfloras of grain crops show the existence of this type of microorganisms in wheat seeds and the absence of them in rye seeds (Fig. 1). True to form, the colonies that correspond to the representatives of bacteria of the genus *Bacillus* (Fig. 1a) have sizes from 2 mm to 5 mm, uneven edges with branchings on a smooth glass surface, a whitish-gray color in the center and a blue/turquoise background, and also a deposit aureole (the egg yolk reaction) up to 5 mm wide.

Table 1. Microbiological standards of grain safety

Parameters	Norm
Total plate count, CFU/g, not more than	5.0×10^3
Escherichia coli group bacteria, not permitted in the mass of the product (g)	0.01
Mold, CFU/g, not more than	50.0
B. cereus, not permitted in the mass of the product (g)	0.1
Pathogenic microorganisms, including salmonellas, are not permitted in the mass of the product (g)	25.0



(a)



(b)

Fig. 1. Visual analysis of presumptive bacteria of the genus *Bacillus* of microflora: (a) of wheat seeds, (b) of rye seeds.

Lack of the colonies that correspond to bacteria of the genus *Bacillus* bacteria in the analysis of bacterial microbiota of rye seeds (Fig. 1b) is explained probably by various susceptibility of plants to this complex of microorganisms, and also by the factors of the external environment of cultivation of seeds [22, 23, 24]. Besides, the rye grain taken for the study differed initially from wheat grains by lower contamination by microorganisms as a result of the initial analysis of content of microorganisms.

As for cultural and morphological features, it is possible to draw a conclusion that this kind of bacterium belongs to *Bacillus subtilis*. This culture forms flat, dry colonies of dense consistence with a specifically white granular deposit that can easily be taken off from the agar. The diameter is 2.5 mm. The edges are almost straight or slightly rugged. Other types of colonies have not been noted.

To confirm the colonies that correspond to representatives of bacteria of the genus *Bacillus subtilis* it has been also established using the microscopy method that the bacteria allocated by us from the microbiota of wheat seeds correspond to this kind. These are Gram-positive thin sticks of 3–5×0.9 microns, they are separate and have the form of threads or chains. They may contain ellipsoidal or cylindrical spores the diameter of which is not higher than the width of a microbic cage (Fig. 2).

On the basis of the obtained data on the quantitative and qualitative composition of microorganisms of the studied grain crops a need of their processing by antimicrobial means to prevent a microbiological damage has been determined.

The establishment of antibacterial activity of SNP solutions depending on the concentration and duration of processing of grain crops was the following stage of work, the obtained data are presented in Table 2.

Proceeding from the basic data on the content of the total viable count in raw grain crops it is possible to note that the least antibacterial effect of SNP can be observed after 2 hours of processing of grain of wheat and rye regardless of the concentrations and the type of colloidal solutions. At the same time, it is known from the studies performed earlier that the access of SNP to the cellular wall is complicated with a high concentration of bacterial cells, and a smaller amount of particles is adsorbed on its surface which provides a decrease in the biocidal effect [25].

It was shown during the subsequent quantitative analysis of bacterial microflora of grain that after 24 hours of processing the colloidal solutions of nanoparticles with the concentration of 0.1 g/dm^3, in general, show a deeper effect against the complex of microorganisms of grain crops in comparison with the lower concentration of SNP of 0.075 g/dm^3.

At the same time it should be noted that the control of the samples of grain processed by SNP after 24 hours has shown almost full compliance with the norms of TR TS 021/2011 [21]. Thus, it is obvious that SNP colloidal solutions are capable to inhibit effectively the development of bacterial microbiota of grain crops.

Analyzing the quantity of microorganisms in the grain processed after 144 hours it is possible to come to a conclusion that the influence of SNP is already insignificant in comparison with the previous period of processing (2–24 h).

At the same time, estimating the antimicrobial effect of colloidal solutions of the chosen concentrations after 144 hours by comparison of their inhibiting influence on microorganisms, it is fair to note that SNP solutions with the concentration both of 0.075 g/dm^3 and 0.1 g/dm^3 have the highest effect in both chosen preparations.

The obtained data have also been presented in the form of diagrams (Fig. 3 a–d).

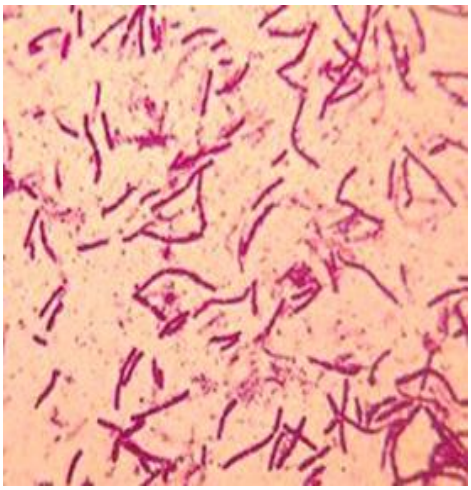


Fig. 2. Microscopic analysis of bacteria of the genus *Bacillus subtilis.*

Table 2. Antimicrobial activity of various concentrations of colloidal solutions of nanoparticles

Cultivation time	Total viable microorganisms in wheat, (CFU/g)				Total viable microorganisms in rye, (CFU/g)			
	Adzhenta		KND-S-K		Adzhenta		KND-S-K	
	0.1 g/dm^3	0.075 g/dm^3	0.1 g/dm^3	0.075 g/dm^3	0.1 g/dm^3	0.075 g/dm^3	0.1 g/dm^3	0.075 g/dm^3
2 h	$8\cdot10^3$	$7\cdot10^3$	$9\cdot10^3$	$8\cdot10^3$	$7\cdot10^3$	$6\cdot10^3$	$7\cdot10^3$	$7\cdot10^3$
24 h	$5\cdot10^3$	$5\cdot10^3$	$6\cdot10^3$	$5\cdot10^3$	$4\cdot10^3$	$5\cdot10^3$	$6\cdot10^3$	$6\cdot10^3$
144 h	$4\cdot10^3$	$3\cdot10^3$	$5\cdot10^3$	$5\cdot10^3$	$3\cdot10^3$	$4\cdot10^3$	$5\cdot10^3$	$4\cdot10^3$

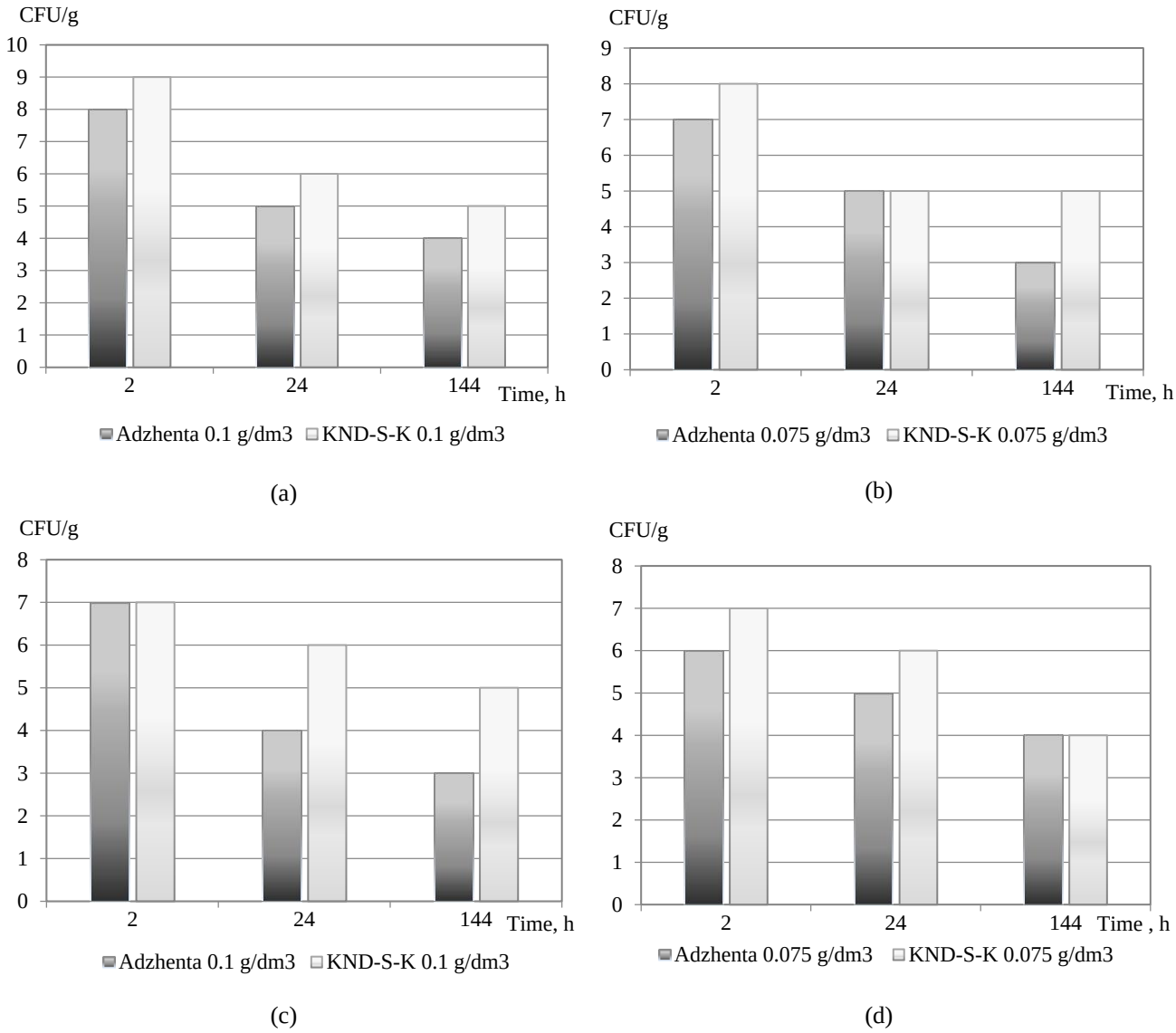


Fig. 3. Diagram of antibacterial activity of silver nanoparticles of various preparations on microorganisms: (a) of wheat with the concentration of 0.1 g/dm^3; (b) of wheat with the concentration of 0.075 g/dm^3; (c) of rye with the concentration of 0.1 g/dm^3; (d) of rye with the concentration of 0.075 g/dm^3.

At the same time, it is necessary, based on the performed studies, to emphasize quite a high antimicrobial influence of Adzhenta colloidal silver after 24 hours of processing in all the samples of grain in comparison with the solution of silver nanoparticles KND-S-K. Most likely, various ways of obtaining and stabilizing SNP in the solution of the used preparations are the reason for that. It is well known that atoms of metals have a high chemical activity which remains in the clusters and nanoparticles, which are formed of atoms, with a large number of atoms which can provide a sharp decrease in their activity [26, 27].

The SNP solutions of colloidal degree of dispersion of KND-S-K stabilized by arabic gum, chitosan and sulfoamber acid with the particles of 6–20 nanometers (Fig. 4) have a high antimicrobial effect, but in many respects depend on the physical and chemical factors of the environment due to the chemical method of stabilization [28, 29]. Chemically, Adzhenta colloidal silver is silver nitrate and is produced without any chemical processes, with the use of an electromagnetic charge which suspends silver particles of 5–15 nanometers (Fig. 5) in water with the formation of solution. Therefore, most likely it shows a more considerable effect.

Besides, as it is reported from the literary data [26, 30], the mechanism of inhibition of SNP is directly related to their size (less than 100 nanometers) and the largest surface area to volume. It is known that with a decrease in the size of particles the specific phase interface and, therefore, the comparative concentration of active silver increases which provides an increase in the area of contact of silver with bacteria.

At the stage of study of influence of SNP colloidal solutions on the presence of a bacterium of the genus *Bacillus subtilis* in the processed wheat sample, the results of the performed study also specify that under the influence of SNP there is destruction of a bacterial cell after 24 hours of cultivation in both chosen preparations. The effect of colloidal solutions was already shown in both cases with the concentration of 0.075 g/dm^3.

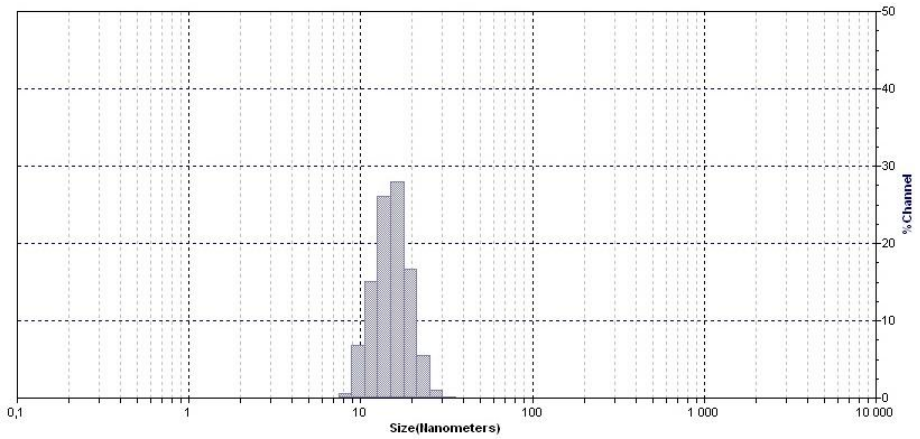


Fig. 4. Histogram of distribution of nanoparticles by size in the KND-S-K colloidal solution.

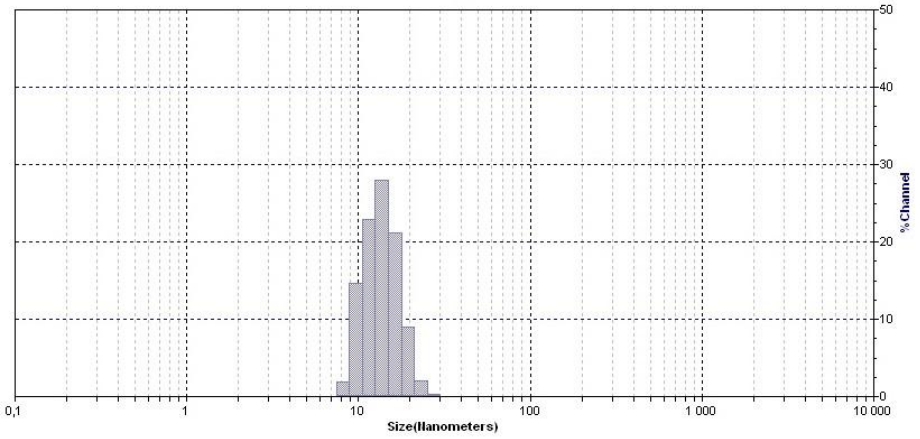


Fig. 5. Histogram of distribution of nanoparticles by size in the Adzhenta colloidal solution.

Thus, based on the results of the performed studies, it is possible to draw a conclusion that the addition of the preparation "Adzhenta colloidal silver" into the grain mass with the concentration of SNP of 0.1 g/dm^3 will allow after 24 hours to prevent the development of microbial contamination, will increase the period of storage and the quality of grain, and also provide the inhibition of further development of spore-forming forms of bacteria of the genus *Bacillus subtilis.* The processing of grain mass using the solution of silver nanoparticles KND-S-K of 0.1 g/dm^3 within 24 hours will also favorably effect the inhibition of bacterial microbiota of grain crops.

CONCLUSION

The performed study was developed to show the efficiency of antibacterial preparations of a new generation – nanodimensional silver dispersions for the food industry.

As a result of the done work, a method of application of preparations of silver nanoparticles to reduce the microbial contamination in the grain processing and baking industry providing an increase in the microbiological purity of grain for the purpose of providing biological safety has been offered.

Antibacterial properties of nanoparticles of Adzhenta colloidal silver and KND-S-K on the basis of understanding of their effect to prove their efficiency against various pathogenic microorganisms of grain crops have been studied.

Various results of effect of SNP preparations of the colloidal degree of dispersion (KND-S-K, Adzhenta) depending on the concentrations in the solution have been obtained and the preferable modes of processing of grain crops have been chosen. On the basis of results of the studies biostatic concentrations of SNP preparations have been determined.

The efficiency of their application against significant pathogenic bacterial microorganisms of grain productions has been proved (in particular, against *Bacillus subtilis*).

It has been established on the basis of study of influence of SNP colloidal solutions on the bacterial microbiota of grain of wheat and rye that SNP are capable to inhibit effectively the activity of the bacterial microorganisms that contaminate grain raw materials.

Finally, the conclusions provided in this work will help us to apply SNP colloidal solutions to inhibit the growth of bacterial microorganisms and reduce considerably the level of microbiological contamination of grain crops.

The current study has been performed within the grant of the President of the Russian Federation No. MK-8362.2016.11.

REFERENCES

1. Tarafdar J.C., Sharma S., and Raliya R. Nanotechnology: Interdisciplinary science of applications. *African Journal of Biotechnology*, 2013, vol. 12, no. 3, pp. 219–226. DOI: 10.5897/AJB12. 2481.
2. Kalpana Sastry R., Anshul S., and Rao N.H. Nanotechnology in food processing sector—An assessment of emerging trends. *Journal of Food Science and Technology*, 2013, vol. 50, no. 5, pp. 831–841. DOI: 10.1007/s13197-012-0873-y.
3. Balandin G.V. *Primenenie nanochastits serebra dlya obespecheniya biologicheskoy bezopasnosti v brodil'nykh proizvodstvakh* [Application of silver nanoparticles for providing biological safety in fermentative productions]. Cand. eng. sci. thesis. Moscow, 2015. 9 p.
4. Singh P.K., Jairath G., and Ahlawat S.S. Nanotechnology: a future tool to improve quality and safety in meat industry. *Journal of Food Science and Technology*, 2016, vol. 53, no. 4, pp. 1739–1749. DOI: 10.1007/s13197-015-2090-y.
5. Ranjan S., Dasgupta N., Chakraborty A.R., et al. Nanoscience and nanotechnologies in food industries: opportunities and research trends. *Journal of Nanoparticle Research*, 2014, vol. 16, no. 6, p. 2464. DOI: 10.1007/s11051-014-2464-5.
6. Rashidi L. and Khosravi-Darani K. The applications of nanotechnology in food industry. *Critical Reviews in Food Science and Nutrition*, 2011, vol. 51, no. 8, pp. 723–730. DOI: 10.1080/10408391003785417.
7. Shulgina T.A., Norkin I.A., and Puchinan D.M. Antibacterial effect of aqueous dispersions of silver nanoparticles on the gram-negative microorganisms (on example of Escherichia coli). *Fundamental Research*, 2012, no. 7, part 2, pp. 424–426. (In Russian).
8. Esteban-Tejeda L., Malpartida F., Esteban- Cubillo A., et al. The antibacterial and antifungal activity of a soda-lime glass containing silver nanoparticles. *Nanotechnology*, 2009, vol. 20, no. 8, pp. 085103. DOI: 10.1088/0957-4484/20/50/505701.
9. Verraes C., Van Boxstael S., Van Meervenne E., et al. Antimicrobial resistance in the food chain: a review. *International Journal of Environmental Research and Public Health*, 2013, vol. 10, no. 7, pp. 2643–2669. DOI: 10.3390/ijerph10072643.
10. Leontiev V.N., Elkaib Kh.M., and Elhedmi A.E. Spoilage of foodstuff: types, causes and ways of prevention. *Proceedings of the Belarusian State University*, 2013, vol. 8, no. 1, pp. 125–130. (In Russian).
11. Smirnova T.A. and Kostrova E.I. *Mikrobiologiya zerna i produktov ego pererabotki* [Microbiology of cereal and products of its processing]. Moscow: Agropromizdat Publ., 1989. 159 p.
12. Medvedev P.V. and Fedotov V.A. Factors contamination grain disputes *Bacillus subtilis* and *Bacillus mesente*. *Vestnik of the Orenburg State University*, 2011, vol. 131, no. 12, pp. 341–343. (In Russian).
13. Tewari A. and Abdullah S. *Bacillus cereus* food poisoning: international and Indian perspective. *Journal of Food Science and Technology*, 2015, vol. 52, no. 5, pp. 2500–2511. DOI: 10.1007/ s13197-014-1344-4.
14. Gorlenko M.V. *Bakterial'nye bolezni rasteniy* [Bacterial diseases of plants]. Moscow: Vysshaya Shkola Publ., 1996. 291 p.
15. Auerman L.Ya. *Tekhnologiya khlebopekarnogo proizvodstva* [Technology of baking production]. St. Petersburg: Professija Publ, 2003. 416 p.
16. Lücking G., Stoeckel M., Atamer Z., et al. Characterization of aerobic spore-forming bacteria associated with industrial dairy processing environments and product spoilage. *International Journal of Food Microbiology*, 2013, vol. 166, no. 2, pp. 270–279. DOI: 10.1016/j.ijfoodmicro.2013.07.004.
17. De Bellis P., Minervini F., Di Biase M., et al. Toxigenic potential and heat survival of spore-forming bacteria isolated from bread and ingredients. *International Journal of Food Microbiology*, 2015, vol. 197, pp. 30–39. DOI: 10.1016/j.ijfoodmicro.2014.12.017.
18. Fewtrell L. *Silver: water disinfection and toxicity*. Spring, 2014. 50 p. Available at: http://www.who.int/water_sanitation_health/dwq/chemicals/Silver_water_disinfection_toxicity_2014V2.pdf?ua=1 (accessed 7 February 2017).
19. *Silver in Drinking-water Background document for development of WHO Guidelines for Drinking-water Quality*. Geneva: World Health Organization, 2003. Available at: http://www.who.int/water_sanitation_health/dwq/chemicals/silver.pdf?ua=1 (accessed 7 February 2017).
20. *GOST ISO 21871-2013. Mikrobiologiya pishchevykh produktov i kormov dlya zhivotnykh. Metod obnaruzheniya i podscheta naibolee veroyatnogo chisla Bacillus cereus* [State Standard ISO 21871-2013. Microbiology of food and animal feeding stuffs. Most probable number count and detection method for *Bacillus cereus*]. Moscow: Standartinform Publ., 2014. 16 p. Available at: http://vsegost.com/Catalog/53/53709.shtml. (accessed 15 February 2017).
21. *TR TS 021/2011 Tekhnicheskiy reglament Tamozhennogo soyuza «O bezopasnosti pishchevoy produktsii»* [Technical Regulations of the Customs Union 021/2011. On food safety]. Moscow: Commission of the Customs Union, 2011. 242 p. Available at: http://www.eurasiancommission.org/ru/act/texnreg/deptexreg/tr/Documents/TR%20TS%20PishevayaProd.pdf (accessed 15 February 2017).
22. Omel'chenko A.V., Jurkova I.N., and Zhizhina M.N. Effects of seed treatments with nanobiosilver on phytopathogens and growth processes of winter wheat seedlings. *Proceedings of Voronezh State University. Series: Chemistry. Biology. Pharmacy*, 2015, no. 3, pp. 71–74. (In Russian).

23. Ibragimov R.I., Yarullina L.G., Shpirnaya I.A., et al. Biokhimicheskie faktory razvitiya ustoychivosti rasteniy k patogenam [Biochemical factors of development of resistance of plants to pathogens]. *Modern high technologies*, 2010, no. 4, pp. 46–49. (In Russian).
24. Nazarenko L.V. Factors of the external ambience, their influence upon growing and development of the agricultural cultures of the long day on example of wheat. *Polythematic online scientific journal of Kuban State Agrarian University*, 2013, no. 93, pp. 1316–1340. (In Russian).
25. Blinov A.V., Kravtsov V.A., Serov A.V., and Blinova A.A. Ispol'zovanie nanochastits serebra v predposevnoy obrabotke semyan [Silver nanoparticles application in preplant treatment of seeds]. *Sbornik nauchnykh trudov Stavropol'skogo nauchno-issledovatel'skogo instituta zhivotnovodstva i kormoproizvodstva* [Collection of scientific works of Stavropol research institute of livestock and forage production], 2014, vol. 2, no. 7, pp. 513.
26. Podkopaev D.O., Shaburova L.N., Balandin G.V., et al. Comparative evaluation of antimicrobial activity of silver nanoparticles. *Nanotechnologies in Russia*, 2014, vol. 9, no. 1–2, pp. 93–97. DOI: 10.1134/S1995078014010121.
27. Zimon A.D. and Pavlov A.N. *Kolloidnaya khimiya nanochastits* [Colloidal chemistry of nanoparticles]. Moscow: Nauchnyy Mir Publ., 2012. 224 p.
28. Krutyakov Yu.A., Kudrinskiy A.A., Olenin A.Yu., and Lisichkin G.V. Synthesis and properties of silver nanoparticles: advances and prospects. *Russian Chemical Reviews*, 2008, vol. 77, no. 3, pp. 233. DOI: 10.1070/RC2008v077n03ABEH003751. (In Russian).
29. Suvorov O.A. and Volozhaninova S.Yu. Sovremennye aspekty primeneniya nanotekhnologicheskikh sredstv v industrii pitaniya [Modern aspects of application of nanotechnology in the food industry]. *Sbornik statey III Vserossiyskoy nauchno-prakticheskoy konferentsii s mezhdunarodnym uchastiem «Innovatsionnye tekhnologii v pishchevoy promyshlennosti»* [Collection of articles of the III All-Russian Scientific and Practical Conference with the international participation “Innovative technologies in the food industry”]. Samara, 2016, pp. 89–92.
30. Sintubin L., De Gusseme B., Van der Meeren P., et al. The antibacterial activity of biogenic silver and its mode of action. *Applied Microbiology and Biotechnology*, 2011, vol. 91, no. 1, pp. 153–162. DOI: 10.1007/s00253-011-3225-3.

Please cite this article in press as: Suvorov O.A., Volozhaninova S.Yu., Balandin G.V., Frolova Yu.V., Kozlovskaya A.E., Fokina E.N., and Labutina N.V. Antibacterial effect of colloidal solutions of silver nanoparticles on microorganisms of cereal crops. *Foods and Raw Materials*, 2017, vol. 5, no. 1, pp. 100–107. DOI: 10.21179/2308-4057-2017-1-100-107.

DETERMINATION OF THE INTENSITY OF BACTERIOCIN PRODUCTION BY STRAINS OF LACTIC ACID BACTERIA AND THEIR EFFECTIVENESS

M. I. Zimina[a,*], A. F. Gazieva[a], J. Pozo-Dengra[b], S. Yu. Noskova[a], and A. Yu. Prosekov[c]

[a] Kemerovo Institute of Food Science and Technology (University), Stroiteley blvd. 47, Kemerovo, 650056, Russian Federation

[b] Biorizon Biotech, Science and Technology Park of Almería (PITA), C/ Albert Einstein 15, 04131 Almeria, Spain

[c] Kemerovo State University, Krasnaya Str. 6, Kemerovo, 650043, Russian Federation

* e-mail: mariia.zimina@list.ru

Received January 18, 2017; Accepted in revised form March 24, 2017; Published June 29, 2017

Abstract: The study of bacteriocins is one of the most relevant areas of research. This is due to the increase in the number of pathogenic microorganisms resistant to antibiotics. The bacteriocins of lactic acid bacteria have the most common application because of their safety in use. To assess the antimicrobial potential of bacteriocins of lactic acid bacteria and the possibilities for their further use, this study deals with the intensity of bacteriocin production by strains of lactic acid bacteria, the minimal inhibitory concentration of bacteriocins produced by these strains with respect to *E. coli B-6954*, as well as the antimicrobial activity of the produced bacteriocins with respect to some strains of pathogenic microorganisms. This work was carried out on the basis of the Kemerovo Technological Institute of Food Industry (Russia). The study objects were strains of microorganisms *Lactobacillus delbrueckii* B2455, *Lactobacillus paracasei* B2430, *Lactobacillus plantarum* B884. Biomass concentration was determined by spectrophotometric method. Study of antimicrobial activity in relation to a number of pathogenic strains was carried out in a culture fluid by optical density, and also by a disk-diffusion test. As a result, the maximum productivity value, characterizing the intensity of bacteriocin production, was observed for strain B884. However, the quality of bacteriocin (antimicrobial activity relative to the *E. coli* strain) with a lower productivity is higher for strain B2430. The minimum inhibitory concentration for the strains studied was: B2430 – $1.0 \cdot 10^6$ CFU/ml, B884 – $1.0 \cdot 10^8$ CFU/ml, B2455 – $1.0 \cdot 10^7$ CFU/ml. The best indicator of the minimum inhibitory concentration was observed for strain B2430. Thus the strain B2430 had the greatest antimicrobial activity, it had an inhibitory effect on 12 test cultures: *Escherichia coli*, *Alcaligenes faecalis*, *Candida albicans*, *Pseudomonas libanensis*, *Staphylococcus warneri*, *Erwinia aphidicola*, *Microbacterium foliorum*, *Bacillus licheniformis*, *Serratia plymuthica*, *Erwinia aphidicola*, *Bacillus endophyticus*, *Leuconostoc mesenteroides*. Thus, among the test Lactobacillus strains, the strain of *Lactobacillus paracasei* B2430 is promising for further study.

Keywords: Lactic acid bacteria, bacteriocins, antimicrobial activity, biomass concentration, minimum inhibitory concentration

DOI 10.21179/2308-4057-2017-1-108-117 *Foods and Raw Materials*, 2017, vol. 5, no. 1, pp. 108–117.

INTRODUCTION

Lactic acid bacteria (LAB) are a group of phylogenetically diverse gram-positive bacteria that have some common morphological characteristics, as well as metabolic and physiological features [1]. Lactic acid bacteria have GRAS safety status and are often used in the production of food products.

Lactic acid bacteria contain in human microbiota and have significant impact on human health [2, 3]. They produce a number of antimicrobial compounds, which include hydrogen peroxide, CO2, diacetyl, acetaldehyde, lactic acid, D-isomers of amino acids, bacteriocins [4].

There is increasing tendency in our society to use more natural and safety products such as biodegradable materials, biofuels and different pruducts, obtained by microbial synthesis (enzymes, polysaccharides, amino acids, vitamins, organic acids, bacteriocins) [5].

Bacteriocins are a heterogeneous group of ribosomally synthesized peptides or proteins that have antimicrobial activity against other bacteria. Action mechanism of bacteriocins is based on creation of

pores in the membrane of targeted cells, which interferes with the membrane potential and kills the cells. Bacteriocins are normally synthesized by strains as a defense system, and they inhibit development of microorganisms related to the producing strain [6]. Currently, one of the most urgent areas of research is the development of new antimicrobial agents, which is associated with a wide spread of pathogenic strains that are resistant to antibiotics [7]. In connection with this, in recent years, the interest of scientists in the study of bacteriocins has been especially increased, this is due to the possibility of their use as bioconservants in food products in order to suppress development of pathogenic microflora [8, 9].

Bacteriocins are divided into separate classes. Lantibiotics of the first class include lantibiotics, which are small (< 10 kDa) thermally stable unmodified proteins. Second-class bacteriocins are divided into pediocin-like (subclass IIa) and bi-peptic bacteriocins (subclass IIb). The third class includes large (> 30 kDa) thermolabile proteins [10].

Due to the high antimicrobial potential of bacteriocins, their use is most common in medicine for the production of antimicrobial agents [11, 12]. Also bacteriocins may be used in the food industry for increasing the shelf life of products and providing food security [13, 14, 15]. The study of new types of bacteriocins is a topical issue in modern science, due to vast possibilities of their application, and in this connection this article is devoted to study of bacteriocins produced by lactic acid bacteria, the intensity of their production and the effectiveness of the action.

Thus, the study was intended to determine the intensity of bacteriocin production by the strains studied, as well as to determine the effectiveness of the action of bacteriocins against pathogenic strains to study the possibility of further use of bacteriocins.

OBJECTS AND METHODS OF STUDY

The following reagents were used as materials at different stages of the study**:** bacto-peptone, meat extract, citric acid ammonium (Component-Reactiv LLC, Russia); acetous sodium, sodium hydrogenphosphate (Belkhim LLC, Belarus); magnesium sulphate 7-water, manganese sulfate 5-water (Cation LLC, Russia); yeast extract, sodium chloride (Component-Reactiv LLC, Russia); Millex-GV filters (0.22 μm, Nihon "Millipore", USA), Müller-Hinton medium, Saburo medium (Lab-Biomed LLC, Russia).

Strains of microorganisms provided by VKPM FSUE "GosNIIgenetika" (http://www.genetika.ru/vkpm) were used as objects of study: *Lactobacillus delbrueckii* B2455, *Lactobacillus paracasei* B2430, *Lactobacillus plantarum* B884.

As test cultures, natural and medical strains of pathogenic microorganisms were used, which were designated as follows: No. 1 – *Bacillus mycoides EMTC 9*, No. 2 – *Salmonella enterica ATCC 14028*, No. 3 – *Micrococcus luteus EMTC 1860*, No. 4 – *Escherichia coli ATCC 25922*, No. 5 – *Bacillus cereus EMTC 1949*, No. 6 – *Alcaligenes faecalis EMTC 1882*, No. 7 – *Proteus vulgaris ATCC 63*, No. 8 – *Pseudomonas fluorescens EMTC 42*, No. 9 – *Candida albicans EMTC 34*, No. 10 – *Pseudomonas aeruginosa ATCC 9027*, No. 11 – *Staphylococcus aureus ATCC 25923*, No. 12 – *Pseudomonas libanensis EMTC 1853*, No. 13 – *Staphylococcus warneri EMTC 1854*, No. 14 – *Erwinia aphidicola EMTC 1857*, No. 15 – *Microbacterium foliorum EMTC 1858*, No. 16 – *Bacillus licheniformis EMTC 1859*, No. 17 – *Serratia plymuthica EMTC 1861*, No. 18 – *Rahnella aquatilis EMTC 1862*, No. 19 – *Erwinia aphidicola EMTC 1863*, No. 20 – *Bacillus endophyticus EMTC 1864*, No. 21 – *Leuconostoc mesenteroides EMTC 1865*, No. 22 – *Enterococcus casseliflavus EMTC 1866*.

All strains were cultured in a fermenter (80% filling) in a liquid MRS medium at 37°C for 3 days. The obtained biomass was separated from the culture medium by centrifuging at 8000 g for 20 minutes. A culture fluid filtered through 0.22 μm membrane filters was used as the bacteriocin solution. The resulting sterile solution of metabolites was used for experiments.

A suspension of nocturnal broth cultures grown on standard culture media was taken for work. The number of microorganisms (titre) in the suspension was determined by the optical density (OD) at a wavelength of 595 nm.

Biomass concentration was determined with the UV-1800 spectrophotometer (Shimadzu, Japan) by measuring the light absorbance at 595 nm. The obtained result was recalculated on the dry biomass basis. The cellular biomass was measured on a dry weight basis. Cells were precipitated on Buprog (pre-boiled) filters with a pore size of 0.24 μm, washed, dried at 80°C and weighed.

The protein concentration was determined spectrophotometrically by measuring the light absorbance at 595 nm. The obtained result was recalculated on the basis of the protein weight according to the albumin calibration table.

Specific productivity, as the value of the product increase per unit time, was determined by the formulas:

$$Q_P(t_i) = \frac{P(t_i) - P(t_0)}{t_i - t_0},\ i = 1,2,3,\ldots, \quad (1)$$

where $t_i \in (0,\infty)$, t_0 is a time at which the lag phase of the periodic cultivation process ends and exponential phase begins; it is obvious that $Q_P(0) = 0$.

The suspension of overnight broth cultures of test strains grown on a standard culture media for 24 hours at a temperature of 37 °C were used for the study. Cells from the agar surface were gathered with an inoculation loop and resuspended in NaCl solution to 0.5 units according to the McFarland standard. The test strains were grown in MRS broth for 24 hours at 37°C, then the culture fluid was centrifuged at 2000 rpm for 10 minutes and the supernatant fluid was separated. To separate cells, the supernatant fluid was filtered through Millex-GV filters. The culture fluid turbidity was adjusted to a value of 0.5 according to the McFarland standard (containing approximately

1.5×10^8 CFU/ml). Suspension optical density was adjusted spectrophotometrically: light absorbance was within the same range as 0.5 in the McFarland units (at OD 450 nm, optical density was within 0.08–0.13). Then, the obtained microbial suspension was subjected to a series of 1:10 dilutions, thus reaching a metabolite concentration from 10^8 to 10^1 CFU/ml. 180 µl of the supernatant fluid of each test strain were added to the plate, then 20 µl of test culture strains were added to each of them. The plate was incubated at 37°C for 24 hours. 200 µl of sterile MRS broth and 180 µl of pure medium with 20 µl of each pathogen solution were used as controls. Bacterial growth was monitored by measuring the optical density during the culture process.

The culture media were prepared as follows: MRS medium, g/l: Bacto-peptone – 10.0; meat extract – 10,0; yeast extract – 5,0; glucose – 20.0; tween – 1.0; ammonium citrate – 2.0; sodium acetate – 5.0; sodium hydrogenphosphate – 2.0; magnesium sulphate 7-water – 0.1; manganese sulphate 5-water – 0.05. MRSA, dense medium, g/l: bacto-peptone – 10.0; meat extract – 10,0; yeast extract – 5,0; glucose – 20.0; tween – 1.0; ammonium citrate – 2.0; sodium acetate – 5.0; sodium hydrogenphosphate – 2.0; magnesium sulphate 7-water – 0.1; manganese sulfate 5-water – 0.05; agar – 20.0.

Antimicrobial activity of strains of lactic acid bacteria was additionally determined by means of agar-diffuse discs [16]. The test strain was plated on an agarized culture medium (MRSA) in the form of lawn and the lawn was covered with paper discs impregnated with lactic acid bacteria metabolites (10 µl/disc). Disc with MRS medium was used as a control, a disc with a ciprofloxacin antibiotic (from a standard kit) was used as a reference substance. The plates were incubated at 37°C for 24 hours. The results were taken into account by the presence and size (in mm) of the transparent zone of non-growth of microorganisms around the disc.

The minimum inhibitory concentration was determined with respect to the isolated strains of bacteria by the microtitration technique. The antimicrobial activity of the bacteriocins produced was evaluated relative to the strain of *E. coli*. A suspension of the *E. coli* strain without addition of bacteriocins was used as a control.

RESULTS AND DISCUSSION

The biomass concentration of strains of lactic acid bacteria and the activity of bacteriocins produced by them were determined by culturing in a MRS culture fluid, the study was carried out for 70 hours. The biomass concentration was determined spectrophotometrically. The antimicrobial activity of bacteriocins was determined by measuring inhibition zones, the study was carried out by a disc-diffusion test. The results obtained in the study of the dependence of concentration of bacteriocins and their activity on the culturing period are presented in Fig. 1–5.

The results obtained allowed to plot a chart showing the intensity of bacteriocins production during culturing of three test strains of lactic acid bacteria, as well as to show the intensity of use of bacteriocins from the culturing period for all three strains. Results are presented in Fig. 4–5.

When analyzing the results presented in Fig. 1–5, we concluded that the period of culturing at which the maximum bacteriocin concentration is observed and the duration at which their maximum antimicrobial activity is observed are different. Thus, the maximum concentration of bacteriocins in the culturing of strain B884 was observed with a culturing duration of 54 hours, while the maximum antimicrobial activity of this strain was observed with a culturing period of 18 hours. In strain B2430, the maximum concentration of bacteriocins was found during culturing for 44 hours, and the maximum activity was observed during culturing for 20 hours. For strain B2455, these values were 57 and 54 hours, respectively. To estimate the intensity of bacteriocin production by microbial strains, the productivity by the target product was calculated, which is defined as the magnitude of the product increase per unit time. The obtained results are represented in Table 1.

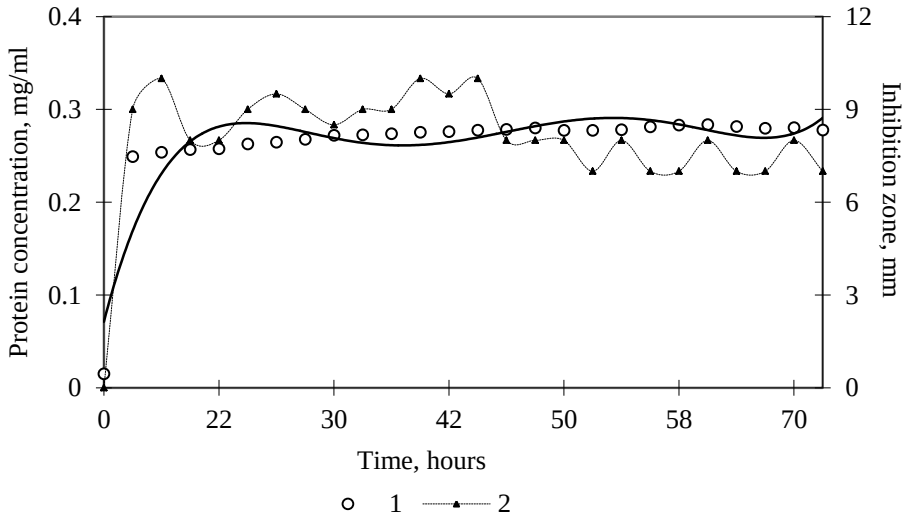


Fig. 1. Dependence of B884 bacteriocins concentration and their activity on the culturing period: (1) protein concentration, (2) activity.

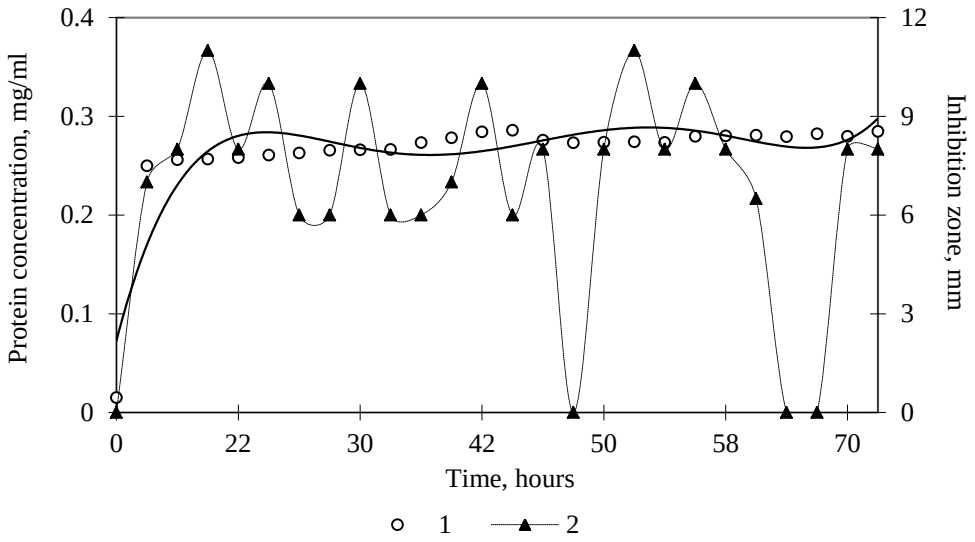


Fig. 2. Dependence of B2430 bacteriocins concentration and their activity on the culturing period: (1) protein concentration, (2) activity.

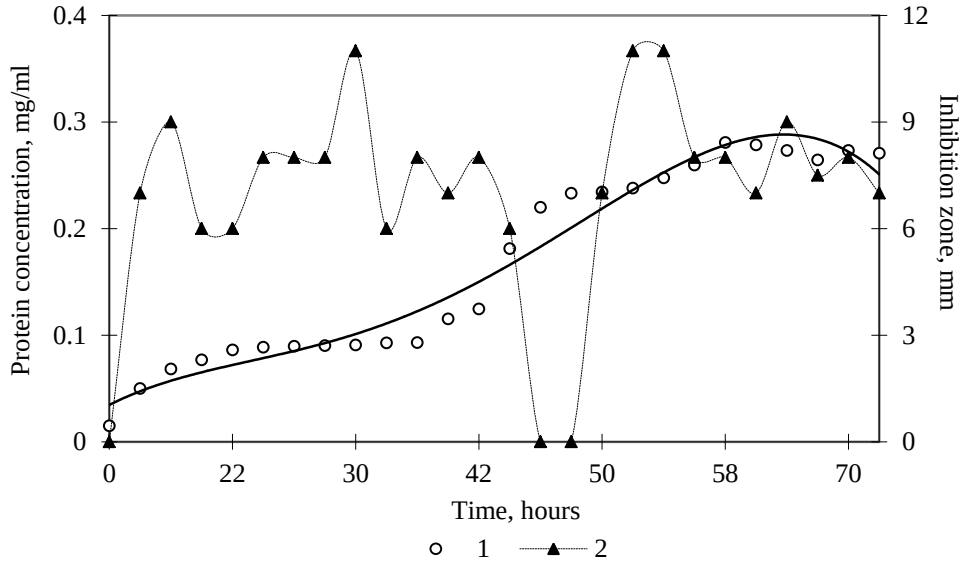


Fig. 3. Dependence of B2455 bacteriocins concentration and their activity on the culturing period: (1) protein concentration, (2) activity.

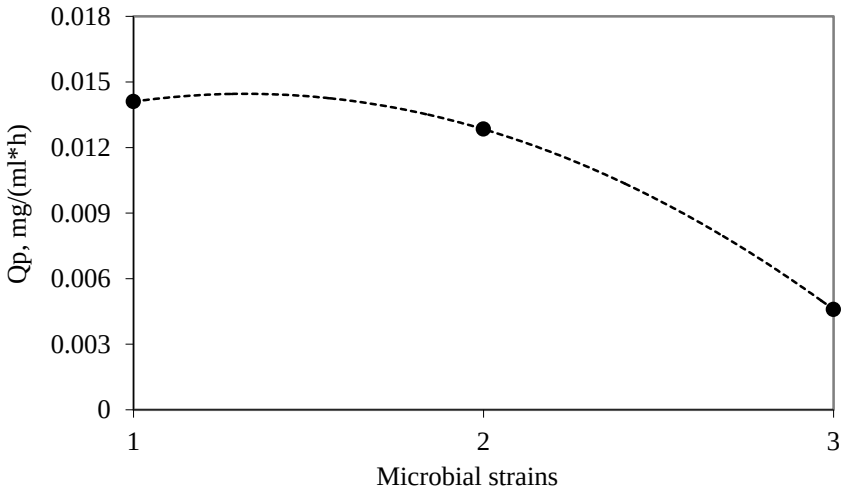


Fig. 4. Maximum intensity of bacteriocin production in the culturing of lactic acid bacteria: (1) B884, (2) B2430, (3) B2455.

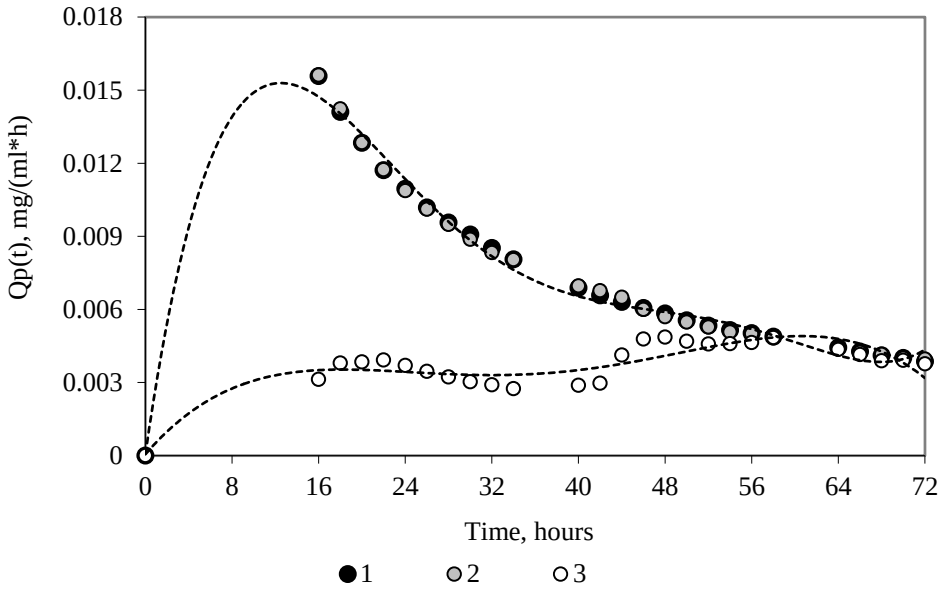


Fig. 5. Dependence of the intensity of bacteriocin production on the lactic acid bacteria culturing period: (1) B884, (2) B2430, (3) B2455.

Table 1. Intensity of bacteriocin production in the course of culturing strains

Strains	Inhibition zone, mm	Culturing period	Specific productivity
B884	10	18	0.0141
B2430	11	20	0.0128
B2455	11	54	0.0046

When analyzing the data given in Table 1, we came to the conclusion that the following productivities were observed for the strains studied: B884 – 0.0141, B2430 – 0.0128, B2455 – 0.0046. In the B884 strain, the inhibition zone of the test culture was 10 mm, in the strains B2430 and B2455 – 11 mm.

The minimal inhibitory concentration of isolated strains was determined. The study was carried out according to the microtitration technique. The antimicrobial activity of the bacteriocins produced was evaluated relative to the strain of *E. coli*. The results of the study are presented in Table 2 and in Figures 6–8.

When analyzing the results obtained in determining the minimum inhibitory concentration, the following conclusion was made. With a bacteriocin concentration of strain B884 of·10^8 CFU/ml, the growth of the *E. coli B-6954* test strain was significantly lower compared to the control. With a concentration of $1.0 \cdot 10^7$ CFU/ml, the growth of *E. coli B-6954* is lower than in the control, up to and including 4 hours of culturing. At the remaining concentrations in the control sample, better indices were observed than in the samples with lactic acid bacteria. Thus, the minimum inhibitory concentration for strain B884 was $1.0 \cdot 10^8$ CFU/ml.

With bacteriocin concentrations of strain B2430 from $1.0 \cdot 10^8$ to $1.0 \cdot 10^6$ CFU/ml, a less intensive growth of the test culture was observed than in the control. With a concentration of $1.0 \cdot 10^5$ CFU/ml, the growth of *E. coli B-6954* is lower than in the control, up to and including 4 hours of culturing. The minimum concentration of strain B2430 was $1.0 \cdot 10^6$ CFU/ml.

When determining the minimum inhibitory concentration of strain B2455, it was found that at bacteriocin concentrations of $1.0 \cdot 10^8$ and $1.0 \cdot 10^7$ CFU/ml, the growth of the *E. coli B-6954* test strain was significantly lower compared to the control. At a concentration of $1.0 \cdot 10^6$ CFU/ml, the growth of *E. coli B-6954* was lower than in the control, up to 6 hours of culturing inclusive, but with a culture time of 24 hours, the *E. coli B-6954* concentration was higher than the control. The minimum inhibitory concentration of strain B2455 with respect to *E. coli B-6954* was $1.0 \cdot 10^7$ CFU/ml.

A study was made of the antimicrobial activity of bacteriocins produced by the strains under investigation, with respect to twenty-two pathogenic strains. The study was carried out by determining the optical density in a MRS culture fluid. The control sample was the culture of a pathogenic strain without the addition of bacteriocins. Results are presented in Fig. 9–11.

Table 2. Results of determination of the minimum inhibitory concentration of strains with respect to the strain *E. coli B-6954*

Culturing period, hrs	Optical density of the mixture at different concentrations of lactic acid bacteria, CFU/ml				
	$1.0 \cdot 10^8$	$1.0 \cdot 10^7$	$1.0 \cdot 10^6$	$1.0 \cdot 10^5$	control
B884					
0	0.0651	0.0689	0.0725	0.0987	0.0719
2	0.0741	0.0934	0.1143	0.1245	0.0955
4	0.0934	0.1629	0.1789	0.1945	0.1631
6	0.1138	0.2289	0.2256	0.2344	0.2166
24	0.1215	0.2713	0.2798	0.2789	0.2517
B2430					
0	0.0354	0.0389	0.0421	0.0600	0.0657
2	0.0400	0.0546	0.0778	0.0856	0.0923
4	0.0536	0.0765	0.0995	0.1110	0.1145
6	0.0876	0.1012	0.1245	0.1600	0.1521
24	0.1090	0.1233	0.1530	0.1855	0.1740
B2455					
0	0.0556	0.0643	0.0734	0.0880	0.0875
2	0.0720	0.0851	0.0965	0.1111	0.1098
4	0.0954	0.1011	0.1142	0.1344	0.1263
6	0.1160	0.1234	0.1536	0.1930	0.1752
24	0.1236	0.1355	0.1944	0.2194	0.1825

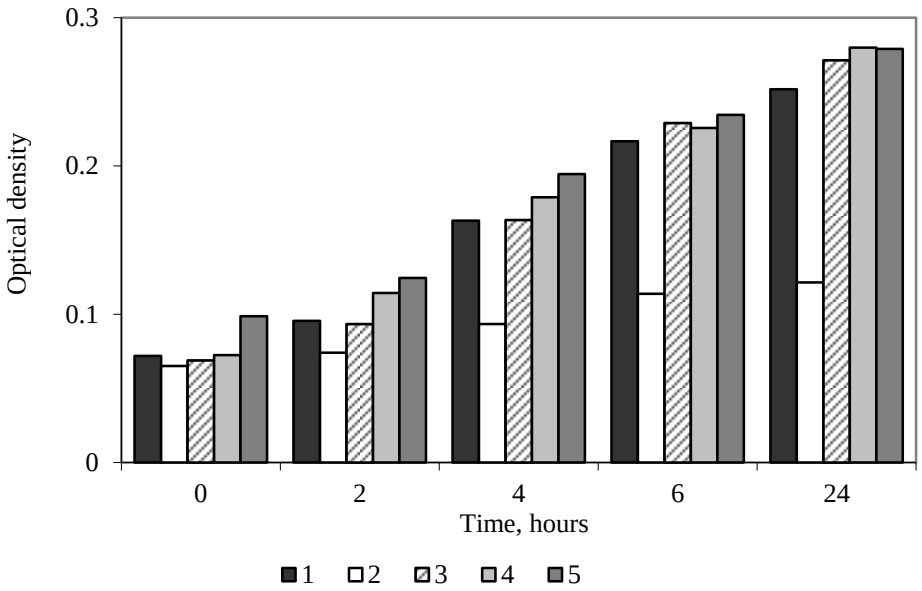


Fig. 6. Change in optical density at different concentrations of bacteriocins of the strain B884, in relation to the test culture *E. coli:* (1) control, (2) $1.0\ 10^8$, (3) $1.0\ 10^7$, (4) $1.0\ 10^6$, (5) $1.0\ 10^5$.

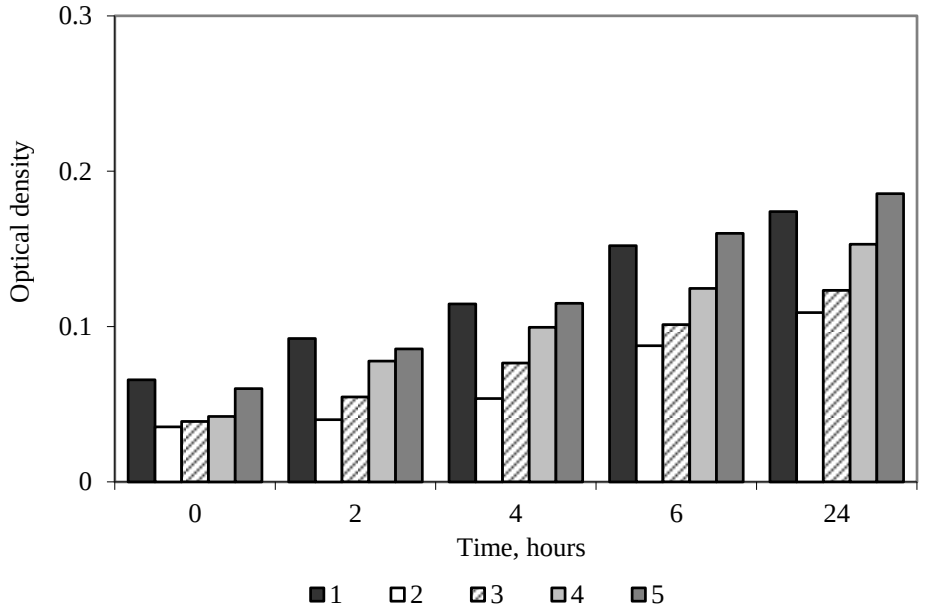


Fig. 7. Change in optical density at different concentrations of bacteriocins of the strain B2430, in relation to the test culture *E. coli:* (1) control, (2) 1.0 10^8, (3) 1.0 10^7, (4) 1.0 10^6, (5) 1.0 10^5.

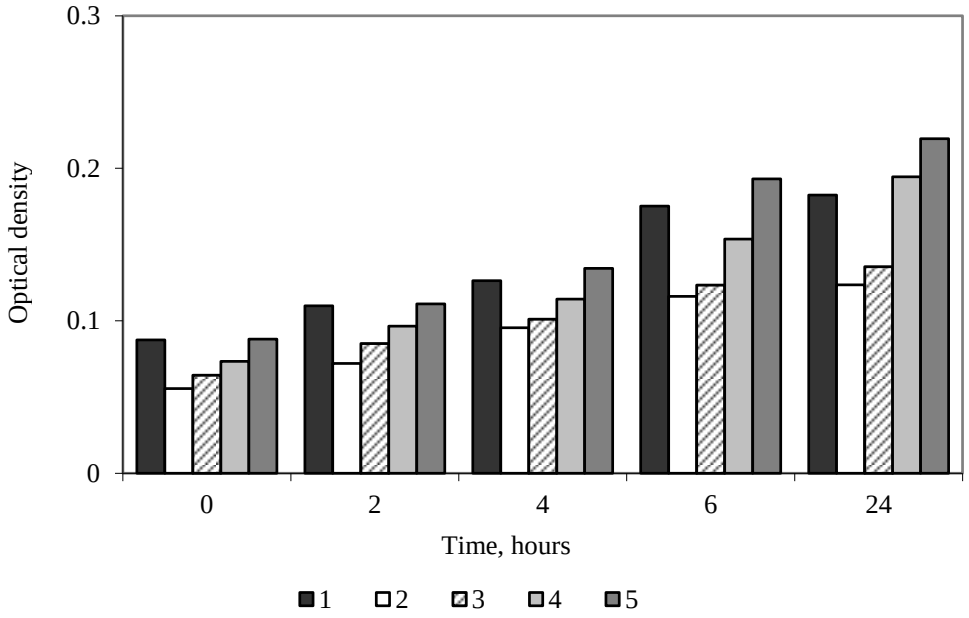


Fig. 8. Change in optical density at different concentrations of bacteriocins of the strain B2455, in relation to the test culture *E. coli*: (1) control, (2) 1.0 10^8, (3) 1.0 10^7, (4) 1.0 10^6, (5) 1.0 10^5.

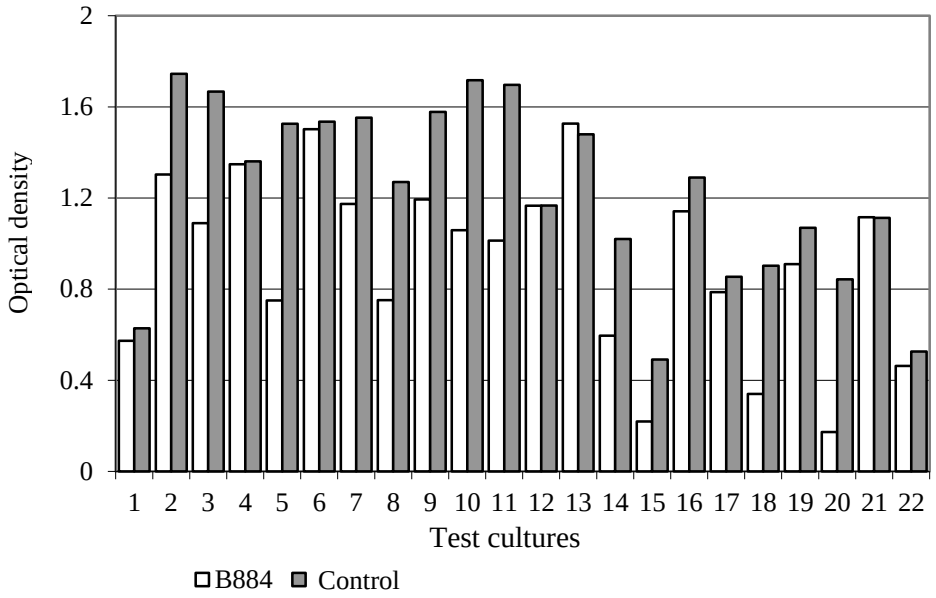


Fig. 9. Antimicrobial activity of strain B884: (1) *Bacillus mycoides*, (2) *Salmonella enterica*, (3) *Micrococcus luteus*, (4) *Escherichia coli*, (5) *Bacillus cereus*, (6) *Alcaligenes faecalis*, (7) *Proteus vulgaris*, (8) *Pseudomonas fluorescens*, (9) *Candida albicans*, (10) *Pseudomonas aeruginosa*, (11) *Staphylococcus aureus*, (12) *Pseudomonas libanensis*, (13) *Staphylococcus warneri*, (14) *Erwinia aphidicola*, (15) *Microbacterium foliorum*, (16) *Bacillus licheniformis*, (17) *Serratia plymuthica*, (18) *Rahnella aquatilis*, (19) *Erwinia aphidicola*, (20) *Bacillus endophyticus*, (21) *Leuconostoc mesenteroides*, (22) *Enterococcus casseliflavus.*

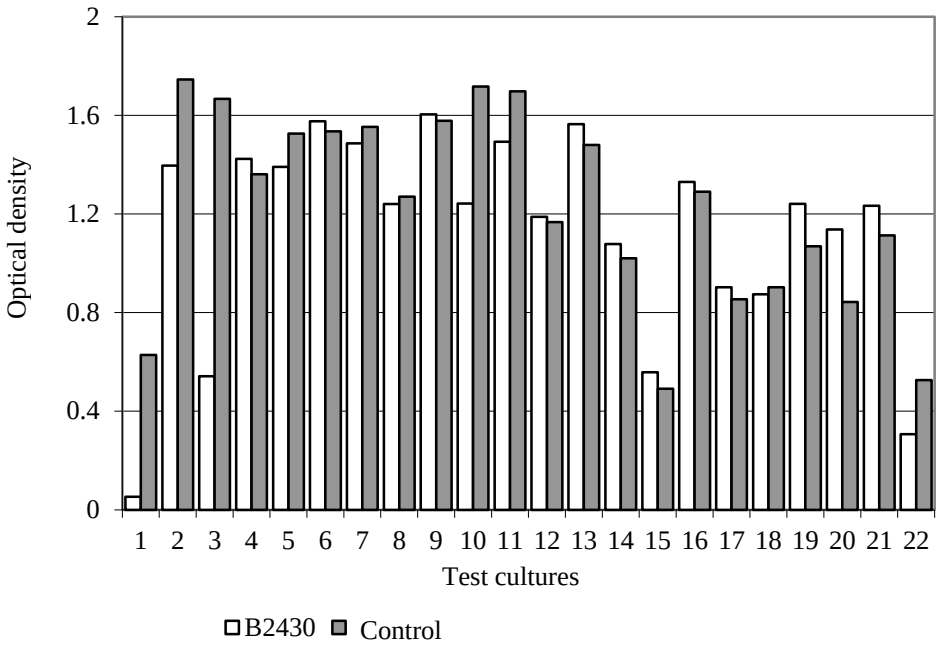


Fig. 10. Antimicrobial activity of strain B2430: (1) *Bacillus mycoides*, (2) *Salmonella enterica*, (3) *Micrococcus luteus*, (4) *Escherichia coli*, (5) *Bacillus cereus*, (6) *Alcaligenes faecalis*, (7) *Proteus vulgaris*, (8) *Pseudomonas fluorescens*, (9) *Candida albicans*, (10) *Pseudomonas aeruginosa*, (11) *Staphylococcus aureus*, (12) *Pseudomonas libanensis*, (13) *Staphylococcus warneri*, (14) *Erwinia aphidicola*, (15) *Microbacterium foliorum*, (16) *Bacillus licheniformis*, (17) *Serratia plymuthica*, (18) *Rahnella aquatilis*, (19) *Erwinia aphidicola*, (20) *Bacillus endophyticus*, (21) *Leuconostoc mesenteroides*, (22) *Enterococcus casseliflavus.*

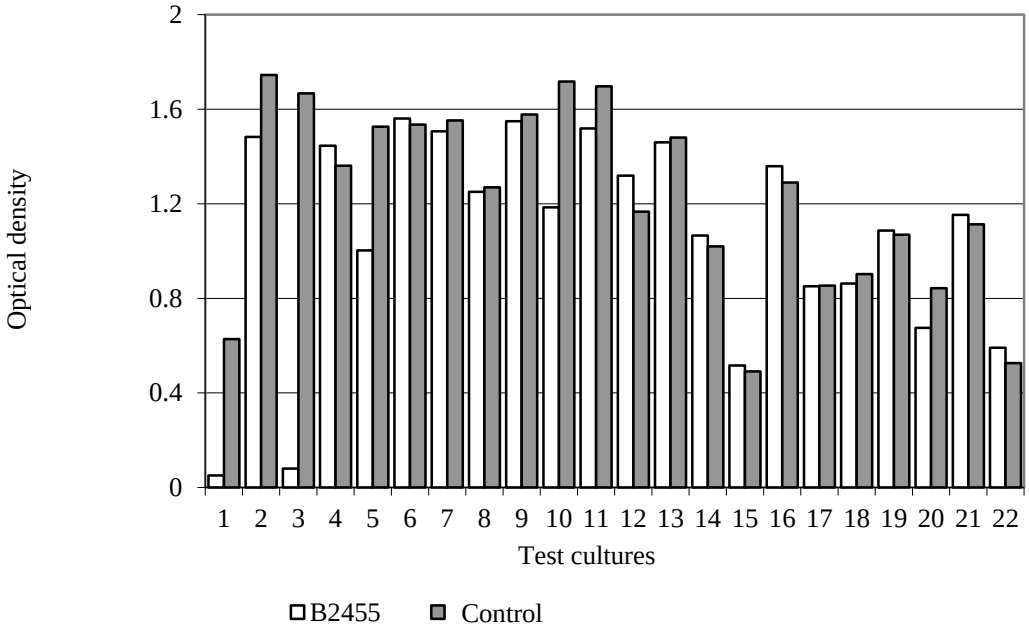


Fig. 11. Antimicrobial activity of strain B2455: (1) *Bacillus mycoides*, (2) *Salmonella enterica*, (3) *Micrococcus luteus*, (4) *Escherichia coli*, (5) *Bacillus cereus*, (6) *Alcaligenes faecalis*, (7) *Proteus vulgaris*, (8) *Pseudomonas fluorescens*, (9) *Candida albicans*, (10) *Pseudomonas aeruginosa*, (11) *Staphylococcus aureus*, (12) *Pseudomonas libanensis*, (13) *Staphylococcus warneri*, (14) *Erwinia aphidicola*, (15) *Microbacterium foliorum*, (16) *Bacillus licheniformis*, (17) *Serratia plymuthica*, (18) *Rahnella aquatilis*, (19) *Erwinia aphidicola*, (20) *Bacillus endophyticus*, (21) *Leuconostoc mesenteroides*, (22) *Enterococcus casseliflavus.*

When estimating the antimicrobial activity of the strains studied, the following conclusion was reached: Bacteriocins of strain B884 exerted an inhibitory effect on two test cultures: *Staphylococcus warneri*, *Leuconostoc mesenteroide*; bacteriocins of strain B2430 – on 12 test cultures: *Escherichia coli*, *Alcaligenes faecalis*, *Candida albicans*, *Pseudomonas libanensis*, *Staphylococcus warneri*, *Erwinia aphidicola*, *Microbacterium foliorum*, *Bacillus licheniformis*, *Serratia plymuthica*, *Erwinia aphidicola*, *Bacillus endophyticus*, *Leuconostoc mesenteroides*; bacteriocins of strain B2455 – on 9 test cultures: *Escherichia coli* , *Alcaligenes faecalis*, *Pseudomonas libanensis*, *Erwinia aphidicola*, *Microbacterium foliorum*, *Bacillus licheniformis*, *Erwinia aphidicola*, *Leuconostoc mesenteroides*, *Enterococcus casseliflavus*.

DISCUSSION

Analysis of the results obtained in determining the intensity of bacteriocin production allowed to distinguish two strains: *Lactobacillus plantarum* B884 and *Lactobacillus paracasei* B2430, showed approximately the same results, but the quality of bacteriocin (antimicrobial activity relative to the strain *E. coli*) for strain *Lactobacillus paracasei* B2430 was higher.

For a more complete determination of the antimicrobial potential of bacteriocins synthesized by strains of lactic acid bacteria and selection of the most effective strain, a minimum inhibitory concentration of strains with respect to the strain *E.coli*. The following results were obtained: the minimum inhibitory concentration for the strain *Lactobacillus plantarum* B884 was $1.0 \cdot 10^8$ CFU/ml, for strain *Lactobacillus paracasei* B2430 – $1.0\ 10^6$ CFU/ml, for strain *Lactobacillus delbrueckii* B2455 – $1.0 \cdot 10^7$ CFU/ml. Thus, the lowest inhibitory concentration was observed for the strain *Lactobacillus paracasei* B2430.

When analysing the antagonistic activity of the bacteriocins of the studied cultures with respect to the 22 cultures of pathogenic strains, it was concluded that bacteriocins of the strain *Lactobacillus paracasei* B2430 possessed the greatest spectrum of antimicrobial activity, as they inhibited the development of most test cultures, compared with the remaining strains and, in addition, this strain demonstrated the best properties and the degree of inhibition of the growth of pathogenic strains.

Based on the results obtained in the study of the intensity of bacteriocin synthesis and their effectiveness, they concluded that bacteriocins of the strain *Lactobacillus paracasei* B2430 have the greatest antimicrobial activity as compared with other strains of lactic acid bacteria, which implies that this strain is promising for further study.

REFERENCES

1. Zimina, M.I., Prosekov, A.J., Babich, O.O., Sukhih, S.A. Identification and studying of the biochemical properties of lactobacillus strains. *Life Science Journal*, 2014, vol. 11, iss. 11, pp. 338–341.
2. Astakhova L., Babich O., Prosekov A., et al. Short chain fatty acids (SCFA) reprogram gene expression in human malignant epithelial and lymphoid cells. *PLoS ONE*, 2016, vol. 11, no. 7, e0154102. DOI: 10.1371/journal.pone.0154102.
3. Shishin M.V. and Prosekov A.Yu. Investigation of morphological and antimicrobial properties of intestinal tract microorganisms. *Food Processing: Techniques and Technology*, 2015, vol. 39, no. 4, pp. 131–137. (In Russian).
4. Walker E.S. Genetic trends in a population evolving antibiotic resistance. *Evolution*, 2001, vol.55, pp. 1–20.
5. Dyshlyuk L., Babich O., Belova D., and Prosekov A. Comparative analysis of physical and chemical properties of biodegradable edible films of various compositions. *Journal of food process engineering*, 2017, vol. 40, n/a, e12331. DOI: 10.1111/jfpe.12331.
6. Zimina M.I., Sukhih S.A., Babich O.O., Noskova S.Yu., Abrashina A.A., and Prosekov A.Yu. Investigating antibiotic activity of the genus Bacillus strains and properties of their bacteriocins in order to develop next-generation pharmaceuticals. *Foods and Raw Materials*, 2016, vol. 4, no.2, pp. 95–100. DOI: 10.21179/2308-4057-2016-2-92-100.
7. Piskaeva A.I., Sidorin Yu.Yu., and Prosekov A.Yu. Comparative Analysis of the Activity of Silver Nanoparticles against Native Microflora from Poultry Processing Plants Wastes. *Nano Hybrids and Composites*, 2017, vol. 13, pp. 176–183. DOI: 10.4028/www.scientific.net/NHC.13.176.
8. Bali V., Panesar P.S., Bera M.B., and Kennedy J.F. Bacteriocins: Recent Trends and Potential Applications. *Critical Reviews in Food Science and Nutrition*, 2016, vol. 56, no. 5, pp. 34–817. DOI: 10.1080/10408398.2012.729231.
9. Cleveland J., Montville T.J., Nes I.F., and Chikindas M.L. Bacteriocins: safe, natural antimicrobials for food preservation. *International Journal of Food Microbiology*, 2001, vol. 71, no. 1, pp. 71–120. DOI: 10.1016/S0168-1605(01)00560-8.
10. Surendran Nair N., Amalaradjou M.A., and Venkitanarayanan K. Chapter One – Antivirulence Properties of Probiotics in Combating Microbial Pathogenesis. *Advances in Applied Microbiology*, 2017, vol. 98, pp. 1–29. DOI: 10.1016/bs.aambs.2016.12.001.
11. Lohans C.T. and Vederas J.C. Development of Class IIa Bacteriocins as Therapeutic Agents. *International Journal of Microbiology*, 2012, pp. 386–410. DOI: http://dx.doi.org/10.1155/2012/386410.
12. Perez R.H., Perez M.T.M., and Elegado F.B. Bacteriocins from lactic acid bacteria: A review of biosynthesis, mode of action, fermentative production, uses and prospects. *International Journal of Philippine Science and Technology*, 2015, vol. 8, no. 2, pp. 61–67.
13. Prosekov A.Yu. and Ivanova S.A. Providing food security in the existing tendencies of population growth and political and economic instability in the world. *Foods and Raw Materials*, 2016, vol. 4, no. 2, pp. 201–211. DOI: 10.21179/2308-4057-2016-2-201-211.
14. Gálvez A., Abriouel H., López R.L., and Omar N.B. Bacteriocin based strategies for food bio-preservation. *International Journal of Food Microbiology*. 2007, vol. 120, no. 1–2, pp. 51–70. DOI: 10.1016/j.ijfoodmicro.2007.06.001.
15. Cotter P.D., Hill C., and Ross R.P. Bacteriocins: developing innate immunity for food. *Nature reviews. Microbiology*, 2005, vol. 3, pp. 777–788. DOI: 10.1038/nrmicro1273.
16. Pilasombut K., Rumjuankiat K., Ngamyeesoon N., and Duy le N.D. In vitro Characterization of Bacteriocin Produced by Lactic Acid Bacteria Isolated from Nem Chua, a Traditional Vietnamese Fermented Pork. *Korean Journal for Food Science of Animal Resources*, 2015, vol. 35, no. 4, pp. 8–473. DOI: 10.5851/kosfa.2015.35.4.473.

Please cite this article in press as: Zimina M.I., Gazieva A.F., Pozo-Dengra J., Noskova S.Yu., and Prosekov A.Yu. Determination of the intensity of bacteriocin production by strains of lactic acid bacteria and their effectiveness. *Foods and Raw Materials*, 2017, vol. 5, no. 1, pp. 108–117. DOI: 10.21179/2308-4057-2017-1-108-117.

PROCESSES, EQUIPMENT, AND APPARATUS FOR FOOD PRODUCTION

THE INFLUENCE OF STRUCTURAL AND KINEMATIC PARAMETERS OF WORKING BODIES OF THE MEAT GRINDERS ON ITS PRODUCTIVITY

A. V. Batrachenko* and N. V. Filimonova

Cherkasy State Technological University,
Shevchenko blvd. 460, Cherkasy, 18006, Ukraine

* e-mail: batrachenko@rambler.ru

Received March 14, 2017; Accepted in revised form April 24, 2017; Published June 29, 2017

Abstract: Meat grinding tops are used in technological lines of production of sausages, canned meat and stuffed semi-finished products. An increase in the specific productivity of tops is economically sound which allows the consumer to reduce significantly the capital and operational costs. It has been established by the authors that not all the area of grating is supplied at any time with meat raw materials by means of the top screw, but only a certain sector is, which significantly reduces the productivity of the top. The researches have been performed using the mathematical modeling of the process of supply of meat raw materials in the top with the subsequent check of adequacy of mathematical model by means of natural experiments under production conditions. As a result, a mathematical model of process of supply of raw materials in the top has been developed that allows to increase significantly the accuracy of determination of its productivity and also to set the most rational structural and kinematic parameters of the working bodies of the top. It has been established that most of the volume of raw materials is supplied by the screw through the grinding knot. The presence of gratings and knives in the grinding knot and their geometrical parameters provide the formation of reverse flows of raw materials through a gap between the screw and the internal surface of the working cylinder and along the screw channel of the screw. The following optimum technological parameters of the process of supply of raw materials in the top have been determined: the outer diameter of the output grating is 0.15–0.155 m; the rotation frequency of the screw is 4.5–5.2 sec^{-1}; the angle of lead of rounds of the screw is 4.8–5.5 degrees; the area of frontal projection of a knife blade is 0.001–0.0011 m^2; the thickness of the output grating is 0.0075–0.0082 m.

Keywords: Meat grinder, productivity, mathematical model, screw, grinding set

DOI 10.21179/2308-4057-2017-1-118-130 *Foods and Raw Materials*, 2017, vol. 5, no. 1, pp. 118–130.

INTRODUCTION

Meat grinding tops are used in technological lines of production of sausages, canned meat and stuffed semi-finished products. They are characterized by quite a simple design, safety in operation and low energy consumption. The most important technical indicator of tops is their productivity which defines a possibility of use of the machine as part of the designed processing line. The increase in productivity in practice is reached, most often, by an increase in the geometry of working bodies - gratings, knives and the screw. However, an increase in the specific productivity of tops is economically sound which allows the consumer to reduce significantly the capital and operational costs. Today the customary ways of increase in specific productivity (an increase in the rotation frequency of the screw, the application of gratings with larger holes, the use of trimmers) mostly exhausted their potential and do not allow to improve significantly the technical and economic indices of the machine.

An approach applied by most of researchers [1] when determining the productivity of the top is of interest in the context of this problem. According to it, the productivity of the top is determined by the formula $G = f\ S_E$ where S_E is screw efficiency (S_E = 0.25–0.35). Such a low value of coefficient is explained [1] by the loss of raw materials through the gaps between the screw and a wall of the working cylinder, by slipping of raw materials during the rotation of the screw and so forth. However, in our opinion, the loss of about 70% of the greatest possible theoretical productivity is an excessively great value for the factors specified by the researchers.

The results of the authors' researches [2] demonstrate the existence of the following features when supplying meat raw materials by means of the top of the screw - not all the area of grating is supplied at any time with meat raw materials by means of the top screw, but only a certain sector is which is

measured from the end of a round of the screw. It makes the productivity of the top twice as low [3]. In our opinion, this effect is the one that causes such a low value of screw efficiency S_E = 0.2–0.35 during the operation of the screw. The development of theoretical provisions and mathematical apparatus technique which would allow to determine the productivity of the top more precisely is urgent, considering all the necessary structural and kinematic parameters of the machine, and also the rheological parameters of raw materials.

Some approaches to the determination of productivity of the top are known. A number of researchers [1] suggest to determine the productivity of the top using the supplying ability of the screw or the grinding ability of the grinding knot. However these approaches cause considerable errors when making a calculation. The approach given in the works [4, 5] allows for more exact results. However it does not allow to display the above stated heterogeneity of supplying the work surface of gratings with raw materials. The approach offered by V. N. Potokin and N. A. Vishelevskiy offers to determine the productivity of the top when counting the pressure of supply of raw materials in the grinding knot of the top. The rheological properties of meat raw materials are described by V. V. Goryachev in the approach based on the provisions of the investigative theory of viscoelasticity. However such a technique of determination of productivity of the top does not allow to display the structural and kinematic parameters of the screw which essentially prevents it from being used in practice.

The purpose of the study is the development of a mathematical model of the process of supply of raw materials in the top which would allow to increase significantly the accuracy of determination of its productivity and also to set the most rational structural and kinematic parameters of the working bodies of the top.

OBJECTS AND METHODS OF STUDY

The researches were conducted using the mathematical modeling of the process of supply of meat raw materials in the top with the subsequent check of adequacy of mathematical model by means of natural experiments under production conditions.

The movement of raw materials in the working cylinder can be described by means of provisions of mechanics of continuous medium. At the same time the specific effect which consists in forcing raw materials only in a certain sector of cross section of the screw is expedient to be considered by means of the productivity coefficient K_Q (the physical sense of productivity coefficient K_Q is revealed in more detail in [6]). Then the productivity of the top is defined by the statement:

$$G = K_Q(Q_{main} - Q_{i.g.} - Q_{s.c.})\rho, \qquad (1)$$

where Q_{main} is the main flow of raw materials through the grinding knot, m^3/s; $Q_{i.g.}$ is a reverse flow of raw materials through the gap between the external surface of rounds of the screw and the internal surface of the working cylinder, m^3/s; $Q_{s.c.}$ is a reverse flow of raw materials along the screw channel of the screw, m^3/s; ρ is the density of raw materials, kg/m^3.

Fig. 1 provides the design scheme of the top. It consists of the working cylinder 1 in which the screw 2 is set. Raw materials are supplied to the working cylinder from the bunker 3, and go out of the working cylinder through the grinding knot 4 in which they are ground.

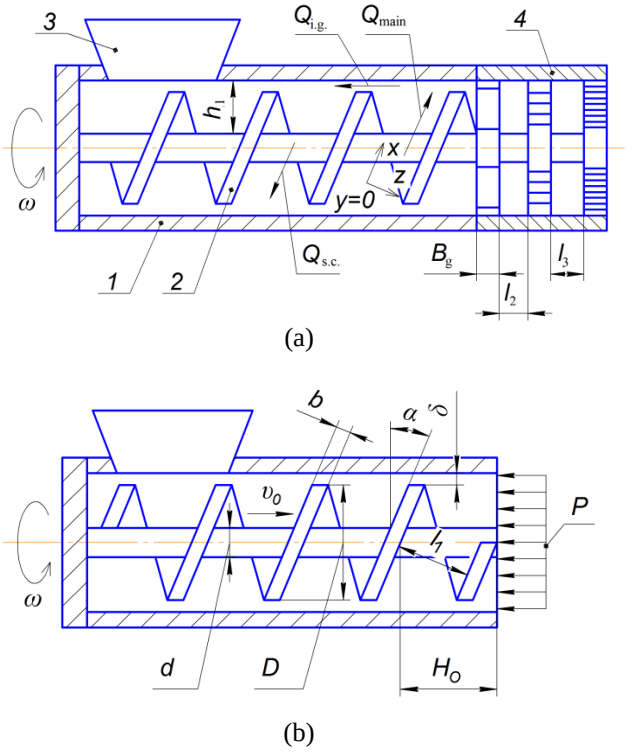


Fig. 1. Design scheme of the mathematical model of the process of supply of raw materials in the top: (a) the structure of the top; (b) the model of the working area.

The productivity of the top is defined, first of all, by the supplying ability of the screw which forms the main flow of raw materials Q_{main} through the grinding knot. In the absence of the grinding knot the value of productivity of the top would be maximum at the output of the working cylinder (we consider that the working screw of the top is supplied with raw materials from the bunker constantly, the holes of gratings of the grinding set are not clogged with particles of raw materials, the gratings and knives are pointed properly, etc.). However the following major factors provide the reduction of productivity.

The presence of gratings and knives in the grinding knot and their corresponding geometrical parameters provide the formation of hydraulic resistance of the grinding knot P, which prevents from the free effluence of raw materials from the working cylinder under the influence of the pressure produced by the screw. Thereof the reverse flows which characterize losses of productivity are formed: through the gap between the external surface of rounds of the screw and the internal surface of the working cylinder $Q_{i.g.}$; along the screw channel of the screw between its rounds $Q_{s.c.}$.

The mathematical description of movement of continuous medium (in this case – meat), can be obtained by the solution of system of the equations which consist of a continuity equation, a motion equation, an energy equation and equations of rheological condition of raw materials. At the same time, to obtain a rigorous solution of such a system of equations in case of supplying the curvilinear channel of the screw with real (with a rather complex set of properties) raw materials is a rather difficult task. However it can be simplified by adding certain assumptions and restrictions.

The rotating screw and the stationary working cylinder are replaced with a fixed screw and a rotating working cylinder. The screw channel which is formed by the space between screw rounds is straightened. That is instead of the rectangular-sectioned screw channel a straightened pipe the length of which is equal to the length of the screw channel is put, and which has a movable (according to the preliminary assumption) upper surface. The system of rectangular coordinates is chosen according to Fig. 1: The *x*-axis is along the channel, the axis *y*-axis is for the height, the z-axis is for the width of the channel.

Further the layer of raw materials which is limited within the enclosed volume to the sizes l_1, h_1, and L is considered. The density of raw materials ρ, the speed of its motion along the axis of the channel υ_0, the tensions p_{ij} which arise in raw materials (which are the result of acts of viscous forces), the pressure P and the temperature T are considered as functions of the time t and the spatial coordinates x, y and z.

When solving problems of mechanics of continuous medium the following are unknown:

- Material density $\rho=\rho$ t, x, y, z ;
- three components of velocity vectors along the axes of the chosen coordinate system:

$$\upsilon_x=\upsilon_x \text{ t, x, y, z} \ , \quad \upsilon_y=\upsilon_y \text{ t, x, y, z} \ ,$$
$$\upsilon_z=\upsilon_z \text{ t, x, y, z} \ ; \qquad (2)$$

- six components of strain tensor (of ten components only six are independent owing to the symmetry of the tensor $p_{ij} = p_{ji}$):

$$\sigma_{xx} = \sigma_{xx} \text{ t, x, y, z} \ , \quad \sigma_{yy} = \sigma_{yy} \text{ t, x, y, z} \ ,$$
$$\sigma_{zz} = \sigma_{zz} \text{ t, x, y, z} \ , \quad \tau_{xy} = \tau_{xy} \text{ t, x, y, z} \ ,$$
$$\tau_{yz} = \tau_{yz} \text{ t, x, y, z} \ , \quad \tau_{zx} = \tau_{zx} \text{ t, x, y, z} \ . \qquad (3)$$

In the equations (3) the first index specifies a normal line to the platform in which this tension takes place, and the second specifies parallel to what axis this tension takes place. Thus, the normal tensions are designated as σ, and tangents as τ;

- the temperature of the supplied raw materials – $T = T$ t, x, y, z .

To define these eleven unknown values it is necessary to make and solve the system consisting of the same quantity of equations:

- the continuity equation (the mathematical expression of law of perdurability of matter according to which the weight remains constant in the closed system):

$$\frac{\partial \rho}{\partial t}+\frac{\partial}{\partial x}(\rho\cdot\upsilon_x)+\frac{\partial}{\partial y}(\rho\cdot\upsilon_y)+\frac{\partial}{\partial z}(\rho\cdot\upsilon_z)=0 \quad , (4)$$

- three motion equations in the chosen coordinate system (which are the mathematical formulation of Newton's second law):

$$\rho\left(\frac{\partial \upsilon_x}{\partial t}+\upsilon_x\frac{\partial \upsilon_x}{\partial x}+\upsilon_y\frac{\partial \upsilon_y}{\partial y}+\upsilon_z\frac{\partial \upsilon_z}{\partial z}\right)=\rho\cdot F_x+\frac{\partial \sigma_{xx}}{\partial x}+\frac{\partial \tau_{yx}}{\partial y}+\frac{\partial \tau_{zx}}{\partial z} \ ,$$
$$\rho\left(\frac{\partial \upsilon_y}{\partial t}+\upsilon_y\frac{\partial \upsilon_y}{\partial x}+\upsilon_y\frac{\partial \upsilon_y}{\partial y}+\upsilon_z\frac{\partial \upsilon_y}{\partial z}\right)=\rho\cdot F_y+\frac{\partial \sigma_{yy}}{\partial y}+\frac{\partial \tau_{xy}}{\partial x}+\frac{\partial \tau_{zy}}{\partial z} \ , (5)$$
$$\rho\left(\frac{\partial \upsilon_z}{\partial t}+\upsilon_x\frac{\partial \upsilon_z}{\partial x}+\upsilon_y\frac{\partial \upsilon_z}{\partial y}+\upsilon_z\frac{\partial \upsilon_y}{\partial z}\right)=\rho\cdot F_z+\frac{\partial \sigma_{zz}}{\partial z}+\frac{\partial \tau_{xz}}{\partial x}+\frac{\partial \tau_{yz}}{\partial y},$$

where F_x, F_y, F_z are the projections of mass forces on to the axes of coordinates;

- six rheological equations connecting the components of tension tensor with the components of tensor of speeds of deformation of raw materials. This connection defines the rheological properties of raw materials;
- the energy equation.

To simplify the calculation when solving the system of equations the following admissible simplifications have been introduced. It is considered that an isothermal task should be considered which would provide an opportunity to do without the energy equation. The raw materials which do not compress, that is $\rho=const$, should be considered. This simplification changes the type of continuity equation - if $\rho=const$, then in that case $\frac{\partial \mathrm{p}}{\partial \mathrm{x}}=0$, then it follows from the continuity equation that:

$$\rho\left(\frac{\partial \upsilon_x}{\partial x}+\frac{\partial \upsilon_y}{\partial y}+\frac{\partial \upsilon_z}{\partial z}\right)=0 \quad , \qquad (6)$$

and as $\rho\neq 0$, the continuity equation takes the following form:

$$\frac{\partial \upsilon_x}{\partial x}+\frac{\partial \upsilon_y}{\partial y}+\frac{\partial \upsilon_z}{\partial z}=0 \quad , \qquad (7)$$

Analyzing the process of supply of raw materials in the top and the known rheological models of food media, we accept that the meat raw materials supplied by the top screw to its grinding knot is a viscoelastic medium the model of which consists of consistently connected bodies of Calvin and Maxwell. In that case the rheological properties of lumpy meat raw materials, according to [7], are displayed by means of the coefficient of viscoelastic properties:

$$\psi = \frac{E_\mu \cdot E_S \left(1 - e^{-\frac{t_1}{t_2}}\right)}{E_S \left(1 - e^{-\frac{t_1}{t_2}}\right) + t_1 \cdot \eta_1 + E_S \left(1 - e^{-\frac{t_1}{t_2}}\right) + E_\mu}, \quad (8)$$

where E_μ is the module of instant deformation of the body, Pa; E_S is the module of equilibrium elasticity and after-effect, Pa; t_1 is the period of relaxation of tensions, sec; t_2 is an after-effect period, sec; η_1 is viscosity, Pa · sec.

Then six rheological equations take the following form:

$$\begin{aligned} \sigma_{xx} &= -p + 2\psi \cdot \frac{\partial \upsilon_x}{\partial x}; & \tau_{xy} &= \tau_{yx} = \psi \left(\frac{\partial \upsilon_x}{\partial y} + \frac{\partial \upsilon_y}{\partial x} \right); \\ \sigma_{yy} &= -p + 2\psi \cdot \frac{\partial \upsilon_y}{\partial y}; & \tau_{yz} &= \tau_{zy} = \psi \left(\frac{\partial \upsilon_y}{\partial z} + \frac{\partial \upsilon_z}{\partial y} \right); \\ \sigma_{zz} &= -p + 2\psi \cdot \frac{\partial \upsilon_z}{\partial z}; & \tau_{zx} &= \tau_{xz} = \psi \left(\frac{\partial \upsilon_z}{\partial x} + \frac{\partial \upsilon_x}{\partial z} \right). \end{aligned} \quad (9)$$

where p is hydrostatic pressure:

$$p = -\frac{1}{3} \left(p_{11} + p_{22} + p_{33} \right), \quad (10)$$

here p_{11}, p_{22} and p_{33} are the main normal tensions.

After the substitution of the corresponding expressions in the equation (5) for the components of tension tensor from the equations (8) and the division of all of them by ρ, three equations of movement of viscous medium written down in the form of Navier-Stokes equation have been obtained:

$$\begin{aligned} &\frac{\partial \upsilon_x}{\partial t} + \upsilon_x \cdot \frac{\partial \upsilon_x}{\partial x} + \upsilon_y \cdot \frac{\partial \upsilon_x}{\partial y} + \upsilon_z \cdot \frac{\partial \upsilon_x}{\partial z} = F_x - \frac{1}{\rho} \cdot \frac{\partial p}{\partial x} + \psi \cdot \left(\frac{\partial^2 \upsilon_x}{\partial x^2} + \frac{\partial^2 \upsilon_x}{\partial y^2} + \frac{\partial^2 \upsilon_x}{\partial z^2} \right); \\ &\frac{\partial \upsilon_y}{\partial t} + \upsilon_x \cdot \frac{\partial \upsilon_y}{\partial x} + \upsilon_y \cdot \frac{\partial \upsilon_y}{\partial y} + \upsilon_z \cdot \frac{\partial \upsilon_y}{\partial z} = F_y - \frac{1}{\rho} \cdot \frac{\partial p}{\partial y} + \psi \cdot \left(\frac{\partial^2 \upsilon_y}{\partial x^2} + \frac{\partial^2 \upsilon_y}{\partial y^2} + \frac{\partial^2 \upsilon_y}{\partial z^2} \right); \\ &\frac{\partial \upsilon_z}{\partial t} + \upsilon_x \cdot \frac{\partial \upsilon_z}{\partial x} + \upsilon_y \cdot \frac{\partial \upsilon_z}{\partial y} + \upsilon_z \cdot \frac{\partial \upsilon_z}{\partial z} = F_z - \frac{1}{\rho} \cdot \frac{\partial p}{\partial z} + \psi \cdot \left(\frac{\partial^2 \upsilon_z}{\partial x^2} + \frac{\partial^2 \upsilon_z}{\partial y^2} + \frac{\partial^2 \upsilon_z}{\partial z^2} \right). \end{aligned} \quad (11)$$

The steady motion of material (the stationary mode) exclusively of the start-up mode and the stop of the screw are being considered. This simplification results in the equality of derivatives of time to zero. For example, $\frac{\partial \upsilon_x}{\partial t} = 0$ etc. The mass forces are neglected, that is it is considered that F_x, F_y and F_z are equal to zero in the equations (10). Gravity is not considered, meaning that the movement of raw materials occurs generally by means of other sources, for example, pressure difference. The speeds of movement of raw materials in the channels are rather small which allows to neglect the inertial loadings arising in motion, as well. The laminar flow which almost always takes place when supplying with high-viscosity media is being considered. In that case, in the absence of turbulence, of three components of speed of raw materials its component on the x-axis of the channel is the only that differs from zero – υ_x, υ_y and υ_z are considered equal to zero.

Thus, for the isothermal movement of medium in case of the steady mode, the possibility to neglect mass forces and lack of turbulence Navier-Stokes equation takes the following form:

$$\begin{aligned} &0 = -\frac{1}{\rho} \cdot \frac{\partial p}{\partial z}; \quad 0 = -\frac{1}{\rho} \cdot \frac{\partial p}{\partial y}; \\ &0 = -\frac{1}{\rho} \cdot \frac{\partial p}{\partial x} + \frac{\psi}{\rho} \cdot \left(\frac{\partial^2 \upsilon_x}{\partial z^2} + \frac{\partial^2 \upsilon_x}{\partial y^2} \right). \end{aligned} \quad (12)$$

The analysis of equations (11) shows that the pressure p is constant throughout the section (it does not change on the y- and z-axes) and depends only on x and changes from section to section with changes of x. In that case the partial derivative $\partial p / \partial x$ is replaced with a full derivative dp / dx in the further calculations. At the same time, assuming that $\upsilon_x = \upsilon_y = 0$, $\partial \upsilon_z / \partial z = 0$ has been obtained from the continuity equation (4). Therefore, unlike the pressure p the speed component υ_z does not change from section to section, and there is only the function x, y, i.e. it changes only throughout the section. Finally:

$$\upsilon_z = \upsilon_z(x, y); \quad \upsilon_z \neq \upsilon_z(z); \quad p = p(z); \quad p \neq p(x, y). \quad (13)$$

The last of the equations (11) can be written down as:

$$\frac{\partial^2 \upsilon_x}{\partial z^2} + \frac{\partial^2 \upsilon_x}{\partial y^2} = \frac{1}{\psi} \cdot \frac{\partial p}{\partial x}. \quad (14)$$

If we consider that the change of pressure p along the length of the channel L is equal to Δp, one equation in the form of Poisson's equation can be obtained for the solution of problem of mechanics of continuous medium taking into account the made assumptions:

$$\frac{\partial^2 \upsilon_x}{\partial z^2} + \frac{\partial^2 \upsilon_x}{\partial y^2} = -\frac{\Delta p}{\psi l}. \quad (15)$$

We accept that the delivery channel of the screw is rather small. Therefore we can neglect the influence of sidewalls of rounds of the screw and consider that we deal with an infinitely narrow gap for which υ_z does not change on the x-axis, that is $\frac{\partial^2 \upsilon_z}{\partial x^2} = 0$. Then Poisson's equation will become still simpler:

$$\frac{\partial^2 \upsilon_x}{\partial y^2} = -\frac{\Delta p}{\psi l} \quad (16)$$

Using double integration on the y-axis and taking into account the boundary conditions ($\bar{\upsilon}_1 = \bar{\upsilon}_0 \neq 0$; $\bar{\upsilon}_2 = 0$), the following will be obtained:

$$\upsilon = \frac{\upsilon_0 y}{h_в} - \frac{h_в y - y^2}{2\psi} \cdot \frac{\partial p}{\partial x}.$$

On the right side of this equation the first element is the speed of direct flow of raw materials along the screw channel of the screw (with the productivity Q_{main}), and the second element is the speed which is directed in the opposite direction, i.e. the reverse flow along the screw channel (with the productivity $Q_{s.c.}$). The sum of both speeds is the speed of net flow.

It follows from the equation (16) that if we integrate the speeds according to the section of the flow, in other words throughout the height h_1 and the width l_1, then the intensity of net flow (the amount of weight which passes along the screw per unit of time) will be stated for the bilamellate model using the formula:

$$Q_{main} = \frac{\upsilon_0 l_1 h_1}{2} - \frac{l_1 h_1^3}{12\psi} \cdot \frac{\partial p}{\partial x}. \quad (17)$$

The first element in the right part of the formula (17) is the direct flow Q_{main}, and the second is the reverse flow $Q_{s.c.}$. At the same time it should be noted that the influence of braking action of sidewalls of the pitch between the rounds of the screw on the flow is not taken into consideration.

Let us apply a change for the parameters which are part of the equation (17):

$$\begin{cases} \upsilon_0 = \pi \cdot D \cdot n \cdot \cos\alpha; \\ l_1 = \pi \cdot D \cdot tg\alpha - l_1 \cdot \cos\alpha = \pi \cdot D \cdot \sin\alpha - l_1 \cdot \cos\alpha; \\ dz = dl \cdot \sin\alpha; \end{cases} \quad (18)$$

where α is the angle of lead of rounds of the screw.

Then the statement (17) of definition of intensity of net flow (without losses through the gap $Q_{i.g.}$) will be written as:

$$Q_{main} = \frac{\pi \cdot D \cdot n \cdot \cos\alpha \cdot \pi \cdot D \cdot \sin\alpha - l_1 \cdot \cos\alpha \cdot h_1}{2} - \frac{\sin\alpha \cdot \pi \cdot D \cdot \sin\alpha - l_1 \cdot \cos\alpha \cdot h_1^3}{12\psi} \cdot \frac{\partial p}{\partial l} \quad (19)$$

Thus, the reverse flow is proportional to the hollow width, and also to the third degree of depth of round and is inversely proportional to the length of rectangular channel between the rounds.

We will obtain the statement of definition of intensity of flow of losses $Q_{i.g.}$through the gap between the screw and the working cylinder. This flow is considered as the one that passes through a rectangular slot with the sides $\pi \cdot D/\cos\alpha$, δ and $b \cdot \cos\alpha$. This flow follows the equation (15) with the corresponding boundary conditions. At the same time it is necessary to take into account that the reverse flow $Q_{i.g.}$in the gap is caused by a considerably greater pressure difference than the reverse flow $Q_{s.c.}$ which is there in the screw channel. The values of pressure differences are related as the length of a pitch of the screw around to the thickness of a round.

Taking this into account:

$$\frac{\pi \cdot D}{\cos\alpha} b \cdot \cos\alpha = \frac{\pi \cdot D}{l_1 \cdot \cos^2\alpha}. \quad (20)$$

Then we will obtain the statement similar to the statement of definition of reverse flow through the screw channel $Q_{s.c.}$. The following replacements are only needed:

$$\begin{cases} \pi \cdot D \cdot \sin\alpha \to \frac{\pi \cdot D}{\cos\alpha}; \\ h_1 \to \delta; \\ \frac{dl}{\sin\alpha} \to b \cdot \cos\alpha; \\ \frac{dp}{dl} \to \pi \cdot D \cdot \sin\alpha \cdot \cos\alpha \cdot \frac{dp}{dl}. \end{cases} \quad (21)$$

It thus appears that we have the following:

$$Q_{s.c.} = \frac{\pi^2 \cdot D^2 \cdot \delta^2 \cdot tg\alpha}{12\psi \cdot b} \cdot \frac{\partial p}{\partial l}. \quad (22)$$

For the purpose of practical application it is expedient to change a little the equations (19, 22) introducing, instead of the local pressure gradient dp/dl which is accepted constant throughout the length of the way of flow of mass of raw materials, the following value:

$$\frac{dp}{dl} = \frac{p_2 - p_1}{L_{1,2}}. \quad (23)$$

where p_1 is the weight pressure in the beginning of supply section; p_2 is the weight pressure in the end of supply section; $L_{1,2}$ is the length of supply section.

Thus, the statements for the definition of separate components of net flow will take the following form:

- the direct flow along the screw type pump:

$$Q_{main} = \frac{\pi^2 \cdot D^2 \cdot n \cdot h_1 \cdot \sin\alpha \cdot \cos\alpha}{2}; \quad (24)$$

- the reverse flow along the screw channel:

$$Q_{s.c.} = \frac{\pi \cdot D \cdot h_1^3 \cdot \sin^2\alpha}{12\psi} \cdot \frac{p_2 - p_1}{L_{1,2}}; \quad (25)$$

- the reverse flow in the gap between the screw and the cylinder:

$$Q_{i.g.} = \frac{\pi^2 \cdot D^2 \cdot \delta^2}{12\psi \cdot b} \cdot tg\alpha \cdot \frac{p_2 - p_1}{L_{1,2}}. \quad (26)$$

The statement, as for the determination of coefficient of productivity of the top K_Q, has the form [6], the scheme of its definition is provided in Fig. 2:

$$K_Q = \frac{\beta_{\max}}{360} - \frac{4S_b^{act} \cdot z_b^{act}}{\varphi \cdot \pi \ \ D_g^2 - d_g^2} = 1 - \frac{4S_b^{act} \cdot z_b^{act}}{\varphi \cdot \pi \ \ D_g^2 - d_g^2} - \left(\theta_{pen} \cdot \left(\frac{1-\varphi}{\varphi}\right) + \theta_{cut} + \left(\frac{q_0}{k_l}\right) \cdot e^{\frac{4f \cdot k_l \cdot B_g}{d_0}} - \frac{q_0}{k_l}\right) \times$$
$$\times \left(\frac{\varphi \cdot k_{int} \cdot H_{o-1}}{E \cdot N_{fil.}}\right) \left(\frac{\pi \cdot n \cdot e^{a_\upsilon} \ \ D - h_1 \ \sin\alpha}{\cos\gamma_{mp}} \cdot \cos\ \alpha + \gamma_{fr}\right)^{b_\upsilon}, \quad (27)$$

where D_g is the outer diameter of the grating; d_g is the diameter of central hole of the grating; S_b^{act} is the area of the front projection of knife blade which is in the section of supply of raw materials contoured by the angle β_{max}; z_b^{act} is the quantity of knife blades which are in the section of supply of raw materials contoured by the angle β_{max}; k_{int} is the empirical coefficient of increase in the resistance of grinding knot due to an increase in the distances between separate gratings by the values of thickness of knives the couples of grinders with gratings are composed of; φ is the coefficient of utilization of working area of the initial grating; θ_{pen} is the tension of penetration of raw materials when flowing around the jumpers between the holes of the grating, Pa; θ_{cut} is the tension of cutoff of raw materials during indention into the holes of the grating, Pa; E is the modulus of elasticity of raw materials during compression, Pa; f is the coefficient of friction of raw materials on the walls of the channel; B_g is the thickness of the grating, m; d_h is the diameter of holes of the grating, m; q_0 is the residual lateral pressure, Pa; k_l is the coefficient of lateral pressure; a_υ and b_υ are the empirical coefficients of increase in the resistance of grinding knot due to an increase in the speed of supply of raw materials the value of which depends on the lengthening of the holes of the grating and the type of raw materials; γ_{fr} is the angle of friction of raw materials on the surface of the screw; h_1 is the depth of the screw channel of the screw; n_s is the rotation frequency of the screw; H_{o-1} is a pitch between the rounds of the screw, within the last round; $N_{fil.}$ is a pitch between the rounds of the screw when the coefficient of its filling with raw materials is equal to 1; α is the angle of lead of rounds of the screw.

The experimental studies of accuracy of the mathematical model were performed in the sausage shop of the meat-processing enterprise LLC Cherkasskaya prodovol'stvennaya kompaniya. The objects of researches were the tops of the models K6-FVZP-200, VVS-180, MP-160 and AL-130 with the gratings with the outer diameter of respectively 200 mm, 180 mm, 160 mm and 130 mm. Fig. 3 provides the external view of the tops during the researches performed by the authors of the work.

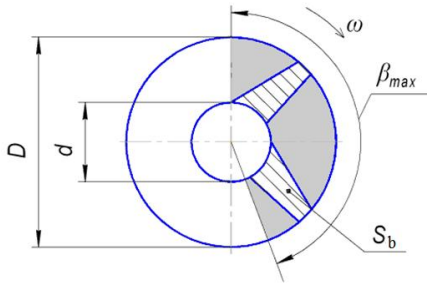


Fig. 2. Design scheme of the last round of the screw (the front view) when determining the coefficient of productivity of the top and K_Q.

RESULTS AND DISCUSSION

According to the obtained results (Fig. 4), the above stated structural and kinematic parameters essentially influence the productivity of the top.

The increase in the outer diameter of grating D_g provides an increase in productivity due to the growth of quantity of holes for passing of raw materials (Fig. 4, a). Thus, with an increase in the diameter of the grating from 130 mm to 170 mm the productivity increases by 2.3 times.

The increase in the angle of lead of rounds of the screw α from 2º to 5º provides an increase in productivity up to 2 times (Fig. 4, b). At the same time the further increase α provides the reduction of productivity of the top. It can be explained by the fact that the screw with a high value α provides the movement of a portion of raw materials to a greater axial distance per one turn (in that case the productivity of the top increases). But at the same time the percentage of force which moves the raw materials in the axial direction of the screw decreases. In the presence of hydraulic resistance from the grinding knot such reduction of force of supply provides the fact that a lower amount of raw materials is pressed through the holes of the grating, the raw materials begin to slip on the rounds of the screw, to move back along the screw

channel and through the gap between the screw and the cylinder. As a result, with low values of hydraulic resistance of the grinding knot (with the reduced values of B_p) the increase in α provides an increase in the productivity of the top (Fig. 4, c), and with the increased hydraulic resistance of the grinding knot (with the increased values of B_g) the increase in α provides a decrease in the production of the top.

For the tops which are designed for operation with the output gratings having small holes (the grinding of raw materials to the state of forcemeat) screws with α = 4–5º can be recommended, and for the tops which are designed for operation with the output gratings having large holes (the grinding of raw materials to the state of meal) screws with α = 5.5–8º can be recommended.

The influence of rotation frequency of the screw n (Fig. 4, d) is similar to the influence of the angle of lead of rounds of the screw - with an increase in frequency the productivity first increases, reaches the maximum and then decreases. The maximum values of productivity are observed at n=4–6 sec^{-1}. The further increase in n reduces productivity. It can be explained by the fact that to a higher speed of movement of raw materials through the holes of grating their higher hydraulic resistance corresponds. And it predetermines, among other things, an increase in the amount of raw materials which move between the rounds of the screw and through the gap between the screw and the cylinder backwards from the grinding knot which provides the reduction of productivity.

The increase in the thickness of the output grating B_g provides the rapid reduction of productivity (Fig. 4, e). It is explained by the growth of hydraulic resistance of holes with an increase in their length (hydraulic resistance grows under the exponential law). As a result, wuth an increase in the thickness of the output grating from 8 mm to 20 mm the productivity decreases, depending on the type of raw materials, by 4.5–6.8 times.

The dependence of productivity of the top on the area S_b of the frontal projection of blades of the knife which operates together with the output grating is inversely proportional (Fig. 4, f). In this case the reduction of productivity of the top with an increase in the total area of blades occurs due to the overlapping of a higher quantity of holes for the passing of raw materials.

(a) (b) (c) (d)

Fig. 3. Tops under study: (a) K6-FVZP-200, (b) VVS-180, (c) MP-160, (d) AL-130.

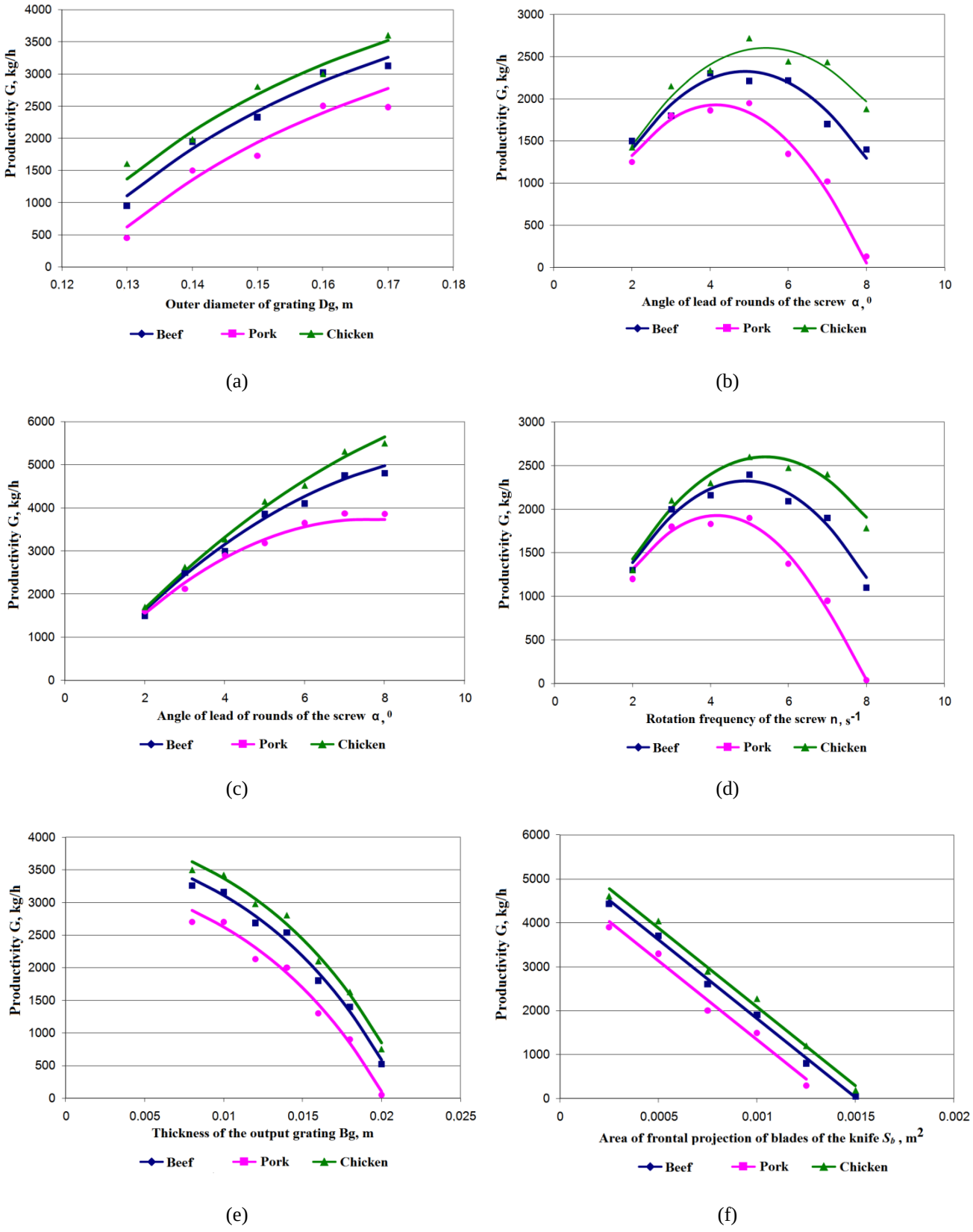


Fig. 4. Dependence of the productivity of the meat grinder on its structural and kinematic parameters: (a) the outer diameter of grating; (b) the angle of lead of rounds of the screw, B_g*=0.016 m*; (c) the angle of lead of rounds of the screw, B_g*=0.008 m*; (d) the rotation frequency of the screw; (e) the thickness of the output grating; (f) the area of frontal projection of blades of the knife.

The performed studies have confirmed the results of mathematical modeling. The curves drawn according to the mathematical model are identical to the experimental ones, the error does not exceed 11%.

The productivity G, kg/h, was determined when revealing the rational parameters of process of grinding using the parameter of optimization:

$$G = f(D_g, n, \alpha, S_b, B_g), \quad (28)$$

where D_g is the outer diameter of the output grating of the grinding knot; n is the rotation frequency of the screw; α is the angle of lead of rounds of the screw; S_b is the area of frontal projection of one knife blade; B_g is the thickness of the initial grating of the grinding knot.

Due to the significant amount of factors in this case an expediently statistical analysis has been performed to obtain functional dependence in the form of multiple regression of the second order by means of central composite rotatable design (CCRD) of multiple-factor experiment. The method of CCRD allows to obtain more precisely the mathematical description of data distribution due to an increase in the number of experiments in the central points of plan matrix and the special choice of "star value".

The analysis of statistical characteristics of the obtained data has shown that the coefficients of their asymmetry tend to zero, that is the distribution of experimental data is symmetric and is approximated according to a normal law. The choice of ranges of variation of factors of functions was made in the way that their any combination provided by the plan of experiment could be realized within these intervals and did not provide contradictions. For this purpose searching experiments have been made to determine the areas in which the necessary combinations of levels of factors would be steadily realized. All the factors that are part of a searching function are the values that have different dimensions, and the values of these factors have various orders. Therefore, to obtain a response surface of these functions an operation of coding of factors has been performed, which is the linear transformation of factorial space.

It has been planned to obtain a multiple regression equation of the 2nd order:

$$y = b_0 + \sum_{i=1}^{n} b_i x_i + \sum_{i=1}^{n} b_{ij} x_i^2 + \sum_{i=1}^{n} b_{ij} x_{ij} x_{ij}, \quad (29)$$

where y is one of high-quality functions; b_{ij} are the regression coefficients obtained using the method of the smallest squares.

For the assessment of adequacy of the obtained regression equation analytical and graphic methods of analysis have been used. The hypothesis of reproducibility of experiences is proved by means of Cochran's criterion which shows that at the level of confidential probability of 95% dispersions are uniform because the design value of criterion is less than the tabular one. The assessment of importance of regression coefficients has been performed using Student criterion t. The assessment of adequacy of the obtained mathematical model has been performed using Fisher criterion which has shown that the design values are much lower than the critical ones, therefore the obtained regression model adequately describes the response surface, and it can be used for the optimization of the studied processes.

The analysis of distribution of the initial residues based on the predicted values has shown that they have a chaotic character of arrangement on the surface and there is no regularity in their behavior. Based on these observations, it is possible to draw a conclusion that the residues have no correlation relationships among themselves, that is the regression model sufficiently describes the interrelation of experimental values and is adequate.

Based on the results of the made experiments, studies and tests of the developed equipment for the process of grinding of meat raw materials, optimum technological parameters of its work (Table 1) the compromise value of which has been obtained using Cramer's method in the mathematical environment "MathCAD 15" have been determined (Fig. 5–7).

As a result of statistical optimization a correlation and regression equation of functional dependence of productivity of the process of supply of raw materials on constructive technology factors has been obtained. After processing of experimental data in the statistical environment STATISTICA 10.0 coefficients of complex equation of multiple regression of the 2nd order were obtained and the following dependence was derived:

$$\begin{aligned} G = {} & -80127 + 702987 D_g + 3249 n + 3256 \alpha + 1224813 S_b + 2151062 B_g - 2550000 D_g^2 - \\ & -367 n^2 - 349 \alpha^2 - 87187500 S_b^2 - 88750000 B_g^2 + 4750 D_g n + 5125 D_p \cdot \alpha + 2468750 D_g \cdot S_b - \\ & -812500 D_g B_g + 4062 n \cdot S_b - 33125 n \cdot B_g - 19063 \alpha \cdot S_b - 36250 \alpha \cdot B_b \end{aligned} \quad (30)$$

Table 1. Optimum technological parameters of the studied grinding process

Technological parameter	Rational value
Outer diameter of the output grating of the grinding knot, m	0.15–0.155
Rotation frequency of the screw, sec^{-1}	4.5–5.2
Angle of lead of rounds of the screw, degrees	4.8–5.5
Area of the frontal projection of one knife blade, m^2	0.001–0.0011
Thickness of the initial grating of the grinding knot, m	0.0075–0.0082

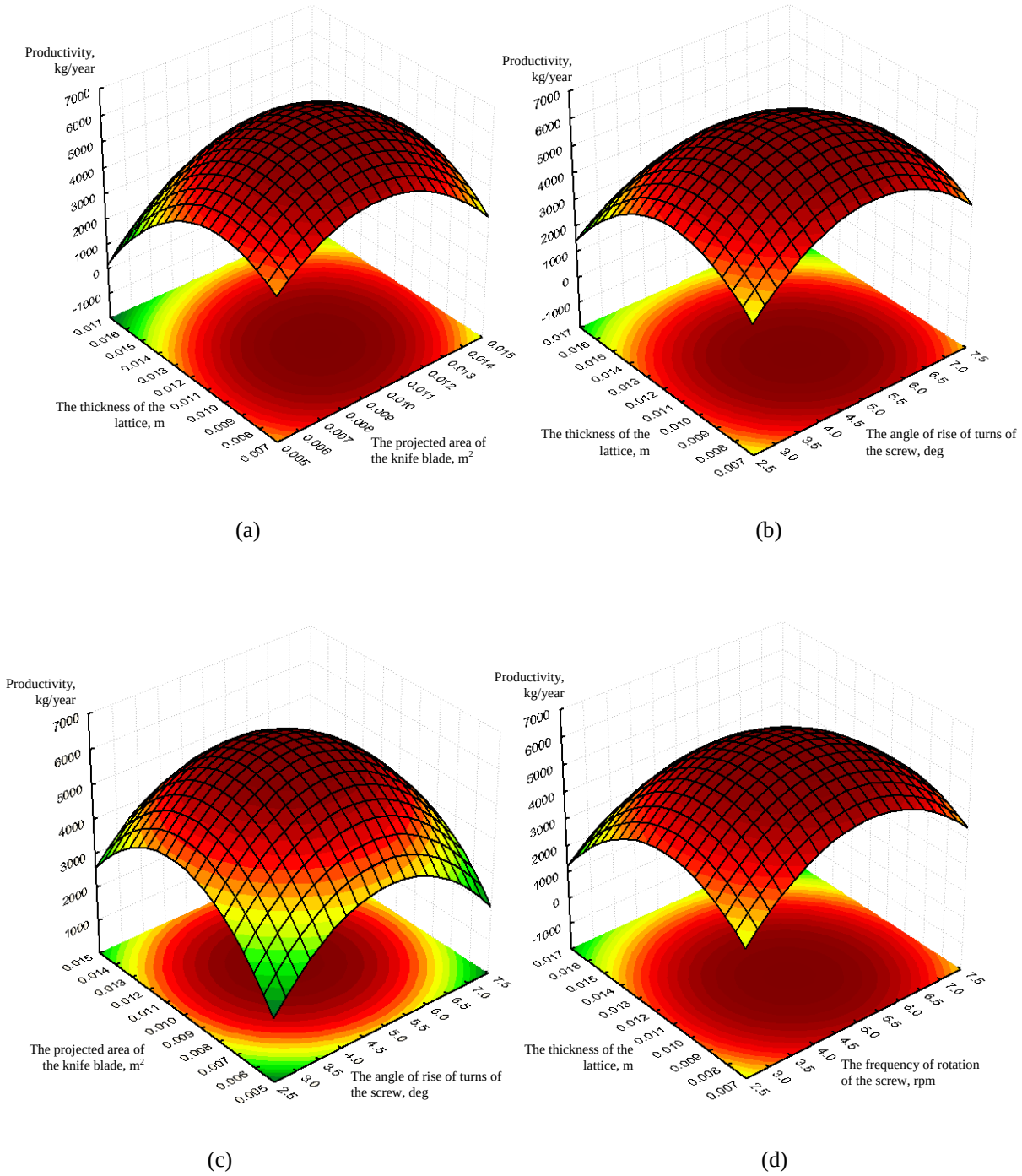


Fig. 5. Surfaces of responses and their projections for productivity in the interaction of major factors: (a) the area of the front projection of one knife blade and the thickness of the initial grating; (b) the thickness of the initial grating and the angle of lead of rounds of the screw; (c) the area of the front projection of one knife blade and the angle of lead of rounds of the screw; (d) the thickness of the initial grating and the rotation frequency of the screw.

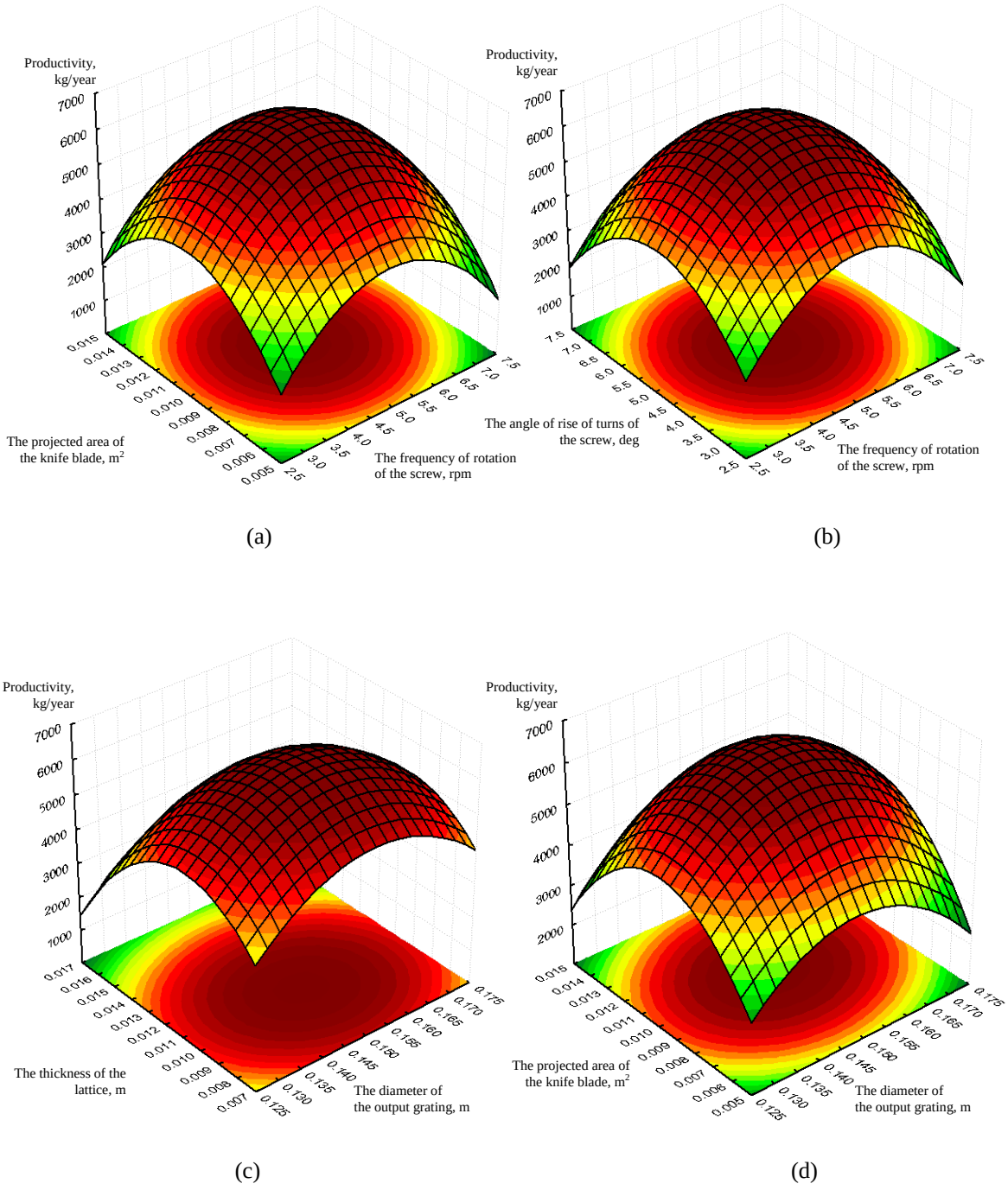


Fig. 6. Surfaces of responses and their projections for productivity in the interaction of major factors: (a) the area of the front projection of one knife blade and the rotation frequency of the screw; (b) the angle of lead of rounds of the screw and the rotation frequency of the screw; (c) the thickness of the initial grating and its outer diameter; (d) the area of the front projection of one knife blade and the outer diameter of the initial grating of the grinding knot.

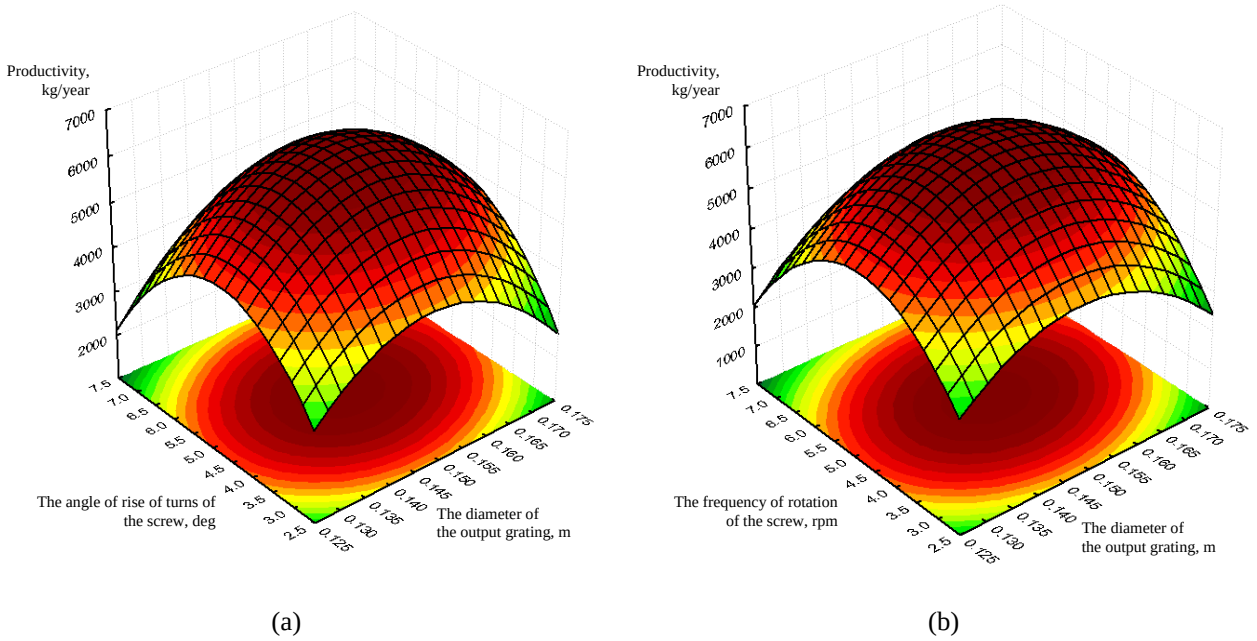


Fig. 7. Response surfaces and their projections for productivity in the interaction of major factors: (a) the angle of lead of rounds of the screw and the diameter of the output grating of the grinding knot; (b) the rotation frequency of the screw and the diameter of the output grating of the grinding knot.

As a result of the work, a mathematical model of the process of supply of raw materials in the top has been developed that allows to increase significantly the accuracy of determination of its productivity and also to set the most rational structural and kinematic parameters of the working bodies of the top.

By means of the obtained mathematical model the influence of structural and kinematic parameters of the top on its productivity has been studied. The model considers the phenomenon of supply of meat raw materials only in a certain sector of the last round of the screw of the top. It has been established that the productivity of the top is defined, first of all, by the supplying ability of the screw which forms the main flow of raw materials through the grinding knot. The presence of gratings and knives in the grinding knot and their corresponding geometrical parameters provide the formation of hydraulic resistance of the grinding knot which prevents from the free effluence of raw materials from the working cylinder under the influence of the pressure produced by the screw. Thereof the reverse flows of raw materials are formed characterizing losses of productivity - through the gap between the external surface of rounds of the screw and the internal surface of the working cylinder and along the screw channel of the screw. An essential increase in the productivity of the top can be reached increasing the rotation frequency of the screw, increasing its outer diameter, reducing the depth of a round, reducing the gap between the screw and the working cylinder, and also increasing the thickness of a screw round.

The following optimum technological parameters of the process of supply of raw materials in the top have been determined as a result of statistical optimization: the outer diameter of the output grating is 0.15–0.155 m; the rotation frequency of the screw is 4.5–5.2 sec^{-1}; the angle of lead of rounds of the screw is 4.8–5.5 degrees; the area of frontal projection of a knife blade is 0.001–0.0011 m^2; the thickness of the output grating is 0.0075–0.0082 m.

The use of the obtained mathematical model allows to increase the accuracy of design calculations of tops and to prove new, highly productive, ways of supply of raw materials to the grinding knot of tops.

REFERENCES

1. Chizhikova T.V. *Mashiny dlya izmel'cheniya myasa i myasnykh produktov* [Machinery for grinding meat and meat products]. Moscow: Legkaya promyshlennost' publ., 1982. 240 p.
2. Nekoz O.I., Filimonova N.V., Filimonov S.O., Batrachenko O.V. and Khom'yak A.V. Research of knife-blades wear intensity of meat-grinder. *Bulletin of Cherkasy State Technological University. Series: Engineering*, 2013, no. 2, pp. 84–96. (In Ukrainian).
3. Haack E., Schnäckel W., and Krickmeier J. Wirkungsgrade deutlich verbessern das leistungspotenzial von industriewolfen ist berechenbar und energieeffizient, *Fleischwirtschaft*, 2012, no. 6, pp. 25–33.
4. Batrachenko O.V. Rozrakhunok osnovnikh tekhnologichniy parametriv m'yasorizal'nikh vovchkiv [Technological calculation of key parameters of meat grinding tops]. *Bulletin of Cherkasy State Technological University*, 2007, no. 3–4, pp. 134–139.

5. Nekoz O.I., Verbits'kiy S.B., Ivanov P.V. and Batrachenko O.V. Metodika rozrakhunku produktivnosti m'yasorizal'nikh vovchkiv [Method of calculation of productivity of meat grinding tops]. *Visnik DonNUET* [Vestnik of Donetsk national university of economics and trade], 2011, no. 1, pp. 26–32.
6. Osipenko V.I., Filimonova N.V., Batrachenko O.V. and Filimonov S.O. Theoretical definition of coefficirnt of productivity of meat grinder. *Herald of Khmelnytskyi national university*, 2015, no. 5, pp. 101–105. (In Ukrainian).
7. Vol'f T.T. Matematicheskoe opisanie reologicheskikh kharakteristik produktov pri mekhanizirovannykh protsessakh izmel'cheniya myasa govyadiny [The mathematical description of rheological characteristics of products in mechanized processes of grinding beef meat]. *Polzunovskiy vestnik* [Polzunovsky Vestnik], 2011, no. 2–1, pp. 214–218.

Please cite this article in press as: Batrachenko A.V. and Filimonova N.V. The influence of structural and kinematic parameters of working bodies of the meat grinders on its productivity. *Foods and Raw Materials*, 2017, vol. 5, no. 1, pp. 118–130. DOI: 10.21179/2308-4057-2017-1-118-130.

ISSN 2310-9599. Foods and Raw Materials, 2017, vol. 5, no. 1

ULTRAFILTRATION CONCENTRATING OF CURD WHEY AFTER ELECTROFLOTATION TREATMENT

I. A. Evdokimov[a,b], S. A. Titov[c], K. K. Polyansky[d], and D. S. Saiko[c]

[a] North Caucasus Federal University,
Kulakova Ave. 2, Stavropol, 355029, Russian Federation

[b] Volga Region Research Institute of Manufacture and Processing of Meat-and-Milk Production,
Rokossovskogo Str. 6, Volgograd, 400131, Russian Federation

[c] Voronezh State University of Engineering Technologies,
Revolyutsii Ave. 19, Voronezh, 394036, Russian Federation

[d] Voronezh Branch of the Plekhanov Russian University of Economics,
Karl Marx Str. 67, Voronezh, 394030, Russian Federation

* e-mail: 125titov@mail.ru

Received March 18, 2017; Accepted in revised form May 10, 2017; Published June 29, 2017

Abstract: This work offers a view on the outcomes of a study focusing on ultrafiltration of curd whey treated on the basis of the membrane electroflotation method in order to ensure more complete extraction of whey proteins when processing recoverable dairy crude. The feature that makes the method different is the presence of membranes between the anode and the cathode while the machines for membrane electroflotation are designed so that current does not run through the whey. To determine the element composition of whey prior to and after electroflotation the method of electron probe X-ray microanalysis was used. It has been shown that the filtration rate of whey treated through electroflotation nearly doubles up if compared to the initial rate. There has also been detected the dependence related to the impact that the concentration of solids and the pressure have on the filtration rate; besides, the kinetics of the ultrafiltration process has been investigated. The method of electron probe X-ray microanalysis was employed to study the element composition of whey both before and after the electroflotation treatment. The increase in the whey ultrafiltration rate after electroflotation can be explained by a growing Hydrogen index and a reduced concentration of Calcium after electroflotation. Besides, a quantitative physical model of whey ultrafiltration was developed, which takes into view specific features of polarization layer formation. The model implies conditional division of whey flow at the membrane surface into two streams – a normal one and a tangential one. Part of the protein molecules transported by the normal flow settles on the membrane surface while the other part of them remains near the surface up until it is pushed into the whey bulk by protein molecules of the tangential flow. That all mentioned above fixes certain elements of newness in the field of membrane technologies. The study was performed at the Voronezh State University of Engineering Technologies and the North Caucasus Federal University (Russian Federation).

Keywords: Whey, ultrafiltration, electroflotation, membrane technology

DOI 10.21179/2308-4057-2017-1-131-136 *Foods and Raw Materials*, 2017, vol. 5, no. 1, pp. 131–136.

INTRODUCTION

Membrane technologies are the basis for low-waste and even non-waste (in case proper arrangements are made) dairy productions [1]. However, their wide implementation is limited, in particular due to low production capacity of membrane machines.

This also holds true for ultrafiltration separation of protein from milk whey [2]. Intensification of this process takes, first of all, minimization of protein deposit on the membrane surface. For instance, preliminary treatment of heated whey with ultrasound will reduce the membrane congestion and the amount of the protein deposit [3]. However, after numerous regular cleanings membranes increase their hydrodynamic resistance, which must be due to the fact that the pores get stuffed with protein from the inside surfaces [4].

If the impact of protein deposit could be minimized in any way, then concentration polarization will be the factor limiting the permeate flow through the membrane [5]. Thus, if for filtering sheep cheese whey membranes are used that are made of composite fluoropolymer, this allows a larger flow of permeate compared to polysulfone membranes, and protein deposits are minimum, while the dependency between the filtration rate

and the pressure is typical of concentration polarization [6].

Whey acidity has a significant impact on the degree of protein deposit. The major role in reducing membrane permeation in case of changing pH belongs, obviously, to β-lactoglobulin. This is suggested with the following experimentally obtained data. In the pH range of 3.9–4.65, the filtration capacity goes down along with the growing pH [7]. At the same time, there is data [8] showing that under a decreasing hydrogen index down to pH 4.65, a high concentration and a low ionic strength of the solution, the solubility of β-lactoglobulin goes down sharply. The results obtained through scanning electron microscope investigation [9] suggest that filtration of β-lacto-globulin solutions leaves the membranes with some deposit appearing as thick layers. Transmission electron microscopy of membrane cross section [10] shows that similar deposits with incorporations of α-lactalbumin globules are also to be found in case of milk whey filtration. The pH range where the whey filtration rate is minimum (pH 4.6–5.5) is close to the range where isoelectric points of various β-lacto-globulins can be found (pI 4.9–5.4) [11, 12].

Since the pH of curd whey lies within this range, its ultrafiltration is more complicated than that of cheese whey. Neutralization of cheese whey with correcting chemical agents in most cases results in its reduced organoleptic features and increased allergenic capacity [13].

This is why there is a lot of interest taken in reducing curd whey acidity with electrophysical methods, e.g. electrodialysis [14] or membrane electroflotation. Membrane electroflotation is different from conventional electroflotation used for protein-containing solutions by the presence of a membrane between the cathode and the anode, while the machines themselves are arranged so that the electric current does not go through whey. Treatment this way improves the product's organoleptic features, while the hydrogen index goes up as well [15].

Electroflotation results in 20–30% of protein eliminated from whey. One of the areas for using floated whey could be ultrafiltration treatment aiming at more thorough extraction of proteins. This is what the present work is focused on.

OBJECTS AND METHODS OF STUDY

In the ultrafiltration device used for the experiment, retentive mechanism/block moves round. There were track-etched polyethylene tetraphtalate membranes used, with a pore diameter of 60 nm. The filtration rate of distilled water in the ultrafiltration cell was 12 ml/min (pressure – 0.2 MPa) (filtration rate her means the volume of filtrate that has passed through the membrane as per a single unit of time). The required level of pH, while the samples of whey were prepared, was reached through adding NaOH or HC1.

For electron probe X-ray microanalysis the whey was first dried, after which scanning electron microscopy was used to select several areas (0.2 mm) within the obtained powders for further microanalysis.

EXPERIMENT OUTCOMES

For 10 minutes following electroflotation, the whey pH goes up from 5.0 to 6.05. The filtration rate of whey that has been treated this way nearly doubles if compared to untreated whey (Fig. 1).

Further electroflotation whey treatment would not increase the filtration rate any more. The results obtained through the experiment indicate that there is a certain value in ultrafiltration of floated whey as well as in further research in the area.

Fig. 2 shows the dependence of curd whey filtration rate on the dry substance concentration, measured under pH = 4.8 and pH = 6.6. The charts demonstrate that the filtration rates at pH close to the values in Fig. 1 reveals a difference of 1.7 times.

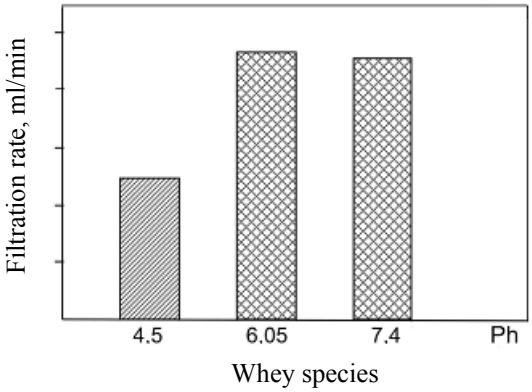


Fig. 1. Filtration rate for initial (pH = 4.5) and floated (pH = 6.05 and pH = 7.4) wheys (t = 30°C, p = 0.2 MPa).

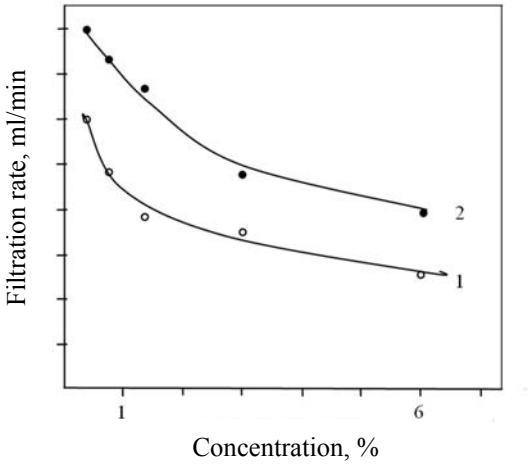


Fig. 2. Relationship between curd whey filtration rate and concentration of dry substances: (1) pH = 4.8; (2) pH = 6.6.

Therefore, the filtration rate growth for the floated whey, if compared to the initial whey, is mostly due to a significant change in the whey hydrogen index through electroflotation. The smaller angles in the charts at 3–6% concentrations of dry substances mean that the 10–15% reduction in the protein concentration in the floated whey, if compared to the initial whey, has virtually no impact on the filtration rate. Therefore, it is most likely that there are two factors

that have an impact on the growth in the floated whey filtration rate. This, first of all, is due to the changing values of pH, while there is some extra impact added by the reducing concentration in Calcium ions.

Calcium ions present in whey are known to speed down its filtration rate [16]. Electron probe analysis done on the whey prior to, and following electroflotation showed a decrease in the Ca ion concentration in the floated whey (Table 1).

Table 1. Whey element composition

Type of whey	Element, share,%				
	Na	P	Cl	K	Ca
Floated whey	1.25	0.43	1.55	0.57	0.52
Non-floated whey	1.06	0.8	1.03	0.45	1.02

The difference in the filtration rate for wheys with various pH value remains in case of changing share of the dry substances in the solution, which should also be true for floated and non-floated wheys. With dry substances concentration tending towards zero, the graphs, as could be expected, tend to intersect. Figures 3 and 4 demonstrate the dependence of filtrate volume on time, and filtration rate on pressure, respectively.

RESULTS AND DISCUSSION, PROCESS MODEL

Fig. 3 shows that 20–30 seconds after filtration is started, the curve indicating the dependence between filtrate volume and time reaches the straight line portion, which means stable filtration rate.

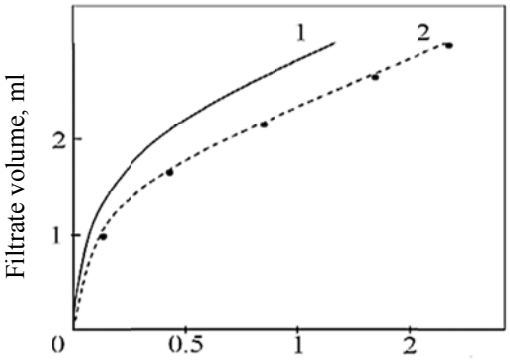


Fig. 3. Theoretical (1) and experimental (2) dependencies of filtrate volume of filtration time.

The grades of the curves were used to determine the rate of steady filtration. At pH = 4.0 the steady rate was v_{st} = 0.7 ml/min; at pH = 10 v_{st} = 1.2 ml/min. Since the process stabilization time is much lower than that of measuring (5 min) in the previous experiments then the average filtration rate determined through these experiments can be considered close to the stable rate. Using the data of the electron microscopy [10] we can suggest that the sublayer with the α-lactalbumin globules coating it, as well as the β-lactoglobulin layer above that, are developed within 20–30 sec.

Therefore, there is proof to the hypothesis stated in [11] and stating that globular formations of α-lact-albumin, casein, and immunoglobulins may deposit on the membrane shaping some sort of bridges above pores, which later on host proteins that can develop layers.

The data obtained make it possible to assume that jellification process in a thick layer of β-lactoglobulin follows a mechanism that is different from, for instance, jellification in rather concentrated protein solutions. Actually, the induction period of jellification in the latest case is from several hours to several days, while it only takes dozens of seconds for gel to develop on a membrane.

This means that polarization layer development could be viewed not from the stance of gel formation yet similarly to particle deposition on solid bodies from gas phase, or in case of sedimentation deposition, from a liquid under the conditions of a tangential flow.

Let us make a conditional division breaking the flow of protein molecules approaching the membrane surface in two – a flow that is normal towards the membrane surface and a tangential one.

Each molecule of the normal flow, when approaching the surface, will stay there for a certain period of time τ_0, until a connection develops between this molecule and other protein molecules. If, within this time, the molecule experiences an impact with a tangential flow molecule then it will be knocked out; however, if this impact takes place after the time of τ_0 then it will get fixed on the surface and will not be knocked out. This metastable condition of a molecule may take place during filtration, unlike other processes of interaction between solutions and solid bodies, due to the fact that a large protein molecule will pressed against the surface with the water flow passing through the membrane.

Let us accept that each molecule of the tangential flow experiences a co-impact with a molecule from the normal flow, so the number of these molecules N_τ approaching a certain point at the surface within the time of t shall be equal to the number of the co-impacts N_c within the same period of time:

$$N_c = N_\tau . \quad (1)$$

Then, all the molecules of the perpendicular flow would approach the same point on the surface in a certain average piece of time t_1 that depends on the solution concentration and the velocity of the molecules v_e:

$$t_1 = \frac{1}{v_e \sqrt[3]{C_0}} . \quad (2)$$

Since we are focusing on a thin layer of the liquid at the membrane surface, the concentration of C_0 in that might be taken as stable.

The period of time t_2, within which the tangential flow molecules reach point A, shall be expressed the following way:

$$t_2 = \frac{1}{v_\tau \sqrt[3]{C_0}}. \quad (3)$$

Within time t the point A will be reached by the N_{cross} number of cross flow molecules:

$$N_{cross} = \frac{t}{t_1}, \quad (4)$$

as well as by those of the tangent ail flow N_t:

$$N_\tau = \frac{t}{t_2}. \quad (5)$$

Now let us calculate the number of the molecules remaining on the surface as a result of impacts:

$$N_{rem} = N_{cross} - N_i \cdot P, \quad (6)$$

where P is the probability of an approaching molecule to be knocked out. Assume that within the time t_2, there were 10 molecules of the normal consequently approaching the boundary between impacts. The time for staying at the boundary for the first molecule is $10t_1$, $2^{nd} - 9t_1$, the last one – t_1. Let us take $\tau_0 = 3t_1$. In this case the tenth, the ninth, and the eighth molecules may be knocked out at impact, while the others may not. The knock out probability P is:

$$P = \frac{3}{10} = \frac{3t_1}{10t_1} = \frac{\tau_0}{10t_1}. \quad (7)$$

Since 10 is the number of the molecules that approached the boundary within a time interval between the impacts, then:

$$10 = \frac{t_2}{t_1}, \quad (8)$$

$$P = \frac{\tau_0}{t_2}. \quad (9)$$

In case the polarization layer is mostly developed faster than steady protein distribution takes place in the boundary layer, then the cross velocity of protein molecules v_e shall be approximately equal to the velocity of the filtrate flow passing through the membrane v_f.

Using (2), (3), (4), (5), (9) in (6), in view of $N_i = N_\tau$ we shall get:

$$N_{rem}(t) = t\left(v_f(t)\sqrt[3]{C_0} - \frac{\tau_0}{t_2^2} \right). \quad (10)$$

The developing polarization layer shapes, on the membrane surface, another membrane, through which whey is filtered.

In view of the hydraulic resistance and the membrane porosity, the Kozeny–Carman equation [17] could be modified as follows:

$$v_f = \frac{\varepsilon_m k_0 \cdot P}{a_1 + l}, \quad (11)$$

where is the coefficient k_0 depends on the filtrate viscosity, the microstructure and porosity of the polarization layer, ε_m is the membrane porosity, a_1 is the parameter taking into account its hydraulic resistance.

Joining the polarization layer thickness l with the number of protein molecules that constitute it, we will have the following formula:

$$l = \frac{m_\mu N_{rem}}{\rho_{pr}\left(S - S_{por}\right)}, \quad (12)$$

Where S is the area of the polarization layer, S_{por} is the total area of the pores that can be determined from the porosity of the polarization layer, m_μ is the mass of a protein molecule, N_{rem} is the number of protein molecules, and ρ_{pr} is its density.

Solving the equation system (10–12) regarding υ_f in view of (3) we shall get:

$$v_f = \frac{k_1 p}{\left[\frac{-(c + k \cdot v_\tau^2 \cdot t) + \sqrt{\left(c + k \cdot v_\tau^2 \cdot t\right)^2 - 4t\left(k \cdot v_\tau^2 \cdot c - k_1 p\right)}}{2} \right] + c}. \quad (13)$$

Here

$$k = \sqrt{C_0^{\,3}} \cdot \tau_0^2, \; k_1 = \varepsilon_m \cdot k_0, \; c = \frac{a_1 \cdot \rho_{pr}\left(S - S_{por}\right)}{m_\mu}.$$

The formula below could be used to calculate the volume of the filtrate developing within the time t:

$$V_f = \int_0^t \frac{k_1 \cdot p \cdot dy}{\left[\frac{-\left(c + k \cdot v_\tau^2 \cdot y\right) + \sqrt{\left(c + k \cdot v_\tau^2 \cdot y\right)^2 - 4y\left(k \cdot v_\tau^2 \cdot c - k_1 \cdot p\right)}}{2} \right] + c}. \quad (14)$$

The dependence of the filtration rate on the pressure, as calculated following the formula (13), as well as the kinetic curve determined through integration of this formula, lay within satisfactory agreement with the experimental ones (Fig. 3, 4). More accurate data could be obtained taking into account the specific hydrodynamic features of whey flowing through a canal of a certain shape.

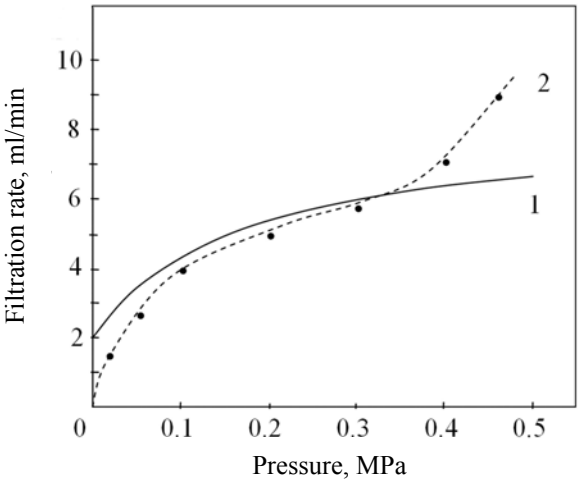


Fig. 4. Theoretical (1) and experimental (2) dependencies of filtration rate on pressure.

Let us accept that, following [18], the major role in β-lactoglobulin molecular interaction belongs to hydrophobic and electrostatic interactions, which may result in aggregation of proteins based o the mechanism described, for instance, in [19]. During that, the electrostatic interactions among protein globules are of local nature [20]. Then the condition for a molecule's getting fixed in the polarization layer will imply three events coming simultaneously – a position of a proper molecule that would ensure its touching the polarization layer with the hydrophobic area; the presence of a hydrophobic area on such a molecule at the spot of contact with the polarization layer, and not very strong an electrostatic repulsion between the areas of globules approaching one another. In case the pH of the solution is high enough, then the last condition often fails to be met, the time τ_0 gets longer and, respectively, following (13), (14) the filtration rate is growing, which is observed in case of floated whey filtration. Electroflotation treatment for curd whey, which leads to a growth in the protein molecule negative charge, is likely to prove especially useful when using negatively charged membranes [21] that improve significantly ultrafiltration productivity. Due to a lower level of Ca in concentrates of curd whey after it has been subjected to electroflotation treatment, they can be recommended to elderly people, since milk and dairy products may have a negative effect on the health in the elderly age, that is due to specific features about calcium absorption, which facilitates atherosclerosis [22].

CONCLUSION

The study has shown that there is a reason to conduct ultrafiltration concentration of curd whey after it has been subjected to electroflotation treatment.

Improved organoleptic properties of floated whey allow using ultrafiltration not only to produce whey protein concentrates with a high concentration factor, yet also to make base for yogurt, dairy drinks, and jellies with a higher content of whey proteins. At the same time it is possible not to exceed the concentration factor of 2–2.5, which reduces the load on the ultrafiltration equipment and decreases its elements, membranes first of all, contamination with protein.

ACKNOWLEDGEMENTS

The work was supported by the Ministry of Education and Science of the Russian Federation (Contract Minobrnauki of Russia № 2017-218-09-162).

REFERENCES

1. Khramtsov A.G. *Fenomen molochnoy syvorotki* [Milk whey phenomenon]. St. Petersburg: Professija Publ., 2011. 804 p.
2. Evdokimov I.A., Zolotareva M.S., Volodin D.N., et al. Efficient technologies for acid milk whey processing. *Molochnaya promyshlennost'* [Dairy industry], 2007, no. 11, pp. 95–96. (In Russian).
3. Koh Li Ling A., Nguyen Hanh Thi Hong, Chandrapala Jayani, et al. The use of ultrasonic feed pre-treatment to reduce membrane fouling in whey ultrafiltration. *Journal of Membrane Science***,** 2014, vol. 453, pp. 230–239. DOI: https://doi.org/10.1016/j.memsci.2013.11.006.
4. Berg Thilo H.A., Knudsen Jes C., Ipsen R., et al. Investigation of consecutive fouling and cleaning cycles of ultrafiltration membranes used for whey processing. *International Journal of Food Engineering*, 2014, vol. 10, no. 3, pp. 321–325.
5. Williams P.S., Giddings S.B., and Giddings J.S. Calculation of flow properties and end effects in field-flow fractionation channels by a conformal mapping procedure. *Analytical Chemistry,* 1986, vol. 58, no. 12, pp. 2397–2403. DOI: DOI: 10.1021/ac00125a010.
6. Macedo A., Duarte E., and Pinho M. The role of concentration polarization in ultrafiltration of ovine cheese whey. *Journal of Membrane Science*, 2011, vol. 381, no. 1–2, pp. 34–40. DOI: 10.1016/j.memsci.2011.07.012.
7. Konrad G., Kleinschmidt T., and Faber W. Ultrafiltration flux of acid whey obtained by lactic acid fermentation. *International Dairy Journal*, 2012, vol. 22, no. 1, pp. 73–77. DOI: 10.1016/j.idairyj.2011.08.005.
8. Díaza O., Pereira C.D., and Cobos A. Functional properties of ovine whey protein concentrates produced by membrane technology after clarification of cheese manufacture by-products. *Food Hidrocolloids*, 2004, vol. 18, no. 4, pp. 601–610. DOI: 10.1016/j.foodhyd.2003.10.003.

9. Lee D.N. and Merson R.L. Examination of cottage cheese whey proteins by scanning electron microscopy relationship to membrane fouling during ultrafiltration. *Journal of Dairy Science*, 1975, vol. 58, no. 10, pp. 1423–1432.
10. Antipov S.T., Titov S.A., Lavrenov A.L., and Soldatenko S.A. Prosvechivayushchaya elektronnaya mikroskopiya polyarizatsionnykh sloev, obrazuyushchikhsya pri ul"trafil"tratsii molochnoy syvorotki [Transmitting electron microscopy of polarization layers formed during ultrafiltration of milk whey]. *Khranenie i pererabotka selkhozsyria* [Storage and processing of farm products], 2009, no. 4, pp. 23–25.
11. Marcus C.R., B. Olivier, and de Haan Edward HF. Whey protein rich in α-lactalbumin increases the ratio of plasma tryptophan to the sum of the other large neutral amino acids and improves cognitive performance in stress-vulnerable subjects. *The American Journal of Clinical Nutrition*, 2002, vol. 75, no. 6, pp. 1051–1056.
12. Permyakov E.A. and Berliner L.J. α-Lactalbumin: structure and function. *FEBS Lett*, 2000, vol. 473, no. 3, pp. 269–274. DOI: 10.1016/S0014-5793(00)01546-5.
13. Beattie D. *Using RO/CEDI to Meet USP 24 on Chloraminated Feed Water Ultrapure Water Expo 2001 Technical Program*. Philadelphia, PA, April 2–4, 2001, p. 216.
14. Evdokimov I.A., Volodin D.N., and Dykalo N.Ya. Elektrodializ - perspektivnyy metod pererabotki molochnoy syvorotki [Electrodialysis is a promising method for processing whey]. *Pererabotka moloka* [Milk Processing[, 2001, no. 2, pp. 5–7.
15. Gorlov I.F., Khramtsov A.G., Titov S.A., et al. High tech of controlled pumping into whole muscle meat food. *Modern Applied Science*, 2015, vol. 9, no. 10, pp. 27–33. DOI: 10.5539/mas.v9n10p27.
16. Hiddink I., de Boer R., and Nooy P.F.C. Effect of various pretreatment on the ultrafiltration of sweet cheese whey at about 55°C. *Milchwissenschaft*, 1981, vol. 36 , pp. 657–663.
17. Mulder M. *Basic principles of membrane technology*. Dordrecht: Kluwer academic publishers, 1995. 510 p.
18. Ye A. and Singh H. Influence of calcium chloride addition on the properties of emulsions stabilized by whey protein concentrate. *Food Hydrocolloids*, 2000, vol. 14, no. 4, pp. 337–346. DOI: 10.1016/S0268-005X(00)00010-2.
19. Dickinson E. and Krishna S. Aggregation in a concentrated model protein system: a mesoscopic simulation of β-casein self-assembly. *Food Hydrocolloids*, 2001, vol. 15, no. 2, pp. 107–115. DOI: 10.1016/S0268-005X(00)00057-6.
20. Boulet M., Britten M., and Lamarche F. Aggregation of some food proteins in aqueous dispersions: effects of concentration, pH and ionic strength. *Food Hydrocolloids*, 2000, vol. 14, no. 2, pp. 135–144. DOI: 10.1016/S0268-005X(99)00059-4.
21. Arunkumar A., and Etzel Mark R. Negatively charged tangential flow ultrafiltration membranes for whey protein concentration. *Journal of Membrane Science*, 2015, vol. 475, pp. 340–348. DOI: 10.1016/j.memsci.2014.10.049.
22. Seely S. Is calcium excess in Western diet a major cause of arterial disease. *International Journal of cardiology*, 1991, vol. 33, pp. 191–198.

Please cite this article in press as: Evdokimov I.A., Titov S.A., Polyansky K.K., and Saiko D.S. Ultrafiltration concentrating of curd whey after electroflotation treatment. *Foods and Raw Materials*, 2017, vol. 5, no. 1, pp. 131–136. DOI: 10.21179/2308-4057-2017-1-131-136.

DETERMINATION OF DEPENDENCE BETWEEN THERMOPHYSICAL PROPERTIES AND STRUCTURAL-AND-PHASE CHARACTERISTICS OF MOIST MATERIALS

A. M. Popov*, K. B. Plotnikov, and D. V. Donya

Kemerovo Institute of Food Science and Technology (University),
Stroiteley blvd. 47, Kemerovo, 650056, Russian Federation

* e-mail: popov4116@yandex.ru

Received October 17, 2016; Accepted in revised form December 18, 2016; Published June 29, 2017

Abstract: Most of foods, raw materials and half-finished products are disperse systems. One of the most energy-consuming processes during foods production is drying. Intensive study of this process allows high-quality final products to be obtained at lower energy consumption. The aim of the research is to determine the interrelation between thermophysical properties and structural-and-phase characteristics of moist materials to establish optimum parameters for drying. A set of experiments has been made to find the influence of temperature on rheological properties of suspensions. A suspension of 40% chokeberry juice and ultradisperse starch from berry meal was used as the object of the research. Thermostatting was carried out in the range from 20 to 50°C with an increment of 10°C. The thermal conductivity coefficient for blocked samples with dimensions of 50×50×75 m^{-3} was determined by means of a continuous plate flat source. Samples were prepared using the plastic mass forming method at the pressure of 50 MPa and the moisture of mass of 15%, and then dried. The results show that yield stress increases with temperature because of coagulation structuring intensification. The material has the highest thermal conductivity at the least capillary moisture of W_{LCM} =14.2%, i.e. when a monomolecular layer of tightly bound water takes on the property of continuity through the material. The obtained results allow us to conclude that the use of volume phase characteristics makes it possible to improve the technique for determining thermophysical characteristics of dry and wet disperse systems to be improved, which in turn allows obtained results to be more accurate.

Keywords: Granulation, granules, powder, drying, phase characteristics

DOI: 10.21179/2308-4057-2017-1-137-143 *Foods and Raw Materials*, 2017, vol. 5, no. 1, pp. 137–143.

INTRODUCTION

Dehydration is the main technological peculiarity when producing foods based on disperse systems. Water – together with smaller particles – forms suspensions and acts as a plasticizing agent during granule formation. Dehydration causes chemical, biochemical, rheological, mechanical and other changes in a material that in turn lead to mass and volume decreases, strength and lifetime increases, and etc. There are physicochemical, mechanical, thermal methods of dehydration [1]. The latter is more often being used to remove water from fine particle fractions.

A factor of drying is the partial pressure difference of vapour on the surface of the material being dried and in ambient medium [2]. The influence of operating parameters on the efficiency and time of drying, and the problems of product shrinkage and crack formation have been studied by such researchers as A.V. Lykov, A.S. Ginzburg, P.S. Kossovich, P.D. Lebedev, B.S. Sazhin, M.Yu. Lur'e, V.I. Mushtaev, B.N. Gak, O.S. Zaytsev [3].

The aim of the research is to determine the interrelation between thermophysical properties of moist materials and their structural-and-phase characteristics.

OBJECTS AND METHODS OF STUDY

In the theory of drying the object of the research are moist materials, their behavior during dehydration under different conditions and prediction of the process with time using drying sensitivity coefficients and crack formation criteria. These coefficients are calculated on the basis of mass balance using the weigh moisture content of materials. When drying free-disperse systems, e.g., wet berry meal, starch, and polysaccharide, it is enough to know mass balance of substances to describe drying. The case is different with structured disperse systems; apart from mass balance (sizes and geometrical form of particles are known preliminarily) total volume balance of mixture components should be used [4]. It is calculated according to the formula:

$$C_G + C_S + C_L = 1, \quad (1)$$

where C_G, C_S and C_L are volume concentrations of gas, solid and liquid phases.

The equation is valid throughout drying independently of materials properties and process rate. When moisture completely is removed, a three-phase system becomes a two-phase one; the following formula is true:

$$C_G + C_S = 1. \quad (2)$$

The use of phase characteristics of disperse systems allows us to evaluate the efficiency of dehydration and the quality of dried foods. At present, the latter is the main criteria for evaluating the former. Quality evaluation is performed visually taking into account the presence of cracks and the degree of linear and volumetric shrinkage [5].

Solid-phase volume concentrations should be used as the criteria to determine the efficiency of dehydration both under static conditions and during material structure forming. At present, mass and heat balances and Ramzin i-d diagram are used when studying drying [6, 7]. This technique allows us to determine the temperature of a drying agent and change in dried material moisture content during the process. Drying of shaped materials requires controlling of such parameters of drying agent as rate, temperature, moisture and geometry of material; it is frequently difficult to do this using the moisture content as a controlling parameter, therefore, the use of volumetric characteristic of the object is possible to exclude errors.

There is a strong relation between structure and phase characteristics of disperse systems. For example, a new system with quite new properties (flowability, homogeneity of material, plastic and strength properties) will be obtained as a result of drying of a two-component "solid – liquid" system. Rheological, structural and mechanical properties of the system and its formability can be predicted if material moisture, porous substance properties (fine particle fraction with high specific surface) and properties of structure-forming framework are known. The amount of liquid component in the system predetermines strength and size of the formed crystallization structure; however, solid phase properties in the newly-formed disperse system do not influence the dependence between solid phase volume concentration and the material moisture content at $W \geq W_{LCM}$, where W is the moisture of material and W_{LCM} is the least capillary moisture [5]:

$$C_S = b \cdot W + a, \quad (3)$$

where *a* and *b* are constants determined empirically.

Drying can be considered as a reverse process of mass forming, i.e. a disperse system consisting of continuous and solid phases; however, Eq. (3) would be valid as well at various factors of changes in material structure during drying. To determine these changes the difference in the processes mentioned should be considered [8]. Assume that a two-component system consists of a structural framework and a porous substance. The latter is fine dispersed particles which bind major part of water and, thereby, form a suspension. Coarse dispersed particles form a framework of a molding compounds and are not able to bind much water. Water-binding mechanism with a fine dispersed fraction having small median sizes has been studied by the following researchers [6]: B.V. Deryagin, A.V. Dumansky, M.H. Carapet'yants, N.N. Kruglitsky, S.P. Nichiporenko, G.V. Kukolev and others. The system consists of liquid and dispersed phases, water-binding capacity of the latter directly depends on its physical and chemical properties, e. g., a large-size starch granule has a layer-like structure, and its top layers are formed mainly by molecules of branch structure known as amylopectin [9]. The decrease of water content inside the starch granule causes pressure increase. As a result X-shaped cracks are formed on its surface. Starch is able to absorb up to 21% of water but only 6% is bound. When temperature increases up to 50–60°C starch granules tend to swell; water penetrates into macromolecules causing hydrogen bonds breakage. Apart from thermal treatment, starch swelling can be achieved by introduction of solutions with high pH (on the order of 10). Jellies contain acids however their concentration causes pH to be 4–7. This is an accepted value in food industry and does not affect the structural framework of granules [10]. Powdered sugar has more water-absorbing ability than starch granules, sucrose crystals are losing their strength when moisture is about 8%. We can conclude that suspension properties of molding compounds or granules depend on sorption activity, wetting ability, swelling ability, ion exchange ability and colloidal and chemical properties. Is should be noted that swelling ability is a essential parameter for forming structure during drying, as water removal from the system leads to volume decrease; i.e., the process is opposite to swelling [1].

Shrinking and swelling of a system takes much time, therefore, the optimum time of drying should be established to prepare the molding compound. It is not easily to perform because of operating costs. Drying is the most expensive process in instant beverage production. The increase of drying rate has both advantages and disadvantages. One of the disadvantages is crack formation, which disrupts obtained product structure [9]. Apart from that, increased temperature leads to increased solubility of such components as lactose, sucrose or fructose that gives rise to the increase of the liquid phase volume that in turn adversely affects obtained granules strength. Consequently, such variables as property of dried material, operating parameters and technical and economic characteristics should be taken into account when determining optimum parameters of drying [11].

Traditional technology of instant beverage production includes drying dump granules. During the process the suspension is heated. A number of experiments have been studied to establish the effect of temperature on rheological properties of the suspension. A suspension of 40% chokeberry juice and ultradisperse starch from berry meal was used as the object of the research. Thermostatting was carried out in the range from 20 to 50°C with an increment of 10°C. Time and conditions of preparing suspension samples were strictly observed and were constant. Table 1 gives rheological parameters of the system as a

function of temperature, where Θ is modulus of elasticity, η is internal friction and Ψ is sharing rate.

Table 1. Effect of temperature on rheological properties of suspension

Rheological parameters	Temperature, °C			
	20	30	40	50
Θ, dyne	270	290	340	470
η_1, poise	2.24	1.68	1.26	1.02
Ψ_1, s^{-1}	113	121	142	196

We can see that yield stress increases with temperature. That is because of coagulation structuring intensification. Viscosity value of the suspension changes twofold; similar situation is observed for water: the increase in temperature from 20 to 50°C reduces its viscosity from 0.001 Pa·s down to 0.00055 Pa·s. Solubility of sucrose in saturated solution of chokeberry juice rises by 25%, i.e., liquid phase volume increases. Taking into account changes in rheological parameters, it follows that plasticity rises sharply with temperature. In practice, we may observe it during the first stage of drying when granulate becomes softer. Dependences obtained can be true only for structured disperse systems that form the single pseudo phase.

Any material is capable of resistance to shrinking stress under certain conditions [12]:

(1) The material must contain minimal amount of capillary moving water before drying. This will help to produce higher homogeneity and less material shrinking, and prevent transfer of soluble substances into the liquid phase.

(2) Adhesive forces acting between structural framework particles must be equal to cohesion ones acting between particles of the suspension.

(3) Whey proteins or surfactants should be used to obtain particles of molecular size which, thus, conduce the balance between adhesive and cohesive forces during drying.

(4) Granulometric composition must insure particles to be packed tightly; this is achieved by structural framework and porous substance quantitative ratio.

(5) It is necessary to reduce suspension shrinking in order to increase hardness of obtained granules during drying and the solid-phase volume concentration. It can be achieved by introduction of a small quantity of modified starch or protein (up to 1.5%). Molecules penetrate into space between large grains, thus limiting mobility of large grains [13].

(6) Granulating should be performed at the drying temperature in order to decrease the volume of the liquid needed for coagulation to occur. Pellets formation process is attended by hydration; the amount of the liquid tends to be reduced, which provides hardness of granules.

Operating parameters of drying directly influence the crystallization rate of sucrose or lactose and the shrinkage of the material [14, 15, 16]. Drying regime, at which the decrease of the system volume is directly proportional to the increase of starch and meal volume during swelling, is the most optimum one. Shrinkage value depends on the drying rate. The higher operating parameters, the faster final shrinkage can be achieved. One should remember that shrinking will go on until capillary moving water is fully removed (even if volume shrinkage is stopped). Moreover, process rate effects distribution of temperature and moisture content across the material, especially for large cross-section granules. It implies irregular water distribution and shrinkage of layers during the process. Consequently, external layers reduce their volume, while internal ones keep their initial volume over time preventing granule shrinkage. It follows that tension forces act on the surface and compressing forces act inside. This leads to serious deformations and crack formation as a result. Professor A.F. Chizhsky has established the crack formation criterion based on the fact that an acting forces magnitude is proportional to the moisture difference between external and internal layers, product thickness being of no importance [17]:

$$\Delta W_{max} = W_{AV} - W_S, \quad (4)$$

where ΔW_{max} is the maximum allowed moisture difference, %; W_{AV} is the average moisture of the sample, %; and W_S is the moisture on the sample surface, %.

For parabolic distribution of water, ΔW_{max} is equal (at constant rate of drying) to:

$$W_{max} = W_C - W_S, \quad (5)$$

where W_C is the moisture in a central layer of the sample, %.

Academician A.V. Lykov suggested dimensionless similarity criteria [7]:

$$K = \frac{(W_{AV} - W_S)}{W_{in}}, \quad (6)$$

$$K_i = \frac{2(W_C - W_S)}{W_{in}}, \quad (7)$$

where K is the crack formation criterion, %; K_i is the Kirpichev's mass exchange criterion; W_{in} is the initial moisture of the material, %.

M.S. Belopol'sky has proved that sensitivity of disperse mass to drying can be described by two coefficients for soft-mud molding products. The first coefficient describes formation of cracks on the surface during surface layer shrinking, while the second one describes formation of internal cracks on the final stage of its shrinking. The values in the expression for determining the sensitivity coefficient of disperse materials to drying characterize structural-and-mechanical and thermophysical properties of the system that effect crack formation.

There are a number of difficulties in describing the process by using differential equations of heat-and-moisture transfer. Therefore, it is more convenient to use such similarity criteria of heat-and-mass transfer as Lykov (Lu), Posnov (Pn), Kirpichev (Ki), Vio (Bi), Kossovich (Ko), Fourier (Fo), Rebinder (Rb) criteria.

Lykov criterion is an analogue of the Lewis number and characterizes the relation between heat and mass transfer in disperse systems. Mass transfer goes on faster than heat transfer if Lu>1 [6]:

$$Lu = \frac{a_m}{a_q}, \quad (8)$$

where a_m is the water conductivity coefficient, m^2/s; a_q is the thermal diffusivity, m^2/s.

Posnov criterion determines the relative fall of moisture content inside the material caused by temperature difference. In other words, the change in water potential depending on that of temperature is estimated [4].

$$Pn = \frac{\delta_T \cdot \Delta t}{\Delta u}, \quad (9)$$

where δ_T is the thermal-gradient coefficient, kg/kg·deg; Δt is the temperature difference, deg; and Δu is the moisture content difference, kg/kg.

Kirpichev number characterizes the relation between intensity of internal and external moisture transfer [6]:

$$K_i = \frac{j_m \cdot l}{a_m \cdot \rho \cdot \Delta u}, \quad (10)$$

where j_m is the evaporation rate, $kg/m^2 \cdot s$); l is geometric dimension, m; and ρ is the liquid density, kg/m^3.

Vio criterion characterizes the ratio of heat input to the surface and heat output from the surface of the body to its inner layers due to thermal conductivity [7]:

$$B_i = \frac{\beta_m \cdot l}{a_m}, \quad (11)$$

where β_m is the mass exchange coefficient divided by the moisture content difference, m/s).

Kossovich criterion shows the ratio of specific heat spent on evaporation of all moisture removed to specific heat used to heat up the moist material [6]:

$$K_o = \frac{r \cdot \Delta u}{c_T \cdot \Delta t}, \quad (12)$$

where r is the specific heat of evaporation, kJ/kg; c_T is the specific heat capacity of the moist material, kJ/kg·deg.

Fourier criterion is a measure of heat saturation of the material and characterizes the process instability and governs change of moisture field (F_{om}) or temperature field (F_{oq}) in the material with time [6, 7]:

$$F_{om} = \frac{a_m \cdot \tau}{2l} \text{ or } F_{oq} = \frac{a_q \cdot \tau}{2l} \quad (13)$$

where τ is time, s.

Rebinder criterion is the main parameter of drying kinetics determining the ratio of heat needed to heat up wet material to heat needed to evaporate moisture for infinitely small period [7, 8]:

$$Rb = \frac{c}{r}\frac{dt}{du}, \quad (14)$$

where c is the specific heat capacity of dry material, kJ/kg·deg; u is the average material moisture content, kg/kg; and t is the average material temperature, deg.

Analysis of parameters mentioned above lets us distinguish four groups of factors that influence drying: properties of liquid (ρ, r), properties of the material being dried (c_T, c, β_T, a_m, a_q), geometry of the body being dried (l), and operating drying parameters (j_m, u, t, τ, Δu, Δt). Two last factors effect irregularity in temperature fields and moisture content distribution across the material: the higher these parameters between the surface of the material and its center in the cross section, the more difficult to ensure continuity of the structure. Liquid component properties in the system influence energy consumption for its evaporation. Properties of the material being dried are characterized by its thermophysical characteristics but thermal diffusivity is more informative [7]:

$$a_w = \frac{\lambda_w}{c_{pw} \cdot \rho_w}, \quad (15)$$

where a_w is the thermal diffusivity, $m^2 \cdot s$; c_{pw} is the wet material heat capacity at constant pressure, kJ/kg·deg; ρ_w is the wet material density, kg/m; λ_w is the wet material thermal conductivity coefficient, W/m·deg; $c_{pw} \cdot \rho_w$ is the volume heat capacity, kJ/m·deg.

The thermal diffusivity in terms of physics is diffusivity of heat. According to eq. (15) and Fourier equation, molecular heat conduction q may be represented:

$$q = -a_p \cdot \rho \nabla H, \quad (16)$$

where a_p is the thermal diffusivity divided by enthalpy, and ∇H is enthalpy gradient. Here, a_P is the diffusivity of enthalpy and $c_p \cdot \rho$ characterizes heat-storage capacity of volume unit of the material. It implies that heat capacity should be determined as the sum of all volume fractions included in the wet material:

$$c_w = c_s \cdot C_s + c_G \cdot C_G + c_L \cdot C_L, \quad (17)$$

where c_G, c_S and c_L are specific heat of gas, solid and liquid phases.

It can be concluded that the thermal conductivity may be calculated in terms of additivity rule and its magnitude does not depend on mass of the material. Kirsher in his researches used follow formulas to determine the thermal conductivity coefficient [3]:

– for heat transfer along layers:

$$\lambda_{mix} = (1 - P)\lambda_S + P\lambda_L, \quad (18)$$

– for heat transfer across layers:

$$\lambda_{mix} = \frac{\lambda_S \cdot \lambda_L}{(1-P)\lambda_S + P\lambda_L}, \quad (19)$$

where P is the porosity of layer; λ_S, λ_L, λ_{mix} are thermal conductivity coefficients of solid, liquid phases and their mixture.

Such Russian scientists as K.S. Krasnov, V.A. Lotov, and B.S. Sazhin suggested various dependencies to determine the thermal conductivity coefficient for moist disperse materials. It should be noted, however, that all of them are empirical because they do not make allowance for volume phase composition compared to Kircher formula. The last takes into account volume concentrations of liquid and

solid phases, nevertheless, the results may have some error. Consequently, the thermal conductivity coefficient of disperse materials should be calculated allowing for all phases volume presented in the system being subject to drying. According to the reference data, thermal conductivity of blocked food systems is within the range from 0.1 to 0.9 W/m·deg (these values for water and air are 0.58 and 0.023 W/m·deg, respectively). Volume fraction of each phase depends on their density, for example, low mass of gas phase has low density as well and occupies more volume in the system. Also gas phase has low thermal conductivity. It means that it will offer resistance to heat transfer during drying. Therefore, thermal conductivity directly depends on each phase volume concentration and their thermal resistance. Taking into account mentioned above, the thermal conductivity coefficient equation for disperse materials will take the following form:

$$\lambda_w = \frac{C_S + C_L \,/\, 1 - C_S}{\frac{C_S \cdot \alpha_1}{\lambda_{S1}} + \frac{C_S \cdot \alpha_2}{\lambda_{S2}} + \frac{C_S \cdot \alpha_3}{\lambda_{S3}} + \frac{C_L}{\lambda_L} + \frac{C_G}{\lambda_G}} \quad (20)$$

where λ_S, λ_L, λ_G, λ_w are thermal conductivity coefficients of solid, liquid, gas phases and disperse material; and α_1, α_2, α_3 are volume concentration factors of solid phase components. All of three phases are taken into consideration in the numerator, however, if C_L = 0, it will include the ratio of solid and gas phases.

$$\alpha_1 + \alpha_2 + \alpha_3 = 1 \quad (21)$$

A number of experiments have made on a model mixture to determine the thermal conductivity coefficient to establish accuracy of eq. (20). Table 2 gives component composition of the mixture.

Table 2. Composition of studying mixture

Component	Content,%
Sugar	60
Starch	25
Chokeberry meal	15
Premixes	0.01 (above 100%)

The thermal conductivity coefficient for blocked samples with dimensions of $50 \times 50 \times 75$ mm was determined by means of the continuous plate flat source Samples were prepared using the plastic mass forming method at the pressure of 50 MPa; the moisture of the mass was 15%. After pressing, samples were subject to air drying and then inside the drier at the constant temperature of 60°C; further, samples have been cooled in the exiccator up to 20°C for 24 hours. The thermal conductivity coefficient of the dry mixture was determined experimentally; its average value was 0.0696 W/m·deg. For the wet mixture, the thermal conductivity coefficient and the heat capacity factor were calculated using eq. (18), (19) on the basis of the data represented in Table 3 and obtained by calculation and experimentally.

According to the reference data, the heat capacity of solid, liquid and gas phases were taken 0.838, 4.19 and 1.005 kJ/kg·K, respectively. The results are given in Table 4. Moisture conduction was computed from the capillary absorption coefficient K_{ci}, m^2/s:

$$W = 0.344 \cdot 10^6 K_{ci} + 0.142, \quad (22)$$

$$C_s = -0.52 \cdot K_{ci} + 0.74. \quad (23)$$

RESULTS AND DISCUSSION

We can see from Table 4 that the capillary absorption coefficient equals zero if the moisture of the mixture is less than the least capillary moisture W_{LCM} (0.142). This water can be removed by drying and Lykov criterion can be found when capillary moving water emerges, implying that $W>W_{LCM}$. If the moisture of the material is 19%, K_{ci}=1 due to the equilibrium rate of iso-concentration and isothermal surfaces. These conditions are optimal for drying. However, at W>0.19, Lu>1 implying that drying would proceed at constant rate and water diffusion rate would be higher than heat diffusion rate. Moreover, all energy supplied to the material is spent on water evaporation from the surface and energy movement from the center to the surface. It implies that when moving capillary water temperature in the center of the material would be much lower than drying temperature; the water movement process dominates. However, when capillary moving water would be removed, the temperature of the material would rise because of water evaporation from internal layers. Therefore, diffusivity dominates on this stage of drying. Figure 1 illustrates the relation between thermophysical properties and moisture content of the studied material.

Table 3. Calculated and experimental properties of studying mixture

W_i, rel.units	P_{press}, MPa	P_w, kg/m^3	P_S, kg/m^3	C_S	C_L	C_G	$\frac{C_L + C_G}{C_S}$	S_v, cm^2/cm^3	$\delta_{envelope} \times 10^{-7}$, m
0.178	18.50	2047	1738	0.690	0.309	0.001	0.449	8816	5.09
0.203	8.80	2003	1665	0.661	0.338	0.001	0.513	8446	6.07
0.228	4.45	1955	1592	0.632	0.363	0.005	0.582	8076	7.20
0.245	3.50	1919	1542	0.612	0.378	0.010	0.634	7822	8.10
0.281	1.71	1835	1433	0.569	0.403	0.028	0.757	7269	10.41
0.307	1.45	1775	1358	0.539	0.417	0.044	0.855	6889	12.41
0.325	0.96	1726	1303	0.517	0.423	0.060	0.934	6610	14.13
0.350	0.70	1652	1224	0.486	0.429	0.085	1.057	6209	17.02
0.369	0.50	1607	1174	0.466	0.433	0.101	1.145	5955	19.22

Table 4. Thermophysical properties of wet mixture

W_{abs}	p_w, kg/m^3	p_{dr}, kg/m^3	C_S	C_L	C_G	λ_w, W/m·deg	c_w, kJ/kg·deg	$a_w\times10^7$, m^2/s	$K_{ci}\times10^6$, m^2/s	Lu
0.051	1235	1156	0.630	0.079	0.290	0.140	1.150	0.206	–	–
0.082	1336	1205	0.650	0.131	0.220	0.208	1.313	0.253	–	–
0.100	1474	1304	0.690	0.170	0.140	0.376	1.510	0.369	–	–
0.121	1587	1373	0.718	0.214	0.068	0.758	1.566	0.676	–	–
0.142	1687	1328	0.740	0.260	–	1.883	1.709	1.466	0.000	0.00
0.158	1647	1368	0.716	0.279	0.005	2.028	1.774	1.550	0.046	0.30
0.181	1612	1304	0.690	0.308	0.002	1.999	1.870	1.475	0.113	0.76
0.198	1576	1250	0.670	0.327	0.003	1.822	1.934	1.324	0.162	1.22
0.218	1536	1190	0.644	0.347	0.009	1.453	2.002	1.041	0.221	2.12
0.236	1491	1130	0.620	0.361	0.019	1.102	2.051	0.789	0.273	3.46
0.252	1445	1074	0.597	0.372	0.031	0.844	2.090	0.607	0.319	5.25
0.275	1378	995	0.565	0.383	0.052	0.582	2.130	0.426	0.386	9.06
0,297	1306	916	0.533	0.391	0.076	0.415	2.161	0.312	0.450	14.42
0.319	1258	857	0.509	0.401	0.090	0.346	2.196	0.263	0.514	19.54
0.335	1182	785	0.480	0.397	0.123	0.249	2.188	0.200	0.561	28.05

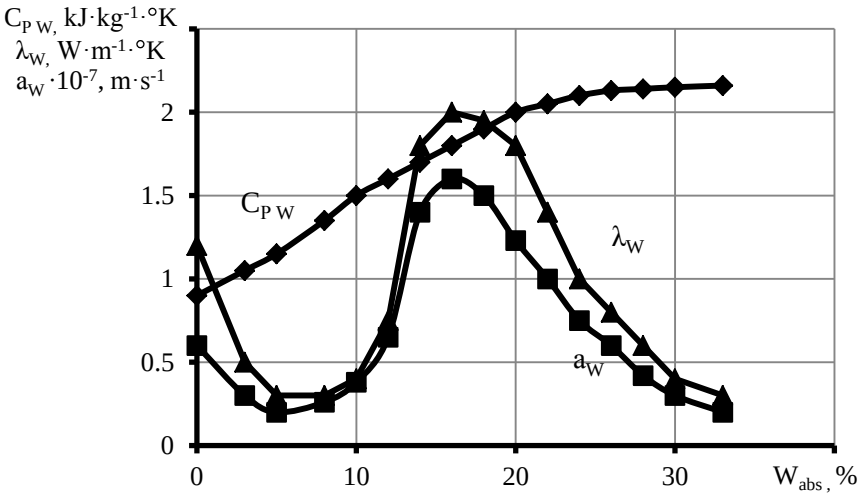


Fig. 1. Relation between thermophysical properties and moisture content of material.

According to Table 4, heat capacity of the studied mixture increases linearly up to its moisture optimal value (W = 0.24) and then heat capacity alters slightly, in spite of change in phase state of the material. This is because moisture content increases more intensively due to the fact that the liquid phase volume concentration alters more than that of solid phase since these phases have different density. Water has the highest heat capacity and with growing of hydration shells it would contribute increasing heat capacity until liquid layer thickness between particles reaches $1.5\cdot10^{-6}$ m. It should be noted that flow of the liquid takes on the property of continuity, and further increase of the liquid layer thickness has no significant effect on the heat-storage capacity of the material. Material with low moisture exhibits high thermal resistance because of gas phase presence; however, thermal conductivity of the material sharply rises up to 16% when moisture is 10–12%. For this moisture value, the thermal conductivity coefficient is higher than for all other phases. This is because of high thermal conductivity of wet materials. For the first time the phenomenon was found by M.S. Metsik: under the influence of force field in solid phase, water molecules are oriented so that the layer of tightly bound water in the form of ice-like crystalline framework is formed. We can presuppose that molecular layers of water do not exhibit significant thermal resistance because of Brownian motion absence. It follows from Fig. 1 that the material has the maximum thermal conductivity at the least capillary moisture W_{LCM} = 14.2%, i.e. when a monomolecular layer of tightly bound water takes on the property of continuity over volume of the material. For the studied mixture, we can obtain water molecule diameter at W_{LCM}-$\delta_{envelope}$ = $7\cdot10^{-7}$m using the equation for calculating the water layer thickness on the particle surface and the data from Table 4; its value is 0.276 nm. It implies that at W_{LCM} the particle surface is capable of retaining of 700/0.276 ≈ 2500 molecular layers of water. The value is relative since some water is held in capillary vessels by capillary forces but it gives general understanding of increase in the least capillary moisture which characterizes quantitative and qualitative changes in the disperse system on any stage of production process.

On the basis of findings obtained we can conclude that the use of volume phase characteristics allows the technique for determining thermophysical characteristics of dry and wet disperse systems to be improved, which in turn allows the obtained results to be more accurate. It may be used for more detailed understanding of thermal conductivity of wet materials to predict both changes in thermophysical properties and behavior of different materials during process taking into account Lykov criterion. Mentioning different materials, we mean materials including different phase contents.

REFERENCES

1. Gharsallaoui A., Roudaut G., Chambin O., Voilley A., and Saurel R. Applications of spray-drying in microencapsulation of food ingredients: An overview. *Food Research International*, vol. 40, no. 9, pp. 1107–1121. DOI: 10.1016/j.foodres.2007.07.004.
2. Zhuzhikov V.A. *Fil'trovanie* [Filtration]. Moscow: Khimiya Publ., 1961. 304 p.
3. Krischer O. *Die wissenschaftlichen Grundlagen der Trocknungstechnik*. Berlin-Gottingen-Heidelberg, 1956. 539 p. (Russ. ed.: Krischer O. *Nauchnye osnovy tekhniki sushki*. Moscow: Inlitizdat Publ., 1961. 540 p.).
4. Lotov V.A. Izmenenie fazovogo sostava sistemy tsement-voda pri gidratatsii i tverdenii [Change in the phase composition of the cement-water system during hydration and hardening]. *Izvestiya Tomskogo politekhnicheskogo universiteta. Inzhiniring georesursov* [Bulletin of the Tomsk Polytechnic University. Geo Assets Engineering], 2012, vol. 321, no. 3, pp. 42–45. (In Russian).
5. Popov A. Sistemic Regularities in the Study and Design of Technological Complexes for the Production of Instant Peverages. *Food and Raw Materials*, 2014, vol. 2, no. 2, pp. 156–160. DOI: 10.12737/547.
6. Lykov A.V. *Teoriya sushki* [Theoretic aspects of drying]. Moscow: Energiya Publ., 1968. 472 p.
7. Baklastov A.M. (ed.), Gorbenko V.A., Danilov O.L., et al. *Promyshlennye teplomassoobmennye protsessy i ustanovki* [Hear and mass transfer processes and apparatus]. Moscow: Energoatomizdat Publ., 1986. 328 p.
8. Lykov A.V. Prognoz razvitiya nauki o sushke kapillyarno-poristykh kolloidnykh tel [Forecast of the development of the science of drying capillary-porous colloidal bodies]. *Inzhenerno-fizicheskiy zhurnal* [Journal of Engineering Physics and Thermophysics], 1970, no. 4, pp. 609–616. (In Russian).
9. Rundgren K., Lyckfeldt O., and Sjöstedt M. Improving Powders with Freeze Granulation. *Ceramic Industry*, 2003, pp. 40–44.
10. Popov A.M., Makkoveev M.A., Astashenko E.B., and Chupin A.V. Identification of granulation process of instantized polydispersed products in plate granulators with activator. *Food Processing: Techniques and Technology*, 2010, vol. 17, no. 2, pp. 60–65. (In Russian).
11. Prosekov A.Yu. and Ivanova S.A. Providing food security in the existing tendencies of population growth and political and economic instability in the world. *Foods and Raw Materials*, 2016, vol. 4, no. 2, pp. 201–211. DOI: 10.21179/2308-4057-2016-2-201-211.
12. Ullah I., Wang J., Chang S.-Y., Wiley G.J., Jain N.B., and Kiang S. Moisture Activated Dry Granulation – Part I: A Guide to Excipient and Equipment Selection and Formulation Development. *Pharmaceutical Technology*, 2009, 33(11), pp. 62–70.
13. Hilker E. Behandlung trockenempfindlicher Rohstoffe. *Ziegelindustrie*, 1974, no. 8, pp. 338–345.
14. Chagin O.V, Kokina N.R., and Pastin V.V. *Oborudovanie dlya sushki pishchevykh produktov* [Drying food equipment]. Ivanovo: IGKhTU Publ., 2007. 138 p.
15. Chokshi R. and Zia H. Hot melt extrusion technique: a review. *Iranian Journal of Pharmaceutical Research*, 2004, no. 3, pp. 3–16.
16. Kozlov S.G., Prosekov A.Yu., and Sorochkina A.S. Aging of whey gels in the presence of organic colloids. *Russian Journal of Applied Chemistry*, 2004, vol. 77, no. 7, pp. 1092–1096.
17. Chizhskiy A.F. *Sushka keramicheskikh materialov i izdeliy* [Drying ceramic materials and products]. Moscow: Stroyizdat Publ., 1971. 178 p.

Please cite this article in press as: Popov A.M., Plotnikov K.B., and Donya D.V. Determination of dependence between thermophysical properties and structural-and-phase characteristics of moist materials. *Foods and Raw Materials*, 2017, vol. 5, no. 1, pp. 137–143. DOI: 10.21179/2308-4057-2017-1-137-143.

STANDARDIZATION, CERTIFICATION, QUALITY AND SAFETY

IDENTIFICATION OF AROMATIC ALDEHYDES IN THE EXPRESS ASSESSMENT OF QUALITY OF HERBAL DISTILLED DRINKS

E. Yu. Egorova[a,*], Yu. V. Morozhenko[a], and I. Yu. Reznichenko[b]

[a] Polzunov Altai State Technical University,
Lenina Ave. 46, Barnaul, 656038, Russian Federation

[b] Kemerovo Institute of Food Science and Technology (University),
Stroiteley blvd. 47, Kemerovo, 650056, Russian Federation

* e-mail: egorovaeyu@mail.ru

Received January 23, 2017; Accepted in revised form March 10, 2017; Published June 29, 2017

Abstract: Despite a long study of main types of the herbs used in the Russian alcoholic beverage production, the structure of the components participating in the formation of "bouquet" of the alcoholic beverages obtained on their basis has not been studied yet. A study of content of aromatic aldehydes characteristic of distilled drinks in aqueous-alcoholic extracts of shell of pine nuts, common St. John's wort herb and wild camomile flowers, and also in the distilled drink simulated on the basis of these extracts became the purpose of this work. The raw materials obtained from the plants growing in the Altai Territory and the Altai Republic of the Russian Federation have been used for this work. The extracts were obtained by infusing the air and dry raw materials of the corresponding type in the 40% water solution of ethyl alcohol within 15 days at a temperature of 20 ± 2°C, with periodic agitation of extraction mixture, separation of extract by decantation and cleaning with filtering. The identification and quantitative determination of aromatic aldehydes were performed using the system of capillary electrophoresis "Kapel'-105M". By the results of studies it has been established that the extracts differ, as for the content of aromatic aldehydes, both from the freshly obtained oak extracts and from the aged cognac distillates. A content of aldehydes has been revealed in the extracts of wild camomile flowers and St. John's wort herb at a level equal and higher than in the extract of shell of pine nuts within the total limits for the three considered extracts of, mg/dm^3: for vanillin – from 18.5 to 96.4, for syringic aldehyde – from 8.5 to 19.4, for sinapic aldehyde – from 9.6 to 17.5, for coniferylic aldehyde – from 22.0 to 47.9. There is no direct correlation between the content of aromatic aldehydes in the imitated distilled drink and the content of these aldehydes in the initial extracts. The obtained data on the content of aromatic aldehydes in the nuts and herbs extracts are one of the evidence of similarity of the processes proceeding when obtaining these extracts and the processes that are the basis of technology of cognacs. In future, the obtained data can be put in a basis of techniques of express control of readiness of extracts and authenticity of new drinks in merchandising and technological practice.

Keywords: Alcoholic beverage products, cognacs, brandy, extracts of vegetable raw materials, pine (cedar) nuts, wild camomile, common St. John's wort, aromatic aldehydes, identification criteria

DOI 10.21179/2308-4057-2017-1-144-153 *Foods and Raw Materials*, 2017, vol. 5, no. 1, pp. 144–153.

INTRODUCTION

A natural consequence of development of the world consumer market of alcoholic products is the increase in the share of the forged drinks and the related search of new ways of prevention of possibility of realization of counterfeits. As for distilled drinks (cognacs, brandy, whisky etc.), this problem has managed to become a global trend as the market of these drinks mostly depends on the state of world economy and is rather unstable [1–3].

Distilled drinks are produced by means of the "enrichment" of distillates of grape wine, fermented fruit juices or aqueous-alcoholic infusions of vegetable raw materials. Such drinks are naturally enriched with volatile aromatic components – the products of biochemical and physical and chemical transformations of polyphenolic substances of vegetable raw materials (for the majority of distillates – oak wood) which considerably distinguishes them from other drinks with a high content of ethyl alcohol.

According to foreign experts, today the share of the forged production grows quicker than the alcohol market develops [4]. This relates to the fact that for the identification of cases of falsification and identification of authenticity of kind, age and the region of origin of the most branded distilled drinks the most modern

methods are applied: thin-layer [5], highly effective liquid [6, 7] and gas-liquid chromatography [8, 9], spectrophotometry [10], fluorescent [11] and chromatic mass spectrometry [12–14] and capillary electrophoresis [15, 16]. The existence and levels of content of such components of structure of drinks as highly volatile ethers [2, 12, 17], tannins and phenolic acids [2, 8], aromatic aldehydes [2, 5, 7, 16] and some ketones, aldehydes, alcohols and low-molecular volatile acids [12, 17–19] characteristic of distilled drinks are considered as the valid and potential criteria of authenticity. As one of the express methods of identification of the forged production it is also offered to use the dependence between the light absorption of test specimen in the infrared spectrum and a concrete type of drink – cognac, armagnac, brandy and others [10].

When searching new approaches to the assessment of authenticity and quality of alcoholic beverages the main attention has been paid for many years to the so-called aged distillates (cognacs, brandy, Calvados, whisky) – the most expensive drinks in the considered segment. The composition of aromatic components of cognacs and brandy as most known and popular drinks with consumers, has been studied in most detail: the main dependences of qualitative structure of aromatic components on the grade and the region of origin of wine material, on the duration of its contact with oak wood or oak staff have been described [17, 20]. Attempts to define the list of the most important substances forming the aromatic profile – the so-called "skeleton of aroma" of drinks [12, 18] have been made. In recent years great importance has been attached also to the search of methods of confirmation of authenticity for other distilled drinks: sherry, whisky, aromatic alcohols of juniper, tequila, mescal, absinthe, vermouths and some other drinks [21–26]. Studies concerning the further improvement of methods of control and identification of drinks fermented on the basis of vegetable raw materials [27, 28] also continue.

A feature of alcohol branch in Russia is the use of distilled drinks of more various vegetable raw materials (including wild-growing raw materials) in production, mainly in the form of extracts and infusions of the flowers, herbs and roots rich with polyphenolic compounds and ethereal oils. In this regard, most often extracts of pine nuts (*Pinussibirica Du Tour*) or their shell, extracts of wild camomile flowers (*Chamomílla recutita (L.) Rauschert*), common St. John's wort herb (*Hypéricum perforatum L.*) and some other species of the plants, wild-growing and those which are specially cultivated for this purpose, are used.

The frequency of application of alcoholic beverages of pine nuts, camomile and common St. John's wort in domestic production is in many respects caused by the fact that the extracts on their basis allow to "smooth" the sharp taste and smell of ethyl alcohol in drinks and to give a characteristic color tone and gloss close to cognac to the finished goods. In turn, the composition of volatile components of these raw materials provides the unique identity of aroma of the obtained drinks.

The analysis of literary data shows that the chemical composition of pine nuts (shell and perikernel film) is slightly similar to oak wood as for the content of polyphenolic substances and lignin [29]. According to the classical technology of cognac production, it is the most important extractive substances that go through hydrolysis and ethanolysis to aromatic aldehydes in the course of ageing cognac materials and necessary for the formation of unique "bouquet" of cognac wine materials and ready-for-use drinks. Besides, as it is noted in some works, there are compounds in the structure of aromatic components of cognacs – in particular, scopoletin, that give a resinous cedar shade of "old" drink to the "bouquet" and a taste of the aged cognacs [30, 31]. The noted data explain to some extent the range of application of pine nuts in the production of Russian alcohol products and cause the theoretical possibility of their use when obtaining the drinks similar to cognac distillates [32, 33].

When studying the properties and composition structure of volatile components of aqueous-alcoholic extracts of wild camomile flowers and common St. John's wort herb the main attention is traditionally paid to the composition of terpens and the polyphenolic compounds various in structure and properties. Among terpenes and polyphenolic compounds, the flavonoids, phenolic acids and anthracene derivatives [34–37] causing the therapeutic properties of the medicinal and cosmetic preparations produced on the basis of these plants by a lot of Russian enterprises are considered to be the most important ones. However the literary data on the existence of aliphatic alcohols, aldehydes, ketones and average esters in the composition of extracts of wild camomile flowers and common St. John's wort herb allow to assume a possibility of formation of more complex compounds including those which have an aromatic molecular structure in the course of extraction, as well.

It is necessary to know the content of the most characteristic compounds the number of which in the drink can also change with its age to authenticate the falsification of a drink.

When authenticating cognac production the confirmation of duration of contact with oak wood determined by the results of analysis of volatile and nonvolatile components is considered to be the major feature.

The main processes in the formation of the volatile compounds characteristic of cognac distillates and necessary for the formation of the "bouquet" typical for cognacs and brandy, include the processes of oxidation of tannins and lignin.

Aromatic aldehydes (Fig. 1) and the products of their subsequent oxidation – aromatic acids – make up to 30% of the polyphenolic complex of cognac distillates and the cognacs aged in contact with oak wood. At the same time, the content of vanillin in cognacs can vary from 0.2 to 2.4 mg/dm^3, the content of sinapic and coniferylic aldehydes is 0.3–2.4 mg/dm^3 and 0.3–2.6 mg/dm^3 respectively. The content of syringic aldehyde – to 7.8 mg/dm^3 of drink [38] can be the most considerable.

The data on the composition of aromatic aldehydes in the aqueous-alcoholic infusions and extracts on the basis of pine nuts or their shell, wild camomile flowers,

common St. John's wort herb and many other types of the vegetable raw materials traditional for domestic alcoholic beverage products, are not available in Russian and foreign literature. In this regard a study of aromatic aldehydes in the extracts obtained from the types of vegetable raw materials which are most popular with the industry and an assessment of the possibility use of these data in merchandising and technological practice for the identification and control of quality of drinks on the basis of such extracts seem appropriate.

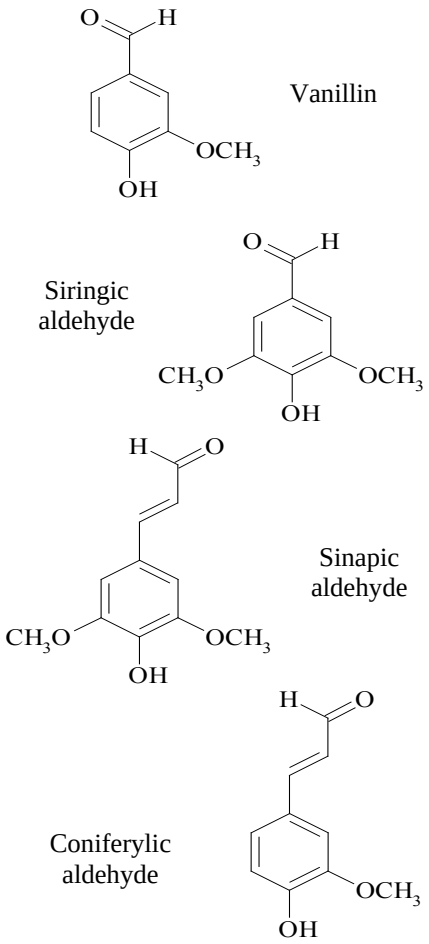


Fig. 1. Characteristic aromatic aldehydes of cognac distillates.

The purpose of work is the research of composition and content of the main aromatic aldehydes in the aqueous-alcoholic extracts of shell of pine nuts, wild camomile flowers and common St. John's wort herb for the identification of these substances in the composition of new distilled drinks.

The following tasks act as solvable in the work:
– the systematization of literary data on the content of aromatic aldehydes in cognac distillates;
– the determination of content of aromatic aldehydes in the composition of aqueous-alcoholic extracts of shell of pine nuts, wild camomile flowers and common St. John's wort herb and the comparative analysis of the obtained results with the literary data on cognac wine materials;
– the assessment of possibility of use of the data on the content of aromatic aldehydes in the studied aqueous-alcoholic extracts in merchandising and technological practice of identification and control of quality of distilled drinks of various producers.

OBJECTS AND METHODS OF STUDY

The following is used as the **study object**:
– raw materials – the pine nuts prepared in the cedar forests of the Republic of Altai (*Pinus sibirica Du Tour*) and their shell, wild camomile flowers (*Chamomílla recutita (L.) Rauschert*) and common St. John's wort herb (*Hypéricum perforatum L.*) prepared in the Biysk district of Altai Krai;
– the aqueous-alcoholic (40% vol.) extracts of shell of pine nuts, wild camomile flowers and common St. John's wort herb;
– the imitation of distilled drink – the blend made by mixing of the obtained aqueous-alcoholic extracts of shell of pine nuts, wild camomile flowers and common St. John's wort herb according to the receipt given below.

Study methods. Methods of data collection and processing, of comparative analysis and systematization of information from scientific publications and periodicals were used when studying the literary data.

The aqueous-alcoholic extracts of shell of pine nuts, wild camomile flowers and common St. John's wort herb were obtained infusing the air and dry raw materials of the corresponding type in the 40% aqueous solution of ethyl rectified alcohol within 15 days (the conditions of extraction had been chosen earlier, by the results of preliminary studies [39]) at a temperature of 20 ± 2°C, with periodic shaking of the extraction mixture and the separation of the obtained infusion (extract) by decantation with the subsequent filtering through the paper filter of the brand "White Ribbon". The ratio raw materials : extragent was chosen by the results of patent search and was 1 : 3 during the extraction of shell of pine nuts, and 1 : 10 for wild camomile flowers and common St. John's wort herb.

The experimental blend of aqueous-alcoholic extracts – an imitation of distilled drink – was prepared by mixing of individual extracts in the ratios providing a characteristic golden and cognac color with "gloss" (see Photo 1) and the aroma of drink close to the cognac one.

Photo 1. Drink with an experimental composition.

The receipt of experimental blend:
– an extract of shell of pine nuts – 91.2 dL;
– an extract of wild camomile flowers – 25.4 dL;
– an extract of common St. John's wort herb – 12.4 dL;
– a water solution of ethyl rectified alcohol, 40% vol. – 871 dL.

The total of tannins in the extracts of shell of pine nuts, wild camomile flowers and common St. John's wort herb was determined in terms of gallic acid according to the method of HPLC using the chromatograph "Waters-Alliance" (USA) with a spectrophotometric detector M 2998.

The identification and quantitative determination of aromatic aldehydes in the individual extracts of shell of pine nuts, wild camomile flowers and common St. John's wort herb were performed in 3 weeks after preparation using the technique M 04–53–2008 [40] based on the system of capillary electrophoresis "Kapel'-105M" (Russia) in the mode of direct detecting with the use of universal borax buffer (0.02 M solution).

The injection of test specimen was performed under conditions recommended by the technique [40]: under the pressure of 30 Mbar for 20 sec. Analysis conditions: the wavelength is 373 nanometers, the temperature is 20°C, the voltage is +25 kV; the analysis duration is 10 minutes.

Characteristics of the capillary: the internal diameter is 75 microns, the effective length is 50 cm, the total length is 60 cm. Calculation method: absolute calibration with the use of standard samples of vanillin, sinapic, coniferylic and syringic aldehydes (the standards of Aldrich, Fluka). The identification of peaks was performed using the method of addition of standard samples.

Under similar conditions the analysis of experimental blend of aqueous-alcoholic extracts was performed, also in 3 weeks after its preparation.

The studies were repeated 3–4 times. The processing of experimental data was performed with the use of IBM PC with the Elforan software (Lumex Group).

RESULTS AND DISCUSSION

According to the literary data, the accumulation of aromatic aldehydes in the distilled drinks like cognac, brandy and whisky is determined by the degree and rate of degradation of lignin of oak wood. It is shown that the maximum rate of decay of lignin is in the distillates with the content of ethyl alcohol of 80% vol.**,** but the maximum concentration of aromatic aldehydes has been recorded in the distillates with the content of ethanol of 65% vol. [38].

At the initial stages of ageing of cognac alcohols there are processes of hydrolysis and ethanolysis of lignin with the transition to the aqueous-alcoholic solution of extractive substances and the formation of sinapic and coniferylic aldehydes. Afterwards there is a process of "saturation of ethylenic bonds" and the formation of syringic aldehyde and vanillin the further oxidation of which produces syringic and vanillic acids [41]. The described sequence of stages is also confirmed during lignin oxidation by chemical means [42]. And if the content of highly volatile aromatic volatile compounds – aliphatic alcohols, ethyl aldehyde, volatile acids and esters – depends in many respects on the ampelography of the grapes [17] processed for alcohol, then the content of aromatic aldehydes in cognac wine materials is substantially interrelated with the type and geography of growth of oak [43, 44] as the source of the extractive substances which are transformed to aromatic components of cognacs in the course of their ageing.

In cognac wine materials all aromatic aldehydes begin to collect during their first year of ageing in contact with oak wood, with a steady tendency to the accumulation of their total content with an increase in the ageing period. It is offered to use the intensity of the chromatographic peak of the syringic aldehyde prevailing in the composition of aromatic aldehydes, that reflects its concentration and is in direct correlation with ageing duration as the "age index" of cognacs and brandy. The value of this index, as a rule, does not exceed 1 for ordinary cognacs and brandy, and it can reach 9 for branded and collection ones [6].

The nature of accumulation of individual aldehydes is considered a feature of no less importance: for vanillin, coniferylic and syringic aldehydes an exact dynamics has been established that reflects a continuous increase in their concentration to a certain age of cognac alcohol after which a reverse trend of slow decrease is observed [1]. One of the natural consequences of these processes is the change of ratio of syringic aldehyde and vanillin in the course of ageing of distillate reaching 2–4 for collection cognacs [6].

Despite long studies in this regard, the published literary data on the content and ratio of aromatic aldehydes in cognacs and cognac semi-finished products are still rather contradictory. The information on the content of vanillin in cognacs and cognac distillates and the possible dependence of content of total and individual aromatic aldehydes, as well as the products of their further oxidation, on the duration of ageing and concentration of distillate (Table 1) is especially ambiguous.

For other drinks of the group of distillates data on the regularities of accumulation of aromatic aldehydes are not provided in scientific literature. At the same time, when obtaining infusions and extracts of vegetable raw materials for blends of alcoholic beverage products in Russia lower concentrations of ethyl alcohol, within 35–50% vol., are used. The choice of extragents in such concentrations is caused by the fact that in these conditions the maximum of the polyphenols [32, 33] that give an attractive color to the extracts and have at the same time a high antioxidant activity are derived [45].

Table 1. Content of phenolic substances and aromatic aldehydes in the aqueous-alcoholic extractsof oak wood and the cognac distillates of different ageing periods (the ageing from 2.5 to 15 years)

Aldehyde	Concentration of aldehydes / Data source					
	in cognac distillates					in extracts, mg/g of raw materials [43]
	[6]	[7]	[16]	[30]*	[38]	
Total of phenolic substances, g/dm^3	not applicable			0.398–1.013	not applicable	29.3–116.8
Vanillin, mg/dm^3	(peak areas in the HPLC)	0.1–1.6	0.19–2.41	2.053–3.953	0.2–2.4	0.013–0.80
Siringic aldehyde, mg/dm^3		0.2–2.8	0.63–7.84	2.275–7.533	up to 7.8	0.008–0.20
Sinapic aldehyde, mg/dm^3		0.5–2.4	0.33–0.87	not applicable	0.3–2.4	0.14–0.88
Coniferylic aldehyde, mg/dm^3		0.9–2.6	0.26–0.79	0.587–1.668	0.3–2.6	0.007–0.66
Syringic aldehyde / vanillin ratio	2–4 : 1	2 : 1	2–4 : 1	1.5–2.5 : 1	2–4 : 1	1 : 2–3

Note. * Data are provided for waterless alcohol.

When receiving extracts from the studied raw materials it is necessary to consider the features of their morphology. The features of morphology of the considered raw materials consist in the following:
– the shell of pine nuts needs 1 year to be formed and is rich with lignin, as well as oak wood is;
– camomile flowers need no more than one month to be formed and are not rich with lignin;
– common St. John's wort herb and blooms need from two to three months to accumulate lignin before the end of blossom time.

Taking into account the features of morphology of the considered raw materials, it is possible to assume that the rate of stages of degradation of lignin and accumulation of aromatic compounds under conditions of receiving extracts from the shell of pine nuts, wild camomile flowers and common St. John's wort herb should be the same (for example, in the extracts of shell of pine nuts), or higher than that of the similar processes in cognac wine materials.

It is also possible to assume the participation of the polyphenolic compounds of extracts of nuts and herbs with a lower molecular weight which constitute more than 50% of extractive substances of these raw materials in the processes of hydrolysis, ethanolysis and oxidation [32, 36, 46]. In particular – tannins (Table 2) with the prevalence of hydrolyzed substances which are part of them [37, 47]. Therefore, it is possible to predict both the equal, and a higher content of aromatic aldehydes in the studied extracts and various alcoholic beverages made on their basis.

The electrophoregrams given in Figures 1–3 show the composition of aromatic aldehydes in the aqueous-alcoholic extracts of shell of pine nuts, wild camomile flowers and common St. John's wort herb. The analysis of electrophoregrams and the comparison of the obtained results (Table 3) to the literary data shows that the content of aromatic aldehydes in the undiluted extracts exceeds the levels of content of the corresponding aldehydes in the cognac distillates of different ages (Table 1).

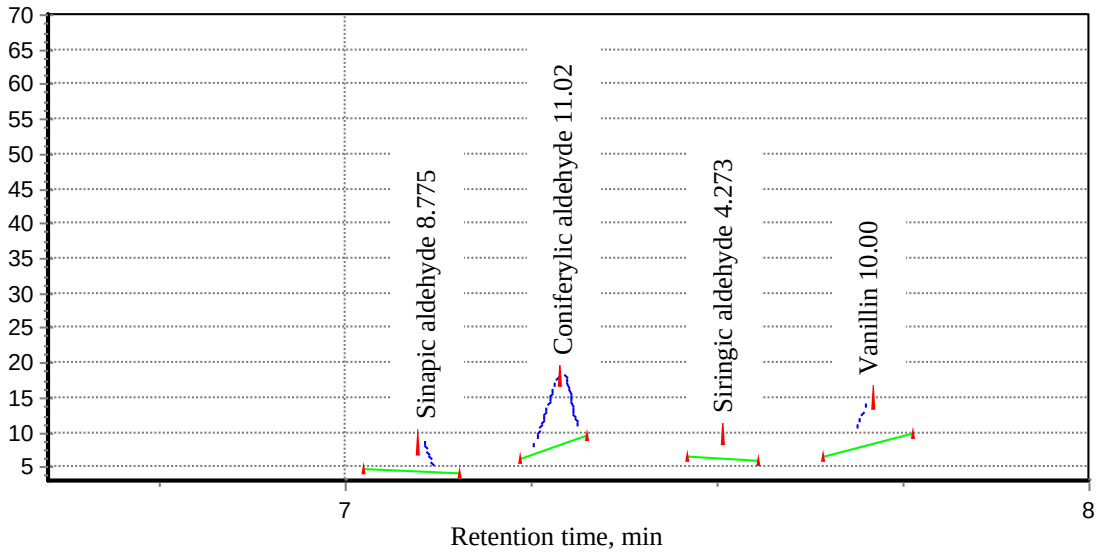


Fig. 1. Electrophoregram of aqueous-alcoholic extract of shell of pine nuts (2-time dilution).

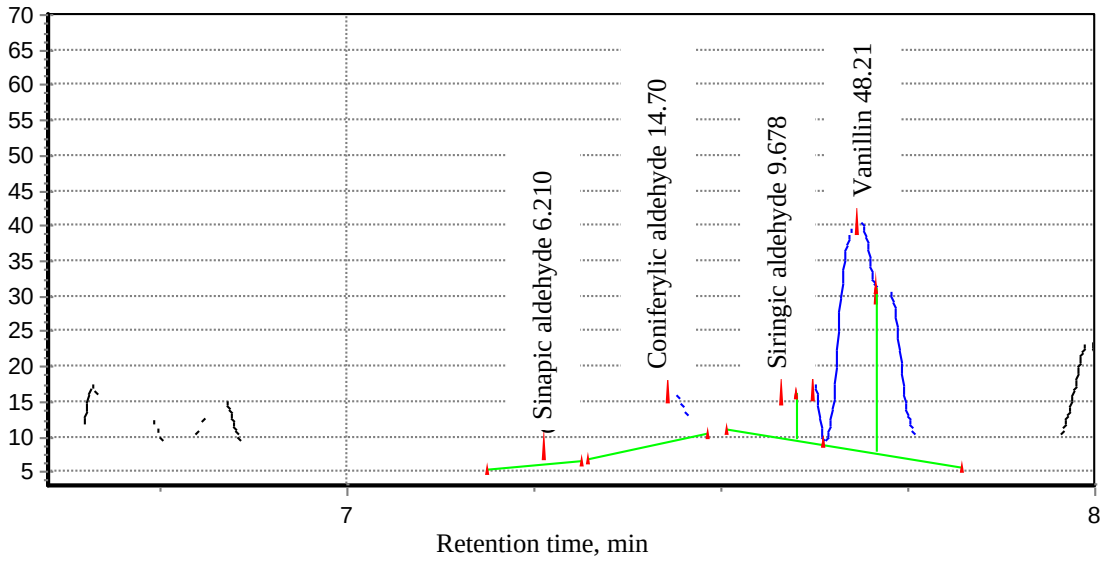


Fig. 2. Electrophoregram of aqueous-alcoholic extract of wild camomile flowers (2-time dilution).

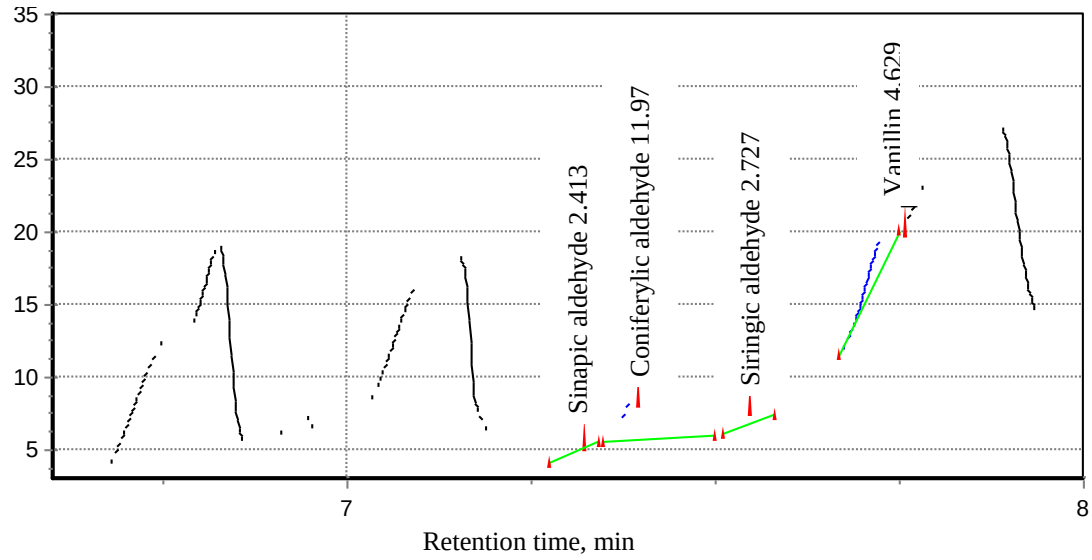


Fig. 3. Electrophoregram of aqueous-alcoholic extract of common St. John's wort herb (4-time dilution).

Table 2. Content of total of tannins in the extracts of shell of pine nuts, wild camomile flowers and common St. John's wort herb

Extract	Content of total of tannins	
	Data of the authors of the article, mg/dm^3 of the extract	Reference data [Source]
Pinus sibirica shell	0.07 ± 0.01	1.5–3.0% in the extract [29]
Hypéricum perforatum herbs	0.48 ± 0.05	10.3–12% in the raw materials [37]
Chamomílla recutita flowers	0.34 ± 0.04	not applicable

No doubt, the choice of extraction module with an increase of which a higher gradient of concentration of lignin containing material on the surface and, respectively, a higher speed of biochemical processes of hydrolysis and the subsequent oxidation of extractive polyphenolic substances is provided is of great importance in the achievement of similar levels of content of aromatic substances in extracts.

It is authentically established that, as for four analyzed aromatic aldehydes, all the three extracts differ both from the freshly obtained oak wood extracts [43], and from the aged cognac distillates. Despite the forecasts, a content of aldehydes at the level equal or even higher than in the extract of shell of pine nuts has been revealed in the extracts of wild camomile flowers and common St. John's wort herb. Vanillin is the strongly prevailing aldehyde in the composition of extract of wild camomile flowers (96.42 ± 9.64 mg/dm^3), the ratio of syringic aldehyde : vanillin in the extract shifts to 1:5. In the extract of

common St. John's wort herb, on the contrary, a predecessor of vanillin – coniferylic aldehyde (47.88 ± 4.80 mg/dm^3) prevails.

The extract of shell of pine nuts for which the established ratio of syringic aldehyde : vanillin is mostly approximated to the corresponding value for cognac distillates and is 1:2.3 can be considered the most balanced as for the ratio of the noted aromatic aldehydes.

It is also necessary to note that there is no direct correlation between the content of aromatic aldehydes in the experimental mixture of extracts – an imitation of distilled drink (Fig. 4) and the content of these aldehydes in the initial extracts (Table 3). Presumably, processes of the second oxidation stage, with the formation of products of oxidation of aromatic aldehydes, first of all – vanillin which is formed of coniferylic aldehyde continued in the simulated drink within three weeks before performing an electrophoretic study.

As an alternative hypothesis, it is also possible to consider the oxidation of aromatic aldehydes to syringic and vanillic acids continuing in the blend. In particular, the actual concentration of syringic aldehyde in the experimental blend is the basis of the similar hypothesis. At the same time, this hypothesis demands additional instrument-based confirmation – a study of composition of aromatic acids in the individual extracts and the experimental blend.

It is known that vanillin and syringic aldehyde have a more characteristic and intensive aroma than their predecessors – coniferylic and sinapic aldehydes, and give pleasant vanilla tones to drinks [38]. The threshold concentration of smell with the concentration of ethyl alcohol in the drink of 40% vol. for vanillin is 0.01 mg/dm^3, and the threshold of taste in cognac alcohols is 0.1 mg/dm^3. The increase in the concentration of vanillin to 30 mg/dm^3 provides the distortion and deterioration in the taste and aroma of drink. The threshold concentration of aroma and taste for coniferylic aldehyde is 3 and 10 mg/dm^3 respectively, for syringic aldehyde is 50 and 100 mg/dm^3. Sinapic aldehyde can be felt only with the concentration of no less than 200 mg/dm^3 [38]. Therefore, taking into account the obtained results and threshold concentrations of taste and smell of individual aromatic aldehydes, the aqueous-alcoholic extracts of the vegetable raw materials considered in the work can be used for the direct simulation of taste and "bouquet" of alcoholic beverages.

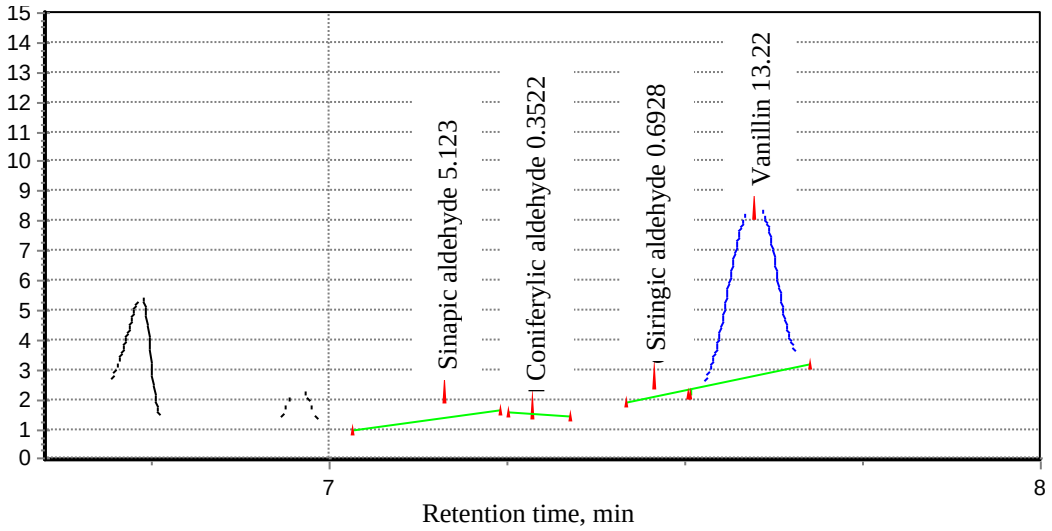


Fig. 4. Electrophoregram of experimental mixture of extracts – imitation of distilled drink.

Table 3. Content of characteristic aromatic aldehydes in the aqueous-alcoholic extracts of vegetable raw materials and the experimental blend (an imitation of distilled drink)

Aldehyde	Concentration of aldehydes, mg/dm^3				
	in aqueous-alcoholic extracts			in a blend of extracts	
	Pinus sibirica shell	*Chamomílla recutita* flowers	*Hypéricum perforatum* herbs	design*	actual
Vanillin	20.00 ± 1.95	96.42 ± 9.64	18.52 ± 1.85	4.51 ± 0.45	13.22 ± 1.30
Syringic aldehyde	8.55 ± 0.90	19.36 ± 1.94	10.91 ± 1.10	1.41 ± 0.15	0.69 ± 0.14
Sinapic aldehyde	17.55 ± 1.80	12.42 ± 1.24	9.65 ± 1.00	2.03 ± 0.20	5.12 ± 0.62
Coniferylic aldehyde	22.04 ± 2.20	29.40 ± 2.94	47.88 ± 4.80	3.35 ± 0.32	0.35 ± 0.03
Syringic aldehyde / vanillin ratio	1 : 2.3	1 : 5	1 : 1.7	1 : 3.2	1 : 19

Note. * The value is calculated on the basis of experimental data on the content of aromatic aldehydes in individual extracts taking into account their prescription dosage when obtaining a blend (see Study methods).

Taking into account that in the course of storage of distilled drinks the hydrolysis and oxidation of polyphenolic compounds and aromatic aldehydes continue, it is possible in our case to predict a further increase in the content of syringic aldehyde and vanillin in the drinks on the basis of the extracts considered in this article. The character and dynamics of these processes demand a further study.

CONCLUSIONS AND RECOMMENDATIONS

The obtained data on the content of aromatic aldehydes in the extracts are one of the evidence of similarity of the processes proceeding when receiving extracts from nuts and herbs, and the processes making a basis of technology of cognac production. The submitted data on the content of aromatic aldehydes in the considered extracts can be used for the direct simulation of "bouquet" of distilled drinks on their basis [48]. In the long term, the obtained data can be put in a basis of techniques of technological express control of readiness of aqueous-alcoholic extracts and authenticity of new drinks in investigation practice.

The existence of four characteristic aromatic aldehydes and other volatile components inherent in cognac production in the composition of the studied extracts testifies to a potential possibility of substitution of cognac distillates to cheaper raw components. In this regard there is a need of collection of information and formation of special statistical database on the structure and content of aromatic aldehydes in extracts and finished goods on the basis of vegetable raw materials which are widely used by Russian enterprises when producing drinks of the distillates group.

REFERENCES

1. Oseledtseva I.V., Guguchkina T.I., and Sobolev E.M. Practical realization of modern ways for determination authenticity of brandy production. *News institutes of higher Education. Food technology*, 2010, no. 2–3, pp. 104–107. (In Russian).
2. Delgado R., Durán E., Castro R., et al. Development of a stir bar sorptive extraction method coupled to gas chromatography-mass spectrometry for the analysis of volatile compounds in Sherry brandy. *Analytica Chimica Acta*, 2010, no. 672 (1–2), pp. 130–136. DOI: https://doi.org/10.1016/j.aca.2010.05.015.
3. *Cognac supplement. Essense of france*. Drinks International (drinksint.com). Zurich House, 2011. 34 p.
4. Von Gesche Wüpper. Die Furcht der Franzosen vor der russischen Cognac-Mafia. *Welt-zeitung*. 17.05.2009.
5. Butskiy K.N. Vozmozhnost' kachestvennoy identifikatsii aromaticheskikh al'degidov metodom tonkosloynoy khromatografii [The possibility of quality identification of aromatic aldehydes using the method of thin-layer chromatography]. *Kriminalistichniy visnik* [Criminal bulletin], 2013, no. 1 (19), pp. 196–202.
6. Kochetova M.V., Larionov O.G., and Ulyanova E.V. The investigation of qualytative composition of cognacs by HPLC. *Sorption and chromatographic processes*, 2008, vol. 8, no. 4, pp. 658–667. (In Russian).
7. Nezalzova E. High-performance liquid chromatography for determination of aromatic aldehydes in wine distillates. *Chemistry Journal of Moldova.* 2011, vol. 6, no. 1, pp. 81–85. DOI: dx.doi.org/10.19261/cjm.2011.06(1).06.
8. Oseledtseva I.V. and Guguchkina T.I. Correlations between Levels of Characteristic Extractive Ingredients in Cognacs and Related Products. *Winemaking and viticulture*, 2011, no. 6, pp. 18–22. (In Russian).
9. Ledauphin J., Le Milbeau C., Barillier D., and Hennequin D. Differences in the volatile compositions of french labeled brandies (Armagnac, Calvados, Cognac, and Mirabelle) using GC-MS and PLS-DA. *Journal of Agricultural and Food Chemistry*. 2010, vol. 58, no. 13, pp. 7782–7793. DOI: 10.1021/jf9045667.
10. Picque D., Lieben P., Corrieu G., et al. Discrimination of cognacs and other distilled drinks by mid-infrared spectropscopy. *Journal of Agricultural and Food Chemistry*, 2006, vol. 54, no. 15, pp. 5220–5226. DOI: 10.1021/jf060465u.
11. Sádecká J., Tóthová J., and Májek P. Classification of brandies and wine distillates using front face fluorescence spectroscopy. *Food Chemistry*, 2009, vol. 117, no. 3, pp. 491–498. DOI: 10.1016/j.foodchem.2009.04.053.
12. Ledauphin J., Saint-Clair J.F., Lablanquie O., et al. Identification of trace volatile compounds in freshly distilled Calvados and Cognac using preparative separations coupled with gas chromatography-mass spectrometry. *Journal of Agricultural and Food Chemistry*, 2004, vol. 52, no. 16, pp. 5124–5134. DOI: 10.1021/jf040052y.
13. Sarvarova N.N., Cherkashina Yu.A., and Evgen′ev M.I. Application of chromatographic methods to the determination of cognac quality indicators. *Journal of Analytical Chemistry*, 2011, vo. 66, no.12, pp. 1190–1195. DOI: 10.1134/S1061934811120094.
14. Zhao Y., Xu Y., Li J., et al. Profile of volatile compounds in 11 brandies by headspace solid-phase microextraction followed by gas chromatography-mass spectrometry. *Journal of Food Science*, 2009, vol. 74, no. 2, pp. 90–99. DOI: 10.1111/j.1750-3841.2008.01029.x.
15. Gun'kin I.N. *Otsenka kachestva kon'yakov elektroforeticheskim i spektroskopicheskim metodami* [Assessment of quality of cognacs using electrophoretic and spectroscopic methods]. Cand. chem. sci. thesis. Krasnodar, 2010. 23 p.
16. Panossian A., Mamikonyan G., Torosyan M., et al. Analysis of aromatic aldehydes in brandy and wine by high-performance capillary electrophoresis. *Analytical Chemistry*, 2001, vol. 73, no. 17, pp. 4379–4383. DOI: 10.1021/ac0014818.
17. Oseledzeva I.V. and Kirpicheva L.S. Assessment of the influence of long factor on variation of parameters of the factions volatile cognac wine materials and young brandy distillate. *Agricultural Bulletin of Stavropol Region*, 2015, no. 1 (17), pp. 246–252. (In Russian).

18. Ferrari G., Lablanquie O., Cantagrel R., et al. Determination of key odorant compounds in freshly distilled cognac using GC-O, GC-MS, and sensory evaluation. *Journal of Agricultural and Food Chemistry*, 2004, vol. 52 (18), pp. 5670–5676. DOI: 10.1021/jf049512d.
19. Savchuk S.A. and Kolesov G.M. Chromatographic determination of fhthalic acid esters as an indicator of adulterated cognacs and cognac spirits. *Journal of Analytical Chemistry*, 2007, vol. 62, no. 8, pp. 761–772. DOI: 10.1134/S1061934807080126.
20. Malfondet N., Gourrat K., Le Quéré J.-L., Brunerie P. Aroma characterization of freshly-distilled french brandies; their specificity and variability within a limited geographic area. *Flavour and Fragrance Journal*, 2016, no. 31 (5), pp. 361–376.
21. Rodríguez Dodero M.C., Guillén Sánchez D.A., Schwarz Rodríguez M., and García Barroso C. Phenolic compounds and furanic derivatives in the characterization and quality control of brandy de Jerez. *Journal of Agricultural and Food Chemistry*, 2010, vol. 58 (2), pp. 990–997. DOI: 10.1021/jf902965p.
22. Mignani A.G., Ciaccheri L., Gordillo B., et al. Identifying the production region of single-malt Scotch whiskies using optical spectroscopy and pattern recognition techniques. *Sensors and Actuators B: Chemical*, 2012, vol. 171–172, pp. 458–462. DOI: https://doi.org/10.1016/j.snb.2012.05.011.
23. Sádecká J., Uríčková V., Hroboňová K., and Májek P. Classification of juniper-flavoured spirit drinks by multivariate analysis of spectroscopic and chromatographic data. *Food Analytical Methods*, 2015, vol. 8, no. 1, pp. 58–69. DOI: 10.1007/s12161-014-9869-8.
24. Magana A.A., Wrobel K., Elguera J.C.T. et al. Determination of small phenolic compounds in tequila by liquid chromatography with ion trap mass spectrometry detection. *Food Analytical Methods*, 2015, vol. 8, no. 4, pp. 864–872. DOI: 10.1007/s12161-014-9967-7.
25. Avila-Reyes J.A., Almaraz-Abarca N., Delgado-Alvarado E.A., et al. Phenol profile and antioxidant capacity of mescal aged in oak wood barrels. *Food Research International*, 2010, vol. 43, no. 1, pp. 296–300. DOI: https://doi.org/10.1016/j.foodres.2009.10.002.
26. Wiśniewska P., Śliwińska M., Dymerski T., et al. Application of gas chromatography to analysis of spirit-based alcoholic beverages. *Critical Reviews in Analytical Chemistry*, 2015, vol. 45, no. 3, pp. 201–225. DOI: 10.1080/10408347.2014.904732.
27. Krasnova T.A., Gora N.V., and Golubeva N.S. Beer quality assurance by controlling wort polyphenolic content with adsorption method. *Foods and Raw materials*, 2016, vol. 4, no. 1, pp. 36–43. DOI: 10.21179/2308-4057-2016-1-36-43.
28. Campo E., Cacho J., and Ferreira V. Solid phase extraction, multidimensional gas chromatography-mass spectrometry determination of four novel aroma powerful ethyl esters: Assessment of their occurrence and importance in wine and other alcoholic beverages. *Journal of Chromatography A*, 2007, vol. 1140, no. 1–2, pp. 180–188. DOI: 10.1016/j.chroma.2006.11.036.
29. Egorova E.Yu. *Nauchnoe obosnovanie i prakticheskaya realizatsiya razrabotki pishchevoy produktsii s ispol'zovaniem produktov pererabotki kedrovykh* orekhov [Scientific substantiation and practical realization of the development of food production with the use of products of processing of cedar nuts]. Dr. eng. sci. diss. Kemerovo, 2012. 484 p.
30. Lukanin A. and Sidorenko A. Kriterii opredeleniya vozrasta kon'yachnykh spirtov [Criteria for determination of age of cognac alcohols]. *Visnyk agrarnoi' nauky* [Bulletin of agricultural science], 2016, no. 10, pp. 51–60.
31. Vivas N. *Manuel de tonnellerie a l'usage des utilisateurs de futaille*. Editions Feret, Bordeaux, 2002. 207 p.
32. Egorova E.Yu., Budaeva V.V., Lobanova A.A., and Ilyasov S.G. Shell of a pine nut in manufacture of alcoholic and non-alcoholic beverages. *Beer and Drinks*. 2005, no. 5, pp. 44–46. (In Russian).
33. Egorova E.Yu. Receiving extracts from an amniotic membrane of pine nuts. *Alcoholic Beverage Production and Winemaking*. 2012, no. 11–12, pp. 23–25. (In Russian).
34. Pavlova L.V., Platonov I.A., Arkhipov V.G., et al. Gas-chromatographic analysis of chamomile (*Chamomilla recutita R.*). *Analytics and Control*, 2013, vol. 17, no. 1, pp. 66–75. DOI: 10.15826/analitika.2013.17.1.009. (In Russian).
35. Bazarnova Yu.G. and Ivanchenko O.B. Investigation of the composition of biologically active substances in extracts of wild plants. *Nutrition problems*, 2016, vol. 85, no. 5, pp. 100–107. (In Russian).
36. Temerdashev Z.A., Milevskaya V.V., Kiseleva N.V., et al. Sorption-chromatographic determination of gallic, caffeic acids, rutin and epicatechin in herbs. *Analytics and control*, 2013, vol. 17, no. 2, pp. 211–218. DOI: 10.15826/analitika.2013.17.2.012. (In Russian).
37. Pravdivtseva O.E. and Kurkin V.A. Issledovaniya po obosnovaniyu novykh podkhodov k standartizatsii syr'ya i preparatov zveroboya prodyryavlennogo [Researches on justification of new approaches to standardization of raw materials and preparations of Hypéricum perforatum L]. *Chemistry of plant raw material*, 2008, no. 1, pp. 81–86.
38. Skurikhin I.M. *Khimiya kon'yaka i brendi* [Chemistry of cognac and brandy]. Moscow: DeLi Print Publ., 2005. 296 p.
39. Egorova E.Yu. and Morozhenko Yu.V. Methodological approaches to the development and quality assessment of new drinks of the group of Distillates. Part 1. Formulation of the new drink. *Polzunovskii Herald*, 2016, no. 3, pp. 4–8. (In Russian).
40. *M 04–53–2008. Kon'yaki, brendi i kon'yachnye spirty. Metodika vypolneniya izmereniy massovoy kontsentratsii vanilina, sinapovogo al'degida, koniferilovogo al'degida, sirenevogo al'degida metodom kapillyarnogo elektroforeza s ispol'zovanie sistem kapillyarnogo elektroforeza «Kapel'-105» i «Kapel'-105M»* [Cognacs, brandy

and cognac alcohols. Technique for mass concentration of vanillin, sinapic aldehyde, coniferylic aldehyde, syringic aldehyde using the method of capillary electrophoresis with the use of capillary electrophoresis systems «Kapel'-105» and «Kapel'-105M»]. St. Petersburg, 2008. n. p.

41. Pochitskaya I. M., Kurchenko V. P., Ursul O. N. Issledovanie fiziko-khimicheskikh protsessov pri vyderzhke kon'yachnykh spirtov [The study of physical and chemical processes when aging cognac]. *Pishchevaya promyshlennost': nauka i tekhnologii* [Food processing industry: science and technology]. 2009, no. 2 (4), pp. 82–89.
42. Koropachinskaya N.V. *Kataliticheskoe okislenie ligninov v aromaticheskie al'degidy v prisutstvii oksida medi* [Catalytic oxidation of lignins in aromatic aldehydes in the presence of copper oxide]. Cand. agr. sci. thesis. Krasnoyarsk, 2004. 18 p.
43. Aksenov P.A. *Otbor duba dlya ispol'zovaniya ego drevesiny v vinodelii* [Selection of oak for the use of its wood in winemaking]. Cand. agr. sci. thesis. Moscow, 2012. 24 p.
44. Oseledtseva I.V., Guguchkina T.I., Markosov V.A., and Prostak M.N. Osobennosti khimicheskogo sostava kon'yachnykh distillyatov, vyrabatyvaemykh v raznykh geograficheskikh zonakh [Peculiarities of the chemical composition of cognac distillates produced in different geographical zones]. *Magarach. Vinogradarstvo i vinodelie* [Grape growing and winemaking], 2013, no. 2, pp. 26–28.
45. Lantto T.A., Dorman H.J.D., et al. Chemical composition, antioxidative activity and cell viability effects of a Siberian pine (*Pinus sibirica* Du Tour) extract. *Food Chemistry*, 2009, vol. 112, no. 4, pp. 936–943. DOI: https://doi.org/10.1016/j.foodchem.2008.07.008.
46. Shefer E.P. *Sovremennye podkhody k izucheniyu khimicheskogo sostava semyan sosny kedrovoy sibirskoy i razrabotka metodov standartizatsii lekarstvennykh preparatov na ikh osnove* [Modern approaches to the study of chemical composition of *Pinus sibirica* seeds and the development of methods for standardization of preparations on their basis]. Cand. pharm. sci. thesis. Moscow, 2000. 24 p.
47. Pozharitskaya O.N., Shikov A.N., Laakso I., et al. Polifenol'nye soedineniya semyan *Pinus sibirica* (*Pinaceae*) [Polyphenolic compounds of *Pinus sibirica* (*Pinaceae*) seeds]. *Rastitel'nye resursy* [Vegetable resources]. 2007, Vol. 43, Iss. 2, pp. 39–46.
48. Egorova E.Yu., Sysoeva D.Yu., Rozhnov E.D., and Morozhenko Yu.V. Aromatic aldehydes of plant product extracts that are used in liqueurs and spirits manufacture. *Polzunovskii Herald*. 2014, no. 4 (2), pp. 126–131. (In Russian).

Please cite this article in press as: Egorova E.Yu., Morozhenko Yu.V., and Reznichenko I.Yu. Identification of aromatic aldehydes in the express assessment of quality of herbal distilled drinks. *Foods and Raw Materials*, 2017, vol. 5, no. 1, pp. 144–153. DOI: 10.21179/2308-4057-2017-1-144-153.

PHYSICAL AND CHEMICAL INDICATORS AND MERCHANDASING ASSESSMENT OF WILD STRAWBERRY, GOOSEBERRY, CHERRY, RASPBERRY, BANANA, WILD ROSE AND KIWI

Yu. V. Golubtsova

Kemerovo Institute of Food Science and Technology (University),
Stroiteley blvd. 47, Kemerovo, 650056, Russian Federation

* e-mail: ula.gol@mail.ru

Received February 22, 2017; Accepted in revised form April 18, 2017; Published June 29, 2017

Abstract: The fruit and berry vegetable raw materials applied in food production technologies have a positive impact on the consumer properties of ready-made product. The qualitative composition and the quantitative content of separate elements in fruit and berry raw materials have been studied in the work (wild strawberry, gooseberry, cherry, raspberry, banana, wild rose and kiwi). The studied samples conformed to the requirements of standards in appearance, coloring, taste and smell. Physical and chemical indicators, such as the content of solids, sugars, pectinaceous substances, organic acids, the titrable acidity of the crude and processed fruit and berry raw materials have been defined. It has been established that the highest quantity of carbohydrates, including sucrose, is in bananas, the lowest quantity is in raspberry. There is no sucrose in wild strawberry and wild rose. Cellulose is in all fruit and berry raw materials, its highest content is in raspberry. Pectinaceous substances are mainly in gooseberry. It has been established that all fruit and berry raw materials are rich with organic acids, except bananas. Apple acid is the only that prevails in bananas. At the same time the acidity of bananas is low. The titrable acidity of wild strawberry is the highest which is proved by the fact of lack of sucrose in it. It has been shown that fruit and berry raw materials contain such vitamins as B_1, B_2, B_6, PP, β-carotene, K_1, E and C. The greatest amount of vitamin C is in wild rose, there are also a lot of group B vitamins in wild rose, tocopherols prevail in wild rose and gooseberry. All types of fruit and berry raw materials are rich with major macro - and microelements. It follows from the obtained data that the physical and chemical indicators can not be the objective criteria of identification of the crude and processed fruit and berry raw materials as their values for different types of raw materials are very close, and sometimes they coincide. Some indicators, such as the content of vitamin C and total of carotinoids can indirectly be suitable for the identification of group of fruit and berry raw materials, but they do not allow to define a type of fruit and berry raw materials.

Keywords: Fruit and berry raw materials, quality, organoleptic properties, physical and chemical properties, identification

DOI 10.21179/2308-4057-2017-1-154-164 *Foods and Raw Materials*, 2017, vol. 5, no. 1, pp. 154–164.

INTRODUCTION

The fruit and berry vegetable raw materials applied in food production technologies have a positive impact on the consumer properties of ready-made product. In particular, it favorably affects the organoleptic characteristics of finished goods: taste, aroma and color. At the same time the vegetable components play a role of natural dyes and fragrances. Thanks to the presence of biologically active agents, fruit and berry vegetable raw materials have a good effect on the human body [1, 2].

Merchandising characteristics of fruit and berry raw materials: the high nutrition and biological value, the simplicity in the preparation for production, the wide range of fruits and berries and their derived products allow to use them effectively in various food technologies, including dairy products technologies [3].

The studied fruits and berries as vegetable objects with the prevalence of water in their composition have no high caloric value: 100 g of the edible part give only 30–100 kcal [4]. Easily digested carbohydrates prevailing in the dry weight are the main energy-yielding material in the composition of fruits and berries. Fruits and berries are of the highest value in nutrition as a source of biologically active agents - vitamins, macro- and microelements, specific substances and food fibers. Thanks to the presence of the listed groups of compounds, fruits and berries improve digestion, the activity of cardiovascular system, the neuroemotional state of the person, therefore a lot of fruits and berries are irreplaceable in nutrition. The average annual need of the person for fruits and berries is 7 kg. [4].

Fruits and berries, first of all, are an effective source of various carbohydrates among which there are sugars, polyols, pectinaceous substances, cellulose and hemicellulose. Sugars are digestible carbohydrates – glucose, fructose, sucrose because of a sweet taste inherent in them. The total content of sugars is from 1.0 to 20% [5, 6, 7]. Monosugars, glucose and fructose prevail. Their content is approximately equal in a lot of fruits and berries. The amount of sucrose (disaccharide) does not exceed 1% in the majority of them. Fructose – the sweetest and most dietary valuable sugar which is expedient for use in the diets with a low caloric content, and also in the food of children and diabetics prevails in the composition of raspberry. Pectinaceous substances and cellulose are carbohydrate polymers, they are not digestible for the human body, but their physiological role is high enough. Pectinaceous substances are part of cells and noncellular clusters. These are derivatives of galacturonic acid. There is soluble pectin and insoluble pectin (protopectin) [8, 9]. The ratio between soluble pectin and protopectin in the composition of fruits and berries changes in the course of growth, maturing and storage. Therefore, changes of consistence become noticeable as well. The content of pectinaceous substances with high jellifying properties which are shown at a certain ratio of pectinaceous substances, sugar and acids [10] in fruits and berries is 0.2–1.8%.

The purpose of work consisted in the determination of parameters of quality of fruit and berry raw materials. The study problems included the determination of titrable acidity, content of vitamins and minerals and also toxic components in fruit and berry raw materials.

OBJECTS AND METHODS OF STUDY

In accordance with the purpose and tasks of the work, the study objects were the following:

– fruit and berry raw materials:

Rubus idaeus (raspberry, the grade “Nagrada”),

Fragaria vesca (remontant wild strawberry, the grade “Berdskaya rannyaya”),

Ribesúva-crispa (garden gooseberry, the grade “Kooperator”),

Prunus fruticosa (ground cherry, the grade “Altayskaya lastochka”),

*Rosa majalis Herrm (*cinnamon rose*)*,

Actinidia deliciosa (kiwi delicatessen),

Músa paradisiaca (banana of "extra" grade);

– model fruit and berry mixtures.

All fruit raw materials used in the work were studied upon the organoleptic and physical and chemical indicators of quality according to the requirements of the relevant normative documents.

The test specimens were selected in accordance with GOST 26313-84 "Products of fruit and vegetable processing. Acceptance rules and methods of sampling". The raw materials are mixed and the single samples are selected from different layers of a product by means of a scoop, a sampler, a siphon and so forth, weighing 100–500 g each. The number of single samples from each unit of transport packing must be not less than two. The total weight of specimen from each selected unit of transport packing must be from 0.3 to 3.0 kg depending on the weight of the product needed for the tests.

The fruits of raspberry were assessed for the compliance with the requirements of GOST R 54691-2011. The appearance, maturity degree, state, smell and taste of berries, the presence of the agricultural fruits and berries damaged by agricultural depredators, the rotten and spoiled berries are assessed in an organoleptic way [11, 12].

The indicators of quality of fruits of wild strawberry were assessed in accordance with GOST 6828-89. The appearance, maturity degree, taste and smell, the presence of the sick and damaged berries of wild strawberry are determined in an organoleptic way; the size of berries - by measuring to a precision of no more than 0.1 mm [13].

Each fraction was weighed. All weighings were performed to a precision of no more than 0.01 kg.

RESULTS AND DISCUSSION

Table 1 presents the carbohydrate composition of fruits and berries.

The analysis of tabular data allows to draw a conclusion that the highest quantity of carbohydrates, including sucrose, is in bananas and the lowest is in raspberry. There is no sucrose in wild strawberry and wild rose. Cellulose is in all fruit and berry raw materials, its highest content is in raspberry. Pectinaceous substances are mainly in gooseberry.

Table 2 presents the titrable acidity and qualitative composition of organic acids of the studied fruits and berries, Table 3 – the content of vitamins.

Fruits and berries are a source of the mineral substances playing an important role in metabolic processes. The total of mineral substances or ash in the composition is 0.2–0.54%. Macro-, micro- and ultramicroelements are found in the composition of ash.

Analyzing these tables, it is possible to note that all fruit and berry raw materials are rich with organic acids, except bananas. Apple acid is the only that prevails in bananas. At the same time the acidity of bananas is low. It is explained by the existence of a large amount of sucrose. The titrable acidity of wild strawberry is the highest which is proved by the fact of lack of sucrose in it.

The qualitative composition and the quantitative content of separate elements are different which is caused by their biological and specific features to accumulate elements, the provision of soils with available forms of elements. In some cases the mineral composition can facilitate the identification of products of processing and prove their naturalness, but is not an objective criterion of specific identification of fruit and berry raw materials.

It follows from the tabular data that fruit and berry raw materials contain such vitamins as B_1, B_2, B_6, PP, β-carotene, K_1, E and C. The greatest amount of vitamin C is in wild rose, there are also a lot of group B vitamins in wild rose, tocopherols prevail in wild rose and gooseberry.

Table 4 presents the content of mineral substances in the studied raw materials.

Analyzing Table 4 it is possible to draw a conclusion that all types of fruit and berry raw materials are rich with major macro - and microelements.

Table 1. Carbohydrate composition of fruits and berries, %

Type of raw materials	Sugars		Pectic substances	Fibre
	Total	Sucrose		
Wild strawberry	3.7–8.1	–	0.7–1.4	4.0
Raspberry	3.6–8.4	0.6	0.5–0.7	5.2
Gooseberry	5.2–13.5	0.3–0.87	3.64–11.0	2-3
Wild rose	8.0–20.0	–	1.8–2.7	4.0
Cherry	6–10.5	0.2–0.31	0.4–0.8	1.8
Bananas	16–19	2.39	–	1.7–2.2
Kiwi	7–7.8	0.3–0.5	0.4–0.45	3.8

Table 2. Titrable acidity and composition of organic acids

Type of raw materials	Titrable acidity, %	Qualitative composition of acids
Wild strawberry	1.6–2.0	Citric, apple, chlorogenic acids and their derivatives, coumaric, salicylic and cinchonic acid
Gooseberry	1.5–3.8	Citric, apple, tartaric, succinic and phosphoric acid
Raspberry	1.3–2.1	Citric, apple, formic, salicylic and chlorogenic acids
Wild rose	0.9–2.5	Apple acid, phenolic acids
Cherry	0.5–0.8	Chlorogenic, ellagic, citric, apple, cinchonic, succinic and salicylic acid
Bananas	0.3–0.4	Apple
Kiwi	0.6–0.8	Apple, citric, salicylic, chlorogenic acids and their derivatives

Table 3. Content of vitamins in fruits and berries, mg / 100g

Type of raw materials	Thiamine (B_1)	Riboflavin (B_2)	Folacin (B_6)	Niacin (PP)	β-Carotene	Phyllochinone (K_1)	Tocopherols (E)	Vitamin C
Wild strawberry	0.03	0.05	13–0.25	0.3	0.03	0.2–0.4	0.3–0.9	20–55
Gooseberry	0.01	0.02	0.03–0.26	0.1	0.7–1.0	0.3–1.0	1.0	Up to 110
Raspberry	0.02	0.05–0.06	0.15–0.32	0.3–0.6	0.2–0.7	0.3–0.6	0.3–0.6	27–93
Wild rose	0.05	0.33–0.88	0.1–0.25	0.6	2.0–2.6	0.6–1.2	1.0–8.8	670–3800
Cherry	0.03	0.03	0.05	0.5	0.1	–	0.3	15
Bananas	0.04	0.05	0.4	0.9	0.12	0.5	0.4	180
Kiwi	0.02	0.04	0.2	0.5	0.09	–	0.3	180

Table 4. Content of the most important minerals in the composition of fruits and berries, mg/kg

Type of berries and fruits	Potassium	Sodium	Calcium	Magnesium	Phosphorus	Iron	Manganese	Cobalt	Molyb-denum
Wild strawberry,	30.8–160	18.0–22.1	27.9	13–18	23–103.6	12.0–103	10–28	0.03–0.052	0.06–0.085
Gooseberry	260	23	22	9	28	0.8	0.45	–	12 mkg
Raspberry	24.9–220	23.4	37.1	12.4	37–88.9	16–69	5.2–25.8	0.06	0.004
Wild rose	23-51	5–6	16–28	6–8	13	24–115	2.2–2.4	–	–
Cherry	256	20	37	26	30	0.3–0.5	0.08	1 mkg	10 mkg
Bananas	380–384	28–31	7–8	40–42	26–28	0.6	0.27	–	–
Kiwi	300	5	40	25	30–34	0.6–0.8	0.19–0.21	1.0 mkg	10 mkg

Table 5 gives the indicators of quality.

As the tabular data show, the quality of the studied raspberry conforms to the requirements of GOST, the content of toxic elements in raspberry does not exceed the admissible level (Table 12), the samples of raspberries can be applied for further studies.

Table 6 provides data on gooseberry.

Analyzing Table 6, it has been established that the samples of gooseberry are typical in shape and coloring, the taste is sourish and sweet, peculiar to this grade, without a foreign smack.

The content of toxic elements in gooseberries did not exceed the admissible level (Table 12).

Table 7 provides data on wild strawberry.

Proceeding from the data of Table 7, it has been established that the samples of berries of wild strawberry are typical in appearance, coloring, taste and smell, and correspond to the high grade. The content of toxic elements does not exceed the admissible level (Table 12), the berries can be used for further tests.

Table 8 presents the indicators of quality of hips.

The tabular data testify that the samples of hips conform to the requirements of GOST for all the indicators and can be used for further tests. The content of toxic elements does not exceed the admissible level (Table 12).

Table 9 gives the indicators of quality of the cherry used for the studies.

Table 5. Indicators of quality of fruits of ***Rubus idaeus*** (raspberry**,** the grade "Nagrada"), n = 5

Name of the indicator	Characteristics and norms	
	in accordance with GOST	in fact
Appearance, size and structure	Aggregate fruits are rounded or cone-shaped complex stone fruits not stuck together in clumps. Consist of a large number (30–60) of separate, grown together stone fruits. The size of the fruit is from 7.5 to 12 mm. Separate small spherical or ellipse stone fruits, with a stone inside, that has a pitted surface	The fruits are rounded and spherical, not stuck together in clumps. Consist of separate stone fruits grown together (48–60). The size of the fruit is from 9 to 17 mm. Meet the requirements.
Color of: surface pulp stones	Grayish and crimson Pinkish Dark yellow	Crimson red
Smell	Specific, pleasant	Pleasant, appropriate
Taste	Sourish and sweet	Mainly sweet
Moisture, %, not more than	15.0	13.0 $\pm$ 0.5
Mass fraction of total ash, %, not more than	3.5	1.5 $\pm$ 0.1
Mass fraction of the blackened fruits, %, not more than	8.0	4 $\pm$ 0.2
Mass fraction of the fruits stuck together in clumps, %, not more than	4.0	2 $\pm$ 0.5
Mass fraction of the fruits with unseparated pedicels and receptacles, %, not more than	2.0	0.5 $\pm$ 0.3
Mass fraction of the crushed particles of the fruits passing through a sieve with a diameter of openings of 2 mm, %, not more than	4.0	1.5 $\pm$ 0.5
Mass fraction of leaves and parts of raspberry stalks, %, not more than	0.5	0.0
Mass fraction of impurities, %, not more than		
organic (fruits and parts of other nonpoisonous plants)	0.5	0.0
mineral (ground, sand, stones)	0.5	0.0
Presence of poisonous plants and their parts	Not allowed	Absent
Presence of mold and decay	The same	Not detected
Presence of persistent foreign smell which does not vanish when ventilating	Not allowed	absent

Table 6. Indicators of quality of fruits of ***Ríbesúva-críspa*** (garden gooseberry, the grade "Kooperator"), n = 5

Name of the indicator	Characteristics and norms	
	in accordance with GOST	in fact
Appearance	The berries are quite developed, healthy, whole, pure, without mechanical damages, the damages caused by depredators and diseases, and excessive external moisture	The berries are mature, healthy, pure, without mechanical damages, depredators and diseases and excessive moisture.
Coloring	Homogeneous	Homogeneous
Taste and smell	Peculiar to the given pomological grade, without foreign smell and (or) taste	Sourish and sweet
Maturity	Harvest	Harvest
Content of berries of % of weight, not more than: Mechanically damaged: In places of shipment At destinations Slightly damaged by powdery mildew	 3.0 5.0 Not allowed	 1.5 ± 0.3 1.5 ± 0.2 absent
Vegetable impurities, % of weight, not more than	0.3	0.1 ± 0.05

Table 7. Indicators of quality of ***Fragaria*** (remontant wild strawberry**,** the grade "Berdskaya rannyaya"), n = 5

Name of the indicator	Characteristics and norms	
	in accordance with GOST	in fact
Appearance	The berries are quite developed, healthy, fresh, whole, mature, pure, without mechanical damages and excessive external moisture, with a pedicel or without it, but with a cup. Separate berries without a cup are allowed	The berries are developed, healthy, whole, mature, pure, without mechanical damages and excessive moisture, with a pedicel.
Taste and smell	Peculiar to the given pomological grade, without a foreign smell and (or) taste	Peculiar, without foreign smells and tastes
Coloring of berries	Homogeneous	homogeneous
Maturity	The berries are uniform in maturity	
Size to the largest cross-section diameter, mm, not less than:		
for fresh consumption	25.0	29 ± 0.5
for industrial processing	25.0 (high grade) Not rated (first grade)	–
Content of berries, % of weight, not more than: mechanically damaged		
in places of shipment	2.0 (high grade) 5.0 (first grade)	1.0 ± 0.2
at destinations	5.0 (high grade) 10.0 (first grade)	1.5 ± 0.5
damaged by depredators and birds	2.0 (high grade) 3.0 (first grade)	1.0 ± 0.1

Table 8. Indicators of quality of fruits of *Rosa majalis Herrm* (cinnamon rose), n = 5

Name of the indicator	Characteristics and norm for the raw materials	
	used as a medicinal preparation in the food industry as well	in fact
Appearance	The whole false fruits of various shape cleared of sepals and pedicels: from spherical, ovoid or oval to strongly extended spindle-shaped; the length of fruits is 0.7–3 cm, the diameter is 0.6–1.7 cm. There is a small round opening or a pentagonal platform on top of the fruit. Fruits consist of the overgrown receptacle (hypanthium) and numerous fruitlets (nutlets) enclosed in its cavity. The fruit walls are dense, fragile, the external surface is glossy, more rarely mat, more or less savoyed. The fruits are thickly covered inside with long and very stiff bristly hairs. The nutlets are small, oblong, with poorly prominent sides.	Whole, pure, from the spherical to the oval shape, the length of fruits is 1.8–3.2 cm, the diameter is 0.8–1.8 cm. There is a round opening on top of the fruit, the fruits consist of hypanthium and the fruitlets (nutlets) enclosed in its cavity. The walls are dense, the external surface is glossy and savoyed. The fruits are covered inside with long stiff bristly hairs. The nutlets are small, oblong, with poorly prominent sides.
Color:		
fruits	From orange-red to brownish-red	Orange-red
nutlets	Light yellow, sometimes brownish	Light yellow
Smell	Peculiar to the given raw materials, without foreign smells	Peculiar, without a foreign smell
Taste	Sourish and sweet, slightly astringent	Slightly astringent, sourish and sweet
Moisture, %, not more than	15.0	12 $\pm$ 0.5
Mass fraction of ascorbic acid, %, not less than	0.2	0.4 $\pm$ 0.01
Mass fraction of total ash, %, not more than	3.0	1.0 $\pm$ 0.1
Mass fraction of other parts of the plant (pieces of branches, leaves, sepals and pedicels), %, not more than	2.0	0.5 $\pm$ 0.1
Mass fraction of the blackened and burnt fruits and the fruits damaged by depredators and diseases, %, not more than	1.0	0,3 $\pm$ 0,1
Mass fraction of the crushed particles of fruits, including the nutlets passing through a sieve in accordance with TU 23.2.2068 with the openings with a diameter of 3 mm, %, not more than	3.0	1.0 $\pm$ 0.5
Mass fraction of immature fruits (from the green to yellow coloring), %, not more than	5.0	1.0 $\pm$ 0.5
Mass fraction of impurities: organic (parts of other nonpoisonous plants), %, not more than	0.5	absent
mineral (ground, sand, stones), %, not more than	0.5	absent

Table 9. Indicators of quality of ***Prunus fruticosa*** (ground cherry, the grade "Altayskaya lastochka"), n = 5

Name of the indicator	Characteristics and norms	
	in accordance with GOST	in fact
Appearance	The fruits typical for this pomological grade (first) in shape and coloring. The fruits typical and untypical for this pomological grade (second) in shape and coloring.	The fruits are typical for this pomological grade in shape and coloring.
Maturity	The fruits uniform in maturity, but not green and not overmature (first grade) The fruits are not uniform in maturity, but not green and not overmature are allowed (second grade)	The fruits are uniform in maturity
Size to the largest cross-section diameter, mm, not less than:	15 (first grade) Not rated (second)	17 ± 0.5
including that for small-fruited grades (Vladimirskaya, Samarkandskaya, Rastun'ya, Kartulialubali, Shubinka) and also that for ground and Nanking cherry	12 (first grade) Not rated (second)	–

Analyzing the data of Table 9, it has been established that the samples of cherry correspond to the first market grade upon the quality indicators, have a typical shape and coloring, the content of toxic elements does not exceed the admissible level (Table 12).

Table 10 gives the indicators of quality of the bananas used for further studies. Mature bananas, i.e. that of the harvest degree of maturity, of extra grade, produced in Ecuador have been studied.

The analysis of tabular data testifies that the samples of bananas correspond to the market extra grade, the content of toxic elements does not exceed the admissible level (Table 12).

Table 11 presents the indicators of quality of the studied fruits of kiwi.

It follows from the tabular data that the samples of kiwi are high-grade and can be used for further studies. The content of toxic elements does not exceed the admissible level (Table 12).

The analysis of tabular data testifies that the quality of the studied types of fruit and berry raw materials conforms to the requirements of normative documents according to the content of toxic elements and can be applied for further tests and the determination of specific identification.

The performed assessment of quality of fruit and berry raw materials with the application of organoleptic and physical and chemical methods of analysis provided by the existing normative documents has shown that the organoleptic method of assessment is the most acceptable for the purpose of identification of fresh fruits and berries. In case of the processed raw materials this method is subjective and is based only on the definition of taste, aroma and color of the applied vegetable raw materials which can be imitated by means of nutritional supplements - dyes and fragrances [14].

The physical and chemical indicators, such as the content of solids, sugars, pectinaceous substances, organic acids and titrable acidity can not be the objective criteria of identification of the crude and processed fruit and berry raw materials as their values are very close, and sometimes coincide in different types of raw materials. Some indicators, such as the content of vitamin C and total of carotinoids can indirectly be suitable for the identification of group of fruit and berry raw materials, but they do not allow to define a type of fruit and berry raw materials [15, 16].

Some physical and chemical methods, for example IR-spectrometry, allows to identify fresh fruit and berry raw materials and to establish the fact of availability of fruit and berry raw materials in foodstuffs, but does not allow to reveal theis species [17].

Thus, the performed studies on the assessment of quality of the fresh and processed fruit and berry raw materials have shown that the organoleptic and physical and chemical methods of analysis regulated by the existing regulatory system have limited capacities in the assessment of species of raw materials.

Table 10. Indicators of quality of *Músa paradisiaca* (banana of "Extra" grade), n = 5

Name of the indicator	Characteristics and norm		
	for the grades		in fact
	extra	first	
Appearance	The fruits are of the same pomological grade. The fruits in brushes are dense, fresh, pure, whole, healthy, developed, not miss-shaped, without flower remains, with highly prominent ridge sides. The crown is green, its cutoffs are plain, smooth, healthy, not overdried		The fruits are of the same pomological grade. The fruits in brushes are dense, fresh, pure, whole, healthy, with highly prominent ridge sides. The crowns are green, their cutoffs are plain, smooth, not overdried
Taste and smell	A specific smell of ripe bananas, the taste is sweet, without a foreign smack and aroma		The taste is specific, sweet, without a foreign smack and aroma.
Maturity	When cutting fruits lacteal juice is well emitted. The fruits are of the harvest degree of maturity with a greenish-yellow or yellow skin but not overmature, dense, roundish, the pulp is creamy		When cutting fruits lacteal juice is well emitted. The fruits are of the harvest degree of maturity with a yellow skin, not overmature, dense, roundish, the pulp is creamy
Sizes of the fruits:			
to the largest cross-section diameter, cm	3.0–4.0		3.0 ± 0.3
in length, cm, not less than	20.0	19.0	21.0 ± 1.2
Quantity of fruits in a brush, pcs.	4–8	4–9	7 ± 1.0
Quantity of brushes per one packing unit, pcs.	15–18	14–18	17 ± 0.9
Content of bananas with deviations from the fixed sizes of no more than:			
to diameter by 0.5 cm, %, not more than	2.0	5.0	1.0 ± 0.2
in length by 1.0 cm, %, not more than	3.0	5.0	2.0 ± 0.7
The surface damages of skin without touching the pulp, mechanical damages and those caused by agricultural depredators on one fruit with the total area of, cm^2, not more than	1.0	2.0	0.5 ± 0.02
Content of fruits with latex streaks (spots), %, not more than:			
- in area not more than 10 cm^2	Not limited		0
- in area more than 10 cm^2	1.0	2.0	0
Content of the broken fruits, with a tear of skin at the pedicel, with deep cuts, strong pressings, skin cracks when the pulp is touched, affected with anthracnose, fusariosis, Sigatoka disease, decayed, rotten, soften, chilled to the 3-4th degree, frozen, mashed, with extensive damages caused by agricultural depredators (skin plagues, deep red spots of nesting of trips), overmature with a dark brown, black or spotty skin	Not allowed		absent

Table 11. *Beginning.* Indicators of quality of fruits of *Actinidia deliciosa* (kiwi delicious), n = 5

Name of the indicator	Characteristics and norm			
	for the market grades			in fact
	high	first	second	
Appearance	The fruits are fresh, whole, pure, healthy, dense, at the stage of market maturity, shaped enough, without a stalk, not overmature, without the damages caused by insect depredators and diseases, without excessive external moisture and shape and coloring typical for the pomological grade			The fruits are fresh, whole, pure, healthy, at the stage of market maturity, Without the damages caused by depredators and diseases, oval-shaped, green
	Slight surface defects of skin which do not affect the quality are allowed	Fruits with slight deficiencies in shape, but without outgrowths and deformations, slight coloring defects, slight skin defects the total area of which does not exceed 1 cm, with small traces from the removed label in the form of longitudinal lines, without hillocks are allowed	Deficiencies in shape, coloring, skin defects in the form of slight cicatrized cracks or scratched/torn off skin the total area of which does not exceed 2 cm, with more prominent traces from the removed label, with small hillocks and slight dents are allowed	
Smell and taste	Peculiar to the given pomological grade, without a foreign smell and taste			peculiar, without foreign
Internal structure	The pulp is dense, juicy and tough, without damages			The pulp is dense, juicy and tough, without damages
The ratio of the minimum diameter to the maximum diameter of the fruit measured in cross section, not less than	0.8	0.7	Not rated	1.0 ± 0.1
Mass of fruits, not less than	90.0	70.0	65.0	91 ± 2.5
Maturity degree	Homogeneous	Homogeneous	Homogeneous, the fruits are of non-uniform maturity, not overmature are allowed	homogeneous
Mass fraction of soluble solids, %, not less than	15.0			17.7 ± 0.8
Mass fraction of the fruits with deviations of more than 10% from the fixed weight, % of weight, not more than	Not allowed	5.0	10.0	–
Mass fraction of the fruits with slight deficiencies in shape and coloring, with slight dents, with small hillocks, %, not more than	Not allowed	5.0	10.0	1.0 ± 0.5
Mass fraction of the fruits with surface skin defects, the total area of which is not more than 1 cm, %, not more than	Not allowed	5.0	10.0	–

Table 11. *Ending.* Indicators of quality of fruits of *Actinidia deliciosa* (kiwi delicious), n = 5

Name of the indicator	Characteristics and norm			
	for the market grades			in fact
	high	first	second	
Mass fraction of the fruits with skin defects in the form of cicatrized cracks or scratched/ torn off skin, the total area of which is not more than 2 cm, %, not more than	Not allowed	Not allowed	5.0	–
Mass fraction of the faded, mushy, watery, overmature, moldy and decayed fruits and the fruits damaged by insect depredators , with mechanical damages, with the damaged pulp, with excessive external moisture, %, not more than	Not allowed			absent
Mass fraction of the fruits grown together, %, not more than	Not allowed			absent

Table 12. Content of toxic elements in berries and fruits

Raw materials	Name of the element			
	plumbum	arsenic	cadmium	mercury
Raspberry	0.023	less than 0.02	0.011	less than 0.00002
Gooseberry	0.029	less than 0.02	0.012	less than 0.00002
Wild strawberry	0.030	less than 0.02	0.013	less than 0.00002
Cherry	0.075	less than 0.04	less than 0.01	less than 0.00002
Wild rose	0.040	less than 0.04	less than 0.01	less than 0.00002
Bananas	0.030	less than 0.03	less than 0.005	less than 0.00002
Kiwi	0.030	less than 0.03	less than 0.005	less than 0.00002
Dichlorophenoxyacetic acid, mg/kg in accordance with SanPiN 2.3.2.1078-01	max. 0.4	max. 0.2	max. 0.03	max. 0.02

REFERENCES

1. Altukhov Yu.P. *Geneticheskie protsessy v populyatsiyakh* [Genetic processes in populations: a study guide]. Moscow: Akademkniga Publ., 2003. 431 p.
2. Biryukova V.A., Zaitsev V.S., Pankin A.A., et al. DNK-genotipirovanie kartofelya i ego dikorastushchikh sorodichei na osnove polimorfizma umerennykh povtornostei semeistva R173 [DNA genotyping of potato and its wild relatives based on polymorphism of moderate repeats of the family R173]. *Materialy Mezhdunarodnoy yubileynoy nauchno-prakticheskoy konferentsii "Nauchnyye Trudy"* [Materials of International jubilee scientific and practical conference "Proceedings"]. Minsk, 2003, Part 1, pp. 313.
3. Kil' V.I. and Gronin V.V. Geneticheskie marker chuvstvitel'nosti populyatsiy koloradskogo zhuka k transgennomu kartofelyu [Genetic markers of sensitivity of the Colorado potato beetle populations to transgenic potatoes]. *Nauka Kubani* [Kuban' Science], 2005, no. 4, pp. 126.

4. Komarova I.N. *Razrabotka PTsR–test–system dlya vidovoi identifikatsii i kolichestvennoi otsenki myasnogo syr'ya v sostave melkoizmel'chennykh polufabrikatov i gotovykh myasnykh produktov* [Development of PCR test systems for species identification and quantification of raw meat in of semi-finished and finely ground meat products]. Diss.Cand.Sci.(Eng.). Moscow, 2005.
5. Lewin B. *Genes*. New York: John Wiley and Sons, 1983. n. p. (Russ. ed.: Lewin B. *Geny*. Moscow: Mir Publ., 1987. 554 p.).
6. Palilova A.N., Urbanowich O.Yu., Dolmatovich T.V., et al. Poisk molekulyarnykh markerov ustoychivosti rasteniy kartofelya k virusnoy infektsii [Search for molecular markers of potato plant resistance to virus infection]. *Materialy Mezhdunarodnoy yubileynoy nauchno-prakticheskoy konferentsii "Nauchnyye trudy"* [Materials of International jubilee scientific and practical conference" Proceedings"]. Minsk, 2003, part 1, pp. 316.
7. Politov D.V. Primenenie molekulyarnykh markerov v lesnom khozyaistve dlya identifikatsii, inventarizatsii i otsenki geneticheskogo raznoobraziya lesnykh resursov [Application of molecular markers in forestry for identification, inventory and assessment of genetic diversity of forest resources]. *Lesokhozyaystvennaya informatsiya* [Forestry Information], 2008, no. 3–4, pp. 24–27.
8. Prosekov A.Yu. And Babich O.O. *Gennaya inzheneriya* [Genetic engineering: a tutorial]. Moscow: Redaktsiya zhurnala "Dostizheniya nauki i tekhniki APK", 2010. 216 p.
9. Prosekov A.Yu., Golubtsova Yu.V., and Shevyakova K.A. Effektivnost vidovoy identifikatsii [Influence of Technological Raw Food Treatment on the Effectiveness of Species Identification]. *Pishchevaya promyshlennost'* [Food processing industry], 2014, no. 6, pp. 8–10
10. Prosekov A.Yu. Theori and practice of prion protein analysis in food products. *Foods and Raw materials*, 2014, vol. 2, no. 2, pp. 106–120. DOI: 10.12737/5467.
11. Prosekov A.Yu., Babich O.O., and Bespomestnykh K.V. Identification of industrially important lactic acid bacteria in foodstuffs. *Foods and Raw Materials*, 2013, vol. 1, no. 2, pp. 42–45. DOI: 10.12737/2053.
12. Romanova O.V. *Identifikatsiya sortov kostochkovykh kul'tur s pomoshch'yu PTsR-analiza* [Identification of the varieties of stone fruit plants by PCR analysis]. Diss.Cand.Sci.(Agr.). Moscow, 2007.
13. Astakhova L., Babich O., Prosekov A., et al. Short chain fatty acids (SCFA) reprogram gene expression in human malignant epithelial and lymphoid cells. *PLoS ONE*, 2016, vol. 11, no. 7, e0154102. DOI: 10.1371/journal.pone.0154102.
14. Coyne V.E., James M.D., and Reid Sh.J. *Molecular biology techniques manual: standard PCR protocol*. 1994.
15. Fulcrand N., Cheynier V., Oszmianski J., and Moutounet M. An oxidized tartaric acid residue as a new bridge potentially competing with acetaldehyde in flavan-3-OL condensation. *Phytochemistry*, 1997, vol. 46, no. 2, pp. 223–227. DOI: 10.1016/S0031-9422(97)00276-8.
16. James S.A., Collins M.D., and Roberts I.N. Use of an rRNA internal transcribed spacer region to distinguish phylogenetically closely related species of the genera Zygosaccharomyces and Torulaspora. *International Journal of Bacteriology*, 1996, vol. 46, pp. 189.
17. Dyshlyuk L., Babich O., Belova D., and Prosekov A. Comparative analysis of physical and chemical properties of biodegradable edible films of various compositions. *Journal of food process engineering*, 2017, vol. 40, n/a, e12331. DOI: 10.1111/jfpe.12331.

Please cite this article in press as: Golubtsova Yu.V. Physical and chemical indicators and merchandasing assessment of wild strawberry, gooseberry, cherry, raspberry, banana, wild rose and kiwi. *Foods and Raw Materials*, 2017, vol. 5, no. 1, pp. 154–164. DOI: 10.21179/2308-4057-2017-1-154-164.

CHEMISTRY AND ECOLOGY

DEPENDENCE OF PURIFIED RUTIN QUALITY ON ACTIVATED CARBON BRAND

E. V. Averyanova*, M. N. Shkolnikova, and A. V. Frolov

Biysk Institute of Technology (branch), Polzunov Altai State Technical University,
Trofimova Str. 27, Biysk, 659305, Russian Federation

* e-mail: lena@bti.secna.ru

Received November 11, 2016; Accepted in revised form January 30, 2017; Published June 29, 2017

Abstract: The main problem of implementation of technology of rutin extraction from grass buckwheat *Fagopyrum sagittatum Gilib.* lies in purification of rutin raw. In this connection the following research object is determined: consideration of the possibility to use for rutin raw purification different commercial carbon brands as adsorbents by the method of preparative chromatography and assessment of their effectiveness to achieve the maximum degree of purification with minimum duration of the elution process. The article presents experimental data on purification of rutin raw sample, extracted from grass buckweat green material by the preparative chromatography method using wood- and coconut-based activated carbons of different brands as sorbents; besides, the following items are presented in the article: dependence of rutin sample melting temperature, qualitative and quantitative flavonoid content, authenticity on chlorophyll and red pigments content depending on sorbent layer height and elution duration in comparison with the GSO [State Standard Samples] control sample. To confirm the reliability of the obtained results, statistical processing of experimental data is conducted using the methods of correlation and regression analysis, as well as using the two-parameter normal distribution of values. It is demonstrated that the use of the following carbon brands, indicated in decreasing effectiveness order, can provide the best purity and stability of parameters values, characterizing the product: NWC-P, NWM-P, OU-A, OU-B; the conducted calculations indicate that the best correlation between the sorbent layer height in a column and the rutin samples quality parameter was achieved when the carbons of the brands NWM-P, OY-A and OY-B were used. Depending on the tasks, rutin purification degree may be regulated by sequential use of NWC-P and NWM-P carbons. When rutin is purified from proximate admixtures, chlorophyll and red pigments, NWC-P adsorbent allows to get a comparable result even when the layer height is from 50 to 70 mm respectively.

Keywords: Grass buckweat, rutin raw, activated carbon, purification, method of preparative chromatography

DOI 10.21179/2308-4057-2017-1-165-173 *Foods and Raw Materials*, 2017, vol. 5, no. 1, pp. 165–173.

INTRODUCTION

Nowadays, a special place in the pharmaceutical market is occupied by medicines and dietary supplements of plant origin, containing flavonoids, one of the most important qualities of which is the ability to increase strength of the capillary walls. P-vitamin activity of these medicines is associated with the antioxidant effect that is important in the treatment of chronic venous insufficiency, hypertension and other cardiovascular diseases, associated with the increased permeability of blood capillaries. The clearest representative of this group of substances is rutin, which not only has a pronounced capillary-strengthening, antioxidant and hepatoprotective action [1, 2], but also improves the treatment of various disorders, associated with physical fatigue [3].

Today the main industrial source of rutin is the buds of Japanese pagoda tree (*Styphnolobium japonicum L.*), however, there is no raw material base of this plant in our country. A promising domestic source of rutin and other flavonoids may be grass buckwheat (*Fagopyrum sagittatum* Gilib.), widely cultivated as a valuable food crop in the Russian Federation. It is known that the rutin content in the cultivated buckwheat sorts is from 2.0 to 8.7% on a dry basis. However, the sorts, the rutin content in which may be 12%, are selected [4, 5].

Despite the broad prospects of the use of grass buckwheat as a raw material for the rutin production, the main difficulty of the implementation of technology of rutin extraction lies in the stage of rutin raw purification and obtaining a product, suitable for use in pharmaceutical industry and dietary supplements production [6]. In view of this, studies have been conducted on the use of commercial carbons of different brands as adsorbents, used for rutin purification, by the method of preparative chromatography, as well as the assessment of their effectiveness to achieve the maximum degree of purification with minimum duration of the elution process was conducted.

OBJECTS AND METHODS OF STUDY

The study objects were rutin raw samples, extracted by the above-mentioned method [7, 8] and purified by the method of preparative chromatography on a layer of wood- and coconut-based activated carbon of six brands. Physical and chemical parameters of the carbons are indicated in Table 1.

Sample melting temperature was measured with the device PTP (M), qualitative and quantitative flavonoid content in the samples was measured by the method of HPLC on high performance liquid chromatograph Milikhrom A-02 with UV radiation and a chromatographic column from stainless steel O 2?75 mm, filled with a reversed-phase sorbent ProntoSIL 120-5C18 AQ, with a software package. The solution of 0.1% acetic acid and acetonitrile was used as an eluent. Flavonoid retention time is 25 minutes. Chlorophyll and red pigments content was measured by spectrometric method. The readings were taken from the devices Shimadzu UV-2401 PC UV-VIS RECORDIGPHOTOMETER (Japan) at wave length of 560 nm, 590 nm, 620 nm, 655 nm and 690 nm in a cuvette with the layer thickness of 1 cm. Isopropyl alcohol was used as a comparison solution. Microscopic examination of rutin samples was conducted with the electron microscope SK 14 28804.

Table 1. Physical and chemical parameters of activated carbons of different brands [9]

Carbon brands	Appearance	Adsorption activity by methylene blue, mg/g	Ash mass fraction, %	Moisture mass fraction, %	Bulk density, g/dm^3	Abrasion capacity, %
OU-A (GOST 4453-74)	Black fine-grained powder	225.0	4.6	4.7	270	60
OU-B (GOST 4453-74)	Black fine-grained powder	75.0	10.0	10.0	290	60
BAU-A (GOST 6217-74)	Black grains	60.0	6.0	10.0	240	60
BAU-MF (GOST 6217-74)	Black grains	70.0	10.0	10.0	Not regulated	60
NWC-P, FCC specification	Black powder	300.0	5.0	15.0	300	> 99
NWM-P, FCC specification	Black powder	280.0	10.0	15.0	300	> 96

RESULTS AND DISCUSSION

Rutin raw was extracted from grass buckweat green material by double extraction with ethanol solution of 70%. The output was 4.44 ± 0.05% (on absolute dry substance), contain of main substance in a sample was 75.74%, melting point was 162°C, crystals were gray-and-green. According to regulating documentation requirements, the rutin content shall be at least 95.0% (State Pharmacopoeia XI); in the GSO [State Standard Sample] sample it was at least 98.5%. For purification of rutin raw we offered the method of preparative chromatography on a layer of activated carbons of different brands – OU-A, OU-B, BAU-A, BAU-MF, NWC-P, NWM-P [10]. 99.5%-methanol was used as a solvent and eluent for chromatography.

In a column with a height of 360 mm and diameter of 15 mm activated carbon is placed (layer height is from 10 to 100 mm). Rutin raw solution is applied to the prepared sorbent layer, eluent feed to the column is produced at a speed of 1 drop in a second. Sorbent layer height in a column corresponds with the number of the sample of purified rutin.

After rutin raw purification with the use of activated carbons of different brands, the rutin samples were analyzed for compliance with the melting temperature, the content of flavonoids and authenticity on the presence of chlorophyll and red pigments in comparison with the GSO [State Standard Samples] control sample. All the used brands of carbons are activated and represented in 87–97 mas.% of composition of elements by carbon. The main structural element of the activated carbon sorption space at the organization molecular level is the graphite basal face, which is formed by carbon atoms in the state of sp^2-hybridization with delocalized fourth electron. Non-specific physical adsorption is realised on them by means of universal forces of dispersion interaction. Besides, non-specific electrostatic induction forces are expressed in carbon like in conductor by means of dipole direction in the sorbate molecule. Their intensity is determined by polarization capacity. Carbons express capacity to sorption by means of addition of these forces. At the same time, oxigenated functional groups and Bronsted acids are present on the surface initially and appear during activation process by overheated moisture vapour. They are represented by hydroxyl, phenol, carboxyl, carbonyl and lactone groupings, content and balance of which are different for different carbon brands [11]. It should be noted that acidic properties of the carbon surface change in the following sequence: NWM-P<NWC-P<OU-A, OU-B<BAU-MF<BAU-A. In other words, on the surface of NWM-P carbon there is minimum number of acidic groups from all the materials under consideration, and on the surface of BAU-A carbon this number is maximum. NWM-P and

NWC-P carbons express high reducing ability in comparison with BAU and OU carbons.

The research results of melting temperature determination are indicated in Fig. 1–3. According to the obtained dependences of Fig. 1, one can achieve the rutin highest melting temperature, which is one of the product characteristics, using NWC-P, NWM-P and OU-B carbons. Moreover, only when these brands of adsorbents are used, there is a dynamic in a positive index changing with carbon layer increase in a column. Rutin samples, purified on NWC-P carbon layer, are the closest to the control sample.

Processing of experimental data results on rutin raw purification with the use of the normal distribution is indicated in Fig. 2.

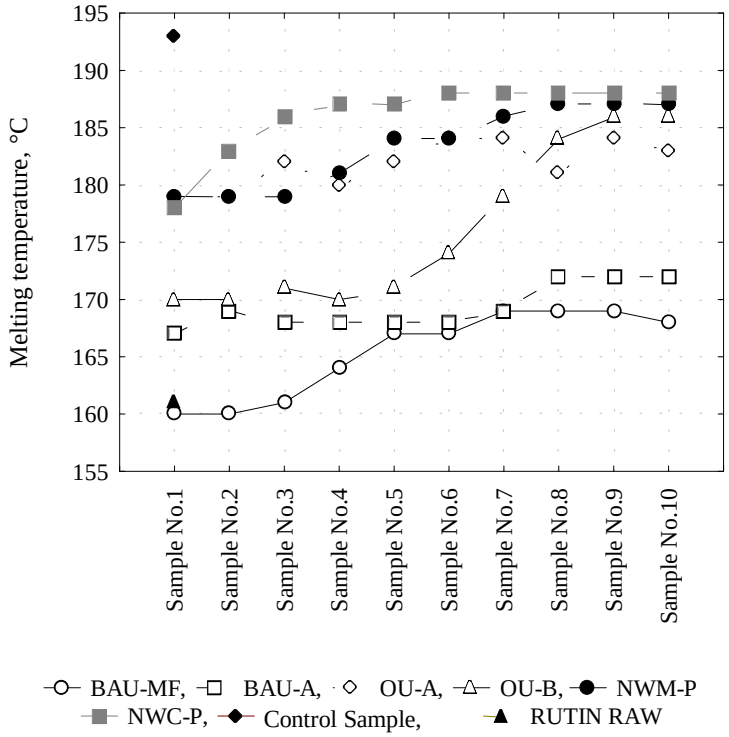


Fig. 1. Dependence of rutin samples melting temperature on carbon brand.

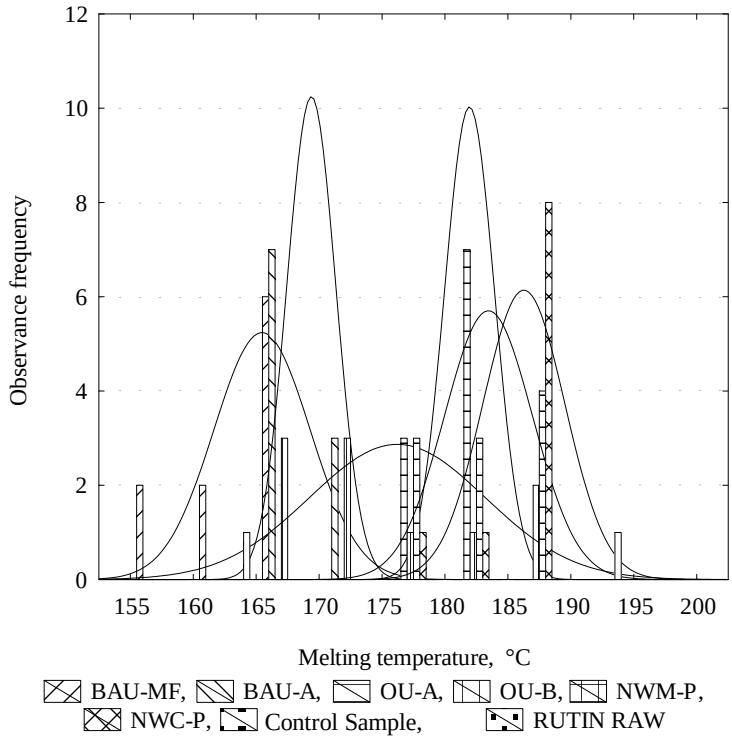


Fig. 2. Normal distribution of melting temperature values of rutin samples depending on carbon brand.

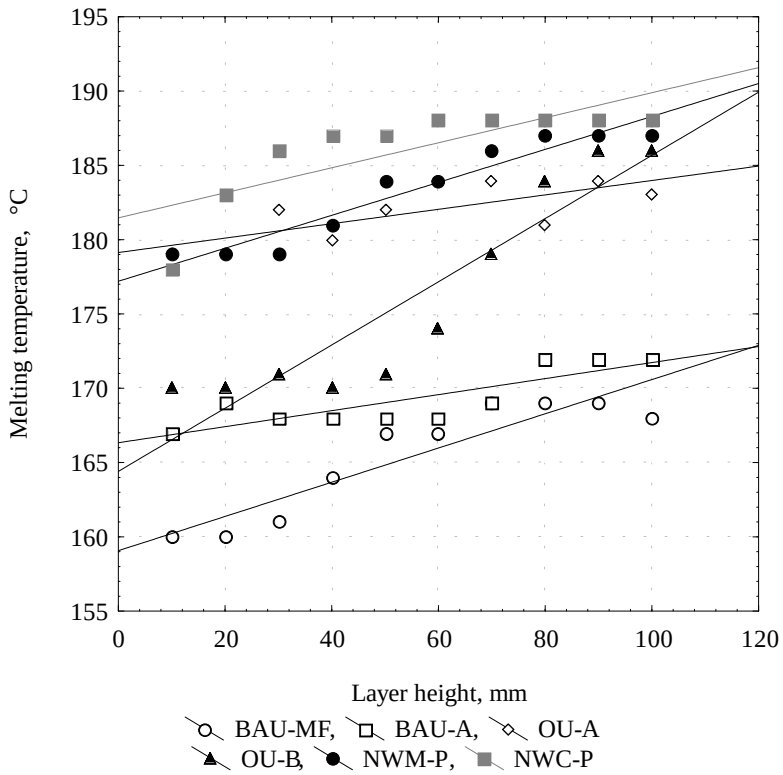
According to Fig. 2, the adsorbent efficiency of BAU-A and OU-A carbons nearly does not depend on the layer height in a column. Herewith, the use of OU-A carbon allows to get a stable result of melting temperature of 181.9°C with narrow distribution. BAU-MF adsorbent is absolutely ineffective, having wide distribution with an average value of 165.4°C. NWM-P and NWC-P adsorbents, having wide distribution, allow to get an average result of 183.3°C and 186.1°C respectively. Maximum purification degree for the carbons of these brands is determined by a much higher specific surface (1.5–2.0 times higher) in comparison with wood-based activated carbon. Coconut-based carbons are sorbents with pores of mixed type with nearly equal volume of micro- and mesopores, whereas wood-based activated carbons are characterized by a large proportion of macropores, acting as transporting channels which bring adsorbate molecules to adsorption space of the activated carbon particles. In this regard, wood-based adsorbents purification efficiency is directly connected with the layer height, it is expressed especially clearly in OU-V activated carbon which has the widest distribution.

Dependence of the use of the studied activated carbon brands on the layer height in a column concerning the melting temperature changing of rutin samples is indicated in Fig. 3.

The calculation results indicate that the highest correlation between the layer height and the achieved result is observed in NWM-P, OU-B and BAU-MF adsorbent brands with a direct correlation coefficient r = 0.9601, r = 0.9265 and r = 0.9159 respectively. Direct correlation coefficient value more that 0.75 indicates strong dependence between the layer height changing and the result obtained. Thereunder, when OU-A carbon is used for rutin raw purification, the results strongly depend on the layer height (r = 0.7381).

Qualitative and quantitative flavonoid contents in the rutin samples were defined with thin-layer chromatography (TLC) and high-efficiency liquid chromatography (HELC) methods. According to TLC, rutin raw contains a foreign admixture - quercetin, which is removed due to purification with the use of NWC-P and OU-B carbons regardless the sorbent layer height. The same effect can be achieved using OU-A and NWM-P carbons with the layer height in a column more than 40 mm. HELC analysis results are indicated in Fig. 4–6.

According to the data of Fig. 4, the greatest purification of the product can be achieved using NWC-P and NWM-P adsorbents. Moreover, only for these activated carbon brands there are stable positive dynamics of admixture reduction when the adsorbent layer in a column increases. However, rutin samples, purified with NWC-P carbon, are the closest to the control sample in their parameters.



Layer height, mm: BAU-MF: r = 0.9159; y = 159.066667 + 0.115151515•x
Layer height, mm: BAU-A: r = 0.8390; y = 166.333333 + 0.0539393939•x
Layer height, mm: OU-A: r = 0.7381; y = 179.133333 + 0.0484848485•x
Layer height, mm: OU-B: r = 0.9265; y = 164.4 + 0.212727273•x
Layer height, mm: NWM-P: r = 0.9601; y = 177.2 + 0.110909091•x
Layer height, mm: NWC-P: r = 0.7855; y = 181.466667 + 0.0842424242•x

Fig. 3. Dependence of rutin melting temperature on adsorbent layer height.

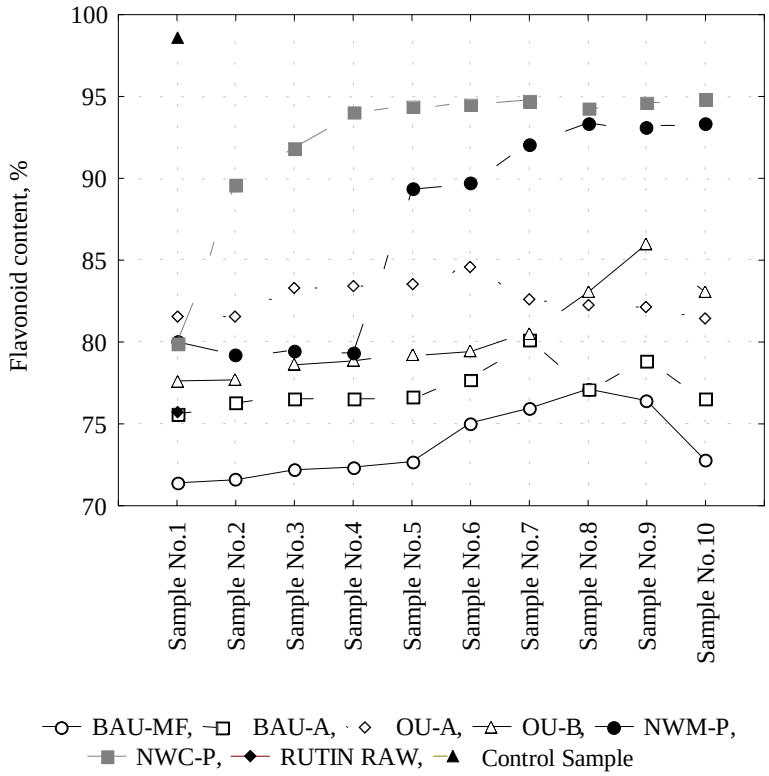


Fig. 4. Dependence of flavonoid amount content in rutin samples on carbon brand.

Processing of experimental data results on rutin raw purification with the method of normal distribution (Fig. 5) showed that the efficiency of BAU-A and OU-A adsorbents nearly does not depend on the layer height in a column. Herewith, use of OU-A carbon allows to get a stable result of 82.6% with narrow distribution. BAU-MF adsorbent is absolutely ineffective, having wide distribution with an average value of 73.8%, and NWM-P and NWC-P adsorbents, having the widest distribution, allow to get an average result of 86.9% and 92.3% respectively.

Dependence of the carbon brand efficiency on the layer height in a column is indicated in Fig. 6. The calculation results indicate that the highest correlation between the layer height and the achieved result is observed in NWM-P and OU-B adsorbent brands with correlation coefficients r = 0.9170 and r = 0.8940 respectively, for BAU-MF and NWC-P activated carbons correlation is less expressed with coefficients r = 0.7142 and r = 0.7235 respectively. Direct correlation coefficient value more that 0.75 indicates strong dependence between the layer height changing and the result obtained. If OU-A activated carbon is used as an adsorbent, there is no correlation among the studied parameters (r = -0.0579). Sorption rutin extraction is far less in comparison with its aglycone–quercetin, which may be connected with different adsorption nature, especially with the structure and the data size of polyphenol molecules. Functional groups on the activated carbon surface interact with phenol compounds due to Van der Waals forces in micropores and hygrogen bonds appearance in mesopores, herewith, the bigger and more polar glycoside molecule is adsorbed slower. Taking into account sub-acid nature of the split flavonoids, adsorption activity of the carbons, used in the present research, will be changed in a sequence, contrary to the surface acidic properties changing.

According to the results, obtained by mathematic treatment of experiments on determination of mass fraction of flavonoid amount, it can be stated that purification has a positive effect on the main substance content, extracted after the use of NWC-P and NWM-P carbons.

Rutin authenticity is confirmed by the results of determination of chlorophyll and red pigments content and is indicated in Fig. 7–9.

The obtained dependences of Fig. 7 show that the use of NWC-P, BAU-MF and BAU-A adsorbents allows to achieve the lowest chlorophyll and red pigments content, whereas using NWM-P carbon, a substantial increase in chlorophyll and red pigments content is observed.

Processing of experimental data results on rutin raw purification with the method of preparative chromatography with the use of normal distribution is indicated in Fig. 8.

According to Fig. 8, the efficiency of BAU-A and BAU-MF carbons nearly does not depend on the layer height in a column and allows to get a stable result of 0.00016% with narrow distribution. NWM-P carbon is absolutely ineffective in this case, having wide distribution with an average value of 0.00056%. It may be connected with the pore structure of the adsorbents under consideration: micropores, presence of which is typical for coconut-based carbons, are especially

suitable for adsorption of small molecules, whereas chlorophyll and red pigments are of quite big sizes. In this case, polymolecular adsorption is most effective which takes place in mesopores at sequential appearance of adsorption layers and which ends with pore filling by a mechanism of capillary condensation.

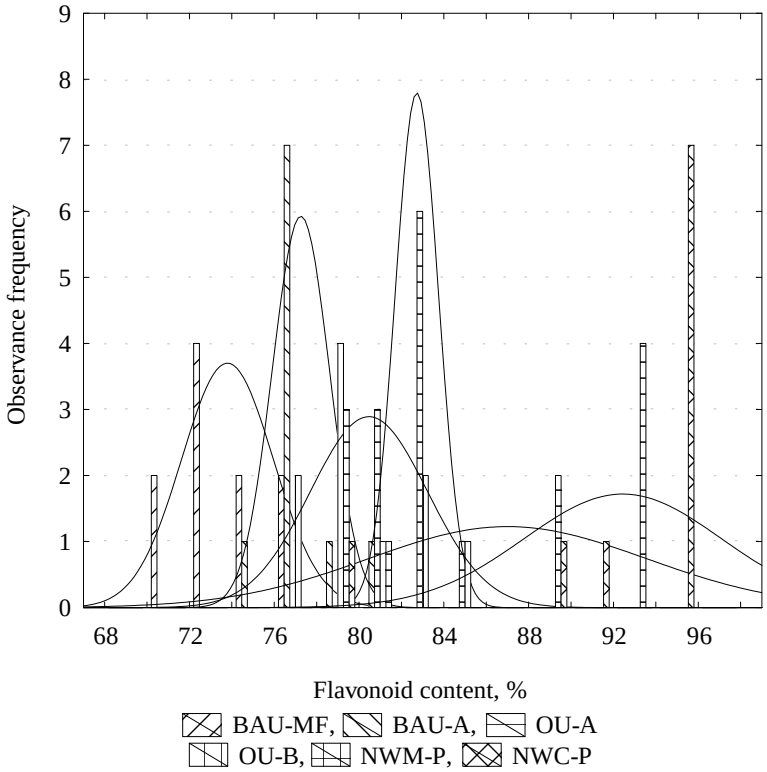


Fig. 5. Normal distribution of flavonoid amount content values in rutin samples depending on carbon brand.

Layer height, mm: NWC-P: r = 0.7235; y = 86.2166667 + 0.110842424•x

Fig. 6. Dependence of flavonoid amount content in rutin samples on adsorbent layer height.

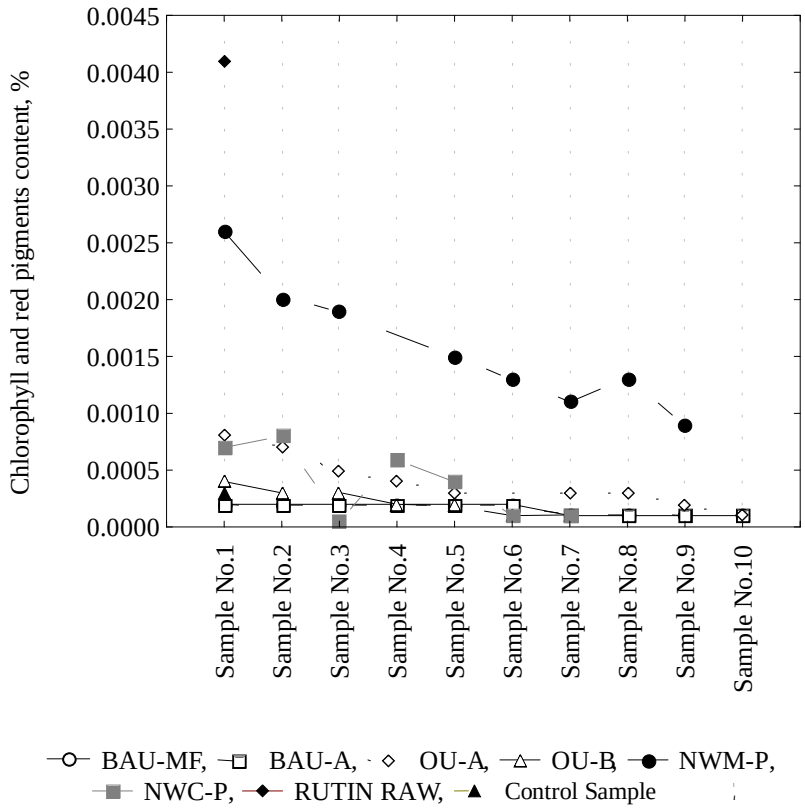


Fig. 7. Dependence of chlorophyll and red pigments content in rutin samples on carbon brand.

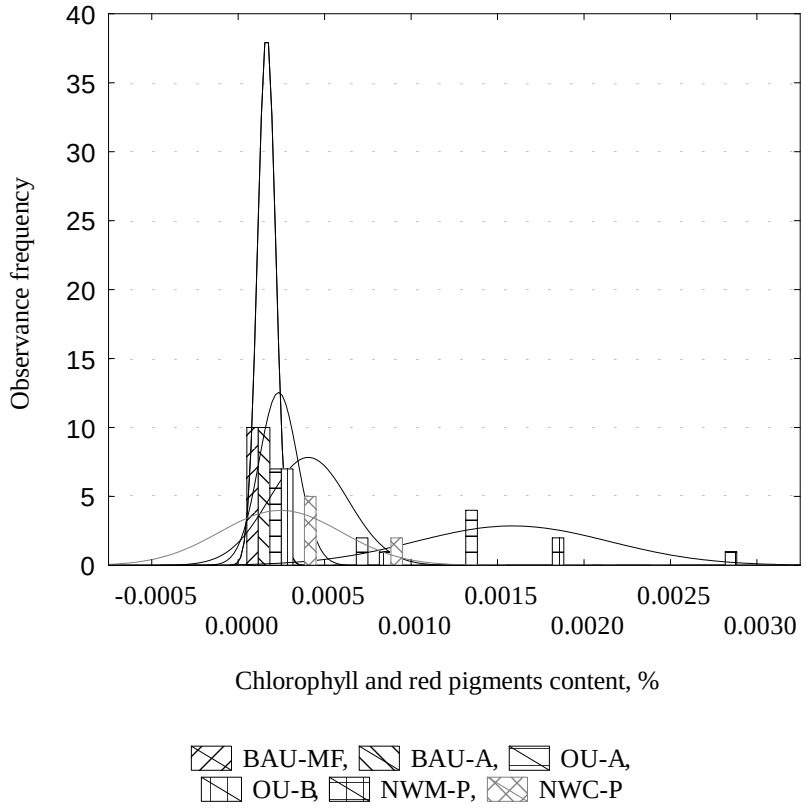


Fig. 8. Normal distribution of chlorophyll and red pigments content values in rutin samples depending on carbon brand.

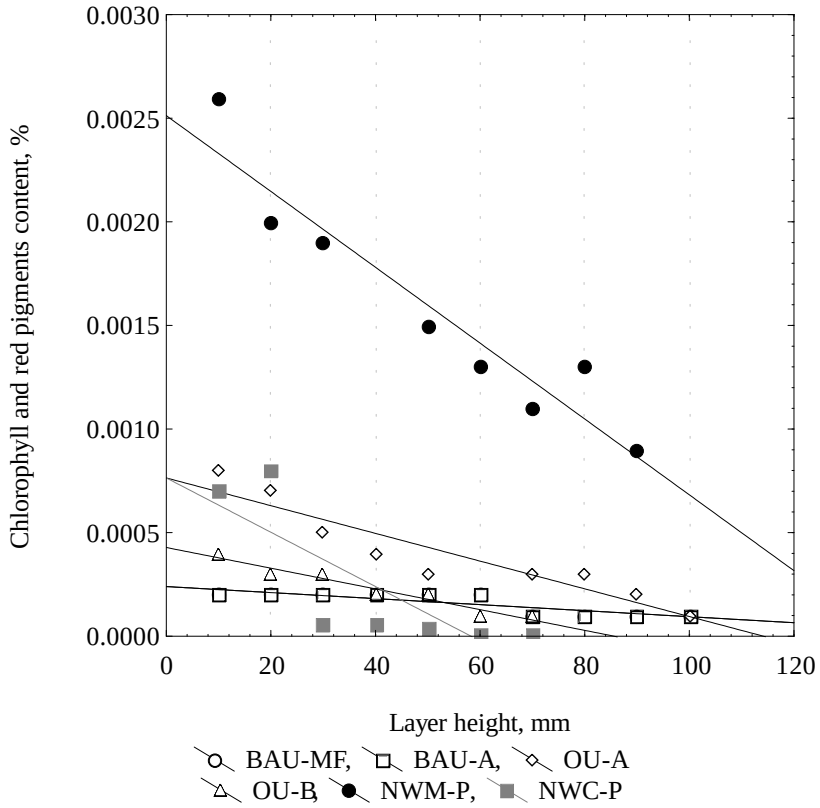
Dependence of the carbon brand efficiency on the layer height in a column is indicated in Fig. 9. The calculation results indicate that the highest correlation between the layer height and the achieved result is observed in OU-A, NWM-P and OU-B adsorbent brands with an invert correlation coefficient r = -0.9707, r = -0.9359 and r = -0.9359 respectively. OU-A and OU-B adsorbents are brightening carbons with mesopore volume of 0.7 cm^3/g and specific surface of 200–450 m^2/g, in contrast to other brands of activated carbons, for which these indexes are much lower and are 0.002–0.10 cm^3/g and 20–70 m^2/g respectively. According to the analysis of the obtained data, authenticity of all tested rutin samples is confirmed, which indicates strong correlation between the parameters under study and the adsorbent brand.

Thus, the use of the following carbon brands, indicated in decreasing effectiveness order, can provide the best purity and stability of parameters values, characterizing the product: NWC-P, NWM-P, OU-A and OU-B, excluding the authenticity index, where NWM-P carbon had the worst result.

The best correlation between the layer height in a column and product quality parameter was achieved, when NWM-P, OU-A and OU-B carbons were used, excluding the experiment on flavonoid amount content, where OU-A carbon showed no dependence.

Depending on the tasks, rutin purification degree may be regulated by sequential use of NWC-P and NWM-P carbons. Moreover, when rutin is purified from proximate admixtures, chlorophyll and red pigments, NWC-P adsorbent allows to get a comparable result even when the layer height is from 50 to 70 mm respectively. These data are proved by rutin samples micro-copying. After purification with NWC-P carbon, the crystal form is needle-like, identical to the GSO [State Standard Samples] control sample, which characterizes substance high purity. These data are indicated in Table 2.

Based on the results of Table 2, it should be noted that physical and chemical properties of the studied rutin samples No. 5 and No. 7 comply with State Pharmacopoeia XI after purification.



Layer height, mm: BAU-MF: r = -0.8528; y = 0.00024 - 0.00000145454545•x
Layer height, mm: BAU-A: r = -0.8528; y = 0.00024 - 0.00000145454545•x
Layer height, mm: OU-A: r = -0.9359; y = 0.000764189189 - 0.00000668918919•x
Layer height, mm: OU-B: r = -0.9707; y = 0.000428571429 - 0.000005•x
Layer height, mm: NWM-P: r = -0.9522; y = 0.00251295117 - 0.0000183014862•x
Layer height, mm: NWC-P: r = -0.7064; y = 0.000802857143 - 0.0000102142857•x

Fig. 9. Dependence of chlorophyll and red pigments content in rutin samples on adsorbent layer height.

Table 2. Rutin physical and chemical parameters

Rutin sample	Crystalls colour	Melting temperature, ◦C	Crystalls form	Crystalls size, μm	Rutin content, %	Flavonoids, different from rutin * (TLC data)	Ultraviolet spectroscopy	
							$D\ max^{I}$, nm	$D\ max^{II}$, nm
GSO	yellow-green	190	needle-like	0.33–153.30	98.56	1; 2	258.0	361.0
Rutin raw	greyish-green	162	irregular	1.66–203.13	75.74	1; 2; 3	258.0	361.0
Sample No. 5	yellow with the greenish cast	189	needle-like	0.42–159.00	96.25	1; 2	257.0	361.0
Sample No. 7	yellow with the greenish cast	189	needle-like	0.66–153.15	97.88	1; 2	258.0	361.0

*Notes.** 1 - kaempferol-3-O-rhamnoside; 2 - isoquercitrin; 3 – quercitrin.

REFERENCES

1. Evdokimova O.V. Preparaty rastitel'nogo proiskhozhdeniya pri khronicheskoy venoznoy nedostatochnosti [Herbal drugs at chronic venous insufficiency]. *Novaya apteka* [New pharmacy], 2006, no. 4, pp.11–12.
2. Krikova A.V., Davydov R.S., and Mokin Yu.N. Biologicheskaya aktivnost' rastitel'nykh istochnikov flavonoidov [Biological activity of flavonoid plant sources]. *Pharmacy*, 2006, vol. 54, no. 3, pp. 17–18.
3. Su K.Y., Yu C.Y., Chen Y.W., Huang Y.T., Chen C.T., Wu H.F., and Chen Y.L.S. Rutin, a Flavonoid and Principal Component of Saussurea Involucrata, Attenuates Physical Fatigue in a Forced Swimming Mouse Model. *International Journal of Medical Sciences*, 2014, vol. 11(5), pp. 528–537. DOI: 10.7150/ijms.8220.
4. Kurkin V.A. *Farmakognoziya. 2-e izd.* [Pharmacognosy. 2nd ed.]. Samara: Ofort Publ., 2007. 1239 p.
5. Kisilev V.E., Kovalenko V.E., and Minaeva V.G. *Grechikha kak istochnik flavonoidov* [Buckweat as a flavonoid source]. Moscow: Nauka Publ., 1995. 96 p.
6. Zhao Z., Dong L., Wu Y., and Lin F. Preliminary separation and purification of rutin and quercetin from *Euonymus alatus* (*Thunb.*) *Siebold* extracts by macroporous resins. *Food and Bioproducts Processing*, 2011, vol. 89, no. 4, pp. 266–272. DOI: https://doi.org/10.1016/j.fbp.2010.11.001.
7. Ryzhov V.M., Kurkin V.A., and Hisyamova D.M. Studying the possibility of waste-free processing the buckwheat sowing grass. *Proceedings of the Samara Scientific Center of the Russian Academy of Sciences*, 2012, vol. 14, no. 1(9), pp. 2282–2284. (In Russian).
8. Pavlovskaya N.E., Gneusheva I.A., Polekhina N.N., Solokhina I.Yu., and Gor'kova I.V. *Sposob polucheniya rutina* [Rutin extraction method]. Patent RF, no. 2505307, 2014.
9. *Obzor rynka aktivirovannogo uglya v SNG: otchet. Ob'edinenie nezavisimykh ekspertov v oblasti mineral'nykh resursov, metallurgii i khimicheskoj promyshlennosti. 7-e izd.* [CIS activated carbon market survey: report. Association of independent experts in the field of mineral resources, metallurgy and chemical industry, 7th edn.], Moscow: OOO INFOMAIN Publ., 2015. 22 p.
10. Averyanova E.V. and Shkolnikova M.N. Effect of activated carbons of different brands on the quality of rutin in the cleaning process. *Bulletin of KrasGAU*, 2015, no. 4, pp. 49–54. (In Russian).
11. Kotelnikova T.A., Kuznetsov B.V., Moreva A.A., and Muraveva G.P. Hydrophiliciti of activated carbons for purification of drinking water according to the nonlinear gas chromatography. *Sorption and chromatographic processes*, 2012, vol. 12, no. 4, pp. 523–531. (In Russian).

Please cite this article in press as: Averyanova E.V., Shkolnikova M.N., and Frolov A.V. Dependence of purified rutin quality on activated carbon brand. *Foods and Raw Materials*, 2017, vol. 5, no. 1, pp. 165–173. DOI: 10.21179/2308-4057-2017-1-165-173.

ECONOMICS

FISCAL TECHNOLOGIES OF BUDGET LIQUIDITY MANAGEMENT AND THEIR ROLE TO ENSURE THE SUSTAINABLE GROWTH OF THE AGRARIAN SECTOR IN THE CONTEXT OF GLOBAL UNCERTAINTY

O. V. Glushakova[a,*], N. V. Fadeykina[a], I. V. Baranova[a], K. Yu. Tsygankov[a], and V. V. Mikhailov[b]

[a] Siberian Academy of Finance and Banking,
Polzunova Str. 7, Novosibirsk, 630051, Russian Federation

[b] Kemerovo Institute (branch), Plekhanov Russian University of Economics,
Kuznetskiy Ave. 39, Kemerovo, 650992, Russian Federation

* e-mail: trinity@oaoktk.ru

Received February 02, 2017; Accepted in revised form April 30, 2017; Published June 29, 2017

Abstract: When the political and economic uncertainty rises, the sustainable functioning of strategically significant industries that first and foremost include the agriculture defines the national security. Comparison of the agricultural output in Russia and some global countries indicate on extensive pattern of the growth in industry. The government too poorly commits to support the agricultural sector. Where the budget revenue declines in the Russian Federation due to unfavorable conditions in the commodity markets, the risks of non compliance with expenditure commitments increase (in particular, program events focused on the agrarian sector support). The purpose of the study was to justify the feasibility to increase the share of government in the activity to ensure the growth of the industry at the brand-new level by using up-to-date fiscal technologies for budget liquidity management. The study was based on the dialectical approach that allows considering components (elements) of the agrarian sector in their flow and development along with systematic and institutional methodological approaches and statistical methods. Fiscal technologies for budget liquidity management are aimed at reducing budgetary risks that arise when implementing budget plans under conditions of global uncertainty. Concentration of financial assets with the Unified Bank Account of the Treasury of Russia and placement of temporarily free budget liquidity in derivative instruments forms conditions to create the innovative and investment-oriented budget deficit and increase of the governmental share in development of the industry at the truly new level.

Keywords: Agriculture, agrarian sector, sustained development, food security, targeting of budget funds remainders, liquidity of the single budget account, budgetary risks, budget data, innovation and investment-oriented budget deficit

DOI 10.21179/2308-4057-2017-1-174-191 *Foods and Raw Materials*, 2017, vol. 5, no. 1, pp. 174–191.

INTRODUCTION

Sustainability of the agricultural sector is one of strategic priorities that specify the national food security. It is obvious that the food security development greatly relates to the matter of programs and policies integrated at the national level, oriented to creation of the environment convenient for business and growth of agricultural output.

For 26 years, quite a long period in history, when Russia was undergoing formation and development of market relations, a range of legislative and regulatory laws were adopted along with documents of state strategic planning system [1] (forecasts, concepts, strategies, programs, activity plans, etc.) to show the opinion and intentions of federal and regional authorities towards agricultural activity, the industry so significant to ensure the national security. Its significance for the national economy is evident from that the term "agriculture" is mentioned 7669 times in the text of the Russian legislation, and 1200 to 8000 and more times in the legislation of the constituent entities.

It is necessary to point out that in the Russian Federation institutional frameworks are mainly formed aimed to ensure the governmental support to agricultural sector.

The Concept of Long-Term Social and Economic Development of the Russian Federation for the period up to 2020 [1], as well as the Food Security Doctrine of the Russian Federation serve as the key instrument that

[1] The documentation system of state strategic planning is defined in the Art. 3 of the Federal Law 3 No. 172-FZ "On Strategic Planning in the Russian Federation" dd. June 28, 2014.

specify major objectives of the governmental agrarian policy for strategic outlook [2]. In December 2010, the Concept of Sustainable Development of Rural Territories of the Russian Federation for the period to 2020 was approved [3], and the Strategy for Agricultural Machinery Development in Russia for the period to 2020 [4] was approved in December 2011.

The Art. 6 of the Federal Law "On Agriculture Development" [5] specifies measures to implement the governmental agrarian policy, including the budgetary funds granted to agricultural producers, and the Art. 7 of the same specifies main areas of public support to this industry. In particular, this includes availability of credit resources for agricultural producers, provided that the share of sale revenue of agricultural products is at least 70% per calendar year of the total income of the entity; development of the risk insurance system in agriculture, of livestock breeding, elite seed production, and others. (sub-clause 1, cl. 1, Art. 7). The federal budget fund is the source of finding of such activities granted as budget subsidies to budgets of the RF constituent entities as prescribed by the Government of the Russian Federation.

In 2007, the State Program for Agriculture Development and Regulation of Agricultural Products, Raw Material and Foodstuff Market for 2008–2012 was adopted [6]. As the list of the RF state programs [7] is approved to integrate the program-targeted principles of budget planning, the program matter was updated, and the timeline was extended to 2020 [8].

Initially, in 2008-2012, the program was assumed to be implemented based on co-financing at the expense of assets as follow: 551.3 billion rubles (39.2%) – federal budget assets; 544.3 billion rubles (38.7%) – budget assets owned by RF entities; 311 billion rubles (22.1%) – extrabudgetary sources, and the total scope of finance under the program amounted to 1406.6 billion rubles. However, the program funding sources were revised. To implement the program within 2013–2020, the federal budget funds were assumed only in the amount of 2126.2 billion rubles (that is, 3.8 times higher compared to the amount scope of budget allocations under the federal budget for 2008–2012).

It should be noted that the RF constituent entities also adopted state programs aimed at support to the agrobusiness. The presence of regions in this process is obviously defined by budget capacity of thereof.

The overarching policy of the Russian Federation to take part in the international agriculture, fisheries and food security activity [9] specifies that the sustainable and predictable development of agriculture is becoming more urgent against the world crises, including food and financial sectors that managed to radically transform the condition related to ensure the food security in Russia in recent days.

The political events of 2014–2016 (the Ukrainian crisis followed by annexation of the Crimea to the Russian Federation, the presence of the National Guard troops in Syria, etc.) fatally resulted in the growth of global political and economic uncertainty. Economic sanctions against Russia by the United States and the European Union countries, the restriction or embargo on the supply of certain food and the similar triggered actions by the President of the Russian Federation and the Government of the Russian Federation to focus on sustainable development of agriculture for the purpose to introduce the policy of import substitution and ensure the national food security.

As the response to economic sanctions by the West, on January 1, 2015, the President of the Russian Federation caused the formation of the Eurasian Economic Union (EEU) with Belarus, Kazakhstan, Armenia as members and Kyrgyzstan that joined them six months later. The purpose of EEU is to ensure the free flow of goods, services, capital assets, labor and introduction of the well-coordinated, consistent or unified policy for economic sectors, including agriculture. The intentions of various countries (Egypt, Thailand, Iran, Mongolia, Serbia) to join the EEU prove their concern.

The purpose of this study is to provide evidence on feasibility to increase the governmental share to ensure the game0changing industrial development through the employment of recent fiscal technologies to manage the budget liquidity based on assessment results for the Russian agrarian sector condition and comparison data of industrial performance between some countries of the world, the development level of institutional environment oriented to the agriculture support, as well as based on the volume of budgetary resources available in the pre-crisis period and in the midst of increasing global uncertainty.

OBJECTS AND METHODS OF STUDY

The target of research is the agrarian sector with reference to processes that characterize its capacity against the growing budget constraints related to fiscal technologies of public liquidity management and the share of such technologies in the sustainable development of the industry to the brand-new level. The research is based on the dialectic approach. In the course of the research, systematic, institutional methodological approaches and statistical methods were applied.

The dialectical approach allows to study agrarian components (elements) on the movement and in process. In turn, the system concept allows assessing the impact of the agrarian sector pattern, as a subsystem, on the supersystem stability that is the national economy as a whole, and considering the interaction between these different systems. The use of the system concept affords to analyze the interaction of the agrarian sector as a national economy subsystem with other subsystems, for instance, with the government sector. The institutional approach is focused on the study of the agrarian sector in terms of assessment of the health, level and directions of the institutional environment development, including such institution as the Federal Treasury and technologies used by thereof to manage budget liquidity.

The analysis of statistical time series makes it possible to track the industrial changes in correlation with a variety of macroeconomic parameters, for example, incomes and expenditures of the consolidated

budgets of the RF budget system, federal budget revenues, oil and gas revenues, oil prices, and so forth.

RESULTS AND DISCUSSION

The comparative analysis and the assessment of the agricultural sector capacity in relation to some macroeconomic parameters

Gross Regional Product (GRP) serves as the summarized performance measure of the state-of-the-art of regional economy and the significance of certain types of economic activity in formation thereof. The analysis of the GRP structure for Russian regions showed that only 21 out of 85 RF entities significantly contribute to ensure the national food security with over 10% share of such business activities as "Agriculture, hunting and fishing" (Fig. 1). If the share of the industry in the GRP structure is taken as 15% and over as the estimation criterion, there are only 11 regions in the Russian Federation with such parameters (Fig. 1). Among them, the Republic of Kalmykia (31.3%), Belgorod (20.3%), Kursk (18.1%), Orel (16.8%), Tambov (21.9%), Stavropol Territory (15.0%), Kabardino-Balkar Republic (16.2%), Karachay-Cherkess Republic (19.2%), and Mariy-El (18.0%), Altai (18.3%) and the Crimea (21.9%) [10].

Moreover, the comparison data on the performance of the most vital types of farm products and foodstuffs in Russia and some countries of the world show that the increasing adjustments are required to be made to lots of indicators to successfully implement the policy of import substitution (with the share rated at about 1.3 trillion rubles to be achieved by 2020) and to ensure the national food security (Table 1).

It is worth pointing out that that despite the statement on accomplishment of the food sovereignty level in the Food Security Doctrine of the Russian Federation by such agricultural products as grain, potato, vegetable oil and sugar, many world countries show much higher performance in the industry with the farmland area much smaller as compared with those in Russia.

So, for example, the area of cultivated lands in such a small country as Belgium is 169.4 times less than in Russia, but the grain output per 1 person is 1.6 times higher. In terms of potato production, Denmark is 1.3 times ahead of Russia, despite the fact that the area of cultivated lands in this country is 84.7 times less. The similar results are reported in terms of production output for other types of agricultural products (Tables 1, 2).

Table 1. Production of most important types of farm products and foodstuffs in 2013 in Russia and in several world countries per capita, kg [11]

Type of agricultural products	Russia	Australia	Austria	Belgium	Hungary	Germany	Denmark	Italy	Canada	Netherlands	Poland	United Kingdom	USA	Finland	France	Japan
Corn**	721	1672	577	1150	1381	585	1628	272	2061	108	748	326	1388	757	1071	93
Including wheat	409	998	188	700	515	305	738	121	1067	79	246	187	183	164	605	6
Potato**	216	56	71	23	45	118	284	22	131	405	164	87	63	115	109	20
Fruits*, berries*, citrus fruits and grapes*	24	156	113	76	130	29	12	276	23	42	109	6	94	4	129	24
Vegetables* and melon and gourds	116	88	70	79	146	42	51	217	63	287	135	40	108	50	82	89
Saluter cattle and poultry (carcass weight basis)*	62	196	106	29	82	99	337	67	123	159	99	57	134	72	87	26
Milk*	211	416	403	179	178	380	910	183	239	74	330	218	289	430	385	59
Eggs, pcs	287	175	200	165	253	167	250	229	225	637	260	39	301	203	246	330
Sugar (of domestic raw materials) **	31.5	149	59	0	12	54	77	6	3	60	50	21	23	16	69	5
Pasta	6.8	…	…	2	8	3	0.4	…	…	…	5	…	…	3	…	7
Vegetable oils**	27.8	21	23	27	36	44	36	20	95	12	22	16	36	20	43	13
Margaric products	3.5	…	…	1.3	…	4.8	11	…	…	15	6	3	…	3	…	2
Cooking salt	3.4	477	…	…	…	232	…	48	311	389	110	96	128	…	96	7
Animal oil	1.7	5.3	4.2	0.2	0.4	5.5	6.9	2	2.5	8	5	2	3	10	7	1

Notes. *By 2020, the imported farm product supply is planned to be reduced as follow: meat of cattle and poultry - by 67.8%, milk - by 29.9%, vegetables - by 70.3%, fruit and berry products - by 20%, grapes - by 54.6%.

** With respect to grain, potatoes, vegetable oil and sugar, the desired level of food food sovereignty as specified by the Food Security Doctrine of the Russian Federation has been achieved.

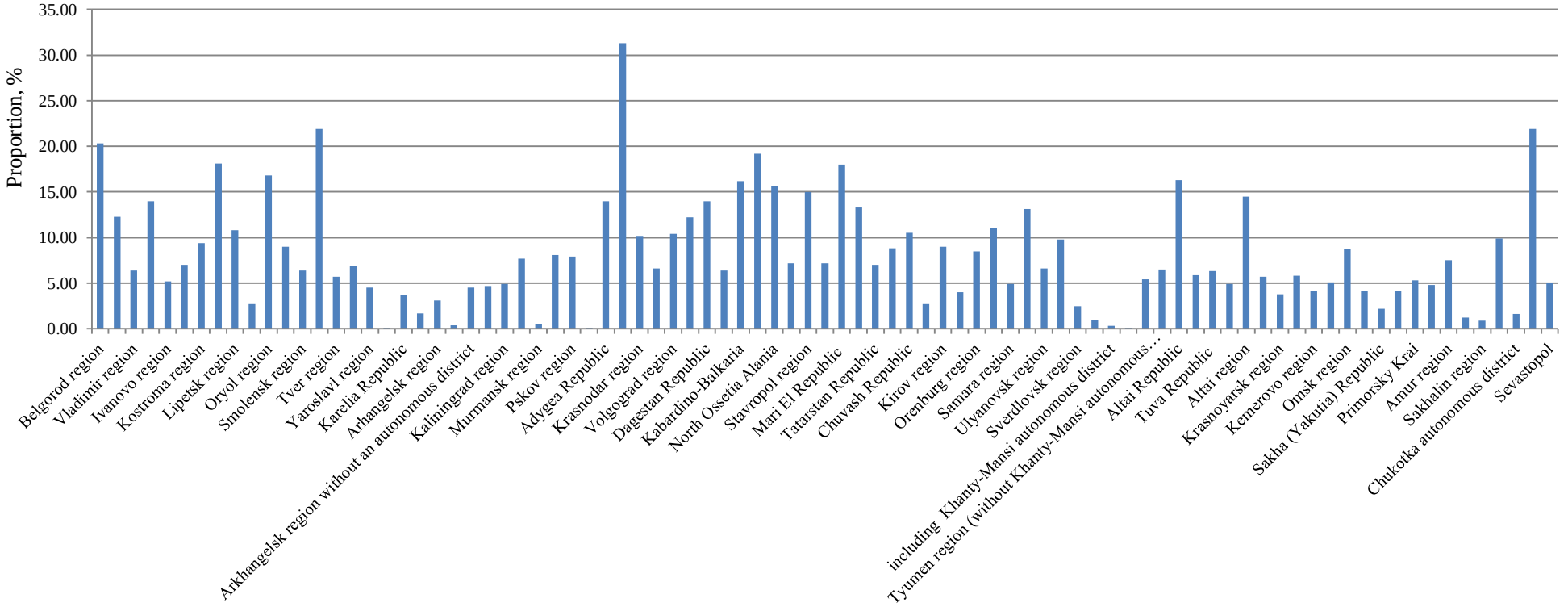


Fig. 1. Share of the "Agriculture, hunting and forestry" in the structure of regional GRP of the Russian Federation entities for 2014 (compiled by the authors to: [10]).

Table 2. The structure of cultivated land in 2013 in Russia and in some parts of the world [11]

Criteria	Russia	Australia	Austria	Belgium	Hungary	Germany	Denmark	Italy	Canada	Netherlands	Poland	United Kingdom	USA	Finland	France	Japan
Total cultivated land, mln hectares	220.2	396.6	3.2	1.3	5.3	16.7	2.6	13.6	65.3	1.8	14.4	17.3	405.4	2.3	28.8	4.5
of them, in percentage																
arable land	55.2	12	43	61	82	71	92	50	70	56	75	36	37	98	64	93
other agricultural land	44.8	88	57	39	18	29	8	50	30	44	25	64	63	2	36	7

The figures above indicate a variety of systemic issues, including the use of morally obsolete equipment and technologies in farm production, high physical depreciation of fixed assets (37% in 2014 as per Rosstat, Federal Service of State Statistics), immaturity of rural area infrastructure, low level of human capital asset development that impedes the industrial re-equipment. Ultimately, the issues above serve as the reason for irrational use of cultivated lands and the extensive nature of the industrial progress.

The financial component is one of key factors of sustainable development in any sector of national economy. In this term, the agriculture is no exception. The financial status of farms remains unstable, as evidenced by parameters of a variety of financial ratios (Table 3). So, the value of working capital financed by equity to total assets ratio remains negative, despite the upward trends that means that entities do not have own resources available to finance their current activities (purchase of raw stock, materials, etc.), and, consequently, it indicates the demand in credit assets. Dependence on external sources of funding is also proved by the value of equity to total assets ratio (Table 3).

Yet, institutional bases are formed, the governmental share in the industrial development remains too low, in our opinion, and the applicable measures are often non-effective. The structure of investments in fixed assets allocated for agricultural sector development was analyzed to prove on inadequate involvement of government in this process (Table 4, Fig. 2). The major sources of financing are own and attracted assets of agricultural producers.

Amendments to the applicable legislation in terms of granting subsidies at the expense of the federal budget to reimburse expenses for the purchase of mineral fertilizers and chemical protection equipment, reimbursement of partial cost for insurance payments, as well as of part of the investment loan interest rate, stimulated attraction of credit resources by agricultural commodity producers. The share of borrowed funds in the investment structure in 2005–2008 increased, reaching its peak value, in 2007, that makes 61.6%. The scope of investments, on whole, showed upward trends, either. As for 1999 to 2015, three critical points may be highlighted where its decrease was required as follow: in 2004 – by 65.1%, in 2009 – by 16.4%, in 2015 – by 5.58%. However, if the negative trend of investments in 2014 to the agriculture development was due to the fall in grain prices and crop failure (production output decreased by more than 25% due to unfavorable agroclimatic conditions), in 2009 and 2015, the negative trend by this parameter related solely to the crisis processes in the economy and the decline in financial capacities of both economic entities and in the budget of the Russian budget system.

When it comes to the governmental involvement in the growth of industry on whole, then, despite the upward trend of budget allocations of the consolidated budget of the Russian Federation (Fig. 3), the share of investments in the capital stock at the expense of the federal budget, starting from 2005, did not exceed 5%, and in 2010–2013 it was a little bit greater than 2%. The involvement of RF entity budgets in the support to the industrial growth was even more inferior (Table 4).

Comparison of the volume of RF consolidated budget subsidies with the federal budget for 2006–2015 by the sub-section of the budget classification of expenditures "Agriculture and Fishery" that enables to report on the sensitivity of the federal budget to crisis processes in the economics. It was in 2009 and 2014, in the course of decline in demands and prices for hydrocarbon raw materials in foreign markets, where financing of the industry was abruptly reduced (Fig. 3–4).

Table 3. Some parameters characterizing the financial standing and financial performance of agricultural entities for 2013–2015 [12]

Criteria	2013	2014	2015
Current liquidity ratio*, %	155	160.9	181.7
Working capital financed by equity to total assets ratio**, %	-41.2	-38.1	-14.2
Equity to total assets ratio***, %	37.8	39.3	44.8
Number of profitable entities, thous.	4.3	4.1	3.7
Balanced financial result, bln rubles	60.9	181.1	280.1

Notes. *Current liquidity ratio – the recommended value is 200%; **Working capital financed by equity to total assets ratio – the recommended value is 10%; ***Equity to total assets ratio – 50 %.

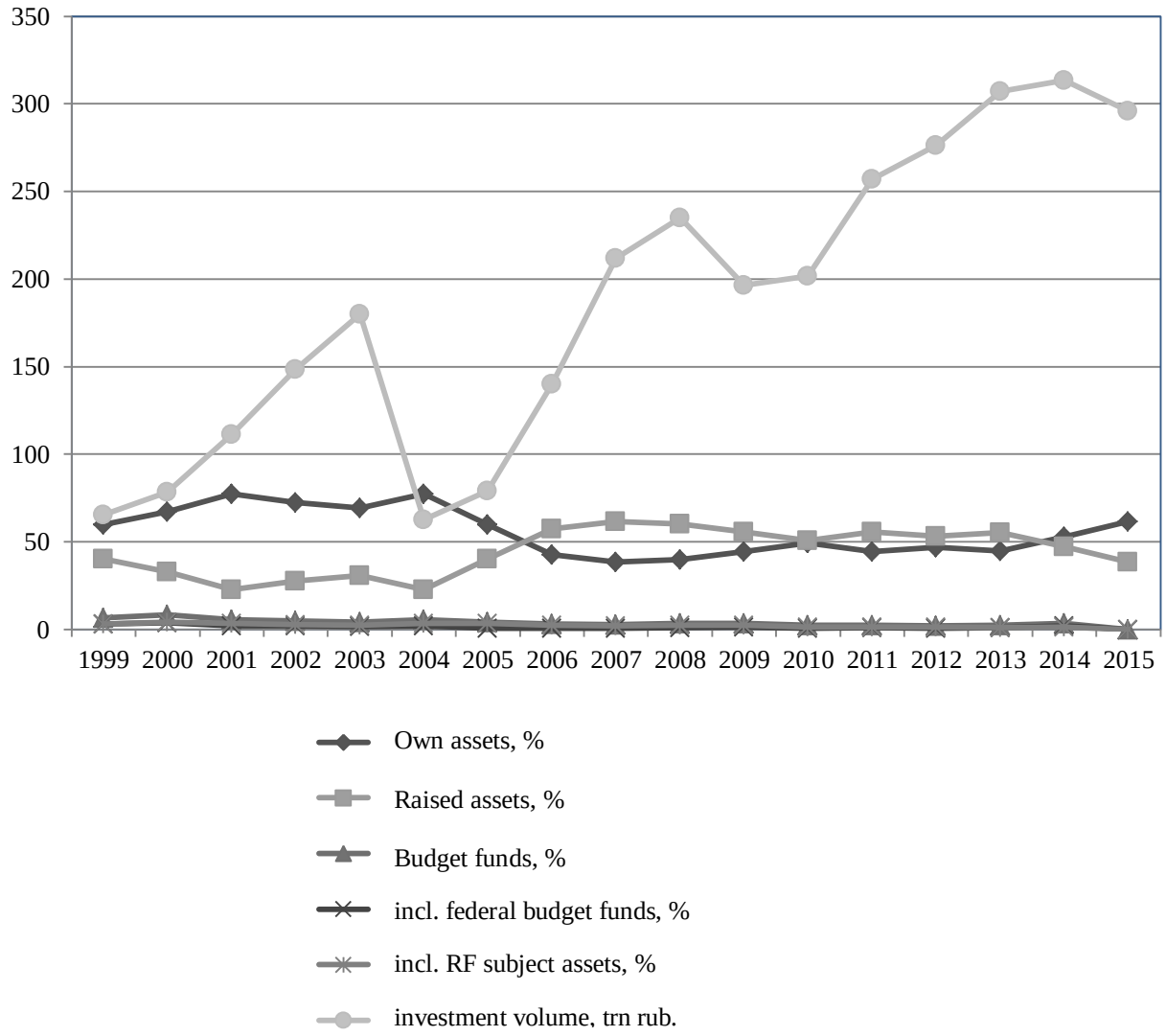


Fig. 2. Graphical view of trends in volume and structure of investments in capital assets to be allotted to agricultural development by sources of funding for 1999–2015 (compiled by authors to: [13]).

Table 4. The structure of investments to the capital stock for agricultural development as per sources of funding for 1999 – 2015, % [13]

Criteria	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015
Investments to fixed assets, total	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
of them:																	
own funds	59.8	67.1	77.4	72.5	69.2	77.4	59.8	42.5	38.4	39.8	44.5	49.3	44.3	46.8	44.8	52.8	61.5
raised funds	40.2	32.9	22.6	27.5	30.8	22.6	40.2	57.5	61.6	60.2	55.5	50.7	55.7	53.2	55.2	47.2	38.5
of which: budgetary funds	6.6	8.5	5.6	5.0	4.1	5.6	4.3	3.1	2.7	3.5	3.6	2.3	2.4	2.0	2.3	3.3	…
including																	
the federal budget	3.0	3.9	2.0	2.1	1.7	2.0	0.7	0.5	0.6	0.9	1.2	0.7	1.0	0.7	1.1	1.9	…
budgets of RF subjects	3.2	4.3	3.4	2.8	2.3	3.4	3.3	2.5	1.9	2.4	2.3	1.4	1.3	1.2	1.0	1.3	…
local budgets	…	…	…	…	…	…	…				…	…	…	…	0.2	0.1	…

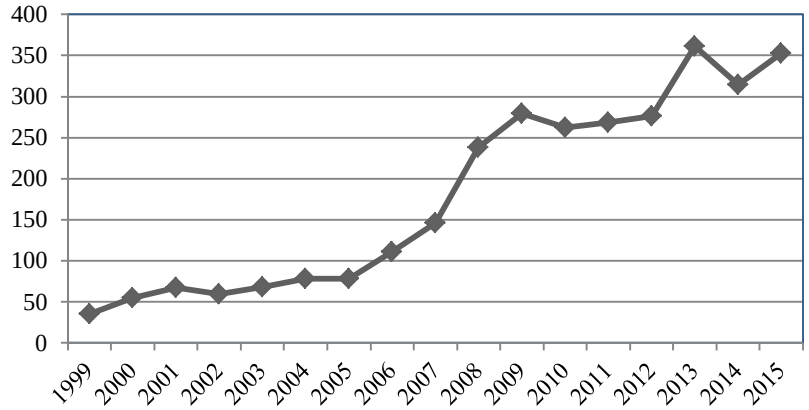


Fig. 3. Volume of the RF consolidated budget subsidies as per the item of budget classification of expenditures "Agriculture and Fishery" for 1999–2015, in bln rubles. compiled by authors to: [14]).

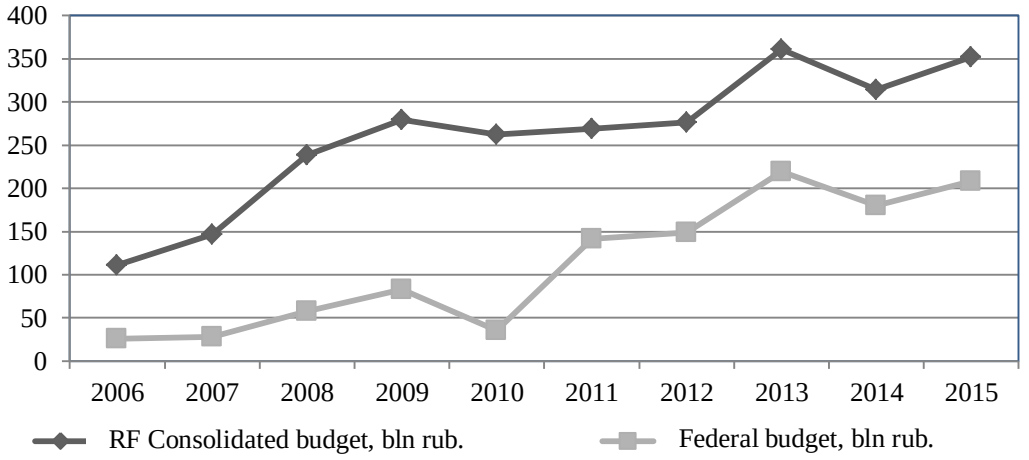


Fig. 4. Comparison of the RF consolidated budget subsidies with the federal budget for 2006–2015 in terms of the sub-section of the budget classification of expenditures "Agriculture and Fishery" in bln rubles (compiled by authors to: [15]).

ISSN 2310-9599. Foods and Raw Materials, 2017, vol. 5, no. 1

Due to the growing global political and economic uncertainty and budgetary constraints, there is an urgent need to search for fundamentally new approaches to manage budget resources available at all levels of the RF budget system to ensure the governmental support to strategically important sectors (including agriculture), but also to raise the required sources of resource support (primarily financial) that will help to overcome the extensive development of the industry and ensure its functioning at a radically new level. Up-to-date treasury technologies offer chances to minimize budgetary risks when reducing budget revenues and are focused to address issues on the shortage of financial resources available by effective management of budget liquidity.

Treasury technologies for budget liquidity management and their role to achieve the budgetary risks reduction under global uncertainty

The financial and economic crisis of 2008–2009 of the subsequently chronic nature that lasts up to date, has boosted the likelihood of budget risks caused by high dependence of the Russian economy on the demand and prices for raw stock.

The budget risk is the potential failure to comply (in full or in part) with certain budget parameters, inefficient liquidity management of the budget account, as well as the inefficient use of budget funds[2]. This is why the liquidity management was accentuated as one of the most urgent issues for discussion at the workshop "Treasury System Upgrading of the Asia-Pacific Economic Cooperation (APEC) Economies" held in March 2012 in Kazan.

The deviation from the cash budget is one of problems that arise when meeting budgets and that results in the liquidity shortage. Irregularity of cash payments that appear as "peak" payments at the end of each quarter and at the end of any financial year, generates risks of cash deficiency on unified budget accounts that synergize in a climate of global political and economic uncertainty.

A distinctive feature of distribution of public financial flows in the RF budget system is the significant concentration thereof in the federal budget. Thus, as per the reports on implementation of the consolidated budget of the Russian Federation and budgets of governmental extra-budgetary funds for 2015, the share of federal budget revenues in total revenue made 50.74%, budgets of governmental extra-budgetary funds – 34.33%, consolidated budgets of RF constituent entities – 34.57%, budgets of territorial state extra-budgetary funds – 5.9% [15]. Utilization of this model of distributive relations is one of reasons for budget imbalance of public and legal entities of sub-federal and municipal level that requires intergovernmental alignment through providing inter-budgetary transfers, attraction of budgetary credits to cover transient cash shortage that arise when executing budgets and utilizing state borrowings. Under the existing model of distributive relations, the fiscal capacity of regions and municipalities largely depends on the utilization of the federal budget capacity. This means that a decrease in its financial capacities involves destabilization in the development of regional and municipal social and economic systems and creates a threat of reducing the national competitiveness of Russia as a whole.

The consolidated [3] budget balance of the RF subjects was analyzed to reveal that consolidated budgets of only 9 regions out of 85 subjects of the Russian Federation were in surplus in 2015. They include the Vladimir Region, Leningrad Region, Sakhalin Region, Tyumen Region, cities of federal significance recognized as RF subjects, namely Moscow, St. Petersburg, Sevastopol, as well as the Khanty-Mansi Autonomous Area and the Chukot Autonomous Area. It should be noted that consolidated budget surplus in Moscow for 2015 was 12.2 times higher than the surplus of the Tyumen Region, one of the most prosperous regional budget in terms of balance (+144,399.3 and +11,788.4 mln rubles, respectively). The remaining 76 consolidated budgets of the RF subjects were short in financial resources. The highest deficit in the consolidated budget in 2015 was reported in the Krasnoyarsk Territory (-37,029.9 mln rubles), followed by Sverdlovsk Region (-17,545.3 mln rubles), Krasnodar Territory (-17,136.5 mln rubles.) [16]). The results of study of consolidated budget balance for the RF constituent entities for 2015 are shown in Fig. 5.

The consolidated budget of the Russian Federation is also in scarcity. As per the data of the budgetary reporting published on the official website of the Federal Treasury, the deficit of the consolidated budget of the Russian Federation as of 01.01.2016 amounted to – 2,819,493.3 mln rubles. [15].

It should be noted that today the world meets pro-active institutions focused to ensure the governmental budget balance since the need to cover budget expenditures at the cost of revenue increasingly assumes not only the political and economic but also the social significance. Thus, the "Fiscal Compact" of the European Union adopted in 2011 specifies introduction of constitutional norms or framework laws known as "debt brakes" in the Eurozone states [17, cl.1]. The substance of these standards is the use of the "golden rule", namely, the requirements to ensure the budget balance. In March 2012, in Brussels, 25 of 27 states, as members to the Economic and Monetary Union (EMU), agreed to sign the Treaty on the Stability, Coordination, and Governance (TSCG). Initially, to ensure sustainability of public finance of the Eurozone states in 1997, the Stability and Growth Pact (SGP) was adopted.

[2] The budget risk in relation to the federal budget is defined in the Order No. 383 of the Ministry of Finance of Russia dd. 10/19/2011 (as amended on January 20, 2014) "On the procedure for strategic monitoring of the quality financial management by the Ministry of Finance of the Russian Federation".

[3] As per the Article 6 of the Budget Code of the Russian Federation No. 145-FZ dd. July 31, 1998 (as amended on November 30, 2013), the consolidated budget is the collection of budgets of the RF budgetary system in the relevant territory (excluding budgets of state non-budgetary funds) regardless of inter-budgetary transfers between these budgets.

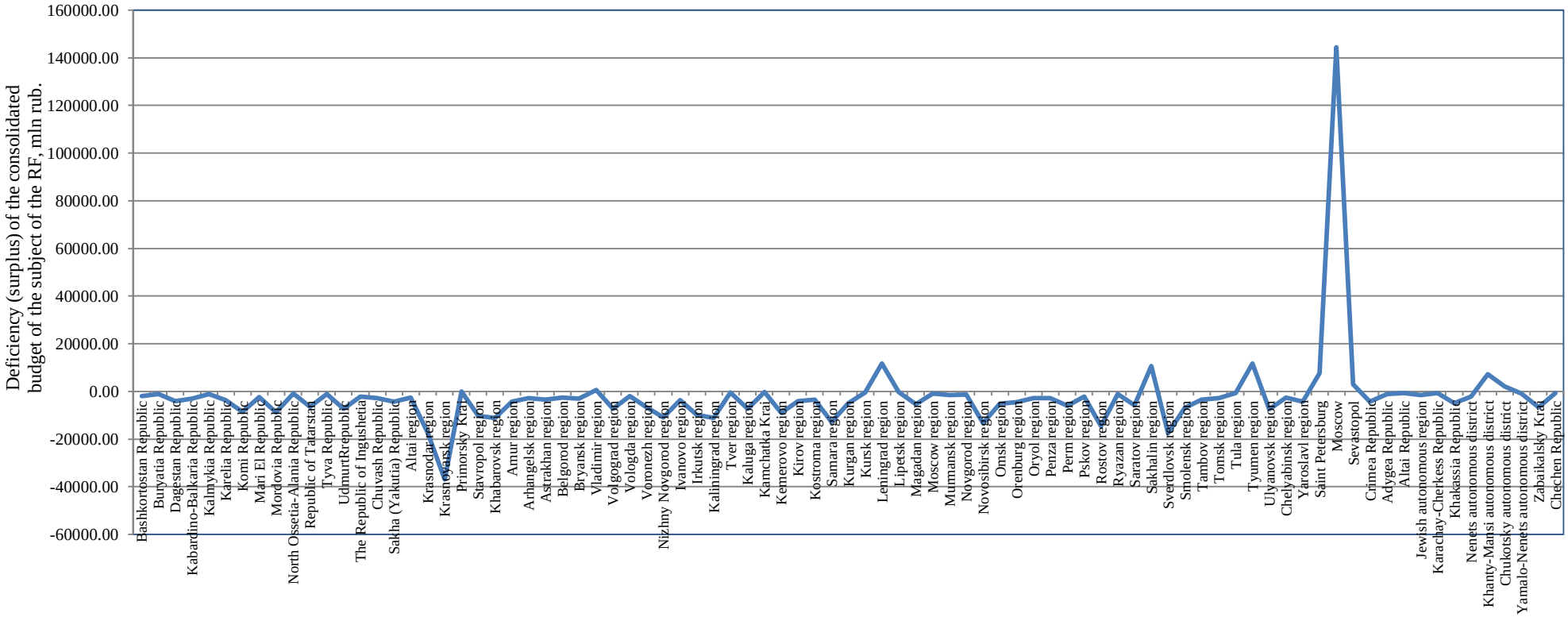


Fig. 5. The results of study of consolidated budget balance of the RF constituent entities for 2015 in mln rubles. compiled by authors to: [16]).

ISSN 2310-9599. Foods and Raw Materials, 2017, vol. 5, no. 1

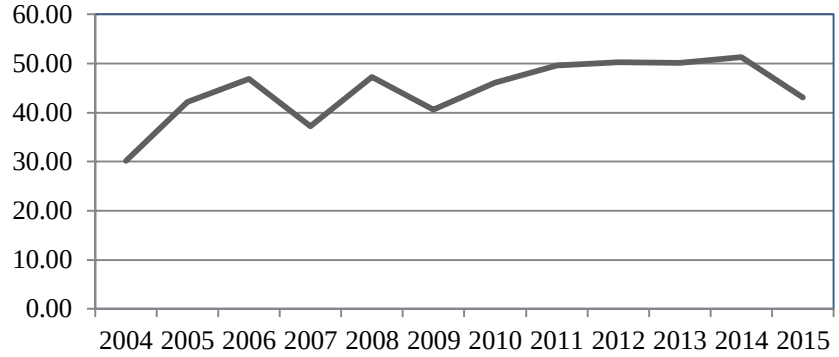


Fig. 6. The share of oil and gas return in the total volume of federal budget revenues for 2004–2015, in % (compiled by the authors to: [20]).

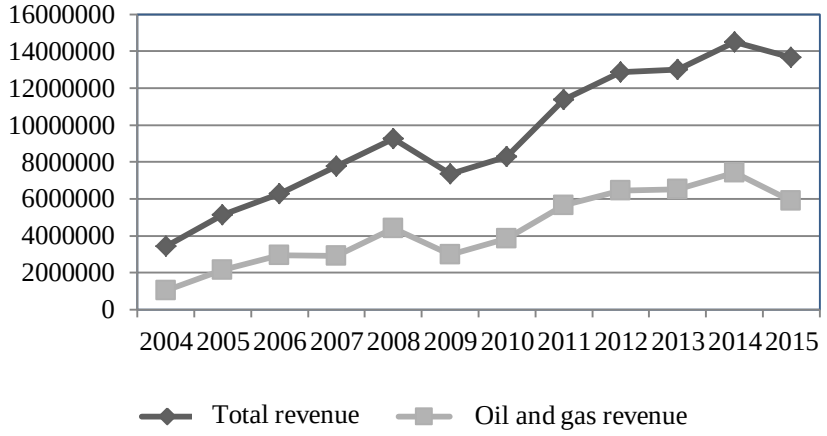


Fig. 7. The trend of federal budget revenues and oil and gas return for 2004-2015, in mln rubles. (compiled by authors to: [20]).

Currently, the protocol annexed to the Treaty of the Functioning of the EU contains requirements to the limit size of the national deficit (not more than 3% GDP) and the upper limit of the government debt (not more than 60% GDP) (See TFEU art 126(2); Protocol No. 12, supra note 14, Art. 1) [18, cl. 2].

In the US, despite the statement by the Ministry of Finance on the need to increase the upper limit of the official debt, the Republican Party urged to make amendments to the constitution to ensure the budget balance whereunder the state budget expenditures should not exceed 18% of the national annual output [19, cl. 195].

In Russia, the requirements to balance budgets are regulated by the Section IV of the RF Budget Code[4]. It sets forth requirements to the volume of expenditures to serve the public debt of a constituent entity of the Russian Federation (municipal entity) that should not exceed 15% of the relevant budget expenditure volume.

The federal budget revenues significantly depend on oil and gas revenues, that, pursuant to provisions of the Article 96.6 of the RF Budget Code, include the federal budget return on tax payment for mineral production of hydrocarbon raw stock and export customs duties on crude oil, natural gas and petroleum products. The trend data for the share of oil and gas returns in the total volume of actual revenues of the federal budget is shown in Fig. 6. The lowest share of oil and gas return was reported in 2004 (30.19%), the peak value of this parameter was reported in 2014 when the share of oil and gas returns in the total revenue of the federal budget made 51.28%[5] .

The close correlation of the total volume of federal budget revenues with the volume of oil and gas return (Fig. 7) raises risks of failure to fulfill expenditure commitments funded with the federal budget against the unfavorable situation at the hydrocarbon market. While the federal budget, since 2014, is designed in view of program-based principles, the failure to fulfill the expenditure obligations primarily concerns governmental programs of the Russian Federation, including program costs associated with the support to agricultural producers. In this situation, destabilization risks arise of the industry potential growth as a whole.

[4] The requirements to the budget deficit limit are set forth for budgets only of the RF constituent entities and local budgets. As for the federal budget deficit, the standard specifying its upper limit is excluded from the Article 92 of the RF Budget Code. Pursuant to provisions of the Article 95 (as amended by the Federal law № 63-FZ dd. 26.04.2007), the federal budget deficit as approved by the Federal Law On the Federal Budget for the next fiscal year and the schedule date, may not be greater than the volume of non-oil and gas deficit of the federal budget.

[5] Calculated by the author based on Laws "On Execution of the Federal Budget" for 2004–2015.

The study of trends in the Urals crude oil prices offers to conclude that from January 2002 to July 2008 sustainable upward trends were reported for this figure to define parameters of the federal budget of those time. Having reached its peak in July 2008, namely, $129.45/barrel, crude oil prices declined for the next five months of 2008. In general, three critical points may be highlighted for the studied period where the crude oil prices were the lowest, that is, the Q1 2002 ($19.82/bbl), December 2008 ($38.50/barrel), January 2016 ($28.53/barrel) (Fig. 8) [21].

The years 2000–2008 should be considered favorable for the development of the Russian economics when the hydrocarbon prices showed steady upward trends, and the federal budget was adopted and implemented with the surplus (Fig. 9). At that particular time a range of measures were taken aimed to develop the human capital capacity, ensure the global competitiveness and financial stability in Russia. First of all, as initiated by the RF President, it refers to implementation of national projects of high priority since 2005, including the top national project "Development of Agrobusiness" to be subsequently transformed to the State Program for the Agriculture Development and Regulation of Agricultural, Raw Materials and Food Markets. During the sustained growth of economics, the Stabilization Fund was formed as part of the federal budget that was subsequently split for two funds – the Reserve Fund and the National Wealth Fund [22]. Pursuant to provisions of the Article 96.9 of the RF Budget Code, the major objective to form the Reserve Fund is to ensure the balance (deficiency payments) of the federal budget. The sources of the Reserve Fund (clause 3, Art. 96.9 of the RF Budget Code) include the extra oil and gas returns, provided that the accumulated assets of the Reserve Fund do not reach its rated volume (7% of GDP predicted) and revenues from the Reserve Fund management. However, due to abrupt decline of hydrocarbon prices, the effect of the cl. 3, Art. 96.9 of the RF Budget Code was suspended [23]. Until February 1, 2020, the returns on the Reserve Fund management are allotted to finance the federal budget expenditures.

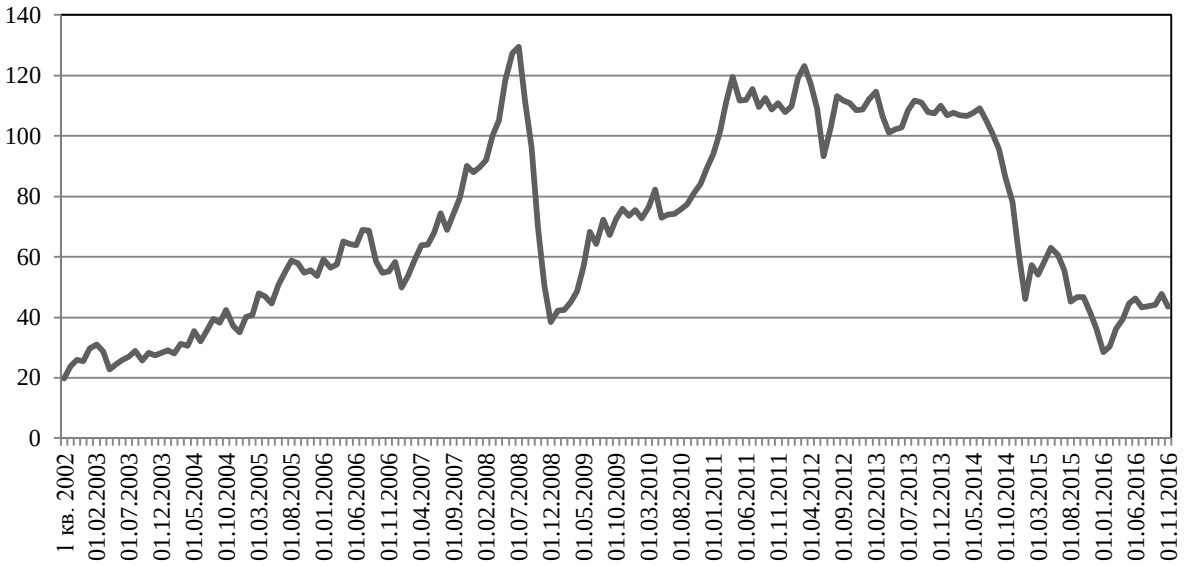


Fig. 8. Price dynamics for the Urals crude oil for 2002–2016, $/per barrel (compiled by authors to: [21]).

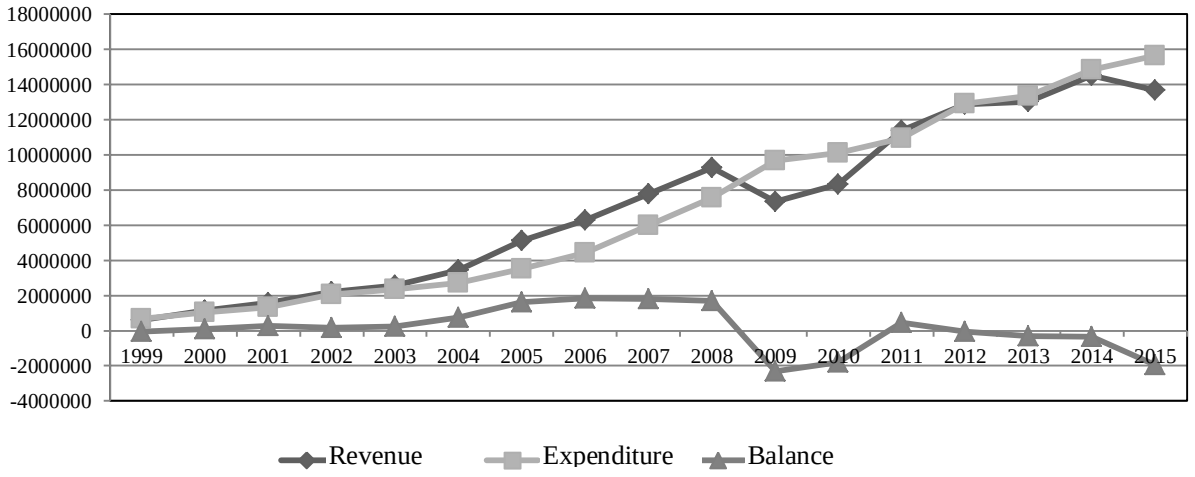


Fig. 9. The federal budget balance for 1999–2015, in mln rubles. (compiled by authors to: [24]).

During the financial and economic crisis of 2009, the Reserve Fund assets were assigned to support the bank liquidity, to finance the federal budget deficit and to take anti-crisis measures in the territory of RF constituent entities. At that particular period, the volume of subsidies to support the regional budget balance increased by 4.2 times [20], since the revenue collection in the RF constituent entities (especially of raw stock) declined drastically (Fig. 10). For example, in January 2009, the regional budget of the Kemerovo Region had the shortfall of profit in the amount of 2 bln rubles. Facing the threat of cash deficiency on the unified account of the regional budget, the priority was given to the costs for remuneration, purchase of medicines, food, payment of utility fees, payment of scholarships, where the costs of construction, reconstruction, upgrading of facilities, including socially significant structures, were provisionally suspended.

By the late 2008, the balance of the Reserve Fund amounted to 9.8% GDP, and resulting from measures to ensure macroeconomic stability by spending about 3 trillion rubles, it made 4.7% GDP (by the late 2009). In late 2010, the Reserve Fund assets amounted to 1.7% GDP (Fig. 11). Nevertheless, against the price advance for hydrocarbon in 2010–2011 thanks to implementation of the policy on saving extra oil and gas returns by the Ministry of Finance, the scope of the Reserve Fund was increased to 3.2% GDP.

The experts of the Ministry of Finance of the Russian Federation hold a view that Russia will not be able to proceed to the Reserve Fund replenishment in view of predicted crude oil prices in the hydrocarbon market and the growth of the federal budget deficit up to 2020.

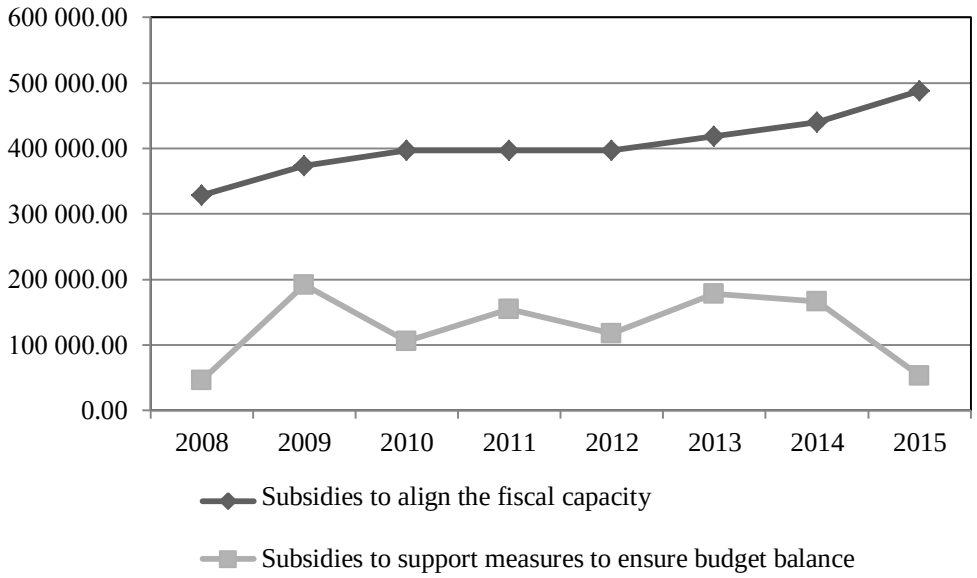


Fig. 10. The trend of the subsidy volume to align the fiscal capacity and to support measures to ensure the budget balance for 2008–2015, in mln rubles (compiled by authors to: [20]).

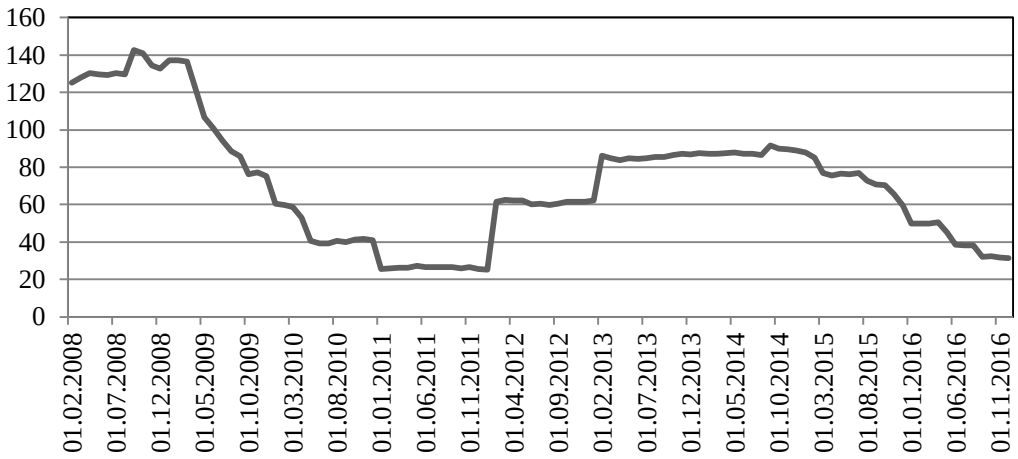


Fig. 11. The trends of volume of the Reserve Fund assets in 2008–2016, in bln USD (compiled by authors to: [25]).

It is obvious that under the growing global uncertainty and budget constraints, the risks arise of cash deficiency and non-fulfillment of expenditure obligations of budgets that conditions the need to seek for brand-new approaches to manage the budget liquidity at all levels of the RF budget system.

One of the key principles of the budgetary system is the principle of cash unity and in compliance with provisions of Art. 38.2 of the RF Budget Code, it means the enrollment of all cash receipts and implementation of all cash payments from the single budget account. It was possible to implement this principle due to the technology of the unified budget account, that, as per the Art. 6 of the RF Budget Code, means an account (totality of accounts for the federal budget, budgets of state extra-budgetary funds of the Russian Federation) opened for purposes of the Federal Treasury with the Central Bank of Russia, separately for each budget of the budgetary system of the Russian Federation to register the budget assets and execute operations on cash receipts to the budget and cash payments from the budget.

The first step to address the issue of budget liquidity management was the Single Account Concept developed by the Ministry of Finance in conjunction with the Russian Treasury and approved by the Decree No.107-r of the Government of the Russian Federation dd. January 23, 2000.

Prior to implement provisions of the Concept, the federal budget assets were dispersed to income and expenditure accounts opened for the Federal Treasury Authorities (FTA) with the Bank of Russia (60% of accounts), in Sberbank facilities (38% of accounts) and in crediting institutions (2% of accounts).

In addition to the expenditure account of the federal budget, 4 accounts were used for revenue recognition and distribution only of the FTA to account returns on payment of:

(1) taxes received from taxpayers and subject to distribution by the FTA in line with statutory regulations specified between budgets of different levels;

(2) revenues of the federal budget;

(3) revenues of the federal budget allotted to finance expenditures;

(4) revenues of the federal budget transferred to the transit account to facilities of the Bank of Russia.

The Concept introduced the term - Single Treasury Account (STA) that is opened with any institution of the Bank of Russia and where assets are accumulated and transactions are registered carried out by federal government authorities to meet the federal budget.

One of fundamental features of STA technology was the account opening to distribute returns between budgets of the budgetary system of the Russian Federation managed by the Federal Treasury Departments (FTD) with institutions of the Bank of Russia that made it possible to combine functions of four profitable personal accounts previously opened with Federal Treasury Branches (FTB). Subsequently, when implementing provisions of the Art. 215.1 of the RF Budget Code that came into force in 2005, the unified budget accounts were opened for RF constituent entities and municipal entities.

In general, the application of STA technology allowed:

– to ensure concentration of federal budget revenues and assets for STA 40105 "Federal Budget Assets";

– to concentrate transactions for revenue recognition of different level budgets on the account 40101 "Revenue distributed by the FTA between the budgets of the budgetary system", opened at the level of the FTD and expense accounting of federal budget at the level of the FTD[6];

– to ensure daily accounting of transactions on revenues and expenditures of the federal budget in the General Ledger of the Federal Treasury conducted at the level of the FTD.

The Federal Law No. 63-FZ dd. April 26, 2007 added an Art. 226.1 to the Budget Code of the Russian Federation on the Limited funding volume where the financial authority specifies the maximum amount of liability payment for the relevant period of the current fiscal year. In addition, the financial authority specifies events, approval and communication thereof to senior custodians, custodians and recipients. Limited funding volumes allow the liquidity management under conditions of strict budget constraints, especially in case of revenue shortfall to the unified budget account in view of crisis in economics and mitigation of the likelihood of cash deficiency on the unified budget account. The financial authority approves the limit budget for senior custodian by using the expert judgment and extrapolation methods, and the decisions may be informed on a quarterly basis with the detailed specification by months within each quarter, in addition. In other words, acceptance of budget commitment by spending unit through conclusion of contracts or agreements with legal entities and individuals takes place within the limits of levels proved, and the assets are granted as part of funding of the budget level proved [7] that may be paid in parts until the limit amount is reached.

Limited funding volume is paid to recipients of budget funds of the RF constituent entities and local budgets, and to the recipients of federal budget funds [26, 27].

The possibility to allocate the federal funds to deposits and their transfer to trust management (Art. 256 of the RF Budget Code) allowed initiation of the budget liquidity management system in RF in 2008 of the Single Treasury Account. However, the system of restrictions under provisions of the article above does not allow the placement of free cash assets of RF subjects with the estimated share of inter-budget transfers from the federal budget (excluding subventions and subsidies from the RF Investment

[6] At the level of FTD, accounts were opened in each RF constituent entity with the Bank of Russia facilities flagged 40101 to distribute revenues received between budgets of the budgetary system of the Russian Federation, as well as accounts flagged 40105 used to account expenditures of territorial federal executive bodies that were recipients of federal assets.

[7] The limit funding cannot exceed the amount of the limits of budget obligations proved for the spending unit (note by O.V.).

Fund) within two of the last three fiscal years did not exceed 20 percent of the consolidated budget own revenues.

The innovative approach to budget liquidity management by the FTA includes the provision, since 2013, of subventions, inter-budget subsidies and other inter-budget transfers for special purpose under the actual need. The implementation of this procedure is set forth in cl. 7 of the Decree No. 1272 of the RF Government dd. December 10, 2012 (as amended on 04.09.2013) on measures to implement the Federal Law *On Federal Budget for 2013 and Scheduled Period 2014-2015*" and allows to exclude unused balance of inter-budget transfers at the end of any fiscal year on unified accounts 40201 "RF Subject Budget Funds". At the same time, expenditures of budget fund recipients for actual needs does not commit to prolong the execution time of payment document and shortens the period of target fund receipt to the regional budget income.

This mechanism is focused on execution of powers of senior custodians of federal budget funds by the territorial bodies of the Federal Treasury and wit this purpose, a personal account flagged 14 is opened to pay liabilities for expenditures of recipients of the RF subject budget sourced by inter-budget transfers from the federal budget to ensure financial security. At the same time, each subsidy, subvention, each other inter-budget transfer of target purpose is assigned with the appropriate target codes which are at all times specified in the expenditure schedule, based on which the personal account flagged 14 accounts for budgetary data (budget allocations, limits of budget obligations and the limit budget level) and in the application for cash expenditures to ensure the adequate accounting for transactions on the personal account and the unified budget account and to form the budgetary reporting on transferred and used inter-budget transfers for targeted purpose.

In 2014, the procedure of transfer provision under the actual need was implemented at the municipal level with the institutional basis as the Order No. 5n of the Treasury of Russia dd. March 26, 2014. Similar orders of the Treasury of Russia were adopted in 2015 and 2016 [28].

However, despite the implementation of this mechanism, on unified accounts flagged 40201 "Funds of the RF Subject Budgets" totaling 85 currently opened with the Bank of Russia, and unified accounts flagged 40204 "Local budget Assets" amounting to over 22000, significant balances of inter-budget transfers accumulate at the beginning and the end of any fiscal year.

It should be noted that the balance of inter-budget transfers is formed due to subsidies, either, to agricultural producers from the federal budget. The information on the movement of inter-budget transfers funded by the federal budget in 2015 is shown in Table 5 [15].

Table 5. Provision of inter-budget transfers to budgets of RF subjects in 2015 by the federal budget, in mln rubles

Balance as of 01.01.2015		Received from FB	Cash flow	Inter-budget transfers for past years restored	Unused balances for past years is returned to FB	Returned to FB within the volume of needs in consumption	Balance as of 01.01.2016
Total	Including those the need for which is proved						
125 980, 13	109 343, 39	952 738, 35	988 424, 21	3 657, 85	132 953, 60	111 278, 22	72 276, 73

This means that methods to assess the need in inter-budget transfers require to be adjusted, on the one hand, and on the other hand, the concentration of resources above on the same account would allow their placement to financial instruments and, thereby, receipt of additional return on free cash management. In our opinion, the use of this methodology, namely, payment of the limit budget to recipients for purposes of expenditure would be rational not only as part of the regulation of the fund transfer from one level of budgetary system to another, but also in terms of the specific budget, since, as proved by more than a decade of practice of one of this article authors in the system of the Federal Treasury, budget data, including limit budget amounts paid to recipients are often of demand in full. Definitely, provisions of Art. 242 of the RF Budget Code do not oblige recipients of budget funds to "zero" accounts thereof based on which the budget subsidies, budget obligation limits and funding limits for the current fiscal year cease to be effective on December 31. Hereat, when forming the consolidated quarterly budget breakdown [8], the budget data are distributed by the financial authority between the senior custodian of budget funds, resulting in "pulling" portions of the budget data by the particular senior custodian (and further by its accountable institutions) which may stay non-demanded in future. Thus, unsatisfactory quality of financial management by budget fund custodians generates, among the others, the problem of ineffective management of budget liquidity on unified budget accounts.

[8] The consolidated quarterly profile is the document compiled and maintained by the financial authority (management authority for the state extra-budgetary fund) to arrange the budget execution by budget expenditures and sources of financing of budget deficit (Art. 6 of the RF Budget Code No. 145-FZ dd. July 31, 1998 (revised on 11/30/2016).

The analysis of the budgetary reporting on the federal budget implementation by expenditures indicates that when clarifying the consolidated quarterly profile and allocating extra budgetary assets to federal budget custodians, they are often used in part. There may be several reasons for this. One of them, already mentioned above, is the low quality of financial management. So, as per the results of monitoring the quality of financial management by the federal budget custodians as of July 1, 2016, the Ministry of Agriculture of the Russian Federation ranked 88th in the rating of 102 liable [29]. The assessment of financial management quality as per the method by the Ministry of Finance of the Russian Federation is conducted in several orientations as part of the approved system of parameters for each of them. So, the budget execution in terms of expenditure is assessed by such indicators as completeness, timeliness of acceptance and execution of budgetary obligations, deviation from the cash budget for federal budget expenditures, quality of management of federal budget funds in terms of inter-budget subsidies and subventions, subsidies and investments to legal entities and other.

Another reason is the time scarcity to hold competitive procedures and conclude government contracts in line with Federal Law 44-FZ [30], since budget recipients are often informed on the budget data by the financial authority at the very end of the fiscal year where there is short of time to execute competitive procedures.

The compliance with the cash budget is impeded by the delay in execution terms by contractors for concluded state (municipal) contracts that negatively affects the uniformity of cash payments from the unified budget account, and, therefore, forms the liquidity deficit.

Irregularity of cash payments from the unified treasury account is one of the urgent challenges announced in budget statements by the President of the Russian Federation in early 2000s, and, despite the improvement of treasury technologies, it remains urgent.

However, for the sake of justice, it should be noted that the irregular budget execution is specific not only for Russia but for other states either since, at the end of the fiscal year, most liabilities are fulfilled under most contracts. Therefore, for example, in Denmark and the Netherlands, it is allowed to transfer the portion of unused budget subsidies for the next year. In France and Sweden, the transfer limit for the next financial year is specified but not more than 3% of the total amount of subsidies allotted [31, p. 49].

In Hungary, to ensure the uniformity of budgetary expenditures, no more than 1/12 of fund allocation as provided for in the budget law is allowed per month, and the need to exceed the amount fixed is approved by the government [32].

In 2015, the document was adopted that, in our view, is of high significance to improve the efficiency of budget liquidity management under conditions of global uncertainty. It is referred to the Concept of budget payment system reforming [33]. The need in development and adoption of this Concept are largely due to a range of problems related to budget liquidity management, including:

– dispersal of budgetary funds to numerous accounts totaling over 50 000 in number[9];
– concurrent duplication of operations on income distribution between budgets of the RF budget system on accounts opened for the Federal Treasury with the Bank of Russia and personal accounts opened with territorial FTAs;
– the limited list of instruments to allocate the free budget liquidity on unified accounts of budgets of the budget system to financial instruments;
– inadequate level of income distribution efficiency from the account flagged 40101 "Incomes distributed among budgets of RF budget system" (more than three days in some cases)[10].
– lack of budgets with revenue administrators, as well as with entities that deliver governmental and municipal services, urgent information on the arrival of funds to accounts, including the information on personal accounts opened with financial institutions;
– significant volume of transactions with cash assets resulting in difficulty to monitor the proper use of budget liquidity.

The main objective of the Concept is to improve the management efficiency of free cash balances of budgets.

As part of the Concept implementation, accounts are planned to close stage by stage that are previously opened by territorial FTA with territorial offices of the Bank of Russia with subsequent opening thereof with the Bank of Russia to ensure accumulation of budget liquidity on the Unified Bank Account of the Treasury of Russia.

Pursuant to provisions of the Concept of the Budget Payment System Reforming, the transition to the Unified Bank Account of the Treasury of Russia will ensure the possibility to target cash balances[11] and will

[9] The status of the current system of budget payments is described by multiple accounts opened with territorial offices of the Bank of Russia by the territorial FTA, namely, accounts to account assets arriving for transient disposal of federal state and budgetary institutions; funds of budgetary, autonomous and other organizations owned by the government; budget funds of RF subjects; funds arriving for transient disposal of state and budgetary institutions of the RF subjects; local budget funds, etc., which finally result in dispersion of the budget liquidity.

[10] It should be noted that, in line with provisions of the Art. 40 of the RF Budget Code, cash assets are deemed to arrive to income of the relevant budget since the date of asset crediting to the single account of this budget. Thus, the delay in schedule to distribute return that arrive to the account 40101, or the delay in asset arrival clarification where, for example, the income code, name of the budget revenue administrator, etc. is wrongly specified, it contributes to the growth of budget liquidity deficit on the unified accounts of budgets, and, consequently, it forms risks of non-fulfillment of budgetary obligations.

[11] The targeting of cash balances on the Unified bank account of the Treasury of Russia as per the Concept is the management of the daily balance amount on the unified bank account by monitoring monetary liabilities of an entity whose personal accounts are opened with territorial FTAs and liquidity provision. The calculation of daily balance and prediction of cash balances on the unified bank account of the Treasury of Russia will be carried out by execution of payment schedule. The data for payment schedule will be contained in cash budgets to meet budgets of the budgeting system of the Russian Federation sent to the Treasury of Russia.

also enable usage of excess liquidity to generate additional return on operations to place free cash in financial instruments.

It is obvious that targeting of cash balances on the Unified Bank Account of the Treasury of Russia predetermines the need to forecast the demand for such funds not only in relation to the unified federal budget account, but also at the level of unified accounts of the budgets of RF subjects and municipalities. Financial authorities, chief administrators (administrators) of budgetary funds of sub-federal and municipal levels and recipients should be involved in this process.

For purposes to target the liquidity on the Unified Bank Account of the Treasury of Russia, the concept and the prototype of the "Cash Management" subsystem are planned to develop along with main functional requirements to the "Cash Planning" module of the prototype of "Cash Management" subsystem under the state integrated information system "Electronic Budget".

CONCLUSIONS

In general, the use of treasury technologies studied above is focused to address issues related to budget constraints and liquidity deficit under conditions of growing global political and economic uncertainty. Moreover, the transition to the new technology of the Unified Bank Account of the Treasury of Russia will allow to target cash balances and use the excessive budget liquidity to obtain additional budget revenues through placement thereof to financial instruments. In this situation, it is possible to transit to the policy of creating an innovation and investment-oriented budget deficit by channeling budgetary allocations for re-industrialization of strategically important industries, including agriculture, to ensure their compliance with the best industrial practices of the world's leading countries. The similar approach was proposed by Keynes in his work The General Theory of Employment, Interest and Money [34], that proved that active governmental participation in the development of economics, especially under the crisis, based on creation of the investment-oriented budget deficit and direct public investments in the economics (in our case, in agriculture), will not only increase the confidence of private investors to governmental authority performance, but will finally ensure the formation of multiplicative economic and social effects.

Ultimately, the development of tools to manage budget liquidity and, thereby, the reduction of budgetary risks (primarily, the risks of non-fulfillment of expenditure obligations of budgets of the RF budgetary system due to the decline in revenue receipts) will contribute not only to its retention but also to an increase in the share of governmental participation in the development of strategically important sectors, including agriculture, under conditions of global political and economic uncertainty, and the growth of Russia's national competitiveness as a whole.

REFERENCES

1. *Rasporyazhenie Pravitel'stva RF ot 17 noyabrya 2008 g. № 1662-r «O Kontseptsii dolgosrochnogo sotsial'no-ekonomicheskogo razvitiya Rossiyskoy Federatsii na period do 2020 goda»* [RF Government Order no. 1662-r dd. November 17, 2008 “On the Concept of long-term social and economic development of the Russian Federation for the period up to 2020”].
2. *Ukaz Prezidenta RF ot 30 yanvarya 2010 g. № 120 «Ob utverzhdenii doktriny prodovol'stvennoy bezopasnosti Rossiyskoy Federatsii»* [Decree no. 120 of the President of the Russian Federation dd. January 30, 2010 “On approval of the Food Security Doctrine of the Russian Federation”].
3. *Rasporyazhenie Pravitel'stva RF ot 30 noyabrya 2010 g. № 2136-r «Ob utverzhdenii Kontseptsii ustoychivogo razvitiya sel'skikh territoriy»* [RF Government Order no. 2136-r dd. November 30, 2010 “On approval of the Concept of Sustained Rural Area Development”].
4. *Prikaz Ministerstva promyshlennosti i torgovli RF ot 22 dekabrya 2011 g. № 1810 «Ob utverzhdenii Strategii razvitiya sel'skokhozyaystvennogo mashinostroeniya Rossii na period do 2020 goda»* [Order no. 1810 of the Ministry of Industry and Trade of the Russian Federation dd. December 22, 2011 “On approval of the Agrarian Machine Industry Strategy for the period up to 2020”].
5. *Federal'nyy zakon RF ot 29 dekabrya 2006 g. № 264-FZ (red. ot 12.02.2015 g.) «O razvitii sel'skogo khozyaystva»* [Federal Law no. 264-FZ of the Russian Federation dd. December 29, 2006 (revised on 12.02.2015) “On agriculture development”].
6. *Postanovlenie Pravitel'stva RF ot 14.07.2007 g. № 446 (red.ot 23.04.2012 g.) «O Gosudarstvennoy programme razvitiya sel'skogo khozyaystva i regulirovaniya rynkov sel'skokhozyaystvennoy produktsii, syr'ya i prodovol'stviya na 2008–2012 gody»* [RF Government Order no. 446 dd. 14.07.2007 (revised on 23.04.2012) “On the State Program for Agriculture Development and Regulation of Agricultural Products, Raw Material and Foodstuff Market for 2008–2012”].
7. *Rasporyazhenie Pravitel'stva RF ot 11 noyabrya 2010 g. № 1950-r «Ob utverzhdenii perechnya gosudarstvennykh programm Rossiyskoy Federatsii»* [RF Government Order 1950-r dd. November 11, 2010 “On approval of the list of state programs of the Russian Federation”].
8. *Postanovlenie Pravitel'stva RF ot 14.07.2012 g. № 717 (red. ot 19.12.2014) «O Gosudarstvennoy programme razvitiya sel'skogo khozyaystva i regulirovaniya rynkov sel'skokhozyaystvennoy produktsii, syr'ya i prodovol'stviya na 2013–2020 gody»* [RF Government Order № 717 dd. 14.07.2012 (rev. on 19.12.2014) “On the State Program for Agriculture Development and Regulation of Agricultural Products, Raw Material and Foodstuff Market for 2013–2020”].

9. *Rasporyazhenie Pravitel'stva RF ot 18.10.2010 g. № 1806-r «Ob utverzhdenii Kompleksnoy programmy uchastiya Rossiyskoy Federatsii v mezhdunarodnom sotrudnichestve v oblasti sel'skogo khozyaystva, rybnogo khozyaystva i prodovol'stvennoy bezopasnosti»* [RF Government Order no. 1806-r dd. 18.10.2010 "On the approval Package Program for Participation of the Russian Federation in International Cooperation in the Field of Agriculture, Fisheries and Food Security"].
10. *Natsional'nye scheta.* Ofitsial'nyy sayt Federal'noy sluzhby gosudarstvennoy statistiki [National accounts. Official website of the Federal State Statistics Service]. Available at: http://www.gks.ru/wps/wcm/connect/rosstat_main/rosstat/ru/statistics/accounts/# (accessed 27 January 2017).
11. *Rossiya i strany mira – 2016.* Ofitsial'nyy sayt Federal'noy sluzhby gosudarstvennoy statistiki [Official website of the Federal State Statistics Service. Russia and world countries – 2016]. Available at: http://www.gks.ru/bgd/regl/b16_39/Main.htm (accessed 28 January 2017).
12. *Sel'skoe khozyaystvo, okhota i okhotnich'e khozyaystvo, lesovodstvo v Rossii. 2015*. Ofitsial'nyy sayt Federal'noy sluzhby gosudarstvennoy statistiki [Agriculture, hunting and hunting industry and forest management in Russia (2015). Official website of the Federal State Statistics Service]. Available at: http://www.gks.ru/bgd/regl/b15_38/Main.htm (accessed 15 January 2017).
13. *Sel'skoe khozyaystvo, okhota i okhotnich'e khozyaystvo, lesovodstvo v Rossii. 2004; 2009; 2013; 2015.* Ofitsial'nyy sayt Federal'noy sluzhby gosudarstvennoy statistiki [Statistics Service. Agriculture, hunting and hunting industry and forest management in Russia. 2004; 2009; 2013; 2015. Official website of the Federal State Statistics Service]. Available at: http://www.gks.ru/bgd/regl/b15_38/Main.htm (accessed 15 January 2017).
14. *Rossiyskiy statisticheskiy ezhegodnik – 2005, 2012, 2015*. Ofitsial'nyy sayt Federal'noy sluzhby gosudarstvennoy statistiki [Russian Statistical Catalog – 2005, 2012, 2015. Official website of the Federal State Statistics Service]. Available at: http://www.gks.ru/wps/wcm/connect/rosstat_main/rosstat/ru/statistics/publications/catalog/doc_1135087342078 (accessed 15 January 2017).
15. *Ispolnenie byudzhetov. Konsolidirovannyy byudzhet RF i byudzhetov gosudarstvennykh vnebyudzhetnykh fondov*. Ofitsial'nyy sayt Federal'nogo kaznacheystva [Budget execution. Consolidated RF budget and budgets of state extra-budgetary funds. Official website of the Federal Treasury]. Available at: http://www.roskazna.ru/ispolnenie-byudzhetov/konsolidirovannyj-byudzhet/ (accessed 25 December 2016).
16. *Ispolnenie byudzhetov. Konsolidirovannye byudzhety sub"ektov RF i byudzhetov territorial'nykh gosudarstvennykh vnebyudzhetnykh fondov*. Ofitsial'nyy sayt Federal'nogo kaznacheystva [Official website of the Federal Treasury. Budget execution. Consolidated RF subject budget and budgets of territorial state extra-budgetary funds]. Available at: http://www.roskazna.ru/ispolnenie-byudzhetov/konsolidirovannye-byudzhety-subektov/ (accessed 25 December 2016).
17. Henning C.R. and Kessler M. Fiscal Federalism: US History for Architects of Europe's Fiscal Union. *Peterson Institute for International Economics*, Working Paper No. 2012-1. Available at SSRN: https://ssrn.com/abstract=1982709 or http://dx.doi.org/10.2139/ssrn.1982709 (accessed 19 January 2017).
18. Fabbrini F. The Fiscal Compact, the 'Golden Rule' and the Paradox of European Federalism. *Boston College International and Comparative Law Review*, 2013, vol. 36, pp. 1–38; *Tilburg Law School Research*, Paper No. 013/2013. Available at SSRN: https://ssrn.com/abstract=2096227 or http://dx.doi.org/10.2139/ssrn.2096227 (accessed 19 January 2017).
19. Bartlett B. The Balanced Budget Amendment: Not Ready for Prime Time. *Tax Notes*, 2011, vol. 132, no. 2, pp. 195–197. Available at SSRN: https://ssrn.com/abstract=1883491 or http://dx.doi.org/10.2139/ssrn.1883491 (accessed 19 January 2017).
20. *Ispolnenie byudzhetov. Federal'nyy byudzhet.* Ofitsial'nyy sayt Federal'nogo kaznacheystva [Budget execution. Federal Budget. Official website of the Federal Treasury]. Available at: http://www.roskazna.ru/ispolnenie-byudzhetov/federalnyj-byudzhet/ (accessed 25 December 2016).
21. *Spravochnaya informatsiya «Dannye, primenyaemye dlya rascheta naloga na dobychu poleznykh iskopaemykh v otnoshenii nefti i gazovogo kondensata» (v tselyakh primeneniya glavy 26.4 Nalogovogo kodeksa RF)* [Reference data "Data used to calculate the tax for mineral development in terms of oil and gas condensate" (for the purpose of applying Chapter 26.4 of the Tax Code of the Russian Federation)]. Available at: http://www.consultant.ru/cons/cgi/online.cgi?req=doc;base=LAW;n=50630#0 (accessed 15 December 2016).
22. *Federal'nyy zakon ot 26.04.2007 № 63-FZ «O vnesenii izmeneniy v Byudzhetnyy kodeks Rossiyskoy Federatsii v chasti regulirovaniya byudzhetnogo protsessa i privedenii v sootvetstvie s byudzhetnym zakonodatel'stvom Rossiyskoy Federatsii otdel'nykh zakonodatel'nykh aktov Rossiyskoy Federatsii» (red. ot 03.07.2016)* [Federal Law no. 63-FZ dd. 26.04.2007 "On amendments to the Budget Code of the Russian Federation as to the budget process regulation and adjustment of certain legislative acts of the Russian Federation with the fiscal legislation of the Russian Federation as follow" (rev. on 03.07.2016)].
23. *Federal'nyy zakon RF ot 03.11.2015 № 301-FZ «O vnesenii izmeneniy v otdel'nye zakonodatel'nye akty Rossiyskoy Federatsii v svyazi s Federal'nym zakonom "O federal'nom byudzhete na 2016 god"» (red. ot 02.06.2016)* [Federal Law no. 301-FZ of the Russian Federation dd. 03.11.2015 "On amendments to certain legislative acts of the Russian Federation in relation to the Federal Law "On the Fiscal Budget for 2016" (rev. on 02.06.2016)].
24. *Ob ispolnenii federal'nogo byudzheta za 1999–2015 gg: federal'nye zakony* [On the Federal Budget execution for 1999–2015: federal laws]. Available at: http://www.consultant.ru/ (accessed 05 January 2017).

25. *Statisticheskaya informatsiya o dinamike ob"ema sredstv Rezervnogo fonda*. Ofitsial'nyy sayt Minfina Rossii [Statistic data on trends of the Reserve Fund asset volume. Official website of the Ministry of Finance of Russia]. Available at: http://minfin.ru/ru/perfomance/reservefund/statistics/volume/ (accessed 15 December 2016).
26. *Prikaz Minfina Rossii ot 21.12.2015 № 204n "O Poryadke utverzhdeniya i dovedeniya do glavnykh rasporyaditeley, rasporyaditeley i poluchateley sredstv federal'nogo byudzheta predel'nogo ob"ema oplaty denezhnykh obyazatel'stv i o vnesenii izmeneniy v nekotorye prikazy Ministerstva finansov Rossiyskoy Federatsii"* (red. ot 29.02.2016) [Order № 204n of the RF Ministry of Finance dd. 21.12.2015 "On Procedure of approval and granting of the limit volume of liability payment to senior custodians, custodians and recipients of federal budget assets and on amendments to certain orders of the Ministry of Finance of Russian Federation" (rev. on 29.02.2016)].
27. *Prikaz Minsotsrazvitiya Novosibirskoy oblasti ot 27.02.2015 № 159 «Ob utverzhdenii Poryadka ispolneniya kassovogo plana i osvoeniya predel'nykh ob"emov finansirovaniya»* [Order no. 159 of the Ministry of Social Development for Novosibirsk region dd. 27.02.2015 "On approval of the Procedure on Cash Budget Execution and installation of limit budget level"].
28. *Prikazy Kaznacheystva Rossii ot 16.02.2015 g. № 3N i ot 22.01.2016 g. № 2n «Ob utverzhdenii poryadka osushchestvleniya territorial'nymi organami Federal'nogo kaznacheystva polnomochiy poluchatelya sredstv byudzheta sub"ekta RF po perechisleniyu mezhbyudzhetnykh transfertov, predostavlyaemykh iz byudzheta sub"ekta RF v mestnyy byudzhet v forme subsidiy, subventsiy i inykh mezhbyudzhetnykh transfertov, imeyushchikh tselevoe naznachenie»* [Order no. 3N of the Russian Treasury dd. 16.02.2015 and Order № 2N dd. 22.01.2016 "On approval of the procedure to execute powers of the RF subject fund recipient by territorial bodies of the Federal Treasury on inter-budget transfers provided from the RF subject budget to the local budget as subsidies, subventions and other inter-budget transfers of special purpose"].
29. *Prikaz Ministerstva finansov RF ot 13.04.2009 № 34n «Ob organizatsii provedeniya monitoringa kachestva finansovogo menedzhmenta, osushchestvlyaemogo glavnymi administratorami sredstv federal'nogo byudzheta» (red. ot 16.05.2016)* [Order no. 34n of the Ministry of Finance of the Russian Federation dd. 13.04.2009 "On arrangement of monitoring of fiscal management quality made by senior administrators of federal budget funds" (rev. on 16.05.2016)].
30. *Federal'nyy zakon ot 05.04.2013 № 44-FZ «O kontraktnoy sisteme v sfere zakupok tovarov, rabot, uslug dlya obespecheniya gosudarstvennykh i munitsipal'nykh nuzhd» (red. ot 03.07.2016)* [Federal Law № 44-FZ dd. 05.04.2013 "On contracting system in procurement of goods, works, services to ensure governmental and municipal needs" (rev. on 03.07.2016)].
31. Morgunov V.I. and Vlasov S.A. Ob upravlenii ostatkami sredstv na schetakh organov gosudarstvennogo upravleniya v Rossii [On management of account balance owned by the governmental authorities in Russia]. *Den'gi i kredit* [Money and Credit], 2012, no. 2, pp. 47–51.
32. Prokofiev S.E. and Sarantsev V.N. Ediniy kaznacheiskiy schyot Federalnogo kaznacheistva [Unified fiscal account of the Federal Treasury]. *Financsy i kredit* [Finance and Credit], 2010, no. 11 (395), pp. 2–7.
33. *Prikaz Minfina Rossii ot 29.08.2013 № 227 «Ob utverzhdenii Kontseptsii reformirovaniya sistemy byudzhetnykh platezhey na period do 2017 goda»* [Order № 227 of the Ministry of Finance of Russia dd. 29.08.2013 "On approval of the Concept to reform budget payment system for the period up to 2017"].
34. Keynes J.M. *Obshchaya teoriya zanyatosti, protsenta i deneg* [General Theory of Employment, Interest and Money]. Moscow: Eksmo Publ., 2007. 960 p.

Please cite this article in press as: Glushakova O.V., Fadeykina N.V., Baranova I.V., Tsygankov K.Yu., and Mikhailov V.V. Fiscal technologies of budget liquidity management and their role to ensure the sustainable growth of the agrarian sector in the context of global uncertainty. *Foods and Raw Materials*, 2017, vol. 5, no. 1, pp. 174–191. DOI: 10.21179/2308-4057-2017-1-174-191.

FORMATION OF AGRO-INDUSTRIAL CLUSTER ON THE PRIORITY SOCIAL AND ECONOMIC DEVELOPMENT AREA OF THE MONO-INDUSTRY TOWN

O. P. Ivanova[a,*], G. D. Antonov[b], V. A. Shabashev[a], L. L. Zobova[a], and A. Yu. Nesterov

[a] Kemerovo State University,
Krasnaya Str. 6, Kemerovo, 650043, Russian Federation

[b] Institute for Advanced Training and Reskilling,
Michurina Str. 13A, Kemerovo, 650000, Russian Federation

* e-mail: prof-ivanova@rambler.ru

Received June 05, 2016; Accepted in revised form December 10, 2016; Published June 29, 2017

Abstract: Issues on the development of mono-industry towns in Russia through diversification of economics thereof may be addressed by formation of the priority social and economic development area (PSEDA). By the results of analysis of conditions to create intraregional (municipal) industrial clusters within the PSEDA mono-industry towns, the feasibility of such clusters is justified to turn into the priority residents of PSEDA, but also to obtain the synergistic effect of taking PSEDA advantages and the cluster approach in diversifying the economies of mono-industry towns. In contrast to previous definitions, the authors consider the intraregional (municipal) industrial cluster as the concept created with favorable involvement of regional and municipal authorities to develop the cluster strategy and use favorable conditions to expand private enterprises, association of entities to implement projects on diversification of mono-industry town economies and investment projects that meet the PSEDA requirements. The principles of PSEDA-based cluster formation in mono-industry towns are formulated. The most significant factors of sustainable development of clusters are highlighted to address mono-town problems. The stage-by-stage creation of municipal clusters proposed by authors is based on their ability to emerge during the extensive market mechanism performance and includes stages to assess the potential to form and develop cluster formations, but also the stages to identify the needs of participating entities in the course of particular interaction, creation and development of entity networks. The analysis of existing agglomerations, systematization of SWOT analysis findings, assessment of factors contributing to cluster formation offered the chance to determine the perspective for the agro-industrial cluster development in Yurga in the Kemerovo Region. The study results represent the particular contribution to the cluster theory, regional economy in terms of development of tools to form municipal industrial clusters within the PSEDA for the purpose to diversify economies of mono-industry towns. The practical significance of the research is the possibility to apply the study results in the activity of regional and municipal authorities when identifying intraregional agglomerations, creating cluster formations as PSEDA mono-town residents.

Keywords: Mono-town, cluster, development, the priority social and economic development area, diversification

DOI 10.21179/2308-4057-2017-1-192-204 *Foods and Raw Materials*, 2017, vol. 5, no. 1, pp. 192–204.

INTRODUCTION

The socio-economic development of mono-industry towns directly depends on functioning of the city-forming enterprise (or a group of related enterprises). For the period from 2008 to 2015, as per various estimates, 200 to 500 settlements belong to RF mono-towns. With the reduction of mono-industry towns of the list approved by the government, the actual number of mono-industry towns and, in particular, the problems they accumulate, is not reduced from 335 in 2009 to 319 in 2015. Options for mono-industry town development: inertial development causing the liquidation of the city-forming entity and population resettlement, upgrading of the city-forming entity with retention of its city-forming purpose, diversification of the mono-industry town economy. Pursuant to the Federal Law No. 473-FZ dd. March 30, 2014 On Priority Social and Economic Development Area in the Russian Federation" [1] and THE Government Decree No. 614 dd. June 22, 2015 On peculiarities to create priority social and economic development areas in the territories of mono-profile municipal entities of the Russian Federation (mono-industry towns)" [2] the tool to address social and economic problems of mono-industry towns is the creation of priority social and economic development areas (PSEDA) based in mono-

towns with the most tough social and economic situation. Despite the PSEDA, along with clusters and special economic zones, are considered as mechanisms to stimulate industrial and innovative development, the authors assume that creation of intraregional (municipal) industrial clusters in the territory of mono-towns as priority ("anchor") residents can afford the synergistic effect by benefiting from PSEDA and cluster approach. The economic meaning of clusterizing is to take advantage of the synergy that arise during interacting between related industry entities concentrated in one territory, and public and private sector organizations. The constructive partnership of all stakeholders in the development of local economy is the defining feature of the cluster. The clusters formation, even during the crisis, boosts the economic growth in territories, contributes to overcome technological backwardness. There is an opinion that cluster formation, involving entities from more than one municipal formation, can strengthen the mono-profile of towns [3]. However, there are examples of effective practice of forming intra-regional clusters. For example, the auto-industry cluster in the Kaluga region (developing based on the governmental support, in particular, tax incentives, access to infrastructure, investor support by administration), "Integrated development of the Lower Angara region" cluster (financed from the federal and regional budgets, banks and enterprises). In this regard, it seems that it makes sense to identify and develop associations of enterprises with the potential to transform into intra-regional clusters as part of PSEDA.

Despite the experience of cluster creation in the Russian Federation, there is a lack in practical formation as part of programs to create PSEDA in mono-industry towns. In addition, the term of cluster is not defined when applied to forms of organization for the purpose of PSEDA creation and development. The practice of cluster formation was reviewed to evidence that they may be formed, firstly, by natural means, as a consequence of gradual development of the certain area of concentration based in the specific territory, and secondly, as a result of purposeful implementation of cluster-forming events. Dirigiste and liberal models of clusters are specified as per these criteria: The dirigiste model is known to assume cluster formation through governmental support. Within the liberal model, the cluster emerges as a result of market rules, and the function of federal authorities is reduced to limiting barriers to its natural development [4]. Both models do not associate the cluster with special economic zones. However, it should be assumed that creation of special conditions favorable for the business development aimed, in particular, to addressing social and economic issues of mono-industry towns, for example, priority social and economic development areas, is the factor initiating the successful emergence and further development of clusters as elements (residents) of such territories. This is how the relevance and practical significance of this study is specified.

OBJECTS AND METHODS OF STUDY

The research object is cluster projects, economic relations of agrobusiness entities of of the mono-town, experience of cluster formation in industry.

Studies of national and foreign scientists primarily focus on the rationale to identify cluster groups, however, the potential of entities, in particular mono-towns, to become the cluster member is not studied, the methods of cluster formation are associated with methods of their identification only [5, 6].

Theoretical and methodological provisions of the cluster theory, official statistic publications, expert opinions form the information base of the research. The calculation-analytical method, system analysis, and method of expert appraisal are used.

When developing the principles of methodological approach to PSEDA-based cluster formation in mono-industry towns, the following provisions of theoretical concepts and studies were taken into account: the opportunity of more effective internal control based on internal information, regulation and coordination of business activities of merging enterprises as a result of intracorporate financial market formation (concept based on the intra-company capital market); efficient creation of networks of suppliers, producers, consumer networks and networks of technological cooperation (D. Ernst); advantages to form industrial chains, commodity chain, supply chains and the creation of value chains (E. Yordon, M. Christopher, T.J. Gallin and M. Handon, M. Garrett and P. Ducuge).

In the methodology for cluster formation analysis, methods for their detection and identification, methods for evaluation thereof and methodological approaches to assess their effectiveness are distinguished. The totality of methods to detect and identify cluster formations in the territory includes the expert assessments, calculation of localization coefficients, factor analysis, statistical cluster and discriminant analysis, use of production inter-branch balances, etc. To determine economic agglomerations capable of cluster forming, tradable or export-oriented industries are determined [7], the coefficient of sectoral employment localization is calculated as the ratio of share of this industry in production structure to the specific share of the same in the country. Similarly, the production localization factor, ratio of sectoral localization by labor productivity, investment and other indicators can be determined [8]. The clusters may be assessed based on SWOT analysis, analysis of industrial potential, methods to evaluate the effectiveness of investment projects, and others. As part of this study, expert assessments, SWOT analysis, assessment of potential of mono-industry sectors, and evaluation of investment project effectiveness were used to locate and identify, as well as to assess cluster structures.

RESULTS AND DISCUSSION

As the economic term, the cluster is a totality of enterprises concentrated on the specific territory, interrelated, but performing in different sectors. And the core of cluster is that its members complement each

other and strengthen their competitive advantages and those of cluster as a whole.

In the concept of M. Porter [9] the interaction between cluster members is distinguished (main manufacturing companies, auxiliary (associated) industries, universities, research organizations and government agencies). The cluster is a more complex formation as compared to a simple association of entities for joint activities, since it involves cooperation through participation in value creation systems, as well as competition.

R. Bro defines the cluster as "the intersectoral concentration of entities that create jobs, export goods and services, have common basic economic needs and unite the public sector of economic development, legislature of different levels, universities, colleges, educational community, funds and all other stakeholders" [10].

The cluster is the form of network intercompany interaction, and unlike entrepreneurial networks, it unites a wider range of embers, including support institutions, production and commercial structures (among them manufacturers, suppliers, as well as higher education institutions and scientific organizations). Within the cluster, members may be associated both by sectors and regions (interindustry).

The cluster member may be a focal enterprise (the core firm), key players, small and medium-sized businesses, supplier agencies, sales intermediaries, trading companies, representatives of workers (trade unions), investment companies, investors, capital investors, financial institutions, local administrations, supporting enterprises, universities, research organizations and think tanks being the part of the cluster companies. It should be noted that the ideas on focal networks with the involvement of a key player are well understood in Russia, but the capacity of small and medium-sized business is underestimated.

The intraregional (municipal) industrial cluster created based on PSEDA mono-town is proposed to be considered as: tool to structure the industry and its network organization; association of organizations, formed to implement projects to diversify the mono-town economy and investment projects meeting PSEDA requirements; network association of industry-related enterprises and organizations in the territory of a mono-industry town; a type of territorial cluster, regional industrial cluster, industrial district.

Its features are as follow:

– combination of competition and cooperation, market and organization;

– extensional and local economic structure, where socio-cultural and production and engineering factors interrelate to ensure competitiveness and activity;

– the form of industrial entity is characterized by the focus of economic and entrepreneurial activity and limited by geography (municipal district, urban district);

– participants are the mono-industry town enterprises with the area of concentration in production of competitive products, suppliers of raw materials, services, cluster infrastructure creating in aggregate the final product and added value;

– availability of internal competition, that distinguishes the cluster against integrated entities.

The most successful and dynamically developing clusters formed based on special economic zones, technology parks and business incubators include clusters in mono-industry towns: cluster of automotive industry - Tolyatti and Naberezhnye Chelny, creation of "titanium valley" in the Upper Ufaley in the Sverdlovsk region, a chemical cluster in Nizhny Tagil, a wood processing cluster using the latest technologies in the city of Sokol, Vologda region and others.

Having analyzed the structure of clusters of mono-profile towns in the Sverdlovsk region, the specialists of the Ural State University compiled a list of most promising new industries for each single-industry town. So, the following industries were named for Nizhny Tagil: manufacture of electrical appliances, pharmaceutical industry, business services, jewelry industry.

The most significant factors for the successful development of clusters are: quality management [11]; mechanisms and organizational forms for knowledge accumulation and dissemination and social capital accumulation [12]; presence of at least 30–50 profile companies in the cluster to realize the potential of innovation diffusion [13].

To describe the communities of technologically related sectors in France, the term "dies" was widely used [14] as the form of interaction of of innovative cluster features. The term "clusters of innovation" has gained a wide popularity among public and private sector leaders after formation of the US cluster named "Clusters of Innovation" [15]. It well reflects the fact that all the world companies have to compete not only in and not so much in terms of productivity as in terms of the ability to innovate.

The methodology and implementation of cluster policy in Russia correspond to conceptual basis of similar European programs on whole, especially of French and German origin [13]. Since 2012, the Ministry of Economic Development of the Russian Federation has competitively selected projects for cluster development in the Russian regions. Around 100 cluster initiatives took part in the competition, 25 of them were selected for pilot support. In 2013–2014, the amount of 3.8 billion rubles was allocated from the federal budget for cluster development on co-financing terms from regional budgets. So, the innovative territorial cluster in the sphere of information and telecommunication technologies of the Novosibirsk region received 269 million rubles, and the information technology cluster in St. Petersburg – 1.3 million rubles. The average size of subsidy for clusters was about 100 million rubles [16].

An analysis of study results of Russian pilot innovation clusters [17] held in 2015 using the European Cluster Improvement Initiative showed the following:

– clusters are mainly located in Russian regions with a high level of innovative development (out of 21 test

clusters, 13 (62%) are based in "strong innovator" regions, 5 (24%) – in "medium-strong innovator" regions, 1 cluster is in the region of "medium innovator" and 2 (9.5%) – in "medium-scale innovator" regions) [18];
– in 13 clusters out of 21 the number of participants was less than 50, and less than 30 in 6 clusters;
– 11 new clusters are specialized in new industries (information technologies, bio-pharmaceuticals and new technologies), while 12 clusters can be referred to traditional high-tech industries founded in the Soviet time (production of aircraft and space vehicles, shipbuilding, nuclear and radiation technology, chemistry and petrochemistry).

Since a large share of Russian clusters is created based on former Soviet enterprises in conventional high-tech industries (aerospace complex, nuclear technologies, etc.), one of their features is a small number of small and medium-sized businesses that act as an active part of foreign clusters created. However, there is diversity among a small number of innovative clusters selected by the Ministry of Economic Development of Russia for subsidization as follow:
– clusters formed of members around large companies (aerospace cluster in Samara);
– networks joining small and medium-sized enterprises (information and pharmaceutical clusters in St. Petersburg and Novosibirsk);
– association of enterprises around the research institute ("Biotechnological Innovative Territorial Cluster "Pushchino") or leading universities (Cluster "Fiztekh XXI" in Dolgoprudniy);
– formed in Closed Administrative Territorial Units (Sarov, Zheleznogorsk);
– created based on large agglomerations.

By the extent of impact on the regional and national economics, on whole, the multi-profile Kamsky Innovative Cluster in Tatarstan, clusters of information and communication technologies in St. Petersburg and the Novosibirsk region, as well as the Samara aerospace and Bashkir petrochemical innovation territorial cluster (ITC) are ranked first as per the study results. The nuclear-innovative cluster in Dimitrovgrad in the Ulyanovsk region, the multiprofile cluster of the Tomsk region, the Zelenograd cluster of microelectronics (Moscow) and the engineering lighting cluster in Mordovia are distinguished by the interaction intensity within the cluster, namely, as per the share of participants in joint projects, number of joint innovation projects and business projects. By the professionalism criteria of the managing company, the multisectoral cluster in Tomsk, the cluster of pharmaceutics, biotechnology and biomedicine in Kaluga, the nuclear-innovation cluster in Dimitrovgrad, ICT cluster in Novosibirsk and cluster of rocket engine building in Perm are ranked first.

The following dependencies are revealed: there is a correlation between the volume of cluster financing through the Ministry of Economic Development of Russia with the level of integration of its participants and the extent of cluster impact on regional development; there is no significant correlation between the support volume and the quality of cluster management [17].

Apart from cluster success, it is necessary to highlight the problems of their development in Russia. So, the cluster development is limited with the lack of knowledge and inability to apply best world practices locally, rapid result orientation, difficulties with investment raising, obsolete and worn-out fixed assets, human resource problems, and poor work-out of the strategy in terms of development priorities choice. Almost all sectors running in the territory are chosen as key areas of growth to result in dispersion of forces, lack of resources to implement all projects.

A particularly significant problem is the weak innovativeness of formed clusters, since the national economy remains weak-responsive to innovations. Among the important reasons the quality of the institutional environment and the specifics of internal industry markets should be accentuated. As a rule, companies are willing to invest in innovations only if the term for innovation and new product marketing is feasible within a year. This is not enough for breakthrough innovations. Even innovative entities are poorly cooperated in terms of creation of new knowledge, technology transfer and interaction with scientific organizations. In addition, the importance of existing barriers between the science, innovation, education and real economic sector should not be excluded, the growing differentiation between sectors in terms of their technological development, regional polarization by innovative performance.

In addition to problems and limitations in cluster development in the Russian Federation, the risks existing in the sphere of cluster formation and cluster policy should be systematized. For example, the global experience shows that when the cluster formation initiated exclusively by the government faces one of major risks, that is the failure to consider business development trends, as well as its economic interests. The "large-scale construction in the open field occurs initiated by officials oriented toward trendy issues" [19]. This results in the artificially created cluster that exists until the state support is granted. Due to certain artificially created cluster initiatives considered by regional authorities as a tool to ensure state support, horizontal links are poorly formed in Russian clusters, the member cooperation is not developed.

The Russian risks of cluster approach execution match those risks highlighted by foreign experts. In particular, Man-Wen T. and Vojer R. [20] focus on the most significant risks faced by foreign governments when forming and promoting cluster development: change of macroeconomic conditions, weak cluster innovation due to the lack of production mechanisms and adaptation of new knowledge, insufficient development of external and internal scientific and technological links that weakens the synergistic effect of clustering and use of inefficient management techniques.

In addition, risks of opportunistic behavior of cluster members, personnel risks (shortage of specialists of the required qualifications to support the cluster entity activities), logistical and marketing risks

should be highlighted. There are also risk groups produced by governmental authorities. For example, infrastructure risks manifested in case of insufficient provision of cluster members with transport, energy, communal and other infrastructure for cluster members, institutional risks that are due to inconsistency of measures of scientific and technical, industrial, regional, socio-demographic, educational policies, resource risks associated with inadequate or inefficient use of budgetary funds.

PSEDA creation in mono-towns is aimed at creating conditions to attract investments avoiding mono-dependence. By implementing projects with multiplier effect, it will be possible to improve the life quality of population by creating the new social infrastructure, work places and by increasing the tax base. The creation of the sustainable system of investment attraction and investment projects implementation will ensure solution of tasks of sustainable social and economic development for the long term. In addition, the PSEDA creation allows solving problems as follow: attracting high-tech enterprises of processing industries with high added value, the growth of competitiveness of the territory by creating conditions to attract investors to the region, including foreign ones and creation of new, up-to-date, export-oriented production, reduction of unemployment through redistribution of labor resources available, growth of tax and non-tax revenues (for example, return of old and emergence of new taxpayers).

PSEDA are created in mono-industry town territory with the most difficult social and economic situation. So, for example, the Yurga municipal district of the Kemerovo region (hereinafter referred to as the "mono-town Yurga") is listed among single-profile municipal entities of the Russian Federation (mono-industry towns) and depending on the risk of their socio-economic deterioration, refers to Category 1 - mono-profile municipal formations of the Russian Federation (mono-industry towns) with the most difficult social and economic situation (including in interrelation with problems of the city-forming entity functioning). The unemployment rate increased from 1.6% to 2.1% between 2000 and 2008 in the mono-town Yurga in the Kemerovo region, By 2009, the level was 3.6%, and by 2016, the figure almost doubled and amounted to 6.4%. In 2016, the staff double reduction is planned and dismissal of more than 1750 peoples at the town-forming entity, that is, the Yurginsky machine-building plant. The Yurginsky Machine-Building Plant LLC faces significant difficulties to obtain orders and, as a result, production volumes have significantly decreased. The city does not dispose of sufficient internal sources for budgeting. In April 2015, the Agreement was signed between the Mono-Town Development Fund and Administration of the Kemerovo Region. To annul infrastructure constraints and develop investment projects, Jurga was allocated assets in the amount of 373.5 mln rubles, and 139.5 million rubles for the construction of a sewage collector.

Formation of the program for PSEDA creation and development in the mono-town requires justification of the list of economic activities that may be internal triggering points. The cluster approach may be used for justification. The cluster approach is one of ways to increase the competitiveness and economic development of territories. In addition, in the paradigm of cluster ideology, the priority today is given to restructuring of the area economy, in particular, to supporting diversification.

It is obvious that single-industry clusters around one or a group of entities may be formed in single-industry towns. Moreover, due to internal structuring, they may be more resistant to the impact of risks associated with external environment of cluster performance. However, failures in cluster functioning may result in the destruction due to weak diversification of the economy of the territory.

When using the cluster approach to form the PSEDA-based mono-town program, one should consider the foreign practice of cluster management of the European Cluster Excellence Initiative [21], the research results of industrial cluster state management, formation of business clusters and high-tech clusters [22, 23, 24, 25, 26, 27], and factors of their sustainable development revealed during the study of national practice of clusters functioning [17].

Prerequisites to create intraregional (municipal) industrial clusters within the PSEDA mono-towns: lack of own opportunities with entities to arrange the effective production activities based on introduction of innovations; the need for economic diversification; the demand for production upgrading; import substitution and the possibility to use favorable conditions for the private entrepreneurship development.

The scenario approach to create municipal clusters based on PSEDA assumes the priority of the top-down movement with the initial development of the cluster strategy and its support under the PSEDA conditions. For example, M. Wickham [28] considers the role of the state when creating clusters as the most important and identifies in the totality of factors for the successful role of the government to create conditions favorable for cluster formation, provision of the necessary infrastructure for cluster development and formation of new leading companies. In addition, it was noted [29] that governments (32%), businesses (27%) and jointly by business and government (35%) are the initiators of cluster formation, cluster is financed by the government (54%), business (18%), jointly by business and government (25%).

An important tool for cluster formation based on PSEDA is the financial and economic mechanism that includes an investment mechanism, and, most importantly, a tax mechanism (creating conditions to foster business development).

As a result of research, analysis and systematization of cluster theory, foreign cluster management practice, methodology and practice of cluster policy implementation in Russia and abroad, Russian pilot innovation clusters, problems, constraints and risks of clusters development, main principles to form intra-

regional (municipal) industrial clusters under PSEDA are in single-industry towns are defined:

– when choosing clusters that can develop within the PSEDA mono-town, the concentration of enterprises carrying out profile, related and supporting lines of activity should be assessed, since high value of activity promotes the spread of innovations. This is also important to stimulate domestic competition, especially in the field of innovation that promotes selection of most effective players and re-flow of labor and investment. When choosing the mono-town to support the mono-industry based on PSEDA are the clusters running in industries with economic indicators that are much higher than the average level in the country;

– use of the network strategy to obtain advantages from the ability to coordinate network structures, adapt to changing conditions, quick response to changes in market conditions, specialization, cost reduction;

– creation of attractive conditions for urban environment for the skilled personnel and innovative entrepreneurship to avoid the domination of the city-forming enterprise and to ensure diversification of the urban economy;

– arrangement of specialized managing companies that implement functions of cluster management, including the coordination of the strategies of participants, interaction with governmental authorities to build effective communications within and between the cluster, as well as to improve skills, training, identify areas of cooperation among participants, intensify cross-sectoral interaction;

– use of outsourcing, that is, clustering through cooperation, involvement of multiple independent companies and competition between them around core enterprises, including, for example, city-forming enterprises and large plants. To form clusters - networks of competing suppliers and contractors, research institutes at certain territories, certain conditions are required, and therefore, the practice of transferring individual business processes for outsourcing is important, since it forms the market for many potential cluster members, the existing organizations and start-ups;

– development of internal competitive environment (in this case, we consider the competition not as an antagonistic struggle between the cluster members and the parallel, simultaneous maintenance (and, therefore, duplication) of same functions). Relying on the functional approach to define the competition (that describes the role of competition in the economy), as per J. Schumpeter who describes under his theory of competition economic development as a rivalry between the old and the new, we consider competition as a mechanism that expels entities that operate inefficiently using obsolete technologies. In justifying the need for internal competition, we rely on perception of the competition not as the conflict between the cluster participants, not as the antagonistic form of competition between enterprises and organizations. The competition is deemed as a form of competitiveness between subjects as an element of market mechanism introduced into the system of functioning and cluster development. In this case, we consider the competition as a driving force to increase the efficiency of activities, including innovation, such as the interaction between cluster members, their coexistence, cooperation, and interconnection to increase the competitiveness of the cluster as a whole. Competition in this case is a selective and flexible mechanism. The first is manifested in the fact that enterprises performing ineffectively can be "absorbed" more efficiently. The flexibility of the mechanism of internal competition is shown in its rapid reaction to any changes in the situation. When changes emerge, the entities emerge in the best position capable to quickly adapt to changes. Thus, the competition is the most important mechanism to ensure the cluster effectiveness.

The prospective development of PSEDA-based clusters determines adoption of the strategy by enterprises based on "open innovation" model [21], the application of incoming and outgoing knowledge flows to strengthen innovative processes within companies. It is important to attract third-party solutions as a result of outsourcing, networking, involvement of customers, and also to involve employees in the innovation creation.

The gradual formation of the intra-regional industrial cluster under PSEDA is defined by the sequence of "formation of certain conditions in the mono-town - key enterprises - related organizations". This chain of events in process of cluster formation considers the operation of market mechanisms and stimulates emergence of key firms capable to form the core of the cluster. The most important elements for the effective cluster functioning are the business climate, infrastructure, access to resources, capital markets, taxation system, administrative barriers, transport infrastructure. In this sense, the conditions formed under PSEDA are favorable to identify and form intra-regional (municipal) industrial clusters in single-industry towns. However, when identifying clusters, their ability should be considered to emerge in the course of extensive manifestation of the market mechanism when enterprises seek concentration due to obvious advantages of the geographic location. For example, Porter and Enright believe that clusters should not be formed from scratch, but rather to develop those agglomerated.

Let's consider the gradual cluster formation.

Stage I. Analysis of social and economic state of single-industry town, identification of promising economic agglomerations, identification of cluster formations, assessment of their formation and development potential, selection of projects to create and develop intra-regional (municipal) industrial clusters.

Stage II. In process of organizational design of clusters, it is required to fist consider the needs of participating entities in certain types of targeted interaction that specify the motivation for association: integration of supply, sales, marketing; use of common economically viable suppliers; integration of the unified scientific and technical policy; exchange of work experience and innovations; coordinated actions to retain and expand positions in the market. The

choice of particular spheres of activity is expedient to justify based on analysis of the marketing research results and perspectives for the sales market development.

The Stage III provides: choice of major cluster activities in the strategic perspective; inclusion of structures actively playing at the market, first of all marketing, supply-marketing, design, etc. (allocation of the group of specialized suppliers and service enterprises); development of future common intra-cluster solutions and approaches; development of principles for the management of the enterprise network.

The formation and development of networks (industrial and business) is based on the combination of key competence of the large enterprise, totality of medium-sized enterprises, a number of small firms (auxiliary, service, service enterprises). The autonomy of unincorporated entities to match with clear rules of inter-organizational interaction, initiates the emergence of sustainable synergies in networks.

Features of network structures: stable nature of cooperation, the need for which is specified by the complexity of final product, its growing science-intensive and long-term research and production cycle. The inter-sectoral principle of cooperation is associated with the involvement in technological process of not only production but also marketing (justification of feasibility to create new products and markets for sale thereof), scientific and technical, sales and service (dealers, leasing companies, maintenance centers, recycling, etc.), financial organizations.

The main feature of the network is that technologies, know-how and other intangible assets are produced and sold created by the request of the managing company of this chain. This requires the use of special network forms of organization of the scientific and production cycle. The networks are distinguished by cooperation (joint creation of value, but not just the market exchange) and the special role of internal infrastructure, interpersonal links, and knowledge transfer.

The cluster that includes a managing company and a network of entities as a core, has a number of advantages to structures that act under strict legal frameworks: freedom to "enter" and "exit" from the network and cooperation ties; the most effective cooperative relations are developed and strengthened, the less effective ones easily die off (with no legal problems); unlimited number of participants, arbitrarily "long" chains of interrelations (technological, economic, financial); ability to integrate resources of different number of participants to the structure to invest in projects aimed at creating new and improving production and cooperation; reduction of transaction costs.

The proposed step-by-step mechanism for cluster formation supposes its gradual increase in its boundaries due to inclusion of participants in the production and business networks. Such a mechanism has advantages as follow: first, it avoids miscalculations and mistakes in determining the structure and types of activities within an intraregional (municipal) cluster; second, the functioning in the network will identify problems of interaction, points of contact, promising areas of joint activities, adjustment of characteristics of joint entities, elaboration of interaction principles.

The effectiveness of cluster project implementation is defined by appearance of the cluster features: synergetic effects, stability of intra-cluster material and information flows, system-forming factors, ability to self-organization and self-development, and continuity of functioning. The cluster should be formed with minimal expenditure of resources, but no compromising of the process effectiveness. The voluntary association of members should be encouraged.

Data analysis of social and economic development of the town as shown on the official website of the Yurga Town Administration makes for the conclusion as follows [30].

First, there is an increase in economic performance figures of the mono-industry town in 2011–2012 followed by the abrupt negative trend in 2013 with some recovery in 2014. Against the overall favorable macroeconomic situation in 2011, there was the upward trend in the economic development. The physical index of industrial production was 122% (12.1 bln rubles), the volume of commodity turnover was 7 bln rubles. The physical index of industrial production in 2012 amounted to 103.2% (13.6 bln rubles). The sales volume reached 7.7 bln rubles (physical volume index is 100.4%). However, yet in 2013, the economic development figures grew to have the negative trend. The index of industrial production in 2013 reduced to 75.6%, and the sales volume – to 75.2%. By the end of 2014, this figure reached 96.6% (see table 1). The transition of the positive trend to negative is reported in the volume of industrial production in the town, especially for manufacturing entities (Table 1) [30], whereas this figure slightly changes for the production and distribution of electricity for the studied period.

Second, the structure of industrial output changed by types of economic activity within 2011–2014. The share of manufacturing entity slightly reduced as follows: from 87.85% in 2011 to 84.24% in 2014. Whereby, the reduction in the volume of shipped products was reported for metallurgical products (by 14% in 2011-2014 from 4186 to 3681.9 mln rubles) and machinery and equipment production (26% growth in 2012 against the previous year and the overall reduction by 84% in 2011 to 2014 from 3,218 to 510.1 mln rubles), while the production of non-metallic mineral products showed an increase by 51% in 2011-2014 (from 1912 to 2893.9 mln rubles) (See Figure 1) [30]. The latter occurs during the construction material industry development in Yurga. The change in the investment pattern to fixed assets of the town also results in the change in the structure of industrial output volume.

Table 1. Changes in industrial output of municipal formation "Yurginsky Municipal District"

No	Types of economic activity	2011	2012	By 2011, in %	2013	By 2012, in %	2014	By 2013, in %
1	Volume of industrial output of the town, mln rubles	12401	13593	110.2	10662	78.4	11331	107
	including for large and medium-sized enterprises	1717	12907	109.6	9924	76.9	10657	107
2	Manufacturing entities, mln rubles	10751	11944	111	9018	75.5	9632	108
	including large and medium-sized enterprises	10071	11263	111.8	8281	73.5	8977	109
3	Production and distribution of energy, gas and water, mln rubles	1650	1649	99.9	1643	99.7	1696	102
	including large and medium-sized enterprises	1646	1644	99.9	1643	99.9	1680	102

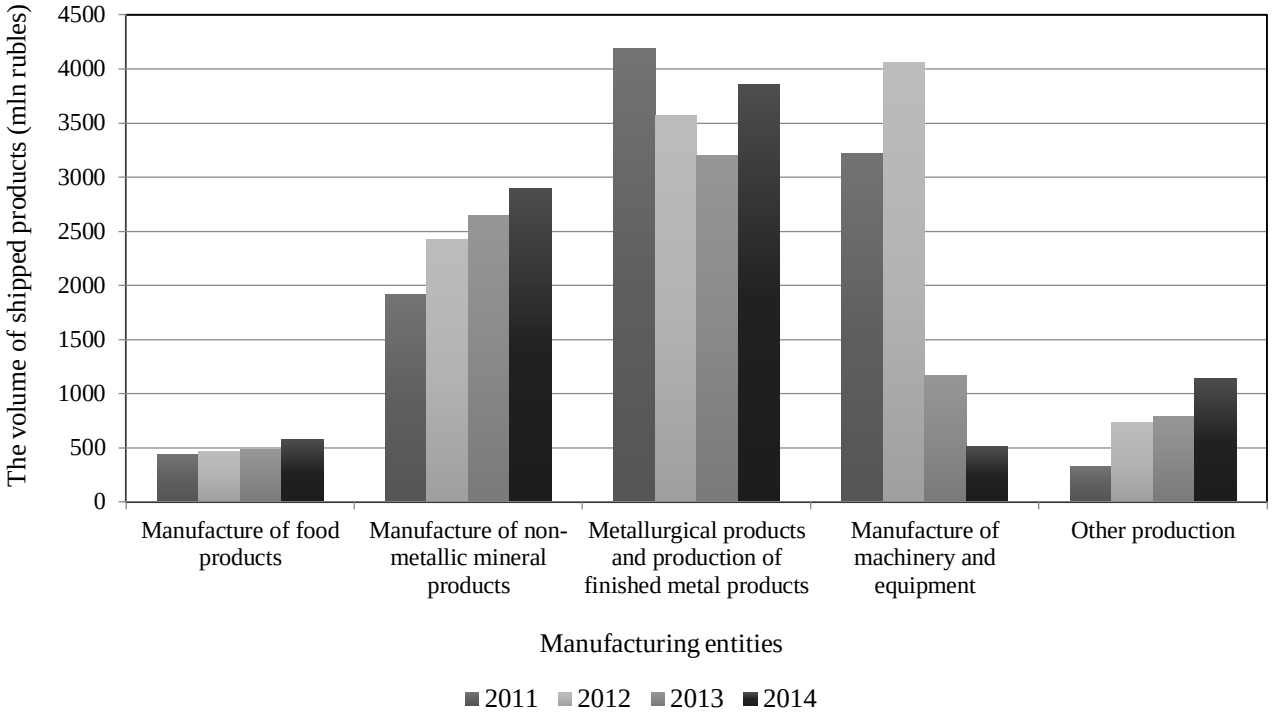


Fig. 1. Changes in the volume of shipped products to manufacturing entities for 2011–2014 (mln rubles).

Third, the structure of real investments has changed: investments in buildings and structures in 2011–2014 significantly increased. The implementation of the Integrated Investment Plan for Upgrading reasonably involves a change in the structure of investments. During the period from 2011 to 2014, the ratio of investments in buildings and structures radically changed (share in 2014 was over 60% against slightly over 30% in 2011) and in machinery, equipment, vehicles and tools (reduction in share from 64% to 35.1% over the same period) (Fig. 2) [30].

Fourth, the structure of investments changed by the types of economic activity towards the reduction in metallurgical products and growth in wholesale and retail trade, repair of vehicles and motorcycles, production of household goods and personal consumables in 2011–2014. [30]. Exemplary is the change in the structure of investment by the types of economic activity. If in 2011 the equity contribution to the capital stock of metallurgical production and production of finished metal products amounted to 62.7% of total investments, by 2014 it declined to 11.02%. Whereas, the equity contribution to capital stock in wholesale and retail trade and repair of motor vehicles and motorcycles, household products and personal consumables increased from 2.4% in 2011 to 47.3% in 2014, the latter figure is the resultant of obvious trends to diversify the economy of the town. These changes cause alterations in the structure of industrial production, reducing the share of city-forming enterprises of a mono-industry town (Fig. 3) [30].

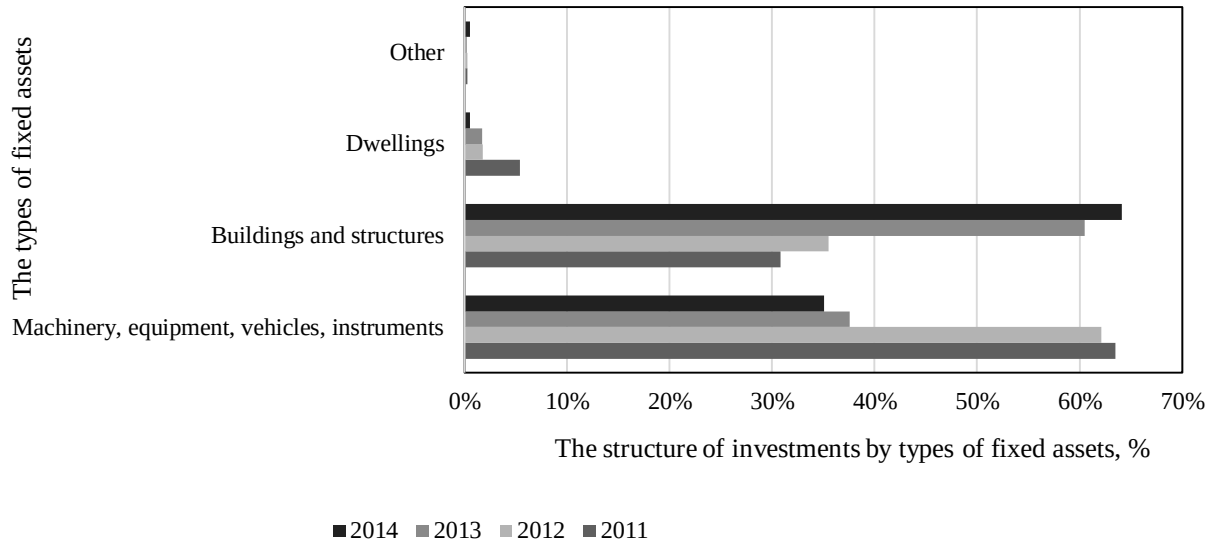


Fig. 2. Trends in changes in the structure of investments by types of fixed assets in 2011–2014.

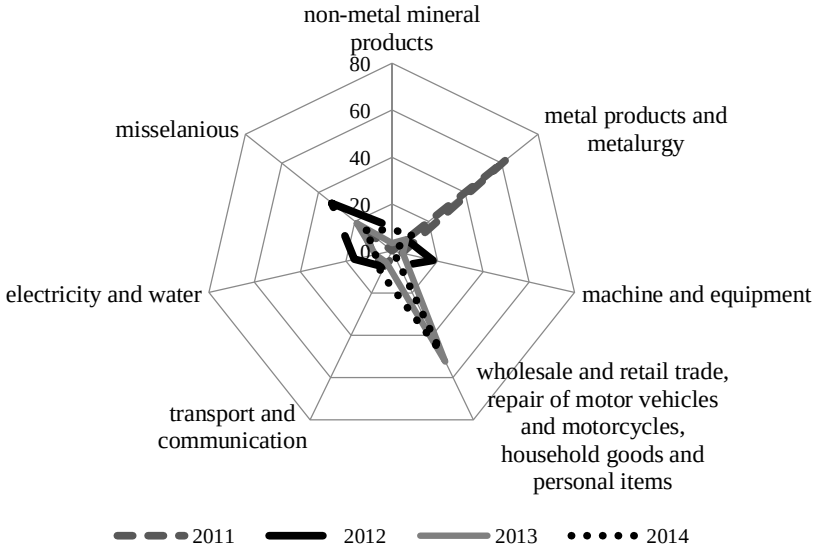


Fig. 3. Change in the structure of investments in the capital stock by types of economic activity in 2011–2014.

The share of town-forming entities is reduced in the total volume of shipped products from 51.2% in 2011 to 12.3% in 2014. Thus, the industrial production index in 2013 was 75.6%, increasing to 96, 6% by 2014. Moreover, the cumulative problems of city-forming entities affected the share reduction therein resulting in the natural decrease in the volume of shipped products and industrial production index of the mono-industry from 90.9% in 2011 to 38.2% in 2014.

In 2011, 9 projects were among projects to create and invest to small enterprises (4 of them were suspended) raising investments from extra-budgetary sources in the amount of 171 mln rubles that made it possible to create 248 new jobs. By 2012, the small business investment projects amounted to 6 with 271.94 million rubles raised and 93 jobs created. However, in 2013 the number of small business projects decreased to 4, and in 2014 – to 3. The joint investments to implementation of these projects in 2013 amounted to 264 mln rubles, in 2014 – only 24 mln rubles, while 218 and 42 work places were created, respectively. At the same time, the volume of extra-budgetary funds to finance projects significantly reduced in 2014 against the figure in previous years.

It should be noted that the share reduction of the Limited Liability Company "Yurginsky Machine Building Plant" in the municipal industrial output does not result in the decrease in the company impact on the mono-town standing to diversify its economy. So, if in 2011–2012 the company succeeded to implemented a range of measures to upgrade, reconstruct and retrofit the entity, introduce up-to-date technologies and equipment at the expense of 350 million rubles allocated, in 2013 the position of the largest system-forming enterprise impeded. That was resulting from macroeconomic deterioration, decrease in consumption

level and coal prices that caused a reduction in investment projects of coal mining companies to acquire the equipment. In this connection, the volume of commodity output of the plant reduced by 50%, and the average monthly salary – by 25%. During 2013–2014, the number of employees decreased by more than 1,700 persons (up to 3959 persons). The resulting state gave rise to the introduction of extreme situation at the Yurginskaya CHPP on the balance of Yurginsky Machine Building Plant LLC. These circumstances make for the conclusion to reduce the share of the enterprise in the volume of municipal commodity output, number of labor force employed in the core enterprise under conditions where the performance of the enterprise highly impacted the social and economic state of the town. The latter circumstance evidence on negligible changes in the dependence on the enterprise activity and mono-profile capacity in case of formal reduction in the mono-town criteria parameters. This conclusion is proposed based on the need to consider both the official level of the mono-town criteria to assess its economy diversification and the reduction in the influence of the city-forming (backbone) enterprise to the municipal economy [30].

Although the economy of the monogorod Yurga over the period 2011-2014 has changed towards a greater variety of economic activities, this was not only due to implementation of modernization program for the mono-industry town, but largely due to a sharp decline in the share of the city-forming enterprise in the mono-industry economy. Such reduction is associated with scheduled measures to restructure the municipal economy as a whole as per the comprehensive plan and with consequences of negative macroeconomic factors.

The existing agglomerations were reviewed to identify cluster entities in Jurga: machine-building, agro-industrial and complex production of building materials. Let's consider the factor assessment in detail that contribute to the creation of agro-industrial cluster.

Apart from Kuznetskie Ferrosplavy JSC, Yurginskiy Ferrosplavny Zavod stand-alone business unit, ZavodTekhnoNikol-Sibir LLC, Komus-upakovka Siberian Plant, among the largest industrial enterprises of the town there Kuzbasskhleb LLC, bakery plant No. 3 in Yurga, "Yurginskiy Gormolzavod" JSC. About 500 small businesses are registered to run in Yurga, 75 of them are engaged in manufacturing industries. In recent years, the distinctive feature in development trends of small business in the town is its production trend.

The SWOT analysis of social and economic conditions in Jurga afford focusing on the following competitive advantages. In terms of geographical location and climatic conditions, these include the density of town location, the proximity to the regional center and major cities of the Siberian region, namely Novosibirsk and Tomsk (intersection of three highways), transport communication support (road, water, railway), location of the West Siberian landfill near the town, the consumer of goods and services of Yurga manufacturers, the supplier of labor force to the town (officers' wives, persons demobilized in reserves from military forces), the factor contributing to social stability in Yurga, strengthening links with federal and regional authorities. In view of demographic potential, the standard of population living and the labor market, it includes an increase in the birth rate since 1997, the reduction in infant mortality rate, in general mortality rate and availability of free man power. As for engineering infrastructure and accommodation, the population in the town is provided with utility services, engineering and transport infrastructure, the housing construction rate doubled since 2000. As for the environmental situation, it covers free and vast lands for the development of agroindustrial cluster and assumes low susceptibility to natural disasters. Along with machine industry and production of building materials, food industry is noted among main industries. Besides, the territorial proximity of the town and the region favorable for agriculture and livestock production allowing supply of agricultural products to the town both for population needs and to food production plants. Among competitive advantages are the following: availability of vocational schools, technical schools, university branches that ensure the adequate number of qualified personnel, the infrastructure for entrepreneurship support available, availability of four manufacturing sites suitable for the construction of various facilities. The city has the advanced infrastructure available in the dense location of the town with the adequate land plots, buildings, facilities available for investment purposes. Geographic and transport availability favorable for investors should be highlighted. There are sufficient land resources for agricultural, industrial and other purposes within the agro-industrial cluster to study.

The known favorable factors include the convenient geographical location of the town (mid location between the regional centers of the Siberian Federal District, namely Kemerovo, Tomsk and Novosibirsk cities, availability of railway communication, good proximity of underground oil and gas mains, high-voltage transmission lines, arrangement of the town on the bank of the Tom River which is the main waterway for the Kemerovo region). The competitive advantages of the town include: the developed system of professional education (Yurga Institute of Technology of the National Research Tomsk Polytechnic University,three colleges (The Yurga Technical College of Machine Industry and Information Technologies, the Yurga Technical School of Agrotechnology and Service, the Yurga College of Technology)), high rate of population with higher and secondary technical education, availability of qualified specialist engineers from the city-forming enterprise (machine-building plant), free investment sites of 549.4 hectares in area and the engineering infrastructure.

As of January 1, 2016, the share of permanent residents in the town amounts to 80484 people, 43214 people are employable population in productive age, 760 people are engaged in the production of food products, including drinks and tobacco goods. In 2014

and 2015, the agricultural output is rated in the amount of over 230 thousand rubles, in 2014 the volume of own-produced goods shipped, delivery of works and services on their own (with no small business involvement) amounted to 12,490.00 thousand rubles, and in 2015 - 514,683.7 thousand rubles.

The agro-industrial cluster will consolidate the greenhousing, the dairy plant, the industrial company for production of beverages and mineral waters "YUSIL", the bakery complex, the greenhouse plant of 5 hectares in area. By 2020, the following is scheduled: implementation of projects to establish a plant for the rainbow trout production of more than a thousand tons per year in volume and fish production recycling (Sibirskaya ryba LLC), expansion of the greenhouse complex (Zeleniy proekt LLC) up to the area of 20 hectares. The cost of projects totals 2165 million rubles. 710 new jobs will be created. In particular, the establishment of the fish-breeding complex for commodity cultivation of rainbow trout will make it possible to saturate the market of the Kemerovo region and other regions with refrigerated and fresh fish products, since production of more than 1,000 tons per year is expected. Peculiarities of cluster strategy implementation and the possibility to create the agricultural complex in Yurga as the standard mono-town of the Kemerovo region is not only PSEDA-based benefits (tax privileges and preferences), food import embargo to Russia from a range of countries (so, for example, in 2014, the volume of Russian trout imports decreased by 50%), but is also based on the identified competitiveness of products bred directly in the region, due to proximity to the consumer, among other things. Public catering establishments and retail chains of Siberian regions compose the target group of consumers. In addition, the higher competitiveness, for example, of trout, will be supported by processing options (smoking, canning, etc.), free delivery management of large batches within Kemerovo, Tomsk, Novosibirsk cities (convenient geography point usage), commercials (brand development and promotion). The consumer similarity is rated as the competitive benefit.

Analysis of figures to identify the agro-industrial cluster, physical output indicators of agricultural and food products, volume of investment in the development of agro-industrial enterprises, as well as opportunities and competitive advantages that ensure investment attraction, the growth of business concern in arrangement of entities and production facilities in the PSEDA of Yurga prove on the high potential to create and develop the agro-industrial cluster in the mono-town.

The following is deemed as positive results of cluster formation in Jurga (predicted by municipal authorities of Jurga): increase in the number of taxpayers and taxable base; emergence of the convenient tool for interaction between large businesses and small and medium-sized businesses; the municipal budget revenue increase; diversification of the economy, use of excess capacity and the territory of the former city-forming enterprise (Table 2).

Among the deterrent factors in Yurga the following may be distinguished: poor quality of business environment (prior to PSEDA), poor development of business associations (chambers of commerce, industry associations) that often fail to achieve the productivity goals and promotion of priorities and interests of the regional business.

As per estimation, the use of cluster approach to form the PSEDA program in Yurga the best effective clusters are identified for the territory. However, it is important to identify the best effective clusters for single-industry towns and establish a specialized entity in a mono-town that executes the cluster management.

PSEDA-based cluster formation contributes to occurrence of synergistic effects, in particular, technological effects due to the spread of technological innovations, resources and infrastructure based on joint use of key resources and PSEDA infrastructure on preferred terms.

Table 2. Estimated figures of cluster formation under PSEDA in the mono-industry town of Yurga, Kemerovo region

Figure	Without PSEDA	With PSEDA (in the first five years)	If there are clusters
Number of enterprises, units	2839	2889	Over 3000
Labor force, pcs	35 600	38 100	40 000
PIT allocations to the municipal budget, rubles	574 609 000	945 208 000	1 172 057920
Insurance contributions from the wage fund, rubles	1 334 860 907	567 124 799	431 014 847
Budget revenues, rubles	912 464 200	1 465 377 000	1 817 067480
Debts of municipal budget, rubles	183 122 000	0	0

CONCLUSION

The PSEDA-based intraregional (municipal) industrial cluster in the mono-town is proposed to consider as the tool to deploy the industry and its network, association of entities to implement projects to diversify the mono-town economy and investment projects meeting the PSEDA requirements. It is indicated, either, that the intraregional (municipal) industrial cluster is the special type (category) of the territorial cluster, regional industrial cluster and the industrial district. In addition, the features distinguishing the intraregional (municipal) industrial cluster from other types are systematized. It is validated that the scenario approach is required to creation of PSEDA municipal clusters based on the priority of from top downward movement with the initial development of the cluster strategy and its support under PSEDA conditions. Basic principles are specified to form the intraregional (municipal) industrial clusters when creating PSEDA in mono-towns that differ from those combination in practice: priority evaluation criteria when choosing clusters with the capacity to develop under the mono-industry town PSEDA; phased networking; use of PSEDA options to create the favorable urban environment; harmonization of participants' strategies; use of outsourcing; development of internal competitive environment as a form of competitiveness of subjects and the market mechanism element integrated into the system of cluster functioning and development. The stages of cluster formation are proposed assuming identification of perspective economic agglomerations, identification and assessment of the cluster formation potential; arrangement of cluster design in view of needs of participants in certain targeted interaction; the choice of basic fields of concern of the cluster in strategic outlook. The staged mechanism for cluster formation assumes a gradual expansion of its boundaries by including participants of manufacturing and business networks. The advantages of the staged mechanism are distinguished to form the cluster. This makes to minimize mistakes when determining the composition and kinds of activities within an intraregional (municipal) cluster, coping with interaction problem. The results of this method evaluation are reviewed with specific reference of cluster formation for PSEDA-based mono-town Yurga. In particular, by the results of analysis of figures obtained for agro-industrial cluster identification and opportunities and competitive benefits of the territory, the high potential is concluded to create and develop the agro-industrial cluster in the mono-town.

ACKNOWLEDGEMENTS

The article was prepared with the financial support of the Russian Humanitarian Scientific Foundation (RHSF). Grant No. 17-02-00453 type a "Development of a methodology for the formation and development of intraregional (municipal) clusters on the territory of advanced social and economic development" (O.P. Ivanova).

REFERENCES

1. *Federal'nyy zakon ot 29.12.2014 N 473-FZ (red. ot 13.07.2015) «O territoriyakh operezhayushchego sotsial'no-ekonomicheskogo razvitiya v Rossiyskoy Federatsii»* [Federal Law N 473-FZ dd. 29.12.2014 (rev. on 13.07.2015) On Priority Social and Economic Development Areas in the Russian Federation"]. Available at: http://www.consultant.ru/document/cons_doc_LAW_172962/ (accessed 27 May 2016).
2. *Postanovlenie Pravitel'stva Rossiyskoy Federatsii ot 22.06.2015 g., № 614 «Ob osobennostyakh sozdaniya territoriy operezhayushchego sotsial'no-ekonomicheskogo razvitiya na territoriyakh monoprofil'nykh munitsipal'nykh obrazovaniy Rossiyskoy Federatsii (monogorodov)»* [The Russian Federation Government Order no. 614, June 22, 2015 “On specifics to form priority social and economic development areas at the territory of mono-profile municipal formations of the Russian Federation (mono-towns)”]. Available at: http://rg.ru/2015/06/30/monogorod-site-dok.html (accessed 27 May 2016).
3. Ilyina I.N. (ed.), et al. *Razvitie monogorodov Rossii* [Mono-town development in Russia]. Moscow: Finansoviy universitet Publ., 2013. 102 p.
4. Mantaeva E.I. and Kurkudinova E.V. Mirovoi opyt klasternoi modeli razvitia [World practice of cluster model development]. *Upravlenie ekonomicheskimi sistemami* [Management of Economic system], 2012, no. 2. Available at: http://www.uecs.ru/uecs-38-382012/item/1085-2012-02-28-05-46-20 (accessed 27 May 2016).
5. Karaeva F.E. *Identifikatsia regionalnykh promyshlennykh klasterov: teoria i praktika* [Regional Industrial Cluster Identification: Theory and Practice]. St. Petersburg: State Institute of Economics, Finance, Law and Technologies Publ., 2014. 160 p.
6. Karaeva F.E. Opredelenie ekonomicheskiy usloviy klasterizatsii regiona clusterization [Determination of economic conditions of regional]. *European Social Science Journal*, 2014, no. 4, vol. 1, pp. 456–461.
7. Lagodyuk A.N. Upravlenie investitsiami v klasterakh: sovremenniy aspekt [Investment Management in Clusters: Modern Aspect]. *Rossiyskoe Predprinimatelstvo* [Russian Journal of Entrepreneurship], 2010, no. 10-1, pp. 60–67. Available at: http://bgscience.ru/com/lib/2604/ (accessed 27 May 2016).
8. Braunerhjelm P. and Carlsson D. Industry clusters in Ohio and Sweden. 1975-1995. *Small Business Economics*, 1999, no. 12, pp. 279–299.
9. Porter M.E. Location, competition, and economic development: Local clusters in a global economy. *Economic development quarterly*, 2000, no. 14 (1), pp. 15–34. DOI: 10.1177/089124240001400105. Available at: http://edq.sagepub.com/content/14/1/15 (accessed 27 May 2016).

10. Breault R. The Evolution of Structured Clusters. *Photonics Tech Briefs*, May 2000. Available at: http://www.photonicsclusters.org/whatisacluster.html (accessed 28 May 2016).
11. *European Cluster Excellence Initiative. The quality label for cluster organizations — criteria, processes, framework of implementation*. February 8, 2015. Available at: http://www.cluster-excellence.eu. (accessed 28.05.2016).
12. Rosenfeld S.A. Creating Smart Systems: A guide to cluster strategies in less favored regions. European Union-Regional Innovation Strategies. *Regional Technology Strategies*. Carrboro, North Carolina, USA, 2002. Available at: http://rtsinc.org/publications/pdf/less_favoured.pdf (accessed 27 May 2016).
13. Kutsenko E. Pilot Innovative Territorial Clusters in Russia: A Sustainable Development Model. *Foresight-Russia*, vol. 9, no. 1, pp. 32–55. DOI: 10.17323/1995-459x.2015.1.32.55 Available at: https://foresight-journal.hse.ru/data/2015/04/07/1096415210/3-Kutsenko-32-55.pdf (accessed 27 May 2016).
14. Toledano J. A propos des? lieres industrielles. *Revue d'Economie Industrielle*, 1978, vol. 6, no. 4, pp. 149–158.
15. *Clusters of Innovation: National Report*. Council on Competitiveness, Monitor Company, and M. Porter. Washington, 2001.
16. *Minekonomrazvitiya Rossii. Realizatsiya klasternoy politiki v Rossiyskoy Federatsii* [Ministry of economic development and trade of the Russian Federation. Implementation of cluster policy in the Russian Federation. Presentation], 2015. Available at: http://www.slideshare.net/semenvuymenkov/ss-48825963. (accessed 27 May 2016).
17. Bortnik I.M., Zemtsov S.P., Ivanova O.V., et al. Stanovlenie innovatsionnykh klasterov v Rossii [Innovatsii Establishment of innovative clusters in Russia]. *Innovatsii* [Innovations], 2015, no. 7, pp. 26–36.
18. *Reyting innovatsionnykh regionov dlya tseley monitoringa i upravleniya (reyting AIRR). Versiya 2015-1.0* [Rating of innovation regions for monitoring and management purposes (AIRR rating). Version 2015-1.0]. Available at: http://www.i-regions.org/files/file_47.pdf (accessed 27 May 2016).
19. Saraev V. Zateryannyy klaster [Lost Cluster]. *Ekspert* [Expert], 2014, no. 51 (928). Available at: http://expert.ru/expert/2014/51/zateryannyij-klaster/ (accessed 27 May 2016).
20. Munn-Venn T. and Voyer R. Clusters of Opportunity, Clusters of Risk. *The Conference Board of Canada Report*, Ottawa, 2004. 32 p.
21. Kutsenko E. Pilot Innovative Territorial Clusters in Russia: A Sustainable Development Mode. *Foresight-Russia*, 2015, vol. 9, no 1, pp. 32–55. DOI: 10.17323/1995-459X.2015.1.32.55. (In Russian).
22. Derudder B. and Witlox F. (eds). *Commodity Chains and World Cities*. Wiley-Blackwell, 2010. 210 p.
23. Stringer C. and Le Heron R. (eds). *Agri-Food Commodity Chains and Globalising Networks* (*The Dynamics of Economic Space*). Routledge, 2016. 258 p.
24. Michael J. Enright Regional clusters: what we know and what we should know. *Innovation clusters and interregional competition*, 2003, pp. 99–129. DOI 10.1007/978-3-540-24760-9_6.
25. Perry M. *Business Clusters: An International Perspective* (*Routledge Studies in Business Organizations and Networks*). Routledge, 2005. 252 p.
26. Braunerhjelm P. and Feldman M.P. (eds). *Cluster Genesis: Technology-Based Industrial Development*. Oxford University Press, 2006. 352 p.
27. Valdaliso J.M. and Wilson J.R. (eds). *Strategies for Shaping Territorial Competitiveness* (*Routledge Studies in Global Competition*). Routledge, 2015. 276 p.
28. Wickham M. *Regional Economic Development: Exploring the 'Role of Government' in Porter's Industrial Cluster Theory*. CRIC Cluster conference. Beyond Cluster- Current Practices & Future Strategies Ballarat, June 30-July 1, 2005. Available at: https://www.researchgate.net/publication/253987774_Regional_Economic_Development_Exploring_the_'Role _of_Government'_in_Porter's_Industrial_Cluster_Theory (accessed 27 May 2016).
29. *The Cluster Initiative Greenbook: New Findings on the Process of Cluster-Based Economic Development*. Available at: http://www.cluster-research.org/greenbook.htm (accessed 27 May 2016).
30. Ivanova O.P., Antonova I.S., and Antonov G.D. *Razvitie monogorodov i upravlenie investitsionnoy privlekatel'nost'yu* [Development of mono-towns and investment appeal management]. Moscow: INFRA-M Publ., 2016. 222 p.

Please cite this article in press as: Ivanova O.P., Antonov G.D., Shabashev V.A., Zobova L.L., and Nesterov A.Yu. Formation of agro-industrial cluster on the priority social and economic development area of the mono-industry town. *Foods and Raw Materials*, 2017, vol. 5, no. 1, pp. 192–204. DOI: 10.21179/2308-4057-2017-1-192-204.

CATERING SERVICE AND ITS QUALITY FOR UNIVERSITY STUDENTS IN MUNICIPAL FORMATION

E. A. Morozova*, E. A. Kranzeeva, and O. P Kochneva

Kemerovo State University,
Krasnaya Str. 6, Kemerovo, 650043, Russian Federation

* e-mail: morea@inbox.ru

Received June 08, 2016; Accepted in revised form September 30, 2016; Published June 29, 2017

Abstract: More and more works are published in scientific literature, concerning the study of students' health and the factors, influencing it, the most important role among which is devoted to rational nutrition. Scientists proved that students' special life style, age-specific peculiarities, intense intellectual and physical activity, irregular studying schedule, lack of money, personal disorderliness and other conditions of students' life demand for special attention to the arrangement of their nutrition. The results of sociological researches, conducted among the Russian students (in Kemerovo and the Kemerovo State University) demonstrate quite a critical relation of students to the quality and functioning of catering service at universities and to price availability of meals in canteens. The analysis of foreign and Russian experience of healthy catering service for students leads to the conclusion that students' centralized nutrition in municipal formation needs to be arranged according to the mechanisms, regulated by the federal program “Shkol'noe pitanie” [School nutrition]. The offered project of the city research and production complex for production of ready meals and semi-finished products for university canteens will allow to increase the students' nutrition quality, improve their health, provide cost efficiency of university public catering, create new workplaces in the city, involve local producers in foodstuffs procurement, develop and implement special programs for students etc.

Keywords: Nutrition, students, health, morbidity, quality of food, canteen, food habits, catering service, municipality

DOI 10.21179/2308-4057-2017-1-205-215 *Foods and Raw Materials*, 2017, vol. 5, no. 1, pp. 205–2015.

INTRODUCTION

According to the Law “Ob obrazovanii v Rossiyskoy Federatsii” [On Education in the Russian Federation] (article 28, clause 15) creation of necessary conditions for preservation and strengthening of health of and catering service for students and employees of educational organizations is established for educational organizations (Federal Law dated as of 29.12.2012 No. 273-FZ (reviewed on 02.03.2016) " Ob obrazovanii v Rossiyskoy Federatsii" [On Education in the Russian Federation]). URL: http://www.consultant.ru/document/cons_doc_LAW_140174/). Despite the fact that nutrition is not the main activity of educational organizations, normal study and upbringing processes are impossible without it, including at universities. Therefore, nutrition quality issues and its effective arrangement at universities should be paid much attention to by management and public organization of university on the one hand, and by scientists on the other.

The issue of students' nutrition is cross-disciplinary. Medics, biologists, ecologists and hygienists consider the issues of rational nutrition, its element-by-element content, caloric content, influence on health and safety. Specialists in the field of foodstuffs production and recycling and in the field of cooking methods study nutrition technological aspects. Sociologists and psychologists study consumer behaviour, stereotypes, nutrition culture and relation to healthy nutrition and pernicious food habits. Topics, dealing with qualitative nutrition arrangement, price policy, cost efficiency of student canteens operation, cafes and buffets belong to economic and administrative science.

Attention to students' nutrition in Russia has been paid to for a long time - even at the end of the 19th century the Russian Society of Public Health Safety offered to arrange "normal canteens" in Moscow and Saint-Petersburg for the studying youth, where nutrition would be based on physiological standards [1]. The results of many researches of the latest decades show that the issues of students' nutrition and its arrangement are relevant and require a serious consideration. Thus, the most frequent nutritional disorders of students, revealed in researches of the 1990s, were irregularity (36%) and dry eating (31%). This resulted either in weight loss (41%), or in overweight, which was found in 9% of students. In surveys students of that time mentioned a sharp increase in food prices at its low quality. Student public catering was becoming unavailable for more than a half [2].

Modern researches (I. P. Balykova et al. [3], E. A. Goreva et al. [4], N. A. Drozhzhina et al. [5], N. N. Zarubina [6], S. A. Krylatov [7], A. V. Noskova [8], Zh. V. Puzanova et al. [9], S. I. Samygin et al. [10], N. V. Semenova et al. [11]) underline preservation of tendencies of nutrition disorder among university students, but nowadays, they are added by rare eating of hot meals and appearance of new food habits – eating a lot of fast food, high-fat, refined products, chips, instant food and drinking a lot of carbonated drinks, made on the basis of chemicals.

Researchers refer lack of money, intensity of studying and lack of attention to their own health to the reasons, causing balance and nutrition disorders of students. They think that high prices and low quality in student canteens together with economy in nutrition leads inevitably to health disorder [12]. It is not surprising that digestive organs diseases have a high position in the structure of morbidity and chronic diseases.

Sector of health social problems of the Institute of Sociology of the Russian Academy of Sciences conducted annually from 2001 till 2008 a monitoring Moscow Students' Health (2363 respondents); according to its results, negative dynamics of students' morbidity are registered. It became clear that the most spread diseases are gastrointestinal (gastritis, colitis), pulmonary and cardiovascular. The monitoring data also revealed a persistent growth in the number of Moscow students with chronic diseases, their number increased by 10% during the observance period. It is stated that there are more junior and senior students among them, then freshmen and sophomores. Researches point out the existence of interdependence between chronic afflictions among students and their level of prosperity. In the low-income group every second person has some chronic disease, in the average-income group each third respondent has it [13].

Foreign scientists [14, 15, 16, 17] also pay much attention to the issues of nutrition of student youth. Their research results should be taken into account, developing the ways of improvement of food quality and nutrition arrangement for students in Russia.

Brief review of the problem under consideration shows that non-standard approach is needed for a significant breakthrough in university catering service. This approach should firstly be based on the best practices of catering service for students and secondly should take into account the specific feature of the territory (region, municipal formation), on which a university (institutions) is located.

The objective of the present paper is to justify the necessity of improvement of catering service for students of universities of a municipal formation (by the example of Kemerovo) to improve quality of their nutrition and to offer a corresponding variant.

OBJECTS AND METHODS OF STUDY

The object of the present research is university students in Kemerovo; the subject is quality and arrangement of their nutrition in educational organizations.

62109 people are studying at universities of Kemerovo Oblast'. Most of students are part-time ones – 30638 people, 29903 people are full-time students and 1668 people are full-and-part-time students (according to the data of October, 2015). The greatest university is the Kemerovo State University. 17289 students are studying at it, including 9164 people, studying at the branches.

There are several universities in Kemerovo: Kemerovo State University (main university – 8125 people), Kuzbass State Technical University (main university – 7339 people), Kemerovo Institute of Food Science and Technology (5265 people), Kemerovo State Medical Academy (3215 people), Kemerovo State Agricultural Institute (2994 people), Kemerovo State Institute of Culture (2821 people), branches of educational organizations in other regions (3651 people). The total number of students at Kemerovo universities is 33410 people or 6% of the city population.

The specific features of studentship are: age-related characteristic from 17 to 25 years old; specificity of educational activity (intellectual nature of labour, regulated by the university curriculum, specific resting time rules), income structure (scholarship, parents' aid, individual earning). The obvious significant feature of this group, which draws attention of researchers, is student age. Thus, it is stated that this period is the most important for formation of personal position, establishment of a wide range of social relations, exploration of the future professional activity, adoption of new behavioural norms and orientation to the desired social roles [18]. Herewith, the researchers do not have a unified position on the essence of the definition of student age. A famous sociologist I. S. Kon analysed the specific features of the student age and pointed out the priority of a social aspect. That is because time boundaries of studentship clash with the period of adolescent age which is complex and contradictory but significant for the social maturity of an individual [19, 20]. M. Ya. Vilenskiy and S. O. Avchinnikova point out the priority of psychophysiological aspect, analysing the student age. They characterise it as a period of peaks of organism physiological potentials [21].

Studying studentship, other aspects are also highlighted, associated with the difficulty of studying at a university. They are organizational conditions and organism psychophysiological peculiarities (V. V. Zashikhina et al. [22], O. F. Kushnerova et al. [23], E. M. Kharlanova [24] etc. [25]).

As it has been stated earlier, one of the incomes (and often the main one) of a student during his/her studying is scholarship. At state universities students are assigned a state academic scholarship, which differentiates, in particular, depending on the location of an educational organization. For example, the minimum size of the state academic scholarship for students of the Kemerovo State University, who have passed exams with good and excellent marks, is 1930 rubles per month and for the students who have only excellent marks it is 2895 rubles (the Russian Federation Government Decree dated as of

18 November, 2011 No. 945 “O poryadke sovershenstvovaniya stipendial'nogo obespecheniya obuchajuschikhsya v federal'nykh gosudarstvennykh obrazovatel'nykh uchrezhdeniyakh professional'nogo obrazovaniya” [On Procedure for Improvement of Scholarship Provision in Federal State Educational Organizations of Professional Education]). URL: http://base.garant.ru/12191951/).

Students, studying at the expense of budget funds and who needs social aid, upon presentation of supporting documents, are assigned a state social scholarship of 2895 rubles per month, students, passing the exams with good and excellent marks, have a scholarship of 4824 rubles, with excellent marks – 5789 rubles.

Mandatory payees of social scholarship in accordance with the law are children-orphans, disabled people of the 1st and the 2nd groups, liquidators of the Chernobyl accident, combat disabled people and veterans.

Senior students may be assigned an enhanced state scholarship if they have good and excellent marks, conduct active scientific-research, cultural and creative, sport and public activity and have achievements in studying. The scholarship size is determined by the University Academic Senate, involving representatives of student government.

In certain cases, freshmen and sophomores in need may also be assigned such a scholarship. Its size for students with excellent marks is 9965 rubles, with good and excellent marks – 9000 rubles (Russian Federation Government Decree dated as of 2nd July, 2012 No. 679 “O povyshenii stipendiy nuzhdayushchimsya studentam pervogo i vtorogo kursov federal'nykh gosudarstvennykh obrazovatel'nykh uchrezhdeniy vysshego professional'nogo obrazovaniya, obuchayushchimsya po ochnoy forme obucheniya za schet byudzhetnykh assignovaniy federal'nogo byudzheta po programmam bakalavriata i programmam podgotovki spetsialista i imeyushchim otsenki uspevaemosti “khorosho” i “otlichno” [“On enhancement of scholarship for full-time freshmen and sophomores in federal state educational institutions of higher professional education, who study bachelor or specialist learning programs at the expense of budgetary funds of the federal budget and who have good and excellent marks”]). URL: http://base.garant.ru/70196772/).

Financial support may be paid to students as a financial aid. Full-time students of the vulnerable category (orphans, disabled people, students from a large family, low-income students) may be provided with a food package.

Students-orphans or students who lost their parents have the right for full state support which presupposes free nutrition or refund for it (from 2014 it is 260 rubles for a working day and 286 rubles for a day off or a calendar day), provision of clothing kit or inventory (or refund of their price according to the norms), right for free accommodation in a dormitory and for free medical care during the whole period of studying (Federal Law "O dopolnitel'nykh garantiyakh po sotsial'noy podderzhke detey-sirot i detey, ostavshikhsya bez popecheniya roditeley" [“On additional guarantees of social support for children-orphans and children, lost their parents”], dated as of 21st December, 1996 No. 159-FZ). URL: http://base.garant.ru/10135206/; (Russian Federation Government Decree dated as of 7th November, 2005 No. 659 “Ob utverzhdenii norm material'nogo obespecheniya detey-sirot i detey, ostavshikhsya bez popecheniya roditeley, lits iz chisla detey-sirot i detey, ostavshikhsya bez popecheniya roditeley, obuchayushchikhsya i vospityvayushchikhsya v federal'nykh gosudarstvennykh obrazovatel'nykh uchrezhdeniyakh, nesovershennoletnikh, obuchayushchikhsya i vospityvayushchikhsya v federal'nykh gosudarstvennykh obrazovatel'nykh uchrezhdeniyakh – spetsial'nykh professional'nykh uchilishchakh otkrytogo i zakrytogo tipa i federal'nom gosudarstvennom uchrezhdenii “Sergievo Posadskiy detskiy dom slepoglukhikh Federal'nogo agentstva po zdravookhraneniyu i sotsial'nomu razvitiyu” [“On approval of norms of financial support for children-orphans and children who lost their parents, persons from among children-orphans and children who lost their parents, who study and are brought up at federal state educational institutions, of persons who have not reached the age of majority, who study and are brought up at federal state educational institutions - open- and closed-type special professional schools and at the federal state institution Sergiev Posad boarding school for children with blindness and deafness of the Federal Agency on healthcare and social development”]. URL: http://base.garant.ru/188814/).

To justify the necessity of improvement of approaches to student catering service, the following methods were used in the present research as the main research methods: analysis of statistics, official documents and other materials; secondary analysis of sociological researches results; comparison and analogy. For a deeper study of catering service system at Kemerovo universities, the Kemerovo State university experience was additionally analysed (results of several representational for the university sociological researches).

RESULTS AND DISCUSSION

In the current context, students experience greater burden at conscientious attitude to learning. The study process requires memory exertion, attention concentration, is often accompanied by stressful situations associated with exams, tests and intermediate control. The consequences of students' mental strain in combination with reduced physical activity may be health deterioration, working capacity decrease and decrease in resistance to various diseases. The process of adaptation to the new social conditions, associated with studying at a university, may cause depletion of body physical reserves, especially during the first semesters [26, 27]. All this requires from students the observance of a healthy lifestyle and, first of all, of healthy nutrition principles.

However, definitive conditions for a healthy nutrition, which meets the requirements of normal functioning of a young organism, have not been created

yet, which is proved by the data of the sociological research "Kuzbass Student", conducted in 2013 in Kemerovo Oblast' by the sociological laboratory of the Kemerovo State University by the decision of Expert Advisory Body of the region universities on monitoring of attitude of educational process subjects to socially significant events, which covered 2973 students of the 9 universities of the federation subject. Let's refer to the data, obtained during this research, on Kemerovo universities as a whole (2444 students of 7 universities) and on the biggest university in the region – the Kemerovo State University (566 students have been questioned).

Defining the most relevant problems of students, respondents have been offered to assess quite a wide range of these problems (21 items), from which one could select up to 6 variants. The data indicate that students of different universities have ranged their difficulties differently, but the lack of money for food appeared to be in the top of ten most significant problems – at the Kemerovo State University 16% pointed out this problem, at other Kemerovo universities – 17%. Data comparative analysis results, depending on social and demographic characteristics, showed that at the Kemerovo State University and at Kemerovo universities totally this problem disturbs, first of all, low-income students, studying on a budgetary basis and living in university dormitories.

In the course of the research under consideration the respondents were questioned about the expenditures which are most relevant for students in terms of financial support (the respondents were offered a list of financial costs, specific for studentship) (see Table 1). The question presupposed the possibility of choosing several answers (up to three), therefore, the sum of percentage in each column exceeds 100%.

Judging by the obtained answers, expenditures for food are the most problematic item of expenditures for the majority of students; 59% of respondents at the Kemerovo State University and 58% of respondents at other Kemerovo universities specified it. Comparison of data on socio-demographic characteristics showed that this measure is more important for freshmen living in dormitories, students studying on a budgetary basis and low-income students.

The represented sociological data on Kemerovo demonstrated the relevance of student qualitative catering service arrangement. But the results of researches, conducted in different years at the Kemerovo State University, allow to make a more detailed justification of the analyzed problem.

Thus, according to the data of representational sociological surveys, dealing with health problems and conducted among the Kemerovo State University students (the researches have been conducted by the sociological laboratory of the Kemerovo State University among students of first to fourth courses of all faculties in April-May, 2012 (covered 1066 respondents) and March-April, 2011 (covered 1096 respondents)) [28], only each forth-fifth respondent kept healthy nutrition to enhance health (see Table 2), they put this measure on a third place after taking vitamins and dietary supplements (55–59%) and sports activity (41–46%).

As well, the results of this research showed that irrational nutrition together with irrational schedule were the main reasons for suffered diseases during the study at the Kemerovo State University (see Table 3).

Moreover, the digestive system diseases are in the second place by frequency among the list of diseases which students suffered during the years of study at university, they have been noted by a quarter of respondents (see Table 4).

Table 1. Material expenditures, most relevant for financial support (% from the number of respondents)

Answers	Kemerovo State University	other universities of Kemerovo
no such expenditures	3	6
expenditures for food	59	58
expenditures for public transport	39	42
expenditures for getting to a place for students living outside the city	36	32
accommodation expenditures	33	27
expenditures for treatment and disease prevention	24	24
expenditures for the Internet	23	20
expenditures for cultural events	16	16
expenditures for study materials	8	6
expenditures for scientific-research activity	3	3
other expenditures	2	3
no answer	4	5

Table 2. Forms of enhancing personal students' health, 2011, 2012 (% from the number of respondents)

Forms of enhancing health	2011	2012
Take vitamins, dietary supplements, herbs	55	59
Do sports	41	46
Keep healthy nutrition	22	25
Do exercises, harden	15	21
Do not enhance health	18	11
Are constantly followed up by a doctor, are treated as outpatients	11	13
Are treated as inpatients periodically	7	7
Are treated in sanatoriums, preventative clinics etc.	4	9
Travel to the sea during holidays	13	14
Take massage or physiological treatment courses periodically	9	9
Visit quacks	2	3
Other forms	2	2

Table 3. Reasons for suffered diseases, 2012

Reasons	% from the number of respondents
Irrational nutrition	37
Irrational schedule	37
Intensity of exams	29
Heavy academic load	29
Careless attitude to the own health	25
Unfavourable accommodation conditions	14
Genetic predisposition	14
Insufficient physical activity	11
Unfavourable studying conditions	10
Pernicious habits	6
Frequent conflicts in a family	2
Frequent conflicts in a group	1
Other	4
No answer	7

Table 4. Diseases, suffered by students during the study at university, 2012

Diseases	% from the number of respondents
Infectious diseases	39
Digestive system diseases	24
Eye diseases	20
Traumas	18
Nervous system diseases	17
Genitourinary system diseases	10
Respiratory system diseases	11
Heart and vascular diseases	9
Ear diseases	6
Other diseases	4
No diseases	25

It should be mentioned, that less than a quarter of respondents (23–24%) considered their nutrition as rational and balanced. More than a half of respondents (54–57%) claimed that they have malnutrition. There are problems also with nutrition regularity: only a third part of students (33–35%) ate regularly during a studying day; approximately the same number (28–36%) ate irregularly; and approximately the same part (31–37%) ate on different days differently.

The represented data obviously prove the necessity of arrangement of effective operation of catering outlets at universities. The opinion of students and lecturers of the biggest university in Kemerovo Oblast' on the functioning of these outlets was studied repeatedly.

The results of sociological research, conducted at the Kemerovo State University in 2012–2013 academic years among the students and teaching staff (2294 of students from a freshman to a senior and 567 lecturers of all faculties took part in a questionnaire survey) showed that only each second lecturer and a little bit more than a half of students (56%) think that there are quite enough or rather enough catering outlets at the university, 41 and 42% of respondents respectively think opposite.

Upon the whole, the negative dynamics are observed concerning the issue of sufficiency of catering outlets at the university - in the course of the 9-year monitoring research University [29] the number of positive answers is decreasing (see Table 5).

Table 5. Assessment by students and lecturers of sufficiency of catering outlets at the university (%, from the total amount of respondents)

Year	2000	2003	2006	2009
Assessment by students				
enough	47	41	32	28
quite enough	38	38	37	38
rather not enough	10	14	15	22
extremely not enough	4	6	15	11
failed to assess	1	1	1	1
total at the university	100	100	100	100
Assessment by lecturers				
enough	33	39	23	22
quite enough	50	42	49	43
rather not enough	9	13	16	23
extremely not enough	1	1	5	5
failed to assess	7	5	7	7
total at the university	100	100	100	100

According to the research data of 2012–2013 academic years, one-third of students used the Kemerovo State University canteen service several times in a week; other one-third part used it every day. The rest of respondents use the university catering service rarely (they are 18%) or those who did not visit canteens (16%). Thus, nutrition of each third student

may be considered a relatively healthy, moreover, according to the data of observation over consumer preferences, students choose meat and fish meals more seldom and cheaper salads, garnish, soups and baking - more often. Lecturers visit canteens more seldom than students – 36% of them have never used its service.

Fig. 1 indicates assessments by students and lecturers of different aspects of canteen operation. The obtained assessments are higher than the theoretical average one (3.0 points), but lower than a "good" level. The highest assessments were given to the food quality and personnel work, price availability got the lowest assessment. On the average, the canteen operation was assessed by students by 3.5 points, by lecturers – by 3.6 points. The comparison of assessments of different university canteens showed that in buildings, located far from the university administrative building, all aspects of canteen operation were assessed lower.

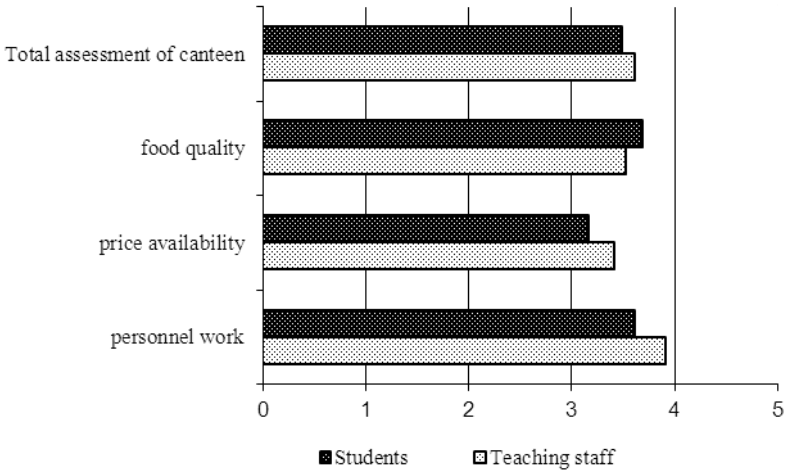


Fig. 1. Assessment of the Kemerovo State University canteen operation, which is visited most often by students and lecturers, by three aspects and upon the whole (by a 5-point scale, where 1 point is very badly, and so on increasingly, 5 points - very good) (points).

Comparison of indicators of students' attitude to canteens operation depending on their prosperity level showed an interesting interdependence - those, who have greater prosperity, gave more loyal assessments to the all items of canteens operation and those, whose financial possibilities are more limited, assessed it more critically. Based on the foregoing, we can state that students are not satisfied with canteens operation because of high prices and food quality, and this causes eating of less healthful food. In general, the opinions of students strongly enough coincided with the views of the teaching staff, which further confirms the reliability of the results.

According to the data of another all-university research, conducted in spring, 2014 (sociological research covered 963 students from freshman to senior of all faculties), less than a half of respondents (42%) could afford a healthy nutrition; almost as many as those who have to economise for it (41%). There are quite a few of those (12%), who "have to economise harmfully for nutrition, because money is not enough at all" (12%). According to the data of comparative analysis, students, having a lower income and living in a dormitory, were in a more vulnerable position.

Thus, a sociological substantiation, built on the data secondary analysis, demonstrated the importance of a more careful attention to students' nutrition arrangement. In this case it is necessary to study the respective experience of different countries, Russian regions and municipal formations, in particular, the experience of nutrition arrangement in comprehensive schools, which has been gained during the Russian reform in school catering service.

In most countries of the world with advanced state welfare activities, systems of pupils' centralised catering service are provided, where state subsidy is up to 80% of the diet price. Parents are also involved in school catering service financing; the method of multi-way financing is implemented. In the context of students, such systems are practiced in the frameworks of general nutrition programs.

In the USA (Food and Nutrition Service. URL: http://www.fns.usda.gov/programs-and-services) healthy children nutrition is implemented due to the current special programs. Thus, the National School Lunch Program is applied to children up to 18 years and covers more than 31 million Americans every day. Under this program school dinners shall comply with the specially designed nutrition standards, which presuppose a certain number of calories, an increased availability of fruits, vegetables and whole-grain products.

School Breakfast Program presupposes that breakfasts shall be included in nutrition regime. The program presupposes measures, motivating and encouraging pupils and their families to use school breakfasts.

Special Milk Program is intended for institutions that do not take part in the above-mentioned nutrition programs. Under this program, children may get milk

for free or buy it at a reduced price (depending on the type of institution and program).

Under the Child and Adult Care Food Program, the standards of rational nutrition are developed. Most of its participants are preschool children who may get a balanced two-meal nutrition. The right to use this program depends on the poverty status of the district or on incomes.

Financial support for nutrition programs is implemented by the United States Department of Agriculture through a compensation for cash and product expenditures, as well as through financial aid to states to cover administrative costs, associated with the programs. Programs control in state institutions and schools is implemented by states individually, and in private schools and non-governmental institutions they act trough special Food and nutrition services.

30.5 million pupils are provided with breakfasts and dinners as a result. Multi-way financing is implemented: each school, participating in the programs, receives federal subsidies directly on the school account or on the account of the district administration, to which it relates; from the nearest agricultural products suppliers schools also receive different food packages in the line of the Department of Agriculture in the amount of 20.75 dollars per dinner per pupil; from parents, who do not have any exemptions, a school receives from 15% to 90% of the pupils' nutrition cost. Totally, under all the programs approximately 12 billion dollars are appropriated in the USA for free nutrition.

In Great Britain (Children's Food Trust. URL: http://www.childrensfoodtrust.org.uk/childrens-food-trust/schools/) systems of centralised catering service have the old-established tradition: in 1906 recommendations for municipal authorities were adopted for provision of free nutrition for pupils.

To the beginning of 1970s the country developed the available centralized nutrition system, which covered the majority of students, and for students from poor families it was free of charge. Since Margaret Thatcher has come to power in 1979, the program was phased out because it was considered costly and bureaucratic.

After school catering service had been criticised by the famous chief cook James Oliver, in 2005 extra-departmental state body was founded under the UK Department of education and training - School Food Trust. The Trust created the biggest national network of healthy culinary clubs for children and families with the support of a grant from the state and commercial organisations. Nowadays, the Trust is a registered philanthropy organization and a special advisor to the government on the issues of school catering service, children nutrition and the skills, associated with it. The main task is to ensure that all children have a balanced diet, cooking skills and education which will help to fully realize their potential. Cooking clubs activity covers 1.7 million people. Nearly all (92%) use their new skills at home, 58% of participants point out that they have a healthy diet due to the fact that they have learned to cook. Another big project of the Trust is training centres School FEAST Network (School Food Excellence And Skills Training Network). Under this project cooks of school canteens may improve their qualification to the 2nd level in accordance with the national standards. It is supposed that cooks of higher qualification will be able to provide better nutrition quality in children institutions.

School nutrition Service in Finland (Finnish Free School Meals are a central part of the food culture. URL: http://www.elo-saatio.fi/finnish-free-school-meals) provides daily free nutrition for approximately 830000 pupils from 7 to 19 years old.

The history of free nutrition is associated with the adoption in 1943 of the law under which municipalities were obliged to provide free breakfasts for pupils. Nutrition complex consists of traditional Finnish products and includes main hot course, vegetables, bread, fat-free or low-fat milk and water.

Special diets are being developed, which include increased content of vegetables, fruits and whole-grain products. According to the recommendations, in educational institutions the number of sweets and sweet carbonated drinks shall be minimised; thus, vending machines and school kiosks shall offer healthy and nutritious products.

Municipal and school training programs define the central nutrition principles. Municipalities allocate resources for school catering service and are responsible for the program implementation. Implementation, quality and efficiency are the components of general education assessment. Pupils have a possibility to take active part in the assessment at obligatory attention to their feedback.

On the average, the price of products for cooking one dinner is 0.6–0.8 euros. Food is more expensive for those who need diet food. The amount of financing of school nutrition is 354 240 euros. Average price of one school dinner is about 2.64 euros. Applying multi-way financing, state obliges municipal budgets by law to provide pupils with free nutrition, which is due to tax revenues to local budgets and revenues from religious communities. Commercial operators and Social-purpose Products Management deal with pupils' nutrition arrangement. Parents are excluded from the number of school catering service investors.

In some countries there are special programs of nutrition for students. Thus, in Canadian Toronto there is a functioning program Student Niutriton (Student Nutrition Program. URL: http://www1.toronto.ca/wps/portal/contentonly?vgnextoid=ecad946d1d592410VgnVCM10000071d60f89RCRD), which covers 160 thousand people daily. Under the program, students get breakfast, lunch and dinner. The founders of this program claim its following tasks: provision of nutrients and energy, creation of healthy food habits, prevention of obesity. The municipality of Toronto allocates grants annually to school/student communities which arrange healthy nutrition for students in educational organisations. However, this financing covers only a small part of total expenditures for the program. The greatest part of program financing comes from parental contributions and local fundraising.

For example, the US Department of Agriculture introduced an electronic debit card instead of meal coupons. Traditionally, meal coupons were offered for working poor and single parents, most working young people older than 18 years old, studying at a college or other university, do not have the right to receive benefits of the supplemental nutrition assistance program (SNAP), but under the certain conditions, for example, presence of dependants, terms of benefits provision are softened (Supplemental Nutrition Assistance Program (SNAP). URL: http://www.fns.usda.gov/snap/students).

In Russia the experience of nutrition programs implementation is realised meanwhile in the system of school catering service. However, nowadays, the project of the federal law on social nutrition is being actively discussed and drafted. At the present time, in the Russian Federation social nutrition is provided for the population groups on the basis of the federal law "Ob osnovakh sotsial'nogo obsluzhivaniya grazhdan v Rossiyskoy Federatsii" [On principles of social service for citizens in the Russian Federation], No. 442-FZ dated as of 28.12.2013 (Federal law dated as of 28 December, 2013 No. 442-FZ " Ob osnovakh sotsial'nogo obsluzhivaniya grazhdan v Rossiyskoy Federatsii" [On principles of social service for citizens in the Russian Federation] URL: http://base.garant.ru/70552648/#help). This law specifies the population groups, provided with social service, as well as indicates that provision of social service recipients with free hot meals is included in the list of social services. The law on social nutrition operates in Saint-Petersburg from 2008 and is being elaborated in Moscow, Tver etc. Experimental sites for implementation of this system are operating in some regions. According to the law, socio-economic system should be created, associated with servicing of various categories of consumers. Social nutrition is a possibility to provide nutrition at the budget expense for certain categories of citizens to ensure social guarantees, stipulated by the current legislation. Under this proposal the following nutrition systems by the consumer contingent are pointed out: working, student, school, children, therapeutic nutrition and the one in military educational institutions. They have a common designated purpose but differ in the significance level and the degree of population coverage.

Norms of catering service at universities will be included in a separate section in this bill. So, we can assume that the catering service system at universities will be built on the model of school catering service.

Under the implementation of the Federal program "Modernizatsiya shkol'nogo pitaniya" [School Catering Service Modernisation], the main aim of which is "complex modernisation of the system of school catering service: provision of 100% of pupils with balanced hot meals in accordance with physiological needs of children and hygiene requirements for catering service", in municipal formations, beginning with 2008 combines of school catering service have been founded in the form of state unitary enterprise and municipal autonomous institutions for the possibility to arrange centrilised production of high-quality products under the single production cycle regardless the personnel qualification level of educational institutions food units.

Thus, for Kemerovo schools the municipal autonomous institution (MAI) "Shkol'noe pitanie" [School Catering Service] produces meals for school canteens (School Catering Service. – URL: http://мау-шп.рф/), which was founded by the decision of the Kemerovo Municipal Property Management Committee (No. 639 dated as of 09.04.2008 in accordance with the Kemerovo Mayor Decree No. 1356 dated as of 04.04.2008). Under the implementation of the project "Shkol'noe pitanie" [School Catering Service] from 2008 till 2011 nearly all school food units were modernised (only a few units, which meet the modern requirements, remained without modifications): facilities were reconstructed, equipment and furniture in dining halls were replaced, cyclic menu was designed, innovative approach to cooking treatment was implemented, the system of quality and nutrition control of pupils was designed.

To involve the maximum number of pupils in rational nutrition, the Kemerovo administration compensates the fifth part of all enterprise expenditures and this allows to ensure the price of school meals lower than the market one. Moreover, the innovations affected also the payment procedure for school catering service, which is made with the use of billing system, which allows parents and form-masters to solve the issues of nutrition process management at the modern level (payment, expenditures control, nutrition orders forming etc.). The module "Shkol'noe pitanie" [School Catering Service] is a part of the service "Elektronnyj zhurnal" [Electronic Journal].

MAI "Shkol'noe pitanie" [School Catering Service] practices production of 20-day menu which is formed in complexes and is regularly renewed (taking into account the season). Meals are not repeated in the menu. The used products have a high nutrition value; they are treated with a low-impact technology, aimed at minimising the loss of nutrient substances during cooking. Careful attention is obligatory paid to the quality and safety of raw materials and finished products. MAI "Shkol'noe pitanie" [School Catering Service] Process Department together with Rospotrebnadzor [Federal Service on Surveillance for Consumer Rights Protection and Human Well-being] and Inspection Committee in an educational institution are responsible for control in this area. The following is conducted under the production control: laboratory control of raw materials and finished products quality; field inspections of food units by the specialists of Rospotrebnadzor [Federal Service on Surveillance for Consumer Rights Protection and Human Well-being] and instrumental examination of microclimate, light and noise. Raw materials and finished products quality are controlled by the specialists of enterprise process department and by the enterprise sanitary inspector.

In conclusion of review of the practice of pupils and students catering service and its regulatory support, it should be mentioned that nowadays, the Common Standard of student nutrition is being developed in Russia, initiated by the Russian Student Community

(RSC). In this Standard a list of approximate products package is alleged, as well as their caloric content, national cuisine peculiarities, price indexes and advice, how to provide a healthy nutrition on a scholarship. Such standards may be differentiated by regions and many federation subjects showed interest in this project (Khromov A. V Rossii k oseni poyavitsya Edinyy standart pitaniya rossiyskikh studentov [In Russia the Common standard of the Russian students nutrition will appear by spring]. URL: http://www.edu.ru/news/education/v-rossii-k-oseni-poyavitsya-edinyy-standart-pitani/).

CONCLUSIONS

The analysis of the foreign and Russian practice of students and pupils catering service shows that principal improvement of student nutrition is possible only at circumspect comprehensive approach to its arrangement. The issue of student rational nutrition should have a status of the state program and there is a hope that the Russian state moves in the appropriate direction. However, taking into account the current economic situation, in the near future one cane face the barriers on the way to the centralised solution of the problem of students nutrition. In these circumstances, the regional and municipal bodies could take this issue under control. In this case, a management difficulty, associated with university departmental subordination, occurs, but when you consider that universities and institutions in remote areas train personnel, primarily for the economy of the respective regions, then this problem can and should be solved.

It seems that the task of centrilised catering service arrangement at universities may be resolved easier in relatively small municipal formations, on the territory of which there are several (up to ten) educational institutions of higher education. Kemerovo is precisely such a municipal formation. The important factor, which should affect the municipal complex arrangement positively and which provides students with healthy nutrition, is the presence in the city of the specialised university - the Kemerovo State Institute of Food Industry (University), which may be a scientific-methodological centre on the alleged production complex.

The new production complex should supply qualitative finished food, products and semi-finished products for cooking meals directly at universities, as well as train personnel of educational organisations canteens and control the nutrition quality in them. The alleged products should have optimum quality-price ratio, i.e. they should guarantee a high quality of products and services in combination with price availability. Enterprise should be equipped with the modern equipment, have experienced personnel, professional dietitians should conduct formulations, there should be a continuous quality control over both the incoming products and semi-finished products and over the outcoming products. Thus, the structure of production complex on centrilised production foodstuffs for universities in the city should include: scientific research laboratory for generation of scientifically grounded menu; laboratory control for conduction of incoming inspection and control over the outcoming products, including measures for production control in canteens and buffets of educational organisations; meat shop (meat and poultry dissection, production of coarse- and fine-lump semi-finished products, forming of semi-finished products; candy production, producing a wide range of small-piece baked products; culinary production of salads and culinary products; logistics centre, where common warehouses are located and raw materials are packaged for universities/buildings; kitchen factory for production of breakfasts and lunches for serveries.

The foundation of scientific research complex for provision of students of the city with nutrition, including dietary one, may solve the following social and economic problems: to improve students nutrition quality and, consequently, improve their health; unload universities from non-specific activities; provide cost efficiency and ability to manage public catering; create new workplaces, including high-technology ones; buy products from local producers more actively; develop and implement special programs (for students with different diseases, for vulnerable students, for students living in dormitories etc.) and others. In any case, centrilised student catering service arrangement in municipal formation is a subject, requiring careful attention and management decisions.

REFERENCES

1. Egorysheva I.V. Russkoe obshchestvo okhraneniya narodnogo zdraviya (k 125-letiyu so dnya osnovaniya) [Russian Society of Public Health Safety (to the 125th anniversary of the foundation)]. *Problemy sotsial'noy gigieny, zdravookhraneniya i istorii* [Problems of Social Hygiene, Public Health and History of Medicine], 2002, no. 6, pp. 56–57.
2. Agadzhanyan N.A. *Zdorov'e studentov* [Students health]. Moscow: Russian University of Nations Friendship Publ., 1997. 199 p.
3. Balykova O.P., Cybusov A.P., Blinov D.S., et al. Research of university students nutrition culture as one of factors of health forming. *Integratsiya obrazovaniya* [Integration of Education], 2012, no. 2, pp. 56–59. (In Russian).
4. Goreva E.A., Petrenko A.V., Khrebtova A.Y., and Fedorov I.A. Sovremennye osobennosti ratsiona pitaniya studencheskoj molodezhi [Modern features of the student youth diet]. *Vestnik Chelyabinskogo gosudarstvennogo universiteta. Obrazovanie i zdravookhranenie* [Chelyaminsk State University Bulletin. Education and science], 2015, no. 1, pp. 44–48.
5. Drozhzhina N.A., Maksimenko L.V., and Kicha D.IFeatures of feeding behavior of students of the Peoples' Friendship University of Russia. *Voprosy pitaniya* [Problems of Nutrition], 2012, vol. 81, no. 1, pp. 57–62. (In Russian).

6. Zarubina N.N. Transformations of the Food Practices in Modern Russia: the Institutional and Discursive Determinants. *Vestnik MGIMO universiteta* [MGIMO Review of International Relations], 2014, no. 6(39), pp. 199–208. (In Russian).
7. Krylatov S.A. Health Assessment of Students: Results of Empirical Research. *Gumanitarnyy vektor. Seriya: Pedagogika, psikhologiya* [Humanitarian Vector. Series Pedagogy and Psychology], 2013, no. 1(33), pp. 98–103. (In Russian).
8. Noskova A.V. Research of the Nutrition Problem: Methodological Approaches and Daily Practices. *Vestnik MGIMO universiteta* [MGIMO Review of International Relations], 2014, no. 6(39), pp. 209–218. (In Russian).
9. Puzanova Zh.V. and Vyalov I.S. The conditions of higher school education and their influence on students' health. *Obschestvo: sotsiologiya, psikhologiya, pedagogika* [Society: sociology, psychology, pedagogics], 2014, no. 4, pp. 12–14. (In Russian).
10. Samygin S.I., Samygin P.S., and Osipova A.A. Youth and health: psychological barriers to self-preservation behaviour. *Gumanitarnye, sotsial'no-ekonomicheskie i obschestvennye nauki* [Humanities, social-economic and social sciences], 2015, no. 6-2, pp. 73–78. (In Russian).
11. Semenova N.V., Lyapin V.A., Grischenko Y.A., et al. Features of stereotypes of a delivery and predisposition to disturbances of alimentary behavior of students of higher education institutions. *Sovremennye problemy nauki i obrazovaniya* [Modern problems of science and education], 2015, no. 4, p. 453. (In Russian).
12. Ushakov I.B., Sokolova N.V., Kordenko A.N., et al. *Provintsiya: kachestvo zhizni i zdorov'e studentov* [Province: life quality and students health]. Moscow – Voronezh: Istoki Publ., 2002. 150 p.
13. Ivakhnenko G.A. Monitoringovoe issledovanie trasnformatsii samosokhranitel'nogo povedeniya moskovskikh studentov [Monitoring research of transformations of self-safety behavior of Moscow students]. *Okhrana zdorov'ya: problemy organizatsii upravleniya i urovni otvetstvennosti* [Health protection: problems of arrangement and management and responsibility levels], 2008, pp. 184–185.
14. Bates B., Lennox A., Prentice A., et al. *National diet and nutrition survey. Results from years 1, 2, 3 and 4 (combined) of the rolling programme (2008/2009 – 2011/2012). A survey carried out on behalf of Public Health England and the Food Standards Agency*. London: Public Health England, 2014. 158 p.
15. Pechey R., Jebb S.A., Kelly M.P., et al. Socioeconomic differences in purchases of more vs. less healthy foods and beverages: analysis of over 25,000 British households in 2010. *Social Science & Medicine*, 2013, vol. 92, pp. 22–26. DOI: https://doi.org/10.1016/j.socscimed.2013.05.012.
16. Salvy S.J., Elmo A., Nitecki L.A., et al. Influence of parents and friends on children's and adolescents' food intake and food selection. *The American Journal of Clinical Nutrition*, 2011, vol. 93, no. 1, pp. 87–92. DOI: doi:10.3945/ajcn.110.002097.
17. Persson M., Soroko R., Musicus A., et al. *A junk-free childhood 2012. The 2012 report of the StanMark project on standards for marketing food and beverages to children in Europe*. London: International Association for the Study of Obesity, 2012. 32 p.
18. Bezrukikh N.A. *Formirovanie ustanovki studentov na zdorovyy obraz zhizni v obrazovatel'nom protsesse professional'noy shkoly* [Formation of the attitude of students to a healthy lifestyle in the educational process of a professional school]. Saratov: Volga academy of public administration, 2007, 47 p.
19. Kon I.S. *V poiskakh sebya: lichnost' i ee samosoznanie* [In quest of myself: personality and identity]. Moscow, 1984. 336 p.
20. Kon I.S. *Psikhologiya ranney yunosti* [Pshycology of early youth]. Moscow: Prosveschenie Publ., 1989. 256 p.
21. Vilenskiy M.Ya. and Avchinnikova S.O. Metodologicheskiy analiz obshchego i osobennogo v ponyatiyakh «zdorovyy obraz zhizni» i «zdorovyy stil' zhizni [Methodological analysis of general and especially in terms of "healthy lifestyle"]. *Teoriya i praktika fizicheskoy kul'tury* [Theory and practice of physical culture], 2004, no. 11, pp. 2–7.
22. Zashikhina V.V. and Tsyganok T.V. Psycho-physiological aspects of adaptation of high school students. *Fundamental'nye issledovaniya* [Fundamental research], 2014, no. 2, pp. 64–68. (In Russian).
23. Kushnerova O.F. and Kushnerova Y.Y. Specificity of social adaptation psihlogicheskoy first-year students to study at university]. *Fundamental'nye issledovaniya* [Fundamental research], 2013, no. 10, part 10, pp. 2314–2317. (In Russian).
24. Kharlanova E.M. Issledovanie sotsial'noy aktivnosti studentov [Research of social activity of students]. *ISOM* [Institute of social and educational management], 2011, no. 5, pp. 173–178.
25. Kranzeeva E.A. and Bogomaz S.A. To the question of studying the creative potential and willingness to innovate reformation. *Vestnik Kemerovskogo gosudarstvennogo universiteta* [Bulletin of Kemerovo State University], 2016, no. 1 (65), pp. 106–110. (In Russian).
26. Baranovskiy A.Yu. *Bolezni narushennogo pitaniya. Lechenie i profilaktika* [Disturbed nutrition diseases. Treatment and prevention]. Moscow: Nauka i tekhnika Publ., 2007. 304 p.
27. Tutel'yan V.A., Spirichev V.B., Sukhanov B.P., and Kudasheva V.A. *Mikronutrienty v pitanii zdorovogo i bol'nogo cheloveka* [Micronutrients in nutrition of healthy and ill people]. Moscow: Kolos Publ., 2002. 424 p.
28. Luzgareva O.I. Otnoshenie studentov k svoemu zdorov'yu [The attitude of students towards one's health]. *Sotsiologicheskiy ezhegodnik KemGU (2011–2012 uch. g., 2012–2013 uch.g.): Sbornik otchetov po rezul'tatam vnutrivuzovskikh sotsiologicheskikh issledovaniy* [Sociologicalannual of the Kemerovo State University (2011–2012

academic years, 2012–2013 academic years): Collectionofreportson results of inter-universities sociaological researches], 2013, pp. 112–165.
29. Bel'chik T.A. Dvukhsub"ektnaya otsenka deyatel'nosti vuza [Two-subject assessment of university activity]. *Sotsiologicheskiy ezhegodnik KemGU (2009–2010 uch.g.): Sbornik otchetov po rezul'tatam vnutrivuzovskikh sotsiologicheskikh issledovaniy* [Sociologicalannual of the Kemerovo State University (2009–2010 academic years): Collectionofreportson results of inter-universities sociaological researches]. Kemerovo, 2010, pp. 65–95.

Please cite this article in press as: Morozova E.A., Kranzeeva E.A., and Kochneva O.P. Catering service and its quality for university students in municipal formation. *Foods and Raw Materials,* 2017, vol. 5, no. 1, pp. 205–215. DOI: 10.21179/2308-4057-2017-1-205-215.

INFORMATION FOR AUTHORS

CONSIDERATION, APPROVAL, AND REJECTION PROCEDURES FOR ARTICLES

The journal is published in printed and electronic versions.

Manuscripts submitted for publication should meet the journal's formatting requirements for articles. The manuscripts presented with violation of the above-mentioned rules shall not be considered by the editorial board.

A manuscript coming to the *Foods and Raw Materials* editorial office is considered as matching the journal specialization and formatting requirements by the person responsible for publication. The manuscript is registered, and receipt is confirmed within 10 days after the manuscript's arrival.

Manuscripts submitted to the editorial board are checked for borrowings from open sources (plagiarism). The check is carried out through the Internet resources, www.antiplagiat.ru.

The manuscript further goes to the scientific consultant who evaluates the validity of data, authenticity, grounds of factual evidence, completeness and representativeness, composition, logic, stylistic quality, and the realization of the goal of the research.

Having been approved by the scientific consultant, the content submitted for publication undergoes reviewing. The reviewer is appointed by the editor-in-chief or the deputy editor.

The journal only publishes the manuscripts recommended by the reviewers. Both the members of the editorial board and highly qualified scientists and specialists from other organizations and enterprises can be invited to review the manuscripts. They are to have profound professional knowledge and experience in the specific field of science and are to be doctors of sciences and professors.

The reviewers are notified that the manuscripts are copyrighted materials and are not subject to public disclosure. The reviewers are not allowed to copy the articles for their private needs. Reviewing is performed confidentially. Violation of confidentiality is impossible unless the reviewer declares unreliability or counterfeiting of the article's materials. The reviews' originals shall be kept by the editorial board for three years since the publication.

If the reviewer says that improvement is necessary, the article shall be sent to the author for follow-on revision. In this case, the return date of the modified article shall be considered the date of the article submission.

If, on the recommendation of the reviewer, the article undergoes a considerable revision by the author, it is again sent to the reviewer who gave the critical remarks. The editorial board reserves the right to reject the articles in case of the author's inability or unwillingness to take into account the editor's recommendations.

In case of two negative manuscript reviews from different experts or one negative review on the article's modified variant, it is rejected without consideration by other members of the editorial board. After reviewing, the possibility of publication is decided upon by the editor-in-chief or, if necessary, by the editorial board as a whole.

The official responsible for publication sends a motivated refusal to the author of the rejected article. The reviewer's name may be reported to the author provided that the former gives consent to it.

The editorial board does not retain rejected articles. Accepted manuscripts are not returned. The manuscripts with negative reviews are neither published nor returned to the author.

As a rule, manuscripts are published in the order of their submission to the editorial board. In exceptional cases the latter has the right to change the order of priority for the articles.

If the editorial board does not share the author’s outlooks completely, it may give a footnote remark on this point. Manuscripts published for the purpose of discussion may be supplied with corresponding remarks.

The editorial board has the right to publish readers’ letters giving evaluations of the printed articles.

The authors assume responsibility for authenticity of the information presented in the article. It should be original and should not have been published before or submitted to other publishing organizations.

The editorial board is not responsible for falsity of the articles’ data. Any copyright violations are prosecuted by law. Reprinting of the journal’s materials is only allowed upon agreement with the editorial board. A written consent of the editorial board for reprinting and references to the journal *Foods and Raw Materials* for citing are compulsory.

The authors are not expected either to pay fees for publication or to be given a reward or free copies of the journal.

FORMATTING REQUIREMENTS FOR ARTICLES

The journal publishes original articles on problems of the food industry and related branches in the English and German languages.

Along with experimental works, the journal publishes descriptions of fundamentally new research techniques and surveys on selected topics, reviews, and news items.

Manuscripts submitted for publication should meet the following basic criteria: validity of data, clarity, conciseness, reproducibility of results, and

compliance with manuscript requirements. In discussing the results, it is mandatory to set forth a sound conclusion on the novelty of the content submitted for publication.

The articles are accepted in the text editor Microsoft Word using the font Times New Roman, font size 10. The manuscript should contain no less than 7–10 pages, typewritten with the single line spacing and having 2-cm-wide margins on all sides. The article size also includes an abstract, tables, figures, and references.

Each article sent to the journal should be structured as described below.

1. In the top left corner of the first page there is the UDC (Universal Decimal Classification) index.

2. Title. It is necessary to give a short, informative, and precise name of the work.

3. Name(s) and initials of the author(s).

4. The name(s) and affiliation to the institution(s) where the research was carried out, the country, city, zip code, e-mail address and phone (of the author).

5. Abstract. An abstract of 180–250 words should reflect fully both the main results and the novelty of the article.

6. Key words (no more than 9).

7*. Introduction. A brief review of the problem dealt with in the study and the validation of the approach taken are presented. References are given in square brackets and numbered (beginning with no. 1) in the order of their appearance in the article. With several references appearing in sequence, they should be placed in the chronological order. The aim of the study should be clearly formulated.

8*. Objects and methods of research.

– For describing experimental work, the section should contain a full description of the object of the study, consecutive steps of the experiment, equipment, and reagents. The original names of equipment and reagents should be specified, and the manufacturer's name (company, country) should be given in parentheses. If a method is not widely known or is considerably modified, please provide a brief description in addition to the reference;

– For presenting theoretical research, the section should contain the tasks, approximations and assumptions, conclusions, and solutions of basic equations. The section should not be overloaded with intermediate data and the description of well-known methods (such as numerical methods of solving equations) unless the authors have introduced some novelty into them.

9*. Results and discussion.

– The section should provide a concise description of experimental and/or theoretical data. Rather than repeating the data of tables and graphs, the text should seek to reveal the principles detected. The past indefinite tense in describing the results is recommended. The discussion should not reiterate the results. This section should be completed with a major conclusion that answers the question specified in the introductory part of the article.

* In case of surveys, these sections do not need to be entitled. The contents may present an analytical survey of the problem chosen and give the widest reflection of the existing points of view and data related to the theme. The article should necessarily contain the grounds for the problem's timeliness and the author's conclusion on the prospects of the approaches given for the solution of the problem analyzed.

Each table is to consist of no less than three columns and have a number and a title. The journal publishes black-and-white photographs and diagrams.

Recommendations for typewriting formulae: mathematical equations forming a separate line should be printed 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, as well as their size and placing. Forced manual changing of individual symbols and formula elements is not allowable!

10. References.

They should be formatted according to the common standard. The list of papers is typed on a separate page in the order of their appearance in the text. All authors of each cited paper are indicated. If there is an English version of the paper, it is necessary to refer to it, indicating the DOI.

For cited journal articles, the names and initials of all authors, the name of the article, the name of the journal (for foreign journals, it is necessary to keep to the CASSI), year, volume, number, and page are indicated.

For cited books, the names and initials of the author(s), the name of the book, publisher, year, volume, number, part, chapter, and page are given.

For cited collections of articles, abstracts; conferences, symposiums, etc., the author(s), the name of the work, the name of the collections (conference, symposium), city (place of holding), publisher, year, volume, number, and the paper's first page are indicated.

References to web resources are to be given in the body of the text.

There should be no references to publications that are not readily available. These include institutional regulations, state standards, technical requirements, unpublished works, proceedings of conferences, extended abstracts of dissertation, and dissertations.

The absence of references to foreign authors and to the cited papers of 2–3 year novelty reduces the chances of a manuscript's publication. The references should reflect the actual impact of representatives of different countries on the investigation of a particular problem.

11. The following information should be sent in English: the title of the article, the authors' initials and surnames, an abstract, key words, the name of the institution (with the mailing address, telephone number, and e-mail).

Documents may be presented in the Russian, English, and German languages.

The following papers are sent to the editorial board.

1. A soft version of the article typewritten in MS Word. The file of the article should be entitled by the first author's surname, e.g., PetrovGP.doc. The data file must only contain a single document.

2. A printed copy of the article identical to its soft version. In case of discrepancies between them, the editor gives preferences to the electronic version of the manuscript.

3. Personal information: the full names of all authors, the place and the mailing address of their places of work, the subdivision and position, the academic degree and rank, the honorary degree, the telephone number, the personal mailing and electronic addresses, the date of birth, and a reference to the author's scientific profile.

The author to contact is indicated by an asterisk. The file should be entitled with the first author's name, e.g., PetrovGP_Anketa.doc.

4. A cover letter to the editor-in-chief from the responsible organization with the conclusion about the work urgency and recommendations for its publication, carrying the date, reference number, and the head's signature.

5. An external review on the article according to the sample, the reviewer's signature being authenticated by the corresponding HR subdivision.

6. A standard copyright agreement. The manuscript's electronic version may be e-mailed to the editorial office at fjournal@mail.ru.

RECOMMENDATIONS

For the article file use the format *.doc. Do not use Russian letters and spaces in the file's name.

The article file is to be identical to the printed original submitted to the editorial board.

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/c^2.

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, Table 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, 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.

Before the year of issue after the publisher's name or city (if no publisher), there is a comma.

Graphic material

The journal publishes black-and-white illustrative material.

While making graphic files, keep to the following recommendations:

Vector pattern, schemes, and diagrams are preferably to be presented in the format of the application in which they were carried out or in EPS. ***For other illustrations***, it is preferable to use TIFF and JPEG formats, optimum resolving capacity being 300 dpi.

Photographs should be submitted in 2 variants. The first one should correspond to the paper-based original, with marks and inscriptions; the second one should not contain any text, captions, etc. The advisable file formats are TIFF and JPEG, the optimum resolving capacity being 300 dpi. The gray color shade is allowed from 9 to 93%.

All illustrations are to be saved as separate files in the folder. Every file contains one picture.