Ministry of Agrarian Policy and Food of Ukraine
Ministry of Education and Science of Ukraine
National University of Food Technologies
Institute of Food Resources, National Academy of Agricultural Sciences of Ukraine
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Resource and Energy Saving Technologies of Production and Packing of Food Products as the Main Fundamentals of Their Competitiveness

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^{1}H NMR-spectroscopy of water-alcohol systems in the process of electrochemical activation of drinking water

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Abstract
The aim of the work is to study the process of establishing the equilibrium state in alcohol water systems at the main stages of creating vodka with electrochemical activation of drinking water. The formation of alcohol-water (drinking) system occurs during the weakening of hydrogen bonds in the presence of water associates and ethanol that have a chemical shift of hydroxyl protons of water δ_{H2O} 4,36 ppm and of ethanol – δ_{EtOH} 4,96 ppm and the difference in chemical shifts between EtOH and H_2O, which is $\Delta\delta$ 0,60 ppm. (Δf 240 Hz), that do not undergo significant changes after the treatment of alcohol water mixture with activated carbon. Conditions for the formation of stable complexes in the system of alcohol-water (drinking) have not been revealed, the absence of formation of ethanol hydrates characterizes a system with unstable equilibrium. Prepared with electrochemical activation drinking water leads to the immediate formation of hydrates of $EtOH \cdot 5H_2O$ type in the alcohol-water system: in the anode cell – an anolyte with ethanol hydrates $EtOH \cdot 4{,}81H_2O$; in a cathode cell – a catholyte with ethanol hydrides $EtOH \cdot 4{,}69H_2O$. The strongest hydrogen bond of OH-groups in the alcohol-water system is observed in water prepared by electrochemical activation that is characterized by a constant equilibrium.

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Introduction

Nowadays, ^{1}H NMR spectroscopy is the most popular among spectroscopic methods due to its simplicity and completeness of information that facilitates chemical researches, especially in the food industry.

The first ^{1}H NMR water and ethanol spectra were obtained more than 60 years ago but even today there are a lot of researches [1-9] of these formally simple systems that demonstrate complex and diverse behavior. In particular, ^{1}H NMR spectroscopy is a highly sensitive method for studying the equilibrium in solutions. Considering that the establishment of the equilibrium state of the alcohol solution in water is being one of the main processes that provide stable and predicted characteristics of vodka products, we used this method for the defining what affect the preliminary water preparation actions may have.

The hydroxyl proton of ethanol can exchange with free ions H^+ in the matrix, that are generated due to dissociation of water, or with the trace amount of acid [7,10-11]. The speed of exchange is proportional to the number of free ions H^+ [11]. For this reason the actual location of the center of ^1H NMR signal, that is averaged for moving forms of protons in this case, depends on the difference in the chemical shifts of protons in two environments – water and alcohol [9].

That is why the creation of an equilibrium state of the solution with help of ^{1}HNMR may become an efficient mean for controlling the efficiency in usage of technical solutions in the process of vodka production.

The aim of the research – applying the method of ^1H NMR spectroscopy to study the process of equilibrium establishment in water-alcohol mixtures at the main stages of vodka production with electrochemical activation of drinking water.

Materials and methods

The following equipment and materials have been used during the research:

– Fourier NMR spectrometer Bruker Avance II – 400 MHz (Fig.1);

– dispenser (15); ampoules 5 mm with specimens (16); capillaries with deuteroacetone;

– external standard and signal for the system LOCK‘a (17); ampoules with capillary (18) (Fig. 1, b);

– drinking water; drinking water – catholyte; drinking water – anolyte;

– rectified ethyl alcohol;

– drinking water based water-alcohol mixture; catholyte based water-alcohol mixture; anolyte based water-alcohol mixture;

– water-alcohol mixture based on drinking water after treatment with activated carbon (vodka); water-alcohol mixture based on catholyte after treatment with activated carbon; water-alcohol mixture based on anolyte after treatment with activated carbon.

Fig.1,a. shows the principal scheme designed for this research experimental stand with the diaphragm electrochemical reactor.

The drinking water (1.0) goes through the open tap into two lines (9) – line for water preparation by electrochemical activation and the line for preparation of water-alcohol mixture. On the electrochemical activation preparation line the water reaches the electrochemical reactor (6), the anodic and cathodic space of which is separated with a porous diaphragm. The electrons are transferred into water near the cathode, and removed from the water – near the anode that leads to the formation of a catholyte (1.1) and anolyte (1.2).

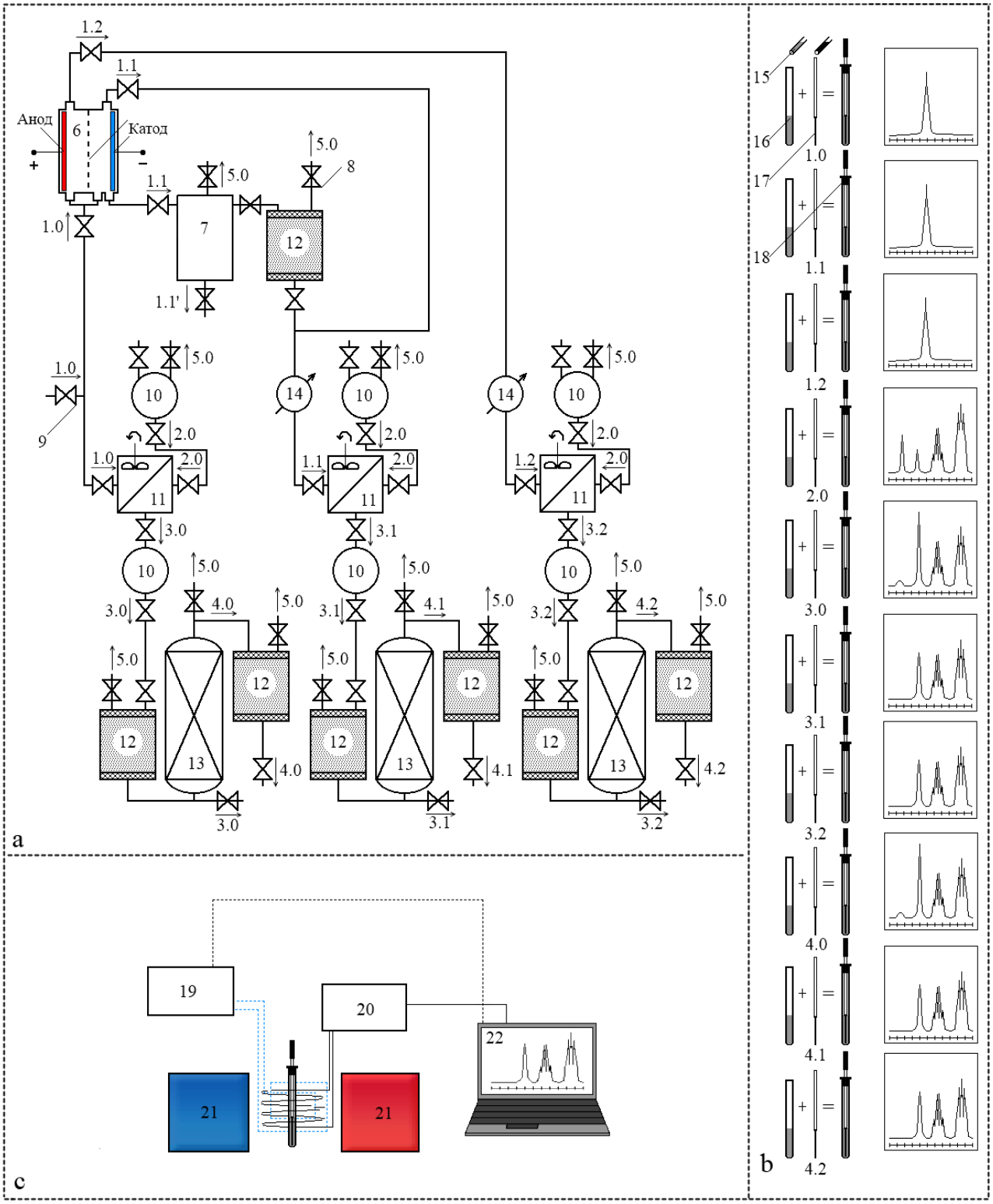

Figure 1. Scheme of conducting the research:
a – the principal scheme of the experimental stand;
b – scheme of sample preparation for ^{1}H NMR research;
c – block scheme of a ^{1}H NMR spectrometer;
1-5 –flows (samples); 6-14 – technological equipment;
15-22 – laboratory equipment

As the result of electrochemical reactions low-solubility calcium and magnesium carbonates, as well as heavy metal and ferrum hydroxides are created in cathode cell. There is an additional line with receiving container (7) for drainage and filtration of the catholyte concentrate (1.1'), sand filter (12) and air taps (8) –for removing the air (5.0).

The electrochemical activation process is accompanied by an increase of water temperature $t_{1\text{-}2}$=32 ºC, that is unacceptable for the production of water alcohol mixture. Consequently, the water flows (1.1, 1.2) are additionally cooled down in the chiller (14).

On the line of the water-alcohol mixture preparation rectified ethyl alcohol (2.0), and afterwards – the water (1.0-1.2), is added to the sorting tanks (11) from gravity tanks (10), where they are mixed with the help of high-speed propeller mixers. In the course of mixing the total volume of water-alcohol mixture undergoes pressure (contraction) with the following heat release. After mixing the strength of water-alcohol mixtures is determined with the help of density analyzer «Anton Paar DMA 4500». In case it is different from the givenparameters, it is adjusted, than mixed again with the following samples collection (3.0-3.2).

Having been mixed the water-alcohol mixture goes to the gravity tanks (10), than it is filtered on the sand filters (12) and treated with the activated carbon in absorbers (13). In order to remove tiny parts of carbonate from the vodka it is filtered again with the following samples collection.

Methodology of ^{1}H NMR research: the study sample is placed with the help of dosimeter (15) into ampoule (16). Necessary for LOCK'a system work – deuterium stabilization of the NMR spectrometer deuteroacetone, an external standard which is separated from study material, is placed into ampoule (16) in the capillary of a specific shape (17); according to the methodology spectrum recording the spectrum of sample in deuteroacetone is recorded. The obtained primary materials, free induction decays, are processed with Bruker TopSpin v2.6 program.

Results and discussions

Fig. 2 shows one-dimensional ^{1}H NMR spectra of CH_3-, CH_2-, OH-groups of protons of study substances, taking into account chemical shift. Rectified ethyl alcohol with a volume fraction of ethanol –96,37% and water ≈ 3,63% have been used in the research. ^{1}H NMR spectra of OH-protons of alcohol are represented by two separate signals of ethanol EtOH and water H_2O (Fig. 2, a). The EtOH component is a symmetric singlet with an expanded base and a top of a regular form with a chemical shift δ_{EtOH} 5,65 ppm. The component H_2O is a singlet from δ_{H2O} 4,85 ppm. The difference in chemical shifts between EtOH and $H_2O$is $\Delta\delta$ 0,80 ppm. (Δf 320 Hz).

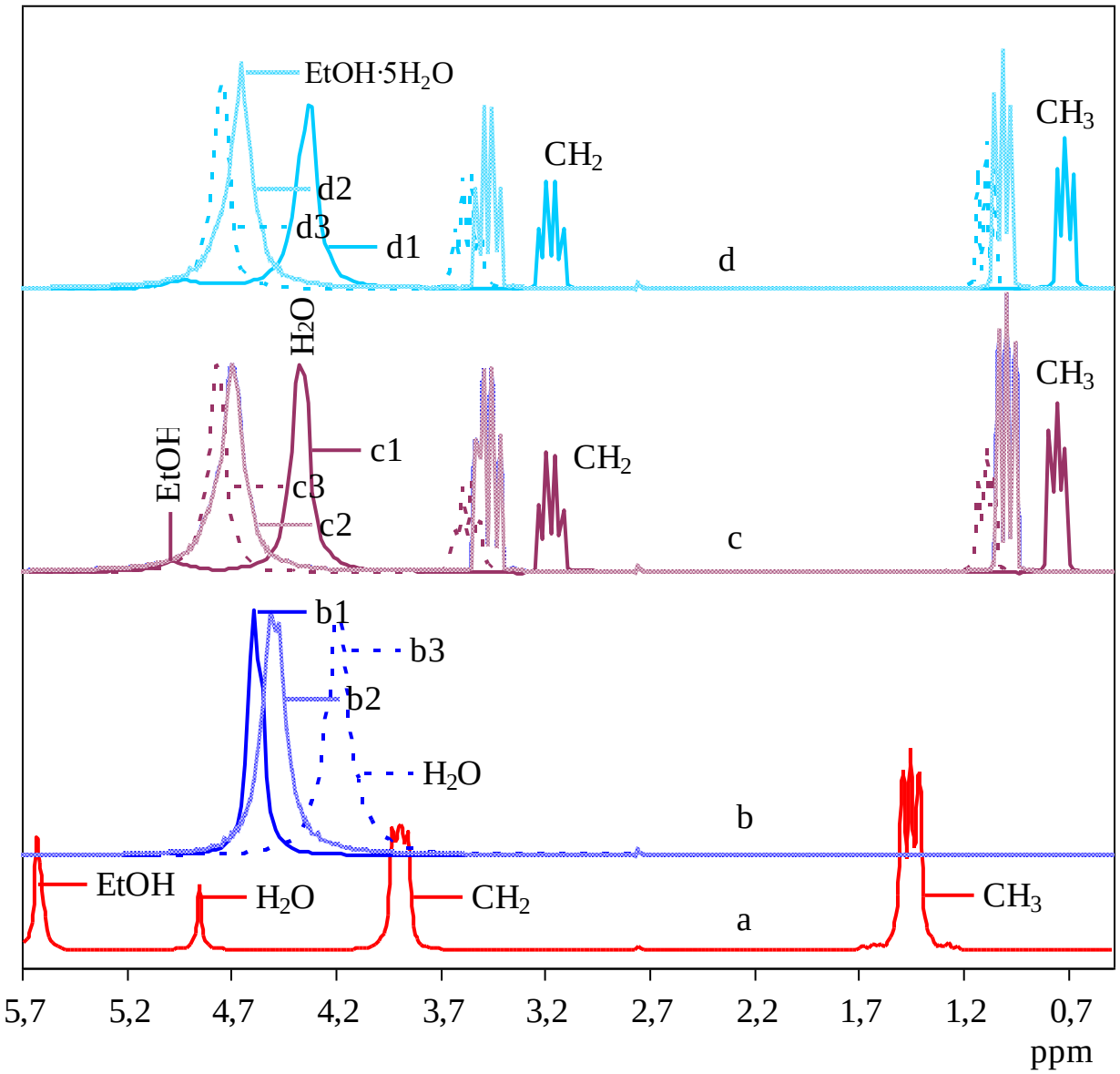

Figure 2. ^{1}H NMR spectra of molecular complexes of resonance CH_3-, CH_2-, OH-groups of protons for water-alcohol mixtures obtained through electrochemical activation of drinking water:

a – rectified ethyl alcohol;
b – water;
c – water-alcohol mixture;
d –water-alcohol mixture after treatment with activated carbon; in the process:
1 – without processing with electrochemical activation;
2 – cathode electrochemical activation;
3 – anode electrochemical activation

The ^{1}H NMR spectrum of drinking water (Fig. 2,b1) has the single signal in the form of a singlet with an expanded base and an irregular vertice at δ_{H2O} 4,60ppm. ^{1}HNMR spectra of drinking water after electrochemical activation: catholyte – singlet from δ_{H2O} (4,50; 4,48) ppm. (Fig. 2, b2); anolyte – singlet with δ_{H2O} (4,19; 4,18)ppm (Fig. 2,b3). In relation to drinking water the catholyte has a displacement of the hydroxyl proton into a «strong field» with an average value of Δδ 0.110 ppm, the anolyte has a displacement into the «strong field» at Δδ 0,415 ppm.

In the process mixing alcohol (Fig. 2,a) with drinking water (Fig. 2,b1), a water-alcohol mixture is created (Fig. 2,c1), ^{1}H NMR spectra of which are represented by two signals of hydroxyl protons EtOH and H_2O. The EtOH component is depicted in the form of a convexity, which is situated in the «weaker field» with δ_{EtOH} 4,96 ppm., the H_2O component is represented as a symmetric singlet with δ_{H2O} 4,36 ppm. The difference in chemical displacements between EtOHiH_2OisΔδ 0,60 ppm (Δ*f* 240 Hz).

The water-alcohol mixture based on drinking water with a pH 6.91 and rectified ethyl alcohol has a pH of 8.32 that corresponds to a lower concentration of ions of hydroxonium H_3O^+in relation to OH^- hydroxyl ions. At constant concentration of alcohol in a water-alcohol mixture (volume fraction of ethanol – 39,94%) and thermostatting system at ^{1}H researches (t = 23,5 ºC), the exchange speed of EtOH is at the intermediate level, with the possibility of separate observation of signals.

While preparing water-alcohol mixture (Fig.2, c2) based on alcohol (Fig. 2, a) with catholyte (Fig. 2, b2) proton spectra are represented by a single total singlet – EtOH +$H_2O$with an extended base and a vertex of the regular form and $\delta_{EtOH+H2O}$ 4,69 ppm. During preparation of the water-alcohol mixture (Fig. 2, c3) based on the anolyte (Fig. 2, b3) the proton spectra are characterized by a total singlet EtOH+$H_2O$with$\delta_{EtOH+H2O}$ (4,82; 4,81; 4,80) ppm. EtOH+H_2Osignal is represented in the form of a distorted Gaussian with an expanded base and a certain asymmetry of the vertex that has one high-polar peak and two additional low-polar peaks. Thus, drinking water prepared with electrochemical activation leads to the instant formation of hydrates of EtOH·5H_2Otype in the alcohol-water system: in the cathode cell – catholyte with ethanol hydrates EtOH·4,69H_2O, in the anode cell – anolyte with ethanol hydrates EtOH·4,81H_2O.

The water-alcohol mixture based on catholyte with pH 9,84 has high alkaline environment (pH 11,60). Due to electrochemical activation while creating a water-alcohol mixture based on anolyte with pH 2,40 and alcohol, the received water-alcohol mixture has pH 3,01, which is a characteristic of an acidic environment. These polar correlations of concentrations H_3O^+до$OH^-$for catholyte and anolyte lead to restructurization in the alcohol-water system, therefore, the proton exchange is accelerated and there is only one common signal of moving protons EtOH+$H_2O$of asymmetric form observed. In this case the electrochemical activation of water intensifies redox reactions during the preparation of water-alcohol mixtures due to the increase of mass concentration of aldehydes and esters. Aldehydes are represented by acetaldehyde, which is created by oxidation of ethanol with oxygen. Esters are

represented by ethylacetate due to oxidation of a part of acetaldehyde to acetic acid and interreacting of acetic acid with ethanol.

After treatment of water-alcohol mixture based on drinking water (Fig. 2, d1), with activated carbon [15] obtained vodka is characterized by two signals of hydroxyl protons EtOHтaH_2O. EtOH component is represented in the form of convexity that is placed in the «weaker field» with δ_{EtOH}=4,93 ppm. The component $H_2O$is represented as a symmetric singlet with δ_{H2O}=4,33 ppm. The difference in chemical shifts between EtOHiH_2Omakes$\Delta\delta$=0,60 ppm. (Δf 240 Hz).

In the process of treatment of water-alcohol mixture based on catholyte (Fig.2, d2) ^{1}H NMR spectra of OH-group are characterized with one total peak – EtOH+H_2O represented in the form symmetric singlet with a chemical shift $\delta_{EtOH+H2O}$ 4,67 ppm. In the process of treatment of water-alcohol mixture with activated carbonate based on the anolyte (Fig. 2, d3), the component is characterized by one total peak –EtOH+H_2O, represented in the form of a symmetric singlet with $\delta_{EtOH+H2O}$ (4,77; 4,76) ppm. The form of the total signal is a distorted Gaussian with an extended base and a vertex that has one main high-polar and an additional low-polar peaks. Thus, the electrochemical activation of drinking water leads to the formation of hydrates in vodka: in the cathode cell – catholyte with ethanol hydrates EtOH·4,67H_2O, in the anode cell – anolyte with ethanol hydrates EtOH·4,765H_2O.

Conclusion

There has been established the fundamental difference between the behavior of water-alcohol mixtures and vodka that are prepared on drinking water and water treated with electrochemical activation. The system with unstable equilibrium is a characteristic of water-alcohol mixture made of alcohol and drinking water.

The alcohol-water system with stable equilibrium and a high degree of protons generalization, as well as specific exchange speed, is a peculiarity of water-alcohol mixture made of alcohol and drinking water that has undergone electrochemical activation in a diaphragm electrolyzer. Thus, the study has confirmed the possibility and practicability of using ^{1}H NMR spectroscopy for the current control of the technological process of production water-alcohol mixtures with water that has undergone electrochemical activation. It is shown that this method is an effective way for establishing the completeness of balance of the alcohol-water system in the presence of additional solution components typical for technological water-alcohol mixtures. There's been demonstrated an efficiency of using electrochemical activation when dealing with water preparation problems during the production of alcohol products.

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Optimization of foaming parameters of the whipped mass with "magnetofood" food additiveusing

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Abstract
The article presents the influence results of "Magnetofood" food additive on the foaming indicators of the whipping confectionery masses in the marsh-mallow technology (foaming capacity, froth resistance, density, plastic strength, effective viscosity, degree of whip and volume kinetics in the storage process). It is proved the surface activity of the nanoparticles of "Magnetofood additive. The mathematical modeling has established the optimal parameters of the whipped masses. The prospects for "Magnetofood" additive using for the creaming confectionery masses as a stabilizer and the structural forming of foamy structures are determined.

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Introduction

The whiiping confectionery (marsh-mallow, pastille, sweets with whipped body) are in the high demand among the population [1–3]. Their value is determined by a significant proportion of the air phase, a high degree of dispersion and the structural properties. The low temperature zones, moderate mechanical stress, the presence of pectin substances which can prevent the oxidation of biologically active substances in the whipped confectionery products production allow you to preserve the beneficial properties of itemized nutrients [4].

However in the modern conditions the production and sale of whiiped confectionery products in the domestic market are the subject to fierce and constantly growing competition. In the current situation (shortage of domestic raw materials, a significant part of imported ingredients with high cost, etc.), Marsh-mallow production is looking for the ways to improve the competitiveness of finished products by improving and stabilizing quality, reducing costs and extending the shelf life of pastry confectionery [2, 3].

The production of whipping confectionery products is complex and difficult to manage the process. Expansion and improvement of this production requires the search

for a simplified technology with the help of reducing the duration of the technological stages, including the preparatory operations and the structure formation of whiipped confectionery products, reducing production space and energy resources, improving the system stability and improving the quality of marsh-mallow production products [4].

The nanopowder food additives using of the mineral origin as a foaming and structure former in the production of whipped confectionery products was not considered.

“Magnetofood” -is a food additive [Patent UA № 126502, МПК A 23L 13/40, A23L 33/10. “Magnetofood”food additive] can influence the processes of structure former of jelly –like sweet pastes and the whipped masses foaming in the production of the whipped confectionery products as well as on the quality indices of finished products. However, these data are missing and the additional studies are needed.

“Magnetofood” additive has a certain functional and technological potential and can both independently form the structural and mechanical properties of jelly masses and foam structures and also affect the gel and foaming agent entering into the chemical and electrostatic interactions. Therefore, “Magnetofood” food additive can perform the several technological functions in the system at once: act as a stabilizer and structure former (foam and jelly formations).

Materials and methods

The study object –is the technology of white pink marshmallows on agar and the apple pectin. The research subject – is the model samples of white pink marshmallows on agar and pectin which are based on the basic formulations № 95 and № 126 and are given in Table 1; and the experimental samples of egg albumen.

The experimental samples of egg white are:

- the experimental sample 9 – control – 30% aqueous solution of dried egg white, [AUSS 30363-2013];
- the experimental sample 10–30% aqueous solution of dried egg white with the introduction of “Magnetofood food additive in the amount of 0,10 % by weight of dried egg white;
- the experimental sample 11–30% aqueous solution of dried egg white with the introduction of “Magnetofood” food additive in the amount of 0,15% to the mass of dried egg white;
- the experimental sample 12–30% aqueous solution of dried egg white with the introduction of “Magnetofood” food additive in the amount of 0,20% by weight of dried egg white.

Table 1

Formulations of white-pink marshmallow on agar and pectin (control) and with different mass fraction of "Magnetofood" food additive (experimenal)

Name of the raw materials	Inputs of the raw material per 1 ton of finished product, kg							
	marshmallow samples on agar				marshmallow samples on pectin			
	№ 1 control	№ 2	№ 3	№ 4	№ 5 control	№ 6	№ 7	№ 8
Granulated sugar	673,0	672,0	671,5	671,0	671,0	670,0	670,5	669,0
Powdered sugar	29,9	29,9	29,9	29,9	29,9	29,9	29,9	29,9
Molasses	139,4	139,4	139,4	139,4	142,9	142,9	142,9	142,9
Apple sauce	390,0	390,0	390,0	390,0	298,0	298,0	298,0	298,0
Egg white	65,0	65,0	65,0	65,0	65,0	65,0	65,0	65,0
Agar	8,6	8,6	8,6	8,6	–	–	–	–
Apple pectin	–	–	–	–	13,4	13,4	13,4	13,4
lactic acid	11,8	11,8	11,8	11,8	8,4	8,4	8,4	8,4
Sodium lactate	–	–	–	–	6,8	6,8	6,8	6,8
Different kinds of essence	2,0	2,0	2,0	2,0	2,0	2,0	2,0	2,0
Dye red	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6
"Magnetofood" food additive	–	1,0	1,5	2,0	–	1,0	1,5	2,0

Foaming ability of egg white and whipped masses was determined by the Lurie method [7]. The change in thefoam stability was recorded on theresiduum of the foam column over time. The active properties were evaluated superficially by the magnitude of the surface tension and determined by "Du Noüy ring" method on the Kruss tensiometers [8]. The expansion foam and the volume concentration of air in the mass were determined by the calculation taking into account the volume of the foam. In our work it was used the optical method for microstructure analyzing of a whipped mass based on image processing obtained by a light in an electron microscope with the use of the personal computer. Marshmallow mass has been obtained and the foaming process was studied on a developed experimental whipping equipment. The structural-mechanical characteristics of whipped marshmallow masses were investigated by the using of the standard and generally accepted methods [8]. The strength of the whipping masses was investigated with the ultimate shear stress – on penetrometers AR-4/1; the rheological properties were determined on Reotest-2 device. The whipping process was optimized by the experimental modeling in order to obtain a criterial equation which describing the whipping process.

Results and discussion

The foaming capacity of protein (PO) which depends both on its concentration, the fractional composition and structure and on the temperature, the presence of salts, sucrose, dietary fiber, etc., significantly affects on the structure formation of whipped masses [9, 10]. Therefore, we studied the effect of "Magnetofood" food additive on the foaming capacity (FC) and the foam stability (FS) of egg white (Fig. 1 and Fig. 2, respectively).

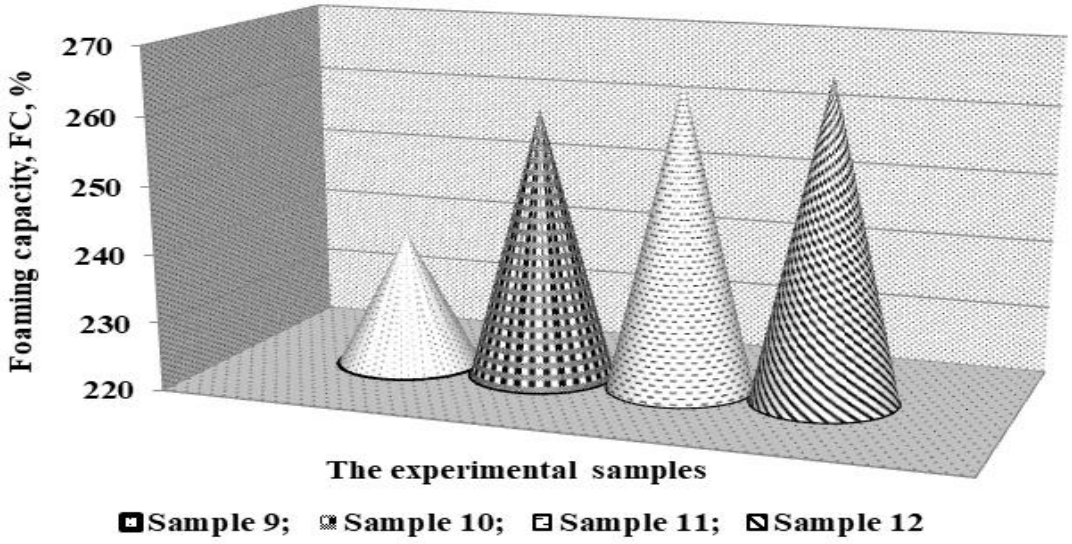

Fig. 1. Influence of "Magnetofood" food additive on the foaming capacity of the egg white (t=20±2 ºC, pH=4,8)

From the data in Fig. 1 it follows that the introduction of "Magnetofood" food additive in egg white in the amount of (0,10–0,20)% by weight of dried egg white increases the software of the "protein-NP "Magnetofood" system by (8,3–11,3)%, which is associated with the capacity of the polarized nanoparticles (NP) of "Magnetofood" food additive to reduce the surface tension of the protein solution and accelerate the coagulation of protein molecules which leads to the increase in the protein solution of the volume concentration of the air phase and a decrease in the size of air bubbles. When using the "Magnetofood" additive due to the amphotericity and nanoparticles, the active acidity of the "protein-NP "Magnetofood"system [8, 11] changes in the direction close to the isoelectric point of the protein in which the maximum FC of protein solutions appears [11].

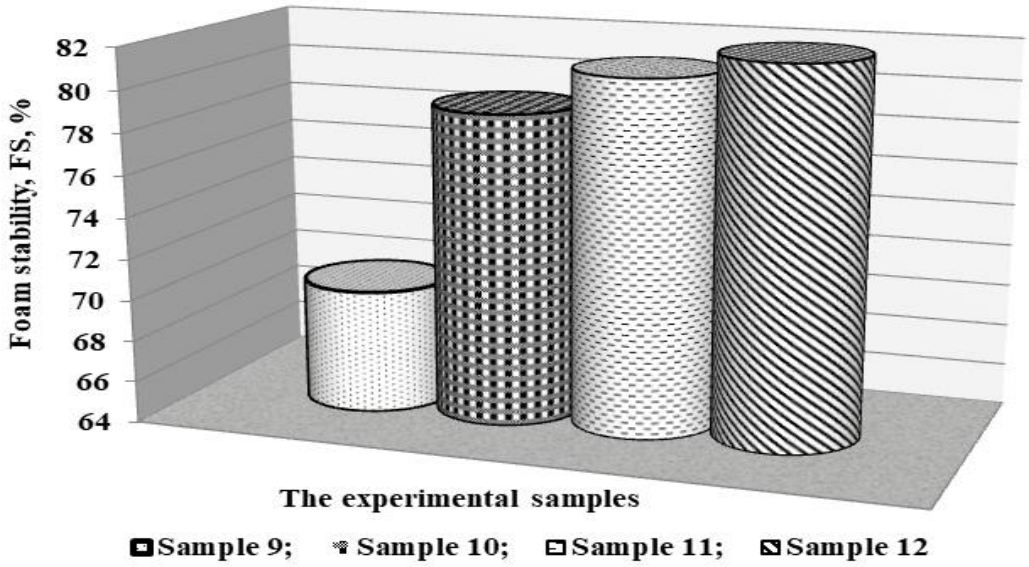

Fig. 2. Influence of "Magnetofood" food additive on the foam stability of the egg white (t=20±2 ºC, sample time τ=30x60 c)

Introduction of "Magnetofood" food additive to egg white in the amount of (0,10–0,20)% by weight of dried egg white increases the FS of the "protein-NP "Magnetofood "system by (12,6–17,1) % (Fig. 2). This is due to the presence of the active magnetic surface of "Magnetofood" additive on the interfacial surface in the adsorption layer of nanoparticles which increase the adhesion force between protein molecules – as a result, fluid mobility decreases and its flow in the film slows down, thereby preventing foam coalescence [12]; the viscosity of the liquid in foam films also increases, slows down their destruction and increases the stability (or stability) of the foam (see Fig. 2).

Correct for a factor in the resultthat the acidity of the medium significantly affects the electrostatic interaction and the properties of protein molecules the effect of the pH of the medium on the foaming capacity of the egg white in the experimental samples 9–12 is further investigated. The dependence picture of the foaming capacity (FC) and the foam stability (FS) of "Magnetofood" system "protein-NP" in the experimental samples 9-12 on pH values was established with the using elements of statistical data processing. As a result, the regression equations (1) and (2) were obtained which adequately describe the relationship between the foaming properties and the pH medium at the different mass fractions of "Magnetofood" food additive.

$$FC=166.7778+ 406.6667x+57.0556y-0,306xy -1200x^2-6.0556y^2 \quad (1)$$

$$FS=64.3523+145.5146x+1.6189y+2.4864xy-517.6136x^2-0.1963y^2 \quad (2)$$

where x – pH y – the mass fraction of "Magnetofood" food additive for unit

From the graphic images of software dependencies FC (Fig. 3, a) and FS (Fig. 3, b) from the pH values of the medium, it can be seen that for 100% egg white (sample 10-control) the values of FC and FS at pH values from 2 to 9 changed by 22,6 % and

by 5,6%, respectively, whereas in the "egg white-NP "Magnetofood "system (samples 10–12), with an increase in the mass fraction of the "Magnetofood" additive, these indicators changed on average by 19,8 % and 3,1% respectively. That is, with the introduction of "Magnetofood",additive the effect of pH on the foaming properties of egg white is less significant which is associated with the stabilizing effect of "Magnetofood" food additive.

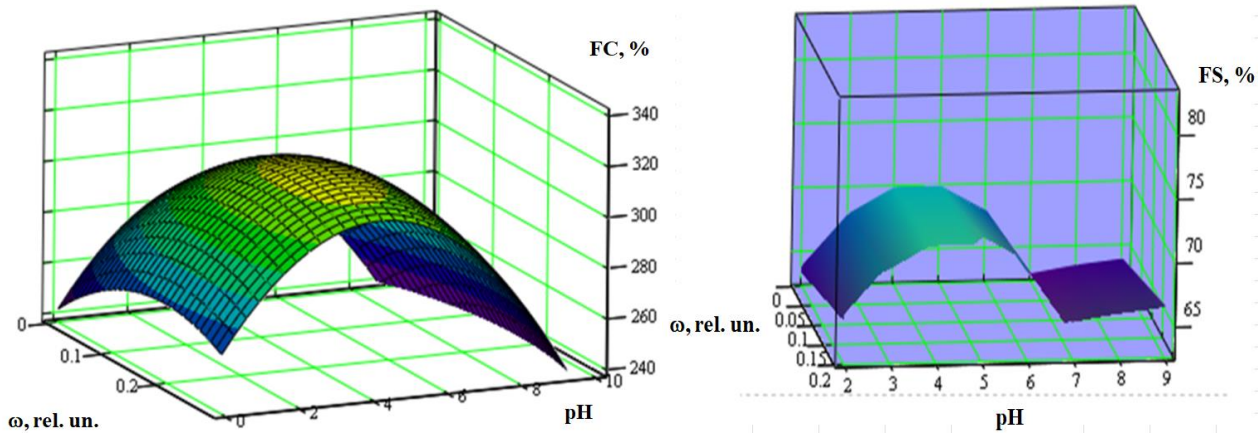

Fig. 3. Dependence of the foaming properties of the experimental samples of the composition "egg white-NP "Magnetofood" on the pH of the medium and the mass fraction of "Magnetofood" food additive, %:
a – foaming capacity (FC); b – foam stability (FS)

From Fig. 3 it follows that the foam stability (FS) and the foaming capacity (FC) of egg white in the experimental samples 9–12 were maximum at pH = 5,0; in the range of pH values of about 7 both of these indicators sharply decreased while at pH more than 7 they slightly increased. The foam stability of the composition "egg white-NPs "Magnetofood "increased with an increase in the mass fraction of "Magnetofood" additive. The foam itself was formed at pH = 4,806 by mass fraction "Magnetofood" 0,155% by weight of dried egg white. Perhaps it was in the acidic medium when egg white molecules acquired a conformation that most contributed to the maximum manifestation of the surface-active properties necessary for the stable foam formation. Thus, the optimal values for the foaming capacity (FC): the content of "Magnetofood" food additive:ω=0,161; pH = 4,904; for the foam stability (FS):ω= 0,159; pH = 4,89.

Conclusion

The obtained results confirm the hypothesis of the foam structure stabilization of marshmallows using “Magnetofood” food additive:

- in all experimental samples of egg white with the introduction of “Magnetofood” food additive in the amount of (0,10–0,20)% by weight of the dried egg white, the foaming capacity (FC) increases by (8,3–11,3) %; the foam stability (FS) – by (12,6–17,1)% compared to control;

- at the introduction of the “Magnetofood” food additive in the amount (0,10-0,20)% of the mass of raw materials there is the effect of the structure stabilizing of the marshmallows samples: during the regulated storage period (90 days), the volume of the contracted structure decreases more slowly by 7,85% in the samples per pectin and 11% in agar compared with control.

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Evaluation of the prospects of using kumquat in sauces technology

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Abstract
The purpose of the work is to study the antioxidant properties of water-alcohol infusions from citrus fruits and to determine the feasibility of their application in the technology of sauces. The theoretical expected value of redox potential (*RP*) Eh_{min} is obtained for monitoring and has a value of 198,0 mV, the maximum value of 450,0 mV (infusion of lemon pulp) is characteristic of plant water-alcohol infusions. The actual measured of $RPEh_{act}$ – from 114,0 mV (control) to 298,0 mV (infusion of pulp lemon). At the same time, the minimum value of the recovery energy (*RE*) is – 84,0 mV and is characteristic for control, and the greatest value of 205,0 mV is the water-alcohol infusion from the kumquat peel. The *pH* level for water-alcohol infusions ranges from 3,50 (lemon infusion pulp) to 5,90 (infusion of lemon peel), the extracts have an acidic medium. According to the results of research, water-alcohol infusions are grouped according to the antioxidant activity – according to *RE*: extracts with average activity (from 100 to 200 mV) – mandarin, lemon, orange, grapefruit infusion; extract with high activity (from 200 mV and above) – infusion of kumquat.

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Introduction

The main directions of creating a new generation of sauces are: increase of antioxidant action, by blocking oxidative reactions [1-4]; reduction of the pH [1] of sauces, due to the obstruction of reproduction of microorganisms increase in terms of storage; improvement organoleptic parameters [1]. All this can be done by adding water-alcohol infusions to plant raw materials.

One of the promising directions for creating sauces is to increase their antioxidant action [5, 6] by introducing natural or identical natural compounds, active chemical compounds that prevent the oxidation of human cells and reduce the risk of developing various diseases, including those related to the action of chemical, physical, radiation, bacteriological and other factors of the environment.

Antioxidant activity [7] is manifested in the ability of compounds to neutralize the activity of free radicals [8, 5]. Free radicals – products of oxidative processes in the body, occurring under the influence the environment [7, 9, 10] (ionization, smoke, environmental pollution, the presence of toxins in food products).

Antioxidants make it possible to prolong the shelf life of food raw materials [11-

14], semi-finished products and finished products, protecting them from damage caused by oxygenation of air, for example, scalding oils and fats or fatty components of food products, biologically valuable substances, and some natural dyes. Direct addition of antioxidants in the sauce leads to a slowdown in the oxidation of unsaturated fatty acids that are part of the lipids. In this case, the addition of antioxidants should not lead to the destruction of the structure and stratification of the sauce. It is very complex because of the fact that it involves a number of factors, stabilizing the effect of each of which manifests itself under certain conditions. Consequently, the technological process of production must be realized in such a way that the substances that are part of the sauce can be active and provide conditions for increasing the strength of the formation of complexes.

Methods of research

Redoxmetry – determination of antioxidant capacity of water-alcohol infusions of plant raw materials; pH-metry; methods of determination of organoleptic parameters.

Results and discussion

Kumquat (fortunel, kinkan) is a group of plant species, which belongs to the family of root, which belongs to the genus citrus [5, 6, 9, 11, 12]. Fruits – small, medium-sized plum, golden-yellow, orange or fiery-orange; peel – smooth, fragrant, sweet-spicy; the pulp is juicy, with sour taste, close to mandarin, and citrus smell [13, 14]. In kumquat there is a significant amount of flavonoids [8, 9], polyphenols [6, 10, 13], carotenoids [14], luteins and tannins, which are known antioxidants [6, 7, 8, 9, 10].

The comparative characteristic of the food and energy value of kumquat in relation to orange, mandarin is presented in the Table 1.

Kumquat is 33,8 % more caloric in relation to orange and 25,4 % in relation to mandarin. In relation to mandarin and orange, kumquat has a higher content of fats, carbohydrates, minerals that perform plastic and protective functions, and also affect the metabolism of humans. Significantly higher vitamin content in kumquat prevents the development of diseases and pathologies, as well as improves the general condition of a person. The exception is vitamins B_1, B_5, B_6, the content of which in kumquat is less than in oranges and mandarins, therefore the use of kumquat in recipes is possible with incomplete replacement for orange or mandarin.

Table 1

Comparative characteristics of the food and energy value of kumquat in relation to orange, mandarin

Nutrient	Quantity in 100 g of orange	Quantity in 100 g of mandarin	Quantity in 100 g of kumquat	Kumquat/ orange, +/–, %	Kumquat/ mandarin, +/–, %
Proteins, g	0,94	0,81	1,88	50,0	56,9
Fat, g	0,12	0,10	0,86	86,0	88,4
Carbohydrates, g: – food fibers; – monosaccharides	11,75 2,40 9,35	8,70 1,20 7,50	15,90 6,50 9,36	26,1 63,1 0,1	45,3 81,5 19,9
Potassium, mg	181,0	37,0	186,0	2,7	80,1
Calcium, mg	40,0	0,0	62,0	35,5	100,0
Magnesium, mg	10,0	12,0	20,0	50,0	40,0
Phosphorus, mg	14,0	20,0	19,0	26,3	–5,3
Sodium, mg	0,0	2,0	10,0	100,0	80,0
Copper, mg	0,045	0,000	0,095	52,6	100,0
Iron, mg	0,10	0,15	0,86	88,4	82,6
Zinc, mg	0,07	0,00	0,17	58,8	100,0
Vitamin C, mg	53,2	26,7	43,9	–21,2	39,2
Vitamin B_1, mg	0,087	0,058	0,037	–135,1	–56,8
Vitamin B_2, mg	0,040	0,036	0,090	55,6	60,0
Vitamin B_3, mg	0,282	0,376	0,429	34,3	12,4
Vitamin B_5, mg	0,250	0,216	0,208	–20,2	–3,8
Vitamin B_6, mg	0,060	0,078	0,036	–66,7	–116,7
Vitamin A, me	225,0	0,0	290,0	22,4	100,0
Vitamin E, mg	0,018	0,000	0,015	–20,0	100,0
Energy value, kcal	47,0	53,0	71,0	33,8	25,4

Water-alcohol infusions were obtained by extraction of a water-alcohol blend (in volume of 100 ml) with a volume fraction of ethyl alcohol rectified 40 % of plant material (size ≈ 3x3 mm, weighing 4 g) with double tension (maceration) at the usual temperature, which consists of the following operations: raw material acceptance and weighing; sorting of raw materials and waste disposal; weighing of waste; shredding of raw materials; preparation of a water-alcohol mixture of required strength; loading of raw material into an emergency capacity; gulf of raw materials with a water-alcohol mixture; insertion of raw materials with a water-alcohol mixture at daily stirring for 5 days depending on the type of raw material; the pumping and pumping of the first draft into the collections for storing and measuring the volume of the received infusion; second gulf of raw materials with a water-alcohol mixture; reintroduction of raw materials with a water-alcohol mixture at daily stirring for 5 days; discharge, pumping and measurement of the volume received by the infusion of the first and second drains; mixing of infusions of the first and second drains; unloading of consumed raw material from an emergency capacity; evaporating the alcohol that was left in the spent raw

material. In the process of extraction, a diffusion phenomenon is used, based on the concentration alignment between the solvent (extractant) and the solution of substances contained in the plant cell.

The indicator of active acidity *pH* was measured on the *pH*-meter pH150MI with a combined glass electrode ESK-10603. *RP* was measured on the *pH*-meter pH150MI with combined redox metric platinum electrode ERP-105.

For not activated inorganic solutions in steady state, there is a right formula that relates the rate of active acidity of *pH* and *RP*[1]:

$$Eh_{min} = 660–60 \cdot pH, \text{ mV} \quad (1)$$

where Eh_{min} – minimal theoretically expected meaning of the *RP*;
pH – active acidity of tested solution.

Acquired meanings of Eh_{min} were compared with the actual measurements of Eh_{act} of solution. The shift of *RP* to the side of the recovered meanings – *RE* was determined by the formula:

$$RE = Eh_{min}–Eh_{act}, \text{ mV} \quad (2)$$

where *RE* – the shift of *RP* to the side of recovered meanings (resilence);
Eh_{min} – minimal theoretically expected meaning of *RP*;
Eh_{act} –actual measured *RP*.

For the study samples of citrus fruits were selected: kumquat, mandarin, orange, lemon, grapefruit, which were evaluated for organoleptic and physico-chemical parameters (table 2).

According to the results of research, water-alcohol infusions are grouped according to the antioxidant activity – according to *RE*: extracts with average activity (from 100 to 200 mV) – mandarin, lemon, orange, grapefruit infusion; extract with high activity (from 200 mV and above) – infusion of kumquat.

In fig. 1-2 graphic dependence of physicochemical and organoleptic parameters of water-alcohol infusions from citrus is presented.

Table 2

Indicators of *RP* of water-alcohol infusions from citrus at *t*=20° C

Raw	*Org*, points	*pH*	Eh_{min}, mV	Eh_{act}, mV	*RE*, mV
Water-alcohol mixture 40% v.	9,680	7,70	198,0	114,0	84,0
Infusion of grapefruit (peel)	9,651	5,53	328,2	202,0	126,2
Infusion of lemon (peel)	9,659	5,90	306,0	169,0	137,0
Infusion of mandarin (peel)	9,590	5,49	330,6	190,0	140,6
Infusion of grapefruit (pulp)	9,573	4,58	385,2	234,0	151,2
Infusion of lemon (pulp)	9,620	3,50	450,0	298,0	152,0
Infusion of orange (peel)	9,597	4,90	366,0	199,0	167,0
Infusion of orange (pulp)	9,583	4,72	376,8	203,0	173,8
Infusion of mandarin (pulp)	9,540	4,63	382,2	196,0	186,2
Infusion of kumquat (pulp)	9,645	3,87	427,8	224,0	203,8
Infusion kumquat (peel)	9,656	5,00	360,0	155,0	205,0
min	9,540	3,50	198,0	114,0	84,0
max	9,680	7,70	450,0	298,0	205,0

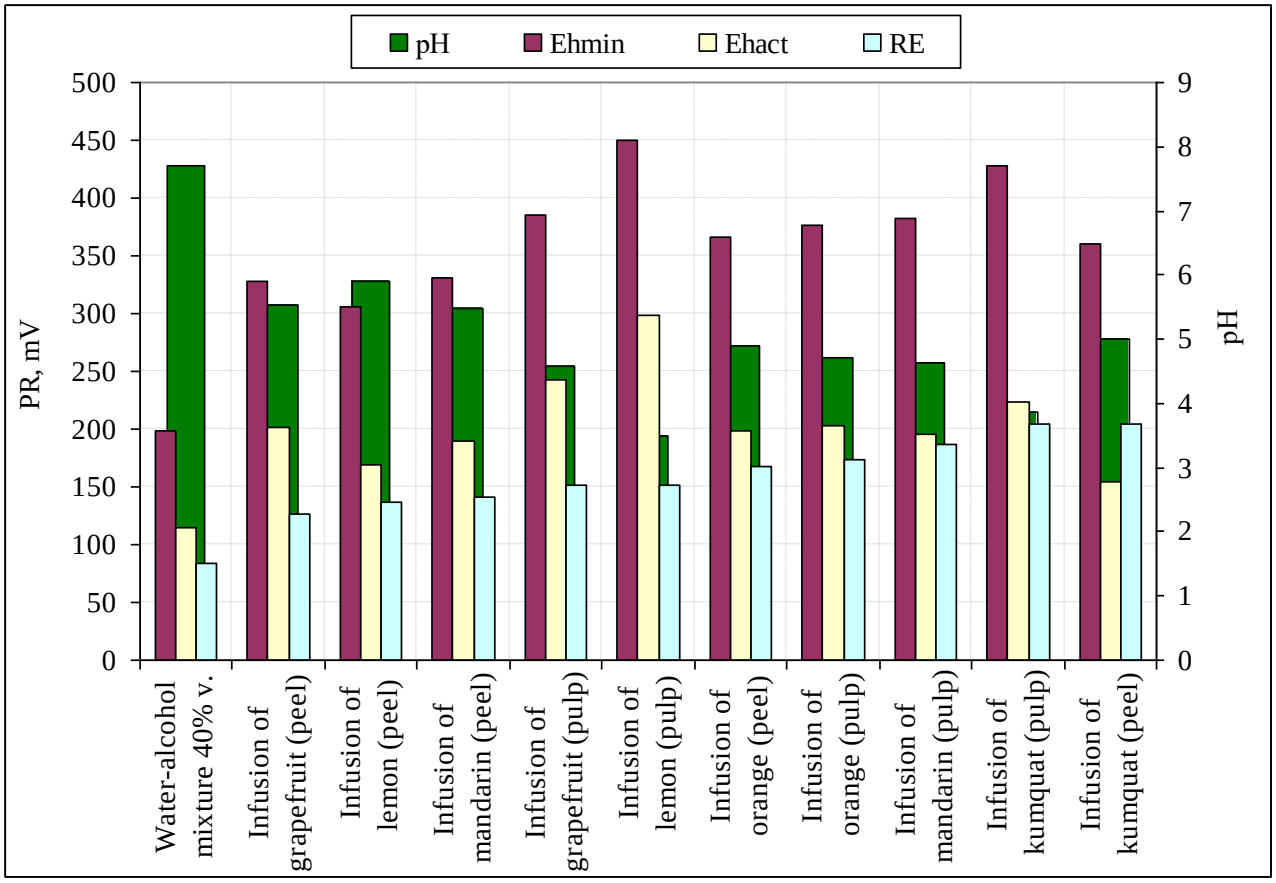

Figure 1. Graphic dependence of physicochemical indices of water-alcohol infusions from citrus

Adding vegetable alcoholic and alcoholic infusions from citrus to sauces regulates their acidity by reducing the pH that prevents the reproduction of microorganisms and enrich them with vitamins and trace elements.

It has been experimentally established that the largest *RP* are infusions from a kumquat. It is expedient to use them in the technology of production of red sauces, for example, red orange sauce, in order to increase antioxidant properties.

The recipe composition of the improved red orange sauce is shown in Table. 3

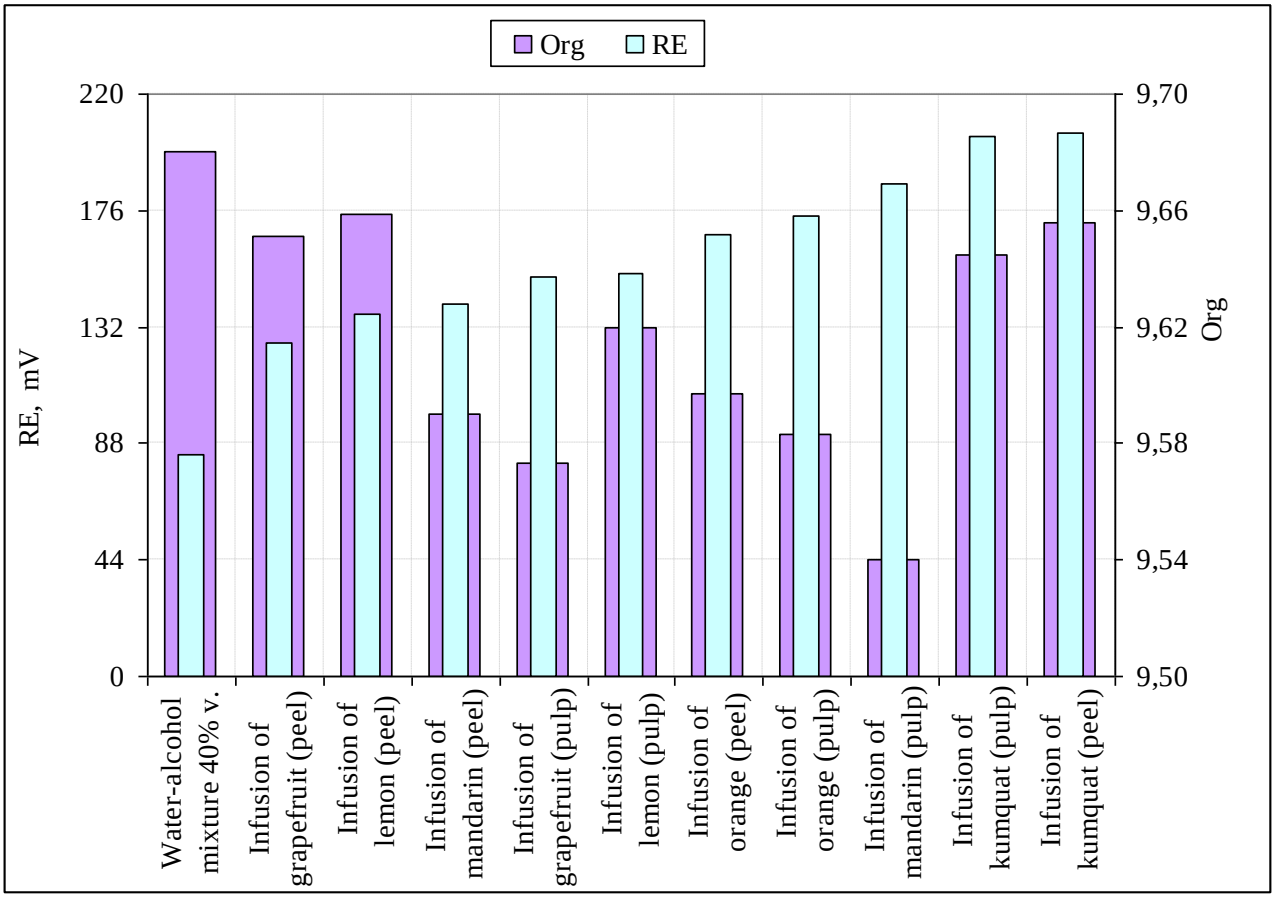

Figure 2. Graphic dependence of organoleptic parameters and energy of restoration of water-alcohol infusions from citrus

Table 3

Composition of the recipes of the red main sauce of oranges

Raw	Content, %
Red turnip sauce №824 or №825	64,1–64,5
Orange (pulp)	8,01–8,05
Oranges (peel)	2,95–2,85
Kumquat (pulp)	8,01–8,05
Kumquat (peel)	2,91–2,85
Wine red	4,37–4,05
Infusion of kumquat	4,45–4,05
Butter	5,2–5,6

Conclusions

The feasibility of using kumquat in sauces is scientifically substantiated. The antioxidant activity of citrus-water alcoholic infusions has been investigated and the rational ratios of the recipe composition of red sauce have been developed.

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Mechanism of water binding and water content of the nanoparticles of "Magnetofood"food additive

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Abstract

It is proposedtheinfluence mechanismof the nanoparticles (NP) of a polyfunctional "Magnetofood"food additive with the functional groups of the complex proteins of rye-wheat flour.

The nanoparticles of "Magnetofood" food additiveinteract with the compound proteins at the expense of the coordination links. Under the influence of the NP of "Magnetofood" additive in the structure of compound proteins there are the structural changes: there are the formation of "cluster" type and the electrostatic complexes of biopolymer with the NP "Magnetofood". The NP of"Magnetofood" food additive affects the association H_2O of lipo- and glucoproteides of the rye - wheat dough. Due to this, the processes of hydration and water content are intensified. This leads to the consumer characteristics improvement of the bakery products.

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Introduction

Bakery products must comply with the quality standards and sanitary standards. Today, the most difficult thing is to find the required quality flour with the help of which it would be possible to slightly improve flour with not very good baking properties.

As a result, bread-making enterprises must use improvers to enhance the quality of flour and correct its deficiencies. Therefore, bread-making industry more often replaces traditional raw materials with cheaper technological powdered raw materials and nutritional supplements, which could increase the nutritional value, enrich a food product with functional ingredients and reduce caloric content.

Dough is a complex hydrophilic colloidal system, composed of the gluten frame, which is filled and surrounded by weakly swollen starch and lipids, sugars and minerals dissolved in it. It was established that lipids, carbohydrates and mineral elements reside in gluten in the chemically bound state – both in the form of adsorption complexes and partially in the form of compounds (glucolipids, lipo- and glucoproteids). At the same

time, starch and shell particles are kept mechanically [1–4].NP of «Magnetofood» food supplement has high-power energy and chemical potential, and bio-relation to biopolymers, namely, proteins, carbohydrates. Therefore, they bear new functional and technological properties, for example, MRA [5–10].

In order to stabilize the structure of the protein carbohydrate frame and supramolecular solvate associates of the protein-carbohydrate complex of flour, we propose applying the multifunctional food supplement «Magnetofood». «Magnetofood» is an ultra-fine ferrous oxide powder of FeO·Fe2O3 with a particle size of ~80 nm.

Materials and methods

We studied the effect of NP of the polyfunctional food additive «Magnetofood» on the technological properties, namely moisture-retaining ability of rye-wheat dough. The object of our study is the technology of the ryewheat bread.The food additive «Magnetofood» was introduced in the form of powder when preparing the test flour samples in the amount of 0.10–0.20 % to the mass of flour [TU U 10.8-2023017824-001:2018].Technology and equipment of food production 65 Under the influence of NP of the food additive «Magnetofood», the structural changes occur in a glucoproteid structure, which are shown in Fig. 1.

Fig. 2 shows formation of solvatocomplexes in the «clusters» of a link of the glucoproteid chain.

An analysis of data in Fig. 2 shows that NP of «Magnetofood» are the active hydrophilic centers along with the ionogenic groups of disaccharide and protein. NP «Magnetofood» activate the formation of solvatoassociates. The content of lipids in wheat flour is (1,5–2,0) %. In flour, lipids are both in the free state and in the form of complexes with proteins (lipoproteids) and carbohydrates (glycolipids). The carboxyl or oxogroups of fats are more polarized and reactive than the alcohol groups of cellulose and hemicellulose. Therefore, under the influence of NP «Magnetofood», lipoproteids and glycolipids undergo structural changes and, when hydrated, can form more stable structures. Fig. 3 shows the process of self-organization of NP from the food additive «Magnetofood» into an electrostatic complex with a lipoproteid stabilized by the electrostatic interaction between atoms and groups.

It follows from data in Fig. 3 that NP of Magnetofood form internal molecular complexes at the expense of coordination bonds with the atoms of nitrogen and oxygen from the remnants of glutamine, proline and 1-linoleyl-2- oleoylglycerol. In addition, there are partial formation of the «clusters» type that make up 30 % of the structured matrix.

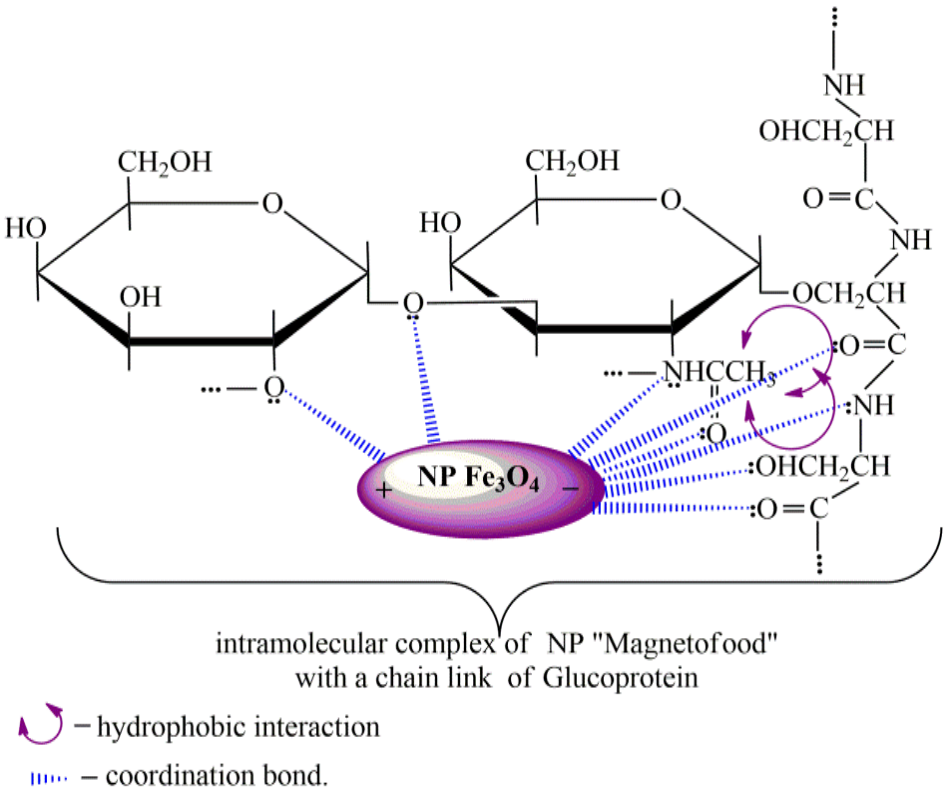

Fig. 1. Self-organization of NP of the food additive «Magnetofood» into the electrostatic complex with a link of glucoproteid chain

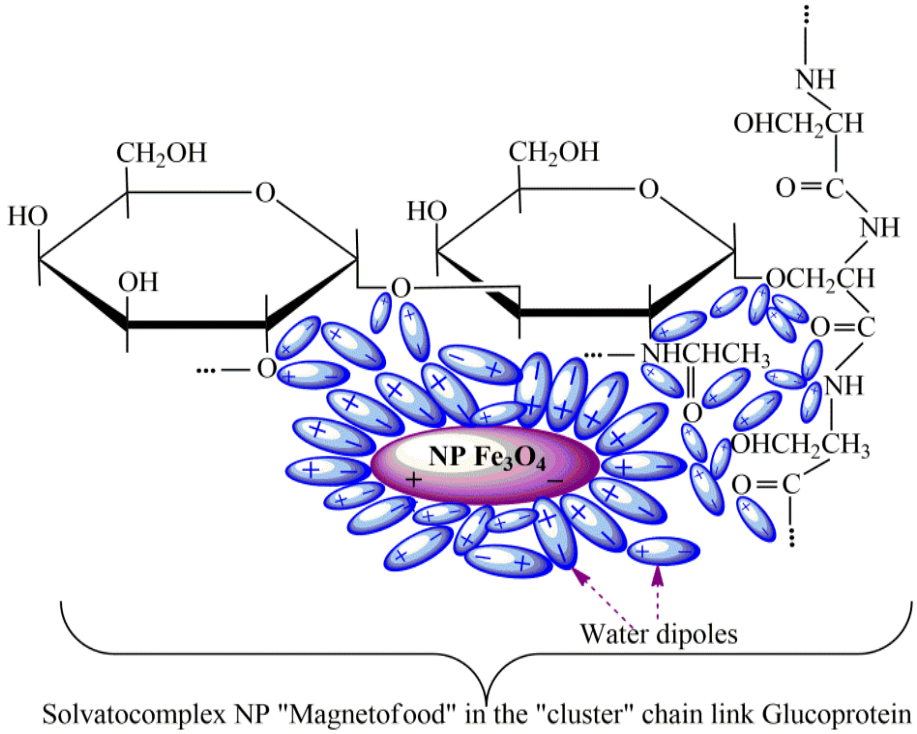

Fig. 2 Solvatocomplexes in the «clusters» of the glucoproteid chain link

Fig. 4 shows the formation of solvatocomplexes in the «clusters» of the lipoproteid chain link.

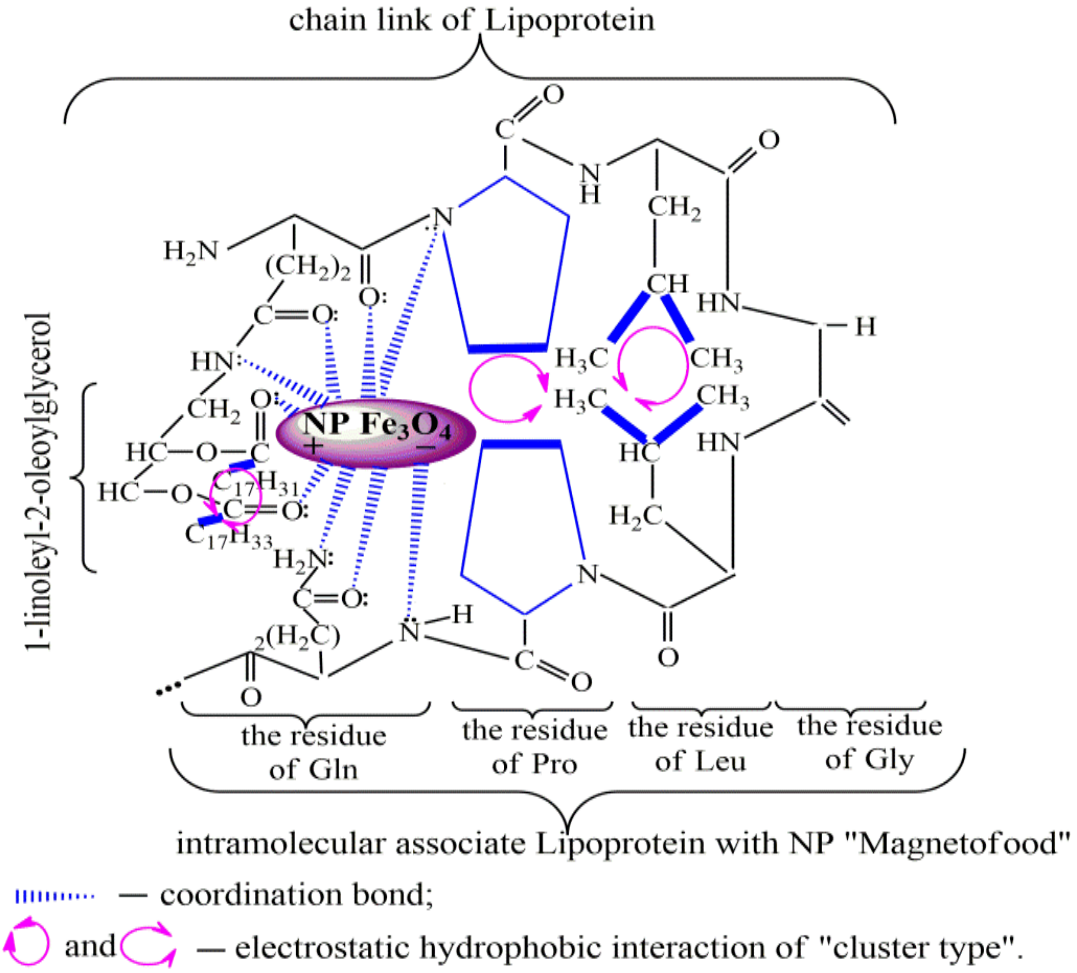

Fig. 3. Formation of the electrostatic complex of NP from the food additive «Magnetofood» with the lipoproteid chain link

An analysis of Fig. 4 shows that due to the presence of the polarized NP of «Magnetofood» and «clusters», as well as the system of hydrogen bonds between water dipoles, the accumulation of water is observed around NP of «Magnetofood» and in the «clusters» of the lipoproteid chain, which contributes to an increase in MRA of rye-wheat dough.

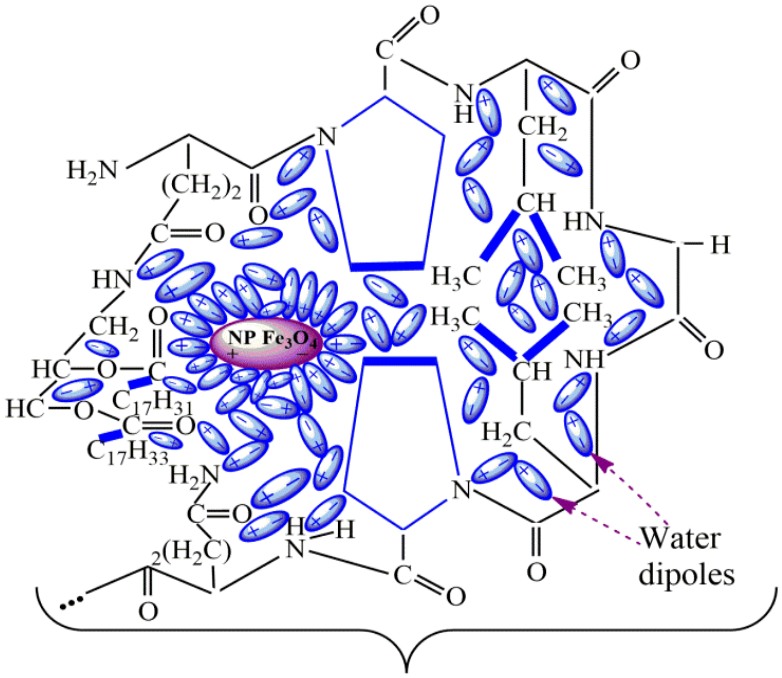

Fig. 4. Solvatocomplexes in the «clusters» of the lipoproteid chain link

Conclusions

1. The mechanism of interaction between nanoparticles (NP) of the food additive «Magnetofood» and functional groups of complex proteins of rye-wheat flour was established. NP from the food additive «Magnetofood» mostly interact with the complex proteins at the expense of coordination links. Under the influence of NP from the additive «Magnetofood», the structure of complex proteins undergoes structural changes: the emergence of formations of the «cluster» type, as well as the electrostatic complexes of biopolymer with NP of «Magnetofood».

2. The mechanism of influence of NP from the food additive «Magnetofood» on the binding of H_2O by the lipo- and glucoproteids of rye-wheat dough was established. NP from «Magnetofood» modify lipo- and glucoproteids, alter the spatial structure, contributing to the strengthening of hydration and water retention processes. The ionized NP of «Magnetofood» activate the formation of solvatoassociates. The «clusters» of complex proteins contain free water and there emerge the aqua-associates (H_2O is retained by means of hydrogen bonds).

3. The mechanism of interaction between the «Magnetofood» nanoparticles and complex proteins and H_2O molecules in rye-wheat dough system is proposed. Owing to the presence of the polarized NP of «Magnetofood» and «clusters», as well as the system of hydrogen bonds between the H_2O dipoles, the accumulation of water is observed around NP of «Magnetofood» and in the «clusters» of chains of lipoand glucoproteids, which promotes the increased MRA of rye-wheat dough. The «clusters» may retain inter-micellar and intra-micellar water, which is bound by the hydrogen,

dipole-ion, and dipole-dipole bonds to the polarized NP of «Magnetofood» and hydrophilic groups of gluco- and lipoproteids. And, finally, water dipoles may simply participate in hydrogen bonds, without breaking their strength. In addition, lateral branches that appear in the polymeric macrostructure contribute to the extension of main chains, without disrupting their «cross-linking». That facilitates the interaction between macromolecules of complex proteins and dipoles of H_2O and improves the hydration of lipo- and glucoproteids of rye-wheat flour.

Thus, when enriching rye-wheat flour with the food additive «Magnetofood,» its water-absorbing capacity and moisture-retaining ability both increase.

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3-D model of the blast freezer

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Abstract
The developed 3-D model of the blast freezer showed its adequacy of simulated processes to those observed in practice. It has shown its versatility and high flexibility as per the range of the variable data which can be changed in the process of simulation, and thus whose influence can be studied. The model allow to determine the optimum positioning of pallets including the distance between them in files and rows providing the highest efficiency of the process, as per the cycle duration and compact loading of freezer per cycle. The model can be used at a stage of freezer and air distribution designing calculations.

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Introduction

Shock freezing technology is the most proper way to extending the shelf life of meat and poultry products along with the preserving the product quality, including its organoleptic properties.This technology involves thermal processing the product with a low temperature air (-35 ... -40 ° C), flowing over the product at a high velocity, which significantly increases the heat fow removed from product, thus reducing freezing time. In shock freezing process water molecules form minute crystals whereas at freezing at moderate speed, macrocrystals are formed that destroy the cellular structure of the product, which badly affects its organoleptic qualities. Particularly negative are the consequences of the macrocrystals formation during the freezing of meat products, since large crystals destroy the structure of fibrous tissues and cell walls. When defrosting, such meat has a laced structure, intensively secretes juice, loosing food quality[1-4,6,10].

Typically, the products in the cages on pallets are placed in rows along the tunnel, which is partitioned a false ceiling. The upper section generates a directed flow of air cooled down to -35 ... -45 0C from the air cooler. The stream of cooled air passes above the distribution ceiling, turning down and then backward, cooling the products and warming up to the entrance to the air cooler thus producing the continuous circulation of air. In [1,2] a number of shock freezer layouts and types is presented . In addition to the above described, there are also designs of shock freezing chambers with

ceiling-mounted air coolers which in contrast to the above does not need a separate compartment for air cooling unit and fan section.

The experience of using shock-frost cameras indicates the following [4, 6, 9-11].

1. Critical for the design and operation of blast freezers is proper air distribution providing uniform and effective air flow around products, which in turn determines short time freezing, lowering energy spent;

2. Optimal placement of cages with cooled down products in the tunnel (chamber) preventing obstructions to high-speed cold air flow to ensure the minimum freezing cycle duration is extremely important;

3. The thermal load of shock freezing in time is extremely uneven and varies from the maximum, and then gradually decreases to a minimum at the end of the freezing cycle, since the heat transfer from the goods decreases gradually as they freeze lowering temperature difference;

The optimum number of blast freezer tunnels (chambers) should be determined with taking into account the attainable uniformity of the total daily cooling load. Thus, the time table of loading- freezing – unloading operations is to be arranged in shifts, whereas each next cycle starts after the cooling load of the previous one has decreased not less than be 40% of its maximum value.

From the stated above, it can be deduced that the critical factor in the design of shock freezing chambers is the adequate calculation of the cooled air velocity fields when it flows around the products in cages [7-9]. In addition, in determining of the distribution of airflow in the freezing chambers, there appears a question of the optimum placement of pallets with cages in the chamber (tunnel), since on the one hand there is a need to fill the chamber as compact as possible and, on the other hand, too dense a loading seriously complicates the circulation of air between the cages and, accordingly, worsens heat transfer, which, in turn, prolongs the freezing cycle [5,6]

Design and calculation practices analysis

For the transient process of product cooling down without phase change within a time increment dτ the heat balance will read:

$$dQ = \rho_m V C_{pm} dT, \quad (1)$$

Where ρ_m −mean product density ,V −product volume, C_{pm}- mean product specific heat , *T-T(τ)*-current product temperature.

The amount of heat removed from the cooled down product to the flowing around air will be:

$$dQ = \alpha F_m [T_m(\tau) - T_\infty] d(\tau), \quad (2)$$

where $T_m(\tau)$ – current temperature of product, T_∞ − temperature of the flowing around air. α – heat transfer coefficient.

Combining (1) and (2) one obtains ordinary differential equation which upon solving yields:

$$\frac{T_m(\tau)-T_\infty}{T_{m0}-T_\infty} = \exp\left(-\frac{\alpha F_m}{\rho_m V * C_{pm}}\tau\right), \quad (3)$$

Or, solved for τ :

$$\tau = \frac{\rho_m V * C_{pm}}{\alpha F_m}\ Ln\ \frac{T_m(\tau)-T_\infty}{T_{m0}-T_\infty}. \quad (4)$$

It should be pointed out that the above equations are valid only under the suggestion of the uniform temperature distribution at any time within a cooled down product. In practice this suggestion never stays true, since at the given conditions the internal heat conduction in the cooled body will be dominant in determining the duration of cooling. The conjugated problem of the external heat transfer and internal heat conduction cannot be solved analytically even for a single cooled body. For a number of cages, being cooled down in a freezer, individual boundary conditions will be different (insofar the air flow around each cage may differ). Being coupled with the uncertainty in the determination of air flows around individual cage in freezer, the problem appears extremely complex. To date, unfortunately, there are no methods and methodology for calculating jets of air from fans flowing through the cage cluttered chambers. Moreover, there are no methods for calculating transient heat transfer from cooled bodies. In most cases, the design of the air distribution in the freezing chambers is solved on the basis of certain design experience and through the application of empirical equations, which, as a rule, have only limited applicability. In these conditions, the most promising is the application of 3-dimensional simulation of blast freezers, including modeling of aerodynamics and heat transfer to airflows in simulated, including the internal heat conduction within a cage itself.

3-D model development

The ANSYS CFX applications provide exceptional capabilities in this sense[].ANSYS Fluent software allows to create a 3-D shock freezer (tunnel) model in 1:1 scale at a given precision of detalization, which is limited only by the available capacity of computers and duration of calculations. This, in turn, allows to adequately displaying all the particulars of the blast freezer, including local aerodynamic parameters, turbulence, temperature distribution etc. Developing a set calculation grids of possible positioning of pallets inside the freezer and respective modeling of the process allows to pick up an optimum placement of cages aimed at the minimizing of freezing duration. The ANSYS CFX built-in grid generator programs allow generating grids of any complexity and boundary fineness (Workbench and ICEFM routines). The generated grid is transmitted to the ANSYS CFX preprocessor unit, which, in fact, runs the individual model. boundary conditions, including the initial temperature of the product, the temperature of the cooled air, boundary conditions on the walls, the ceiling

and the floor, which allows to take into account the individual features of a particular project. It is also possible to enter parameters that allow to perform a variational calculations, aimed at the determining of optimal designs of air coolers, air deflectors, distributors etc [5,7,9].

The simulation was carried out at the Department of Thermal Power Engineering and Refrigeration Technology of NNIITI named after Academician Guliy I.S. NUFT using the licensed ANSYS 15 Lic No 1023420 Acad software. The developed calculation grid of the modeled freezer is shown in Fig.1.

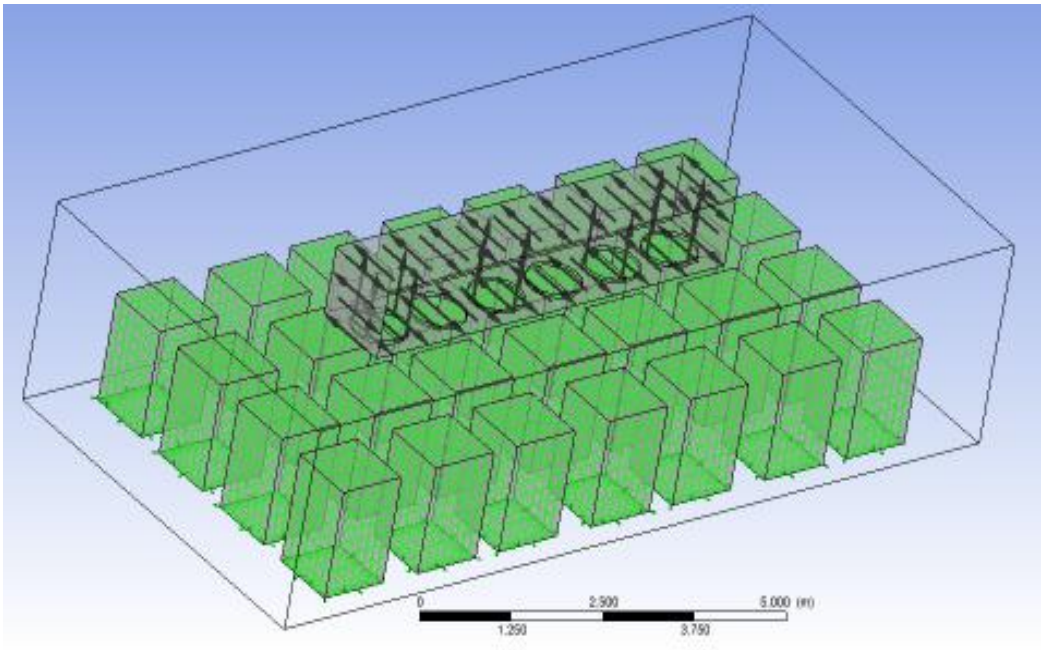

Fig.1. Calculation grid of the freezer with product cages on pallets and over hanging air cooler

Accepted size of the cage -1x1,2x1,6, which corresponds to the pallet size adopted in the meat industry. In this arrangement of pallets in the tunnel, the production capacity will be 17-20 t per cycle. The ANSYS CFX actually creates an environment in which it is possible to form a geometric entity that comprises two sub-domains. One is a cooling cabinet which forms a fluid sub-domain, in which the flow of cooled air takes place. The other- is a solid domain which includes a set of caged boxes on pallets arranged in a certain way and enveloped by the fluid sub-domain. The two sub-domains are thermally connected at the boundaries of every cage by postulating the heat flux conservation on the sub-domains" interfaces. This allows us to adequately capture all of the local aerodynamic parameters, including the turbulence scaling and the flow parameters in the wall boundary layers without the need for preliminary determination of the local heat transfer. As it is seen from Fig.1., the air is cooled down in the

overhanging cooler with the fan intakes at the bottom of the cooler and the side wall grill distributors.

Results and discussion

The simulation of the transient regime of product cooling down has been performed with the variation of the cooling duration at 1 hr. step. The obtained results have sown their close adequacy to the data observed in practice. The analysis of the flow pattern through the snuggly packed freezer allowed discovering and locating the zones of poor air circulation and as a result of this poor heat transfer from the cages. Configuration of streamlines exiting the side grills of air coolers showed the necessity to address the issue of the special air distributor –deflector which will even the air flow and direct it uniformly towards the periphery of the side rows of pallets. This is in conformity with the results presented in[9].The temperature distribution along the line passing through the center of the row of cages adjacent to the axial line at different heights is presented in Fig 2 and 3.

As it is clearly seen from the data in Fig.2 and 3. The most efficient cooling takes place in the central part of rows (cages No 3,4,5). Which is quite clear due to the fact that the fan intakes create a powerful stream of air in this zone. In the contrast, the periphery cages remote from the fan intakes are located in the zones of poor circulation which is caused by the improper design of air distribution. Poor cooling in the lower parts of cages is also the result of weak streams of air penetrating a whole depth of the freezer, since there is no air deflector directing flow downwards, instead the air stream tend to move along the least resistance way – to turn backward and move to the fan intakes along the shortest unobstructed way.

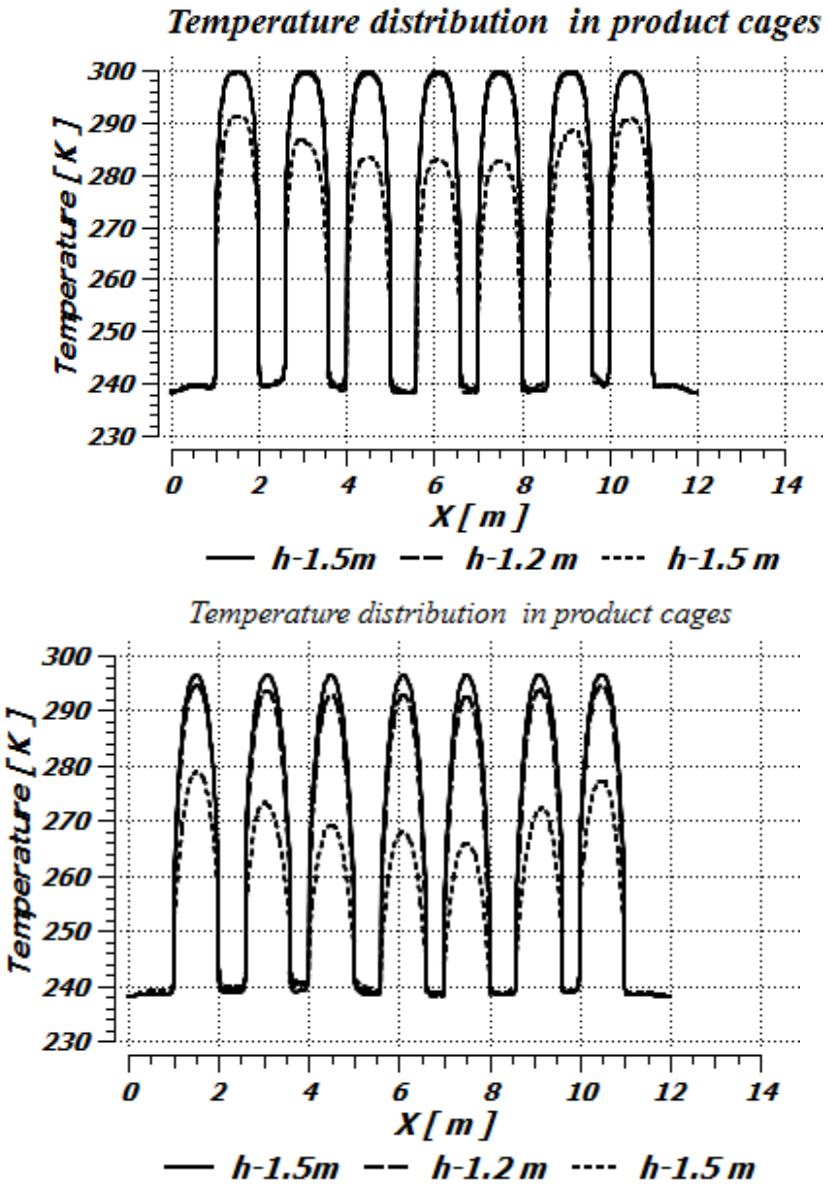

Fig. 3. Temperature distribution in freezer and cages. 12 hrs. cooling.

Conclusions

The developed 3-D model of the blast freezer showed its adequacy of simulated processes to those observed in practice. It has shown its versatility and high flexibility as per the range of the variable data which can be changed in the process of simulation, and thus whose influence can be studied. The model allow to determine the optimum positioning of pallets including the distance between them in files and rows providing the highest efficiency of the process, as per the cycle duration and compact loading of freezer per cycle. The model can be used at a stage of freezer and air distribution designing calculations.

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Development of the white-pink marshmallow formulas with using of "Magnetofood" food additive

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Abstract
It was investigated the effect of "Magnetofood" food additive in the powder form in the amount of 0,10 %; 0,15 % and 0,20% by weight of the raw materials, on the process of structure formation of the gelling agent and foaming of the whipped mass in the whipped confectionery production as well as on the quality indicators of the finished product. It has been improved the marshmallow technology formulas of the white-pink marshmallow on agar and pectin. The formulations and technological schemes of the white-pink marshmallow on agar and pectin with "Magnetofood" additive in the amount of 0,15% by weight of raw materials were developed.

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Introduction

The confectionery industry is one of the active users of food additives and the improving agent in the products production. The use of food additives in the industry of whipped pastry, in particular marshmallow is due to a number of circumstances; the reasons and the directions of food additives using by the confectionery industry. The analysis of the information sources [1–32] shows the insufficiency of data on the marshmallow technologies with the using of nanopowder additives which have thickening, foam-and gelling, stabilizing capacities; improving the structural and mechanical properties of whipped masses and the quality indicators and the storage-life extender of marshmallows. As an additive – improving agent for food systems we have developed and proposed the "Magnetofood" food additive [TA Ter Admin/U 10.8-2023017824-001:2018]. It is the ultra-fine powder with a large specific and highly active surface.

In the food systems "Magnetofood" exhibits antioxidant, sorption, bacteriostatic, complexing, emulsifying, moisture-containing fat-containing, water-binding, stabilizing, structure-forming properties [1–4]. In this regard, it is relevant to improve the formulation and the existing technology of the white-pink marshmallow with the introduction to the formulating composition of "Magnetofood" food additive.

Results and discussion

The study object is the technology of the white-pink marshmallow on agar and pectin. The research subject is the marshmallow model samples on agar and pectin based on basic recipes № 95 and № 126 are listed in Table 1.

The experimental samples preparation of the marshmallow was carried out according to the traditional technology of the white-pink marshmallow according to the classic recipe Table 1.

Table 1

Formulations of white-pink marshmallow on agar and pecti (control) and with different mass fraction of "Magnetofood" food additive (Experimenal)

Name of the raw materials	Inputs of the raw material per 1 ton of finished product, kg							
	marshmallow samples on agar				marshmallow samples on pectin			
	№ 1 Control	№ 2	№ 3	№ 4	№ 5 Control	№ 6	№ 7	№ 8
Granulated sugar	673,0	672,0	671,5	671,0	671,0	670,0	670,5	669,0
Powdered sugar	29,9	29,9	29,9	29,9	29,9	29,9	29,9	29,9
Molasses	139,4	139,4	139,4	139,4	142,9	142,9	142,9	142,9
Apple sauce	390,0	390,0	390,0	390,0	298,0	298,0	298,0	298,0
Egg white	65,0	65,0	65,0	65,0	65,0	65,0	65,0	65,0
Agar	8,6	8,6	8,6	8,6	–	–	–	–
Apple pectin	–	–	–	–	13,4	13,4	13,4	13,4
lactic acid	11,8	11,8	11,8	11,8	8,4	8,4	8,4	8,4
Sodium lactate	–	–	–	–	6,8	6,8	6,8	6,8
Different kinds of essence	2,0	2,0	2,0	2,0	2,0	2,0	2,0	2,0
Colouring agent	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6
"Magnetofood" food additive	–	1,0	1,5	2,0	–	1,0	1,5	2,0

The data on the influence of "Magnetofood" food additive on the basic physico-chemical and technological parameters of the experimental samples of the white-pink marshmallow are presented in Table 2.

Table 2

The influence of the "Magnetofood" food additive on the physico-chemical and technological indicators of the experimental samples of white – pink marshmallow on agar and pectin

(n = 3, p ≤ 0,05)

Quality indicators	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8
Mass fraction of moisture, %	17±0,3	17,3±0,3	17,4±0,3	17,5±0,3	17±0,3	17,4±0,3	17,5±0,3	17,6±0,3
Total acidity, deg.	0,7±0,02	0,6±0,02	0,5±0,02	0,5±0,02	5,90±0,2	5,4±0,2	5,30±0,2	5,2±0,2
Density, kg / m^3(the smallest value)	545±2	490±2	485±2	484±2	550±2	485±2	480±2	479±2
*Duration of whipping, min.	16	14	14	14	10	8	8	8
Plastic strength κPa	9,0±0,5	10,3±0,5	10,8±0,5	10,9±0,5	6,5±0,5	7,0±0,5	7,4±0,5	7,5±0,5

**Duration of whipping, min – the time to achieve the lowest density value pf the experimental samples of the marshmallows mass.*

Conclusion

From the experimental data Table 2 it follows that the introduction of "Magnetofood" food additive in the amount of (0,10–0,20)% of the prescription composition contributes to the improvement of physico-chemical and technological indicators of the experimental samples of white-pink marshmallow on agar and pectin:

- the mass fraction of moisture is increased by (1,7–2,9) % in the samples on agar and (2,3–3,5)% in the samples on pectin due to water binding and water-containing capacity of the "Magnetofood" additive;

- decreases the acidity of $(0,1–0,2)^0$ in the samples on agar and on (0,5–0,7)° in the samples on pectin due to the amphoteric nature of "Magnetofood" additive;

- the density value decreases, in particular the smallest value, by (55–61) kg/m^3 for agar, by (65–71) kg/$m^3$for pectin and the duration of whipping during~2 minutes. This can be explained as follows: "Magnetofood" surface-active nanoparticles with the complexing and structure-forming properties contribute to

branching of the main chains of egg white macromolecules in a dispersion medium, slowing down the process of the loss of liquid and thinning the walls of the air bubbles, with the result that in a decrease in the density of the experimental samples of the whipping masses is decreasing in comparison with the control samples.

- the plastic strength increases by (1,3–1,9) kPa in the samples on agar and (0,5-1,0) kPa in the samples on pectin due to the structure-forming and stabilizing effect of the nanoparticles "Magnetofood" additive which contributes to gel-forming capacities of pectin and agar which allows to increase the viscosity in the Gibbs-Plateau channels, slow down the weeping process and stabilize the gel framework of the foamy structure**.**

It should be noted that the best results were obtained with the content of the "Magnetofood" additive 0,15% by weight of the raw materials.

Conducted researches allowed to scientifically substantiate the recipe (Table 1) and the technological parameters of the production of the white-pink marshmallow. Fig. 1 shows the technological scheme of the white-pink marshmallow on agar with the addition of "Magnetofood" food additive. A distinctive feature of the new technology is the blending mixing of "Magnetofood" food additive with the gelling agents which are used before the technological operation ofsteeping with the gelling agents in the cold water. The production technology of the white-pink marshmallow on pectin with the addition of "Magnetofood" food additive includes the same stages but has some differences in the technological regimes.

The technological process of the white pink marshmallows production involves the following stages: *the selection and preparation of the prescription components* – the bulk components are sifted, essence, lactic acid, colouring agent, egg white are dissolved, glucose syrup is heated and filtered; the obtained dry mixture by gelling agents with "Magnetofood" food additive, followed by soaking and swelling in the cold water at the temperature of (20±2)ºC for (2,5–3,0)·3600 s– for agar.

Swelling of the pectin-magnetofood mixture is added to the apple sauce (pre-mixed with sugar in an amount equal to the amount of pectin) for (4,0–8,0)· 3600 s at (20±2) °C and thoroughly mixing for the good distribution and pectin swelling. It should be noted that at the stage of soaking and swelling, the solvation of "Magnetofood" food additive is and swelling of thegelling agents with its partial structuring under the nanoparticles action of "Magnetofood" additive which facilitating the water ingress into the most organized sections of the gelling agents chain.

Next, *the solution* of agar mixture with "Magnetofood" additive *is heated* to the temperature of (95–100) ºC and held for (10–15)·60 s. Then add the sugar and mix thoroughly at the temperature (95–98) ºC for (20–30)·60 s and a solids content of DS=(84,5±0,5)%. Get *agar-sugar syrup*. At this stage, "Magnetofood" additive increases of the agar solubility due to its water-holding capacity and the interaction of its ionized nanoparticles with polarized agar groups which lead to branching of the molecules main chains of the gel components which contributes to their chain and better penetration of the water molecules. A pectin-apple-magnetofood mixture is wiped through a sieve with a hole diameter $d=0,8\cdot10^{-3}$ m and sent for the whipping

(which depending on the acidity of the puree used, make sodium lactate) with the prepared egg white. The duration of whipping (4–6)·60 s. Get protein-pectin-apple mixture with “Magnetofood” addition.

The cooking of agar-sugar-dextrose syrup with "Magnetofood"food additive. In the agar-sugar-magnetofood syrup is added the prepared molasses and mixed at (95–100) ºС for (8–10)·60 s. In the case of the marshmallow preparation on pectin the sugar-dextrose syrup is prepared by boiling sugar with glucose syrup at a temperature of (105–110) ºС until the solids content is DS=(82,5±2)%.

The cooking of the whipped protein-apple mass. The apple puree with sugar and half an egg white (in the form of a solution) are whipped for (5–8)·60 s at a temperature (20±2) ºС. Then add the second half of the egg whites by continuing to whip another (5–8)·60 s.

The cooking marshmallow mass. To the agar-sugar-syrup with “Magnetofood” food additive add a whipped protein-apple mass, taste and aromatic emulsion, and the mixture is kneaded on a slow stirrer at a temperature of (54±1) ºС for (3–4)·60s with for the same distribution of the gel and flavoring substances in the whipped mass. For marshmallow on pectin, the process is identical.

Formation, structure formation and drying. The molded products are sent for holding. The duration of structure formation and drying (6–8)·3600 s at a temperature (35–40) °С

Packing, packaging, labeling and storage. The ready marshmallows are packed and stored in the storage conditions at a relative humidity of (75±2)%.

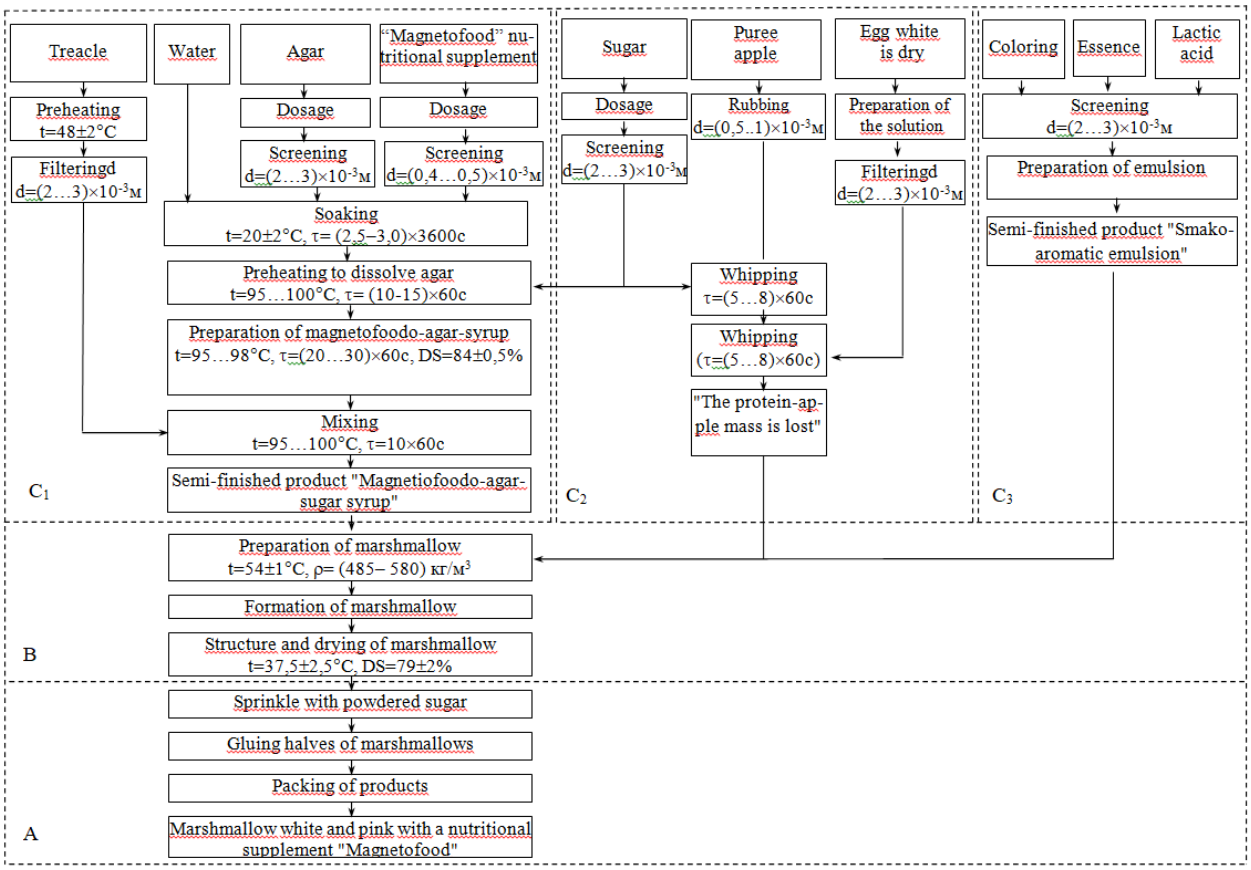

Figure 1. The technological scheme of white-pink marshmallows on agar with "Magnetofood" food additive: A, B, C_1, C_2, C_3 are the subsystem of the technological scheme of the marshmallows production

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Insurance's impact on food safety and food security

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Abstract
The research analyzes the impact and role of insurance in ensuring and improving food safety and food security in accordance with international and national experience. The findings reveal that food security and safety is one of the biggest issue today facing humanity, but insurance can be a big instrument to mitigate to food safety and security risks.
The study also suggest that there are a lot of effective methods providing food safety and security. The analysis shows that there are four types of insurance product related to the food safety and security: commercial general liability; business interruption; product recall; product liability. Liability insurance has influence and contribute to food safety by follows reasons and methods as follows: reduction the insurance premiums; terms and conditions of the insurance policies; insurance companies' assistance with the aim to reduce food safety risks. The results indicate, that liability law could have influence of food safety and food security (liability claims; liability insurance; direct effects of liability law on management strategy).
Keywords: insurance, liability insurance, food industry, food safety, food security.

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Introduction

The analysis of studies and publications showed that a lot of researchers are engaged in research into the insurance market and food safety and food security. The purpose of the study is to analyse the main interconnections of insurance and food safety and food security.

The complexity of the food safety and security problem justifies the performance of researches not only in agriculture, but in other branches of activity too. The insurance is to be noted by its struggles to adapt to the new challenges [10]. According to the *Lloyd's Food Report (2013)* insurance can be a big instrument to mitigate and management related to food safety and security risks (financial risks for growers, manufacturers, distributors, retailers and food-service providers) [1]. In addition, innovative insurance methods and multi-stakeholder cooperation can make a big impact in progressing towards a more food security and safety [1].

Food security and safety is one of the biggest problem and issue today facing humanity [10]. There are a lot of modern and effective methods and instruments providing food safety and security, but this article develops the influence of insurance on food safety and security. In addition, according to the *Lloyd's Food Report (2013)* food insecurity will be one of the issue to global society in the future [1]. Besides, *Swiss Reinsurance Company Ltd (2015)* indicates, for example, the insurance products for food contamination and studies the crisis management in food safety in a globalized world in in the 21st century [2]. The impact of insurance for food safety and security are object of studying for many scientists and international organizations across the world. *Lloyd's* analyzes the business and insurance implications of food safety and security [1]. *Havinga (2012)* discussed the influence of liability law (preventive effects of liability claims and liability insurance) on food safety, and stated that three ways in which liability law could have influence of food safety controls as follows [6]:

- liability claims;
- liability insurance;
- direct effects of liability law on management strategy [6].

This paper presents research into two parts: firstly, liability insurance and food safety; and, secondly, insurance and food security.

Materials and methods

Materials

The study of the insurance's impact on food safety and food security was conducted on the international scientific researches and reports. The most important research results were obtained from studies as follow: *Swiss Reinsurance Company Ltd (2015)* [2]; *Connally (2009)* [3]; *Havinga (2012)* [6]; *Cogan and Aloysius (2016)* [8]; *Omri Ben-Shahar (2015)* [5]; *Isaboke et al. (2016)* [9]; *Mârzaa et al. (2015)* [10] etc.

Methods

Scientific research of the insurance's impact on food safety and food security was based on the application of the following methods: abstract-logical, system analysis and grouping for studying the insurance's impact on food safety and food security. Observation, generalizations and descriptions methods were used to analyse the advantages and disadvantages of using insurance as instrument to increase the food safety and food security.

Results and discussion

Liability insurance and food safety

Studying the crisis management in food safety in a globalized world in in the 21st century *the Swiss Reinsurance Company Ltd (2015)* shows that there are three insurance products for food contamination as follows [2]:

1) Product liability insurance (compensation of third party liability claims for injury or damage caused by the contaminated food);

2) Product recall insurance (food industry): expenses for the recall of any accidentally contaminated;

3) Contamination products insurance [2].

Altogether, according to the *Connally (2009)* it can be four types of insurance product related to the food safety and security: commercial general liability; business interruption; product recall; product liability [3]. Furthermore, insurers may also encourage safe food handling practices through the terms and conditions of the insurance agreement or by decreasing the insurance premiums based on the level of food safety [3].

Havinga (2012) have proposed three ways in which liability law could induce preventive measures for food safety as follows [6]:

1) Claims from injured consumers or damaged business.

2) Covering the risks of liability claims by insuring the risk (through insurance). Insurers may induce food safety controls through the terms of an insurance policy

3. Liability law has impact on business directly inducing businesses to assure food safety [6].

In addition, *Cogan and Aloysius (2016)* have proposed that combined these three methodologically distinct approaches food safety liability insurance is a weak regulator of food safety [8].

Analysis by *Havinga (2012)* shows that liability insurance has influence and contribute to food safety by follows reasons and methods [6]:

- reduction the insurance premiums;
- terms and conditions of the insurance policies;
- insurance companies assistance with the aim to reduce food safety risks [6].

The opposite arguments and measures to the positive insurance contribute to food safety are as follows [6]:

1) insufficient knowledge with insurers;

2) decreasing the financial incentive to produce safe food;

3) insurers does not interact with food safety officers [6].

Altogether, scholars have argued that that compulsory food safety liability insurance could supplement government regulation of food safety. As a result, *Cogan and Aloysius (2016)* stated that governments are exploring the benefits of food safety insurance [8].

Connally (2009) studied the problem of managing risks to reduce or avoid legal liability through the good food safety practices (GFSP) and argued that for the food industry enterprises with insurance, the policy may require the food supplier to follow the GFSP and do what is possible to minimize the incident of foodborne illness [3].

Omri Ben-Shahar (2015) explores regulation of food safety through compulsory insurance and the role of insurance as a substitute for government regulation of food safety. The results of the research papers show that the insurance sector has advantages in collecting and administering the information relevant to setting standards. Additionally, compulsory food liability insurance is an important way in which regulation of food safety [5].

In addition, *Havinga (2012)* argued that liability law could stimulate a culture within firms to take responsibility for food safety. Altogether, author distinguished the factors that encourage food safety measures in firms as follows:

1. Market (firms that produce unsafe food risk losing their reputation, market share and sales);
2. Food safety laws and regulations (firms that violate food laws risk penalties);
3. Product liability law (firms that are legally responsible for a product) [6].

Cogan and Aloysius (2016) have make research about the liability insurance as a regulator of food safety through three distinct perspectives as follows [8]:

- an economics of information framework;
- an analysis of the empirical evidence of under deterrence of foodborne illness;
- a review of emerging evidence of food suppliers' cognitive biases with regard to food safety.

Insurance and food security

In addition, according to the report of the *Agricultural Insurance Conference (Berlin, 2014)* agricultural insurance should be seen as one component to the agricultural system and it is related to food security [11].

Altogether, *Isaboke et al. (2016)* described the effect of weather index based micro-insurance on food security status of smallholders, and find that a positive impact on food security is associated with the uptake of index insurance [9]. *Mârzaa et al. (2015)* suggest that insurance alone cannot provide food security. It can make a big impact in raising awareness of the importance of risk reducing and encouraging investments in increasing the agricultural industry development [10].

The research results by *Isaboke et al. (2016)* showed that many factors (age of household head, education level, household size, access to extension, distance to nearest market) are important variables that influence farmer’s propensity to adopt the weather index insurance [9].

Mârzaa et al. (2015) discussed the interconnections between insurance and food security taking into account the climate change challenges. Authors have the ways in which insurance has a big impact for the food security as follows [10]:

1. Food security factors;
2. Factors impacting on the development of agricultural insurances;
3. European agricultural insurance systems [10].

Massachusetts department of agricultural resources analyzes the interconnection the food security and liability insurance. Scientific organization argued that buyers may have special concerns about food safety and they may require the producers to buy special insurance to protect them [4].

Conclusion

The article has investigated the practice of using insurance as an instrument for improving and ensuring food safety and food security in modern conditions. The results have indicated that insurance has a big impact for the food security in follow directions: food security factors; factors influencing the development of agricultural insurances; European agricultural insurance systems. The analysis shows that liability law could induce preventive measures for food safety and food safety. In addition, liability law could stimulate a culture within firms to take responsibility for food safety. Furthermore, our results confirmed that there are factors that encourage food safety measures in firms (market; food safety laws and regulations; product liability law). Altogether, it was indicated the opposite arguments to the positive insurance contribute of insurance to food safety and food security **(**insufficient knowledge with insurers; decreasing the financial incentive to produce safe food; insurers does not interact with food safety officers).

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Mechanism of fat-binding and fat-contenting of the nanoparticles of the "Magnetofood" food additive

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Abstract

The goal of research is the mechanism study of interaction of Fe_3O_4 nanoparticles ("Magnetofood" food additive) with linoleic acid and sunflower oil which is represented by the "Two-layer coordination" model. The chemical composition of the surface layers and the chemical state of elements on the surface ofFe_3O_4 nanoparticles coated with linoleic acid and unrefined sunflower oil was studied by X-ray photoelectron pectroscopy. It was established that on the spectra lack the C 1s absorption band at 290 eV which corresponds to carboxyl carbon (-COOH), that is, there is no Estern group. Thisallows for the conclusionabout the fat-binding and fat-contentingcapacity of the nanoparticles of"Magnetofood" food additive.

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Introduction

One of the important functionally and technological properties of the food raw materials and the food ingredients which determines the technological processes course and thefinished product quality is the fat-retainingcapacity (FRC). FRCis the capacity to bind and retain fat. Fats are triglycerides. The edible fatspeciation. besides triglycerides, also contains the higher fatty acids (oleinic linoleic, linoleic ones are in oils; palmitic, stearic are in animal fats). Therefore, when studying of the FRC mechanism it is necessary to consider the physical chemical interactions of the food systems ingredients with the main components of fats and oils – triglycerides and higher fatty acids. Knowledge of the binding mechanisms and the fat content of the raw materials will allow the rational use of new types of the food raw materials and the food additives and predict the raw ingredients behavior in the food systems (dough and confectionery masses, minced meat, etc.) in the process of the processing and storage of finished products.

Thus, the food fibers have the high fat-binding capability (FBC) of the mechanism of which is not well understood. There is an opinion that FRC and FBC are determined by lignin presence and are not affected by the particles size [1, 2]. The following scientific studies of the mechanism of FRC and FBC and the food fibers in the meat systems [3–6] showed the dependence of the fat-retaining capacities and the fat burning properties on the number and size of the raw particles. This suggested that the fat absorption mechanism by the food fibers can be determined not only by the lignin sorption activity the availability of which increases during grinding, but also by the surface adsorption [3–6].

Materials and methods

Research subjects

Sample 1 – Fe_3O_4 nanoparticles coveredby linoleicacid. It was obtained by the dispergating 1 g of Fe_3O_4 nanoparticles (sample 1) and 0,2 g oflinoleic acid in 10 ml of dymethylformamide for 12 hours at a temperature of (50±1) °C and nitrogen stream blowing over the surface of the reaction mixture. After cooling the suspension to (20–25) °C, Fe_3O_4 nanoparticles coveredby linoleic acid were isolated by magnetic filtration and washed with the water-ethanol mixtures (1: 1) in 5–7 times. The final product was dried in vacuum at (60 ± 1) ° C for 24 hours;

Sample 2 – Fe_3O_4 nanoparticles coveredbythe unrefined sunflower oil or 1-linoleyl-2-oleoyl-3-linole-noylglycerol. Dispersed 1 g of Fe_3O_4 nanoparticles (sample 1) and 0,2 g of the unrefined sunflower oil or 1-lino-leyl-2-oleoyl-3-linolenoylglycerol in 10 ml of dimethylformamide for 12 hours at a temperature of (50 ± 1) °C and the nitrogen stream of above the surface of the reaction mixture. After cooling the suspension to (20–25) °C, Fe_3O_4 nanoparticles covered bythe unrefined sunflower oil or 1-linoleyl-2-oleoyl-3-linolenoylglycerol were isolated by magnetic filtration and washed with the water-ethanol mixture (1:1) in 5–7 times. The final product was dried in vacuum at (60 ± 1) °C for 24 hours.

X-ray photoelectron spectroscopy (XPES or XPS)

The study of the chemical composition of the surface layers and the chemical state of the elements on the surface of the experimental samples 1, 2 was carried out on the Kratos Axis Ultra DLD electron spectrometer (“Kratos Analytical Limited”, UK). As an exciting X-ray, the Al K_α line with photon energy hv = 1486,6 eV, voltage at the 15 kV tube and the emission current of 10 mA were used. The recording of XPE-spectra was carried out in the constant energy mode of the analyzer passing through which was 160 eV when recording observation spectra and 40 eV – for the registration of the spectra of the internal electronic levels of the main elements: Fe 2p, O 1s, C 1s. The scales of the association energy (E_{as}) of the spectrometer were pre-calibrated on the

peaks position of the main levels Au $4f_{5/2}$ (E_{bond}=83,96 eV), Ag $3d_{5/2}$ ($E_{as.}$=368,21 eV) i Cu $2p_{3/2}$ (E_{bond} =932,62 eV) on the surface spectra of the samples of elemental standards (Aurum, Argentum, Kuprum); calibration accuracy ± 0,03 eV. Charge samples were evaluated for Carbon C 1s spectra (284,5 eV).

The analysis samples were prepared in a pre-fabricated thin layer of the sample (50,0 mg) in metallic In, which is located directly in the holder of the measuring chamber of the device.

For a detailed analysis of the chemical states of atoms we used the spectra decomposition into the individual components according to a program that takes into account the mixed Lorentz – Gaussian shape of the peaks and the area under the peaks while simultaneously optimizing the background parameters by using the minimizing principle of the number of bands needed to describe the experimental spectra.

The error in the peak position determining was ± 0,01 eV. The analysis of the chemical state of the atoms (Ferum, Oxygen and Carbon) on the surface of the samples consisted in a detailed study of the spectra of the electronic levels:Fe 2p (705 – 740 eV), O 1s (525 – 554 eV) and C 1s (275 – 295 eV) which allowed to quantify the phase composition of the surface of the samples.

X-ray photoelectron spectroscopy (RPES or XPS)

The chemical composition of the surface layers of the “lipid-NP Fe_3O_4” system and the chemical state of the elements on its top arefurther investigated by the X-ray photoelectron spectroscopy (RPES) method. Fig. 1 shows the X-ray photoelectron spectra (RPES or XPS-spectra) of the internal electronic levels of C 1s and Fe 2p of the experimental samples 1 (Fig. 1, a, b) and 2 (Fig. 1, c, d) of the compositions “lipid-NP Fe_3O_4”.

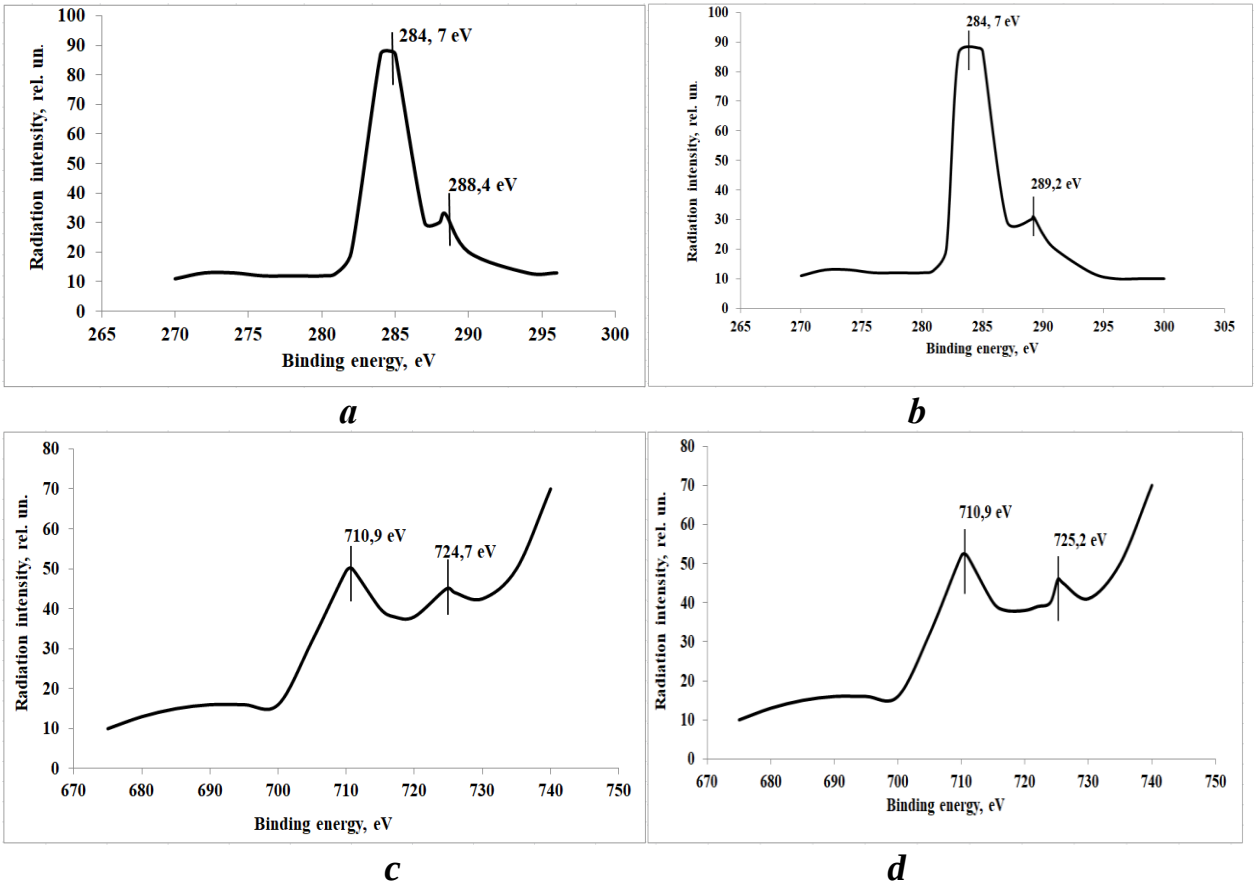

Fig. 1. XPS images of C 1s and Fe 2p internal electronic levels: C 1s level of Fe_3O_4 nanoparticles coated with linoleic acid (a); C 1s lvel of Fe_3O_4 nanoparticles coated with sunflower oil (b); Fe 2p level of Fe_3O_4 nanoparticles coated with linoleic acid (c) and Fe 2p level of Fe_3O_4 nanoparticles coated with sunflower oil (d)

Results and discussion

On the spectra (Fig. 1, *a,b*), there is no absorption band C 1s at 290 eV which corresponds to carboxylic Carbon (–COOH)[20]. And this indicates the absence of free carboxylic acid or ester group of triglyceride on Fe_3O_4 nanoparticles coated with lipids. Thepeak at 284,7 eV (Fig. 1, *a, b)* is attributed to the Carbon atoms in the aliphatic chain (C–C); and the peaks at 288,4 eV (Fig. 1, *a*) and 289,2 eV (Fig. 1, *b*) are related to carboxylate ($–COO^{-}–$). That agrees with the received data from the previous literature [9].

On the spectra (Fig. 1, *c, d*) the characteristic peak of oxides and ferric hydroxides at 710,9 eV is not observed which characterizes the binding of energy to the electron of the basic level of Fe2 $p_{3/2}$ [9]. However, in the experimental samples 1 (d) and 2 (e),

an absorption band appeared in the area ofhigher binding energies 724,7 eV (Fig. 1, в) and 725,2 eV (Fig. 1 , *d*). This absorption band is related to the carboxylate of the ferrum [9].

The spectra of X-ray photoelectron spectroscopy (RPEC) of the level C 1s and Fe 2 p give one more confirmation of the chemical structure of the experimental samples of the system of "lipid-NPs Fe_3O_4" system. Indicating the formation of the chemical bonds between the atoms of the Ferrums NPs Fe_3O_4 and lipids Oxygen atoms (higher fatty acids, in particular, linoleic, and triglycerides of oils and fats, in particular sunflower oil).

Conclusions

The chemical composition of the surface layers in the experimental samples of the system "lipid-NPs Fe_3O_4" was established by the method of X-ray photoelectron spectroscopy (RPES). On the spectra of samples 1, 2, the absorption band C 1s at 290 eV is not observed which corresponds to carboxylic Carbon (–COOH). That is no free carbonic acid or ester group. The peak at 284,7 eV (in samples 1, 2) is attributed to Carbon atoms in the aliphatic chain (C–C); and the peaks at 288,4 eV (sample 1) and 289,2 eV (sample 2) are bound to carboxylate (–COO^-–). The spectra of samples 1, 2 do not show the characteristic peak of oxides and ferrous hydroxides at 710,9 eV, however, the absorption band appeared at 724,7 eV (sample 1) and 725,2 eV (sample 2). This absorption band is related to the carboxylate of the ferrum. All this points to the formation of the chemical bonds between the atoms of Ferrum of NPs Fe_3O_4, and the lipids Oxygen atoms.

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The structure of the Abstract:

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