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CONTENT

ASSESSMENT OF COLOR OF MEAT USING THE METHOD OF COMPUTER COLORIMETRY

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Abstract

In the article is considered a possibility to use the accessible modern digital technique: flatbet scanners, digital photocameras and web-cameras for determination of color of foodstuff.

The offered method allows get the digital image of studied sample and count information about the values of color coordinates of its every pixel that characterizes the color of meat half-finished product such as meat powder. The assessment of this raw material was carried out in dry and restored state.

At measurement of color coordinates of the meat powders in native state there was determined the method of sample preparation for getting the mean value of color with the least standard deviation ~20 %. Thus, according to the studies, the sample of dry meat half-finished product must be reduced to fragments less than 0,2 mm.

Availability of this method allows use it for assessment of the quality of dry meat half-finished products according to color parameter.

Keywords: color coordinates, computed colorimetry, dry meat half-finished product, analysis of image, yellowness index.

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1. Introduction

According to traditional interpretation, color it is a characteristic of luminous stimulus that creates certain visual perception [1]. From the other side, color is subjective characteristic of the light, it reflects the ability of human eye to recognize the length of wave of electromagnetic radiation in visible spectrum with wave length 360...780 nm [2].

In practice the color of most raw material and ready production is determined organoleptically [3]. The sensor method is insufficiently precise because of possible subjectivity of taster's views [4], but this very method gives the best definition of product for consumer. Physical-chemical methods of assessment of coloring are most precise but need the long sample preparation, special equipment and use of expensive reagents [5].

Progressive development of digital technique gave impulse to creation of direction – the method of computer colorimetry, which essence is in assessment of color in the system of color coordinates after analysis of digital images of the studied sample [6–9].

The aim of the work was to carry out an experimental verification of possibility to use the method of computer colorimetry for the control of quality of powdery foodstuff. For attaining this aim it is necessary to solve the following problems: to study the color of powders from the meat row materials dried by the different methods, in dry and restored state using computer colorimetry.

2. Materials and methods of research

The essence of the method of computer colorimetry is in digitization of image of studied sample and its further computer processing for the control of production quality on color, fragments form or surface morphology [9, 10]. This method allows realize the analysis of studied products fast, automatically and objectively.

On the **Fig. 1** is schematically presented the principle of used methodology.

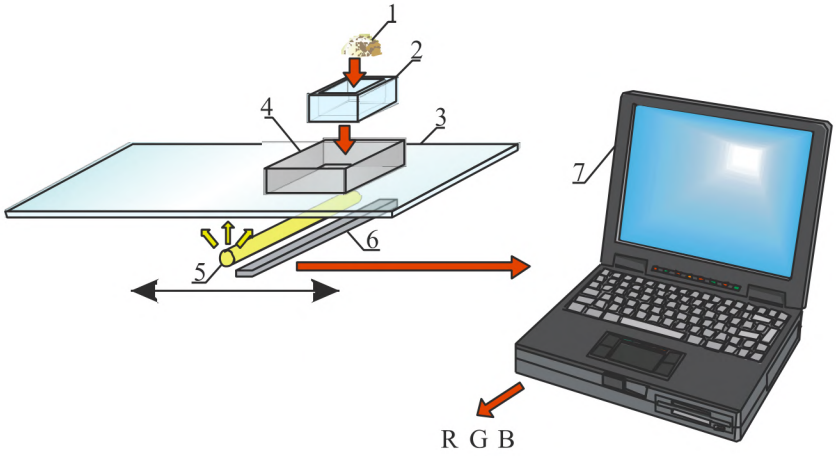

Fig. 1. Scheme of measurement of color coordinates of the studied sample: 1 – studied sample; 2 – cell of transparent glass; 3 – working glass of flatbet scanner; 4 – cell section; 5 – lighting source; 6 – radiations receiver; 7 – personal computer

The samples 1, that is powder or dense substance (powder restored with water) ~5 g (**Fig. 1**) were evenly placed in the glass cell 2 (glass does not distort the received digital image), set in the special box – cell section, that allows standardize conditions of sample lighting, exclude highlights and side flares. The cell section is placed on working plane of flatbet scanner 3 Epson Perfection V370 Photo (Indonesia). To get the digital image there was selected the mode of usual scanning of non-transparent objects.

The mobile matrix of analogous-digital converter 6 – Epson matrix CCD (Indonesia), with diode light 5 – LED white (China), transforms photons energy, reflected from the object into eclectic signal that is subjected to digitization.

The coded signal comes on personal computer 7 (minimal requirements: operational system Windows 7 64-bit, main memory >2 GB) as digital image with amplification JPG.

Assessment of color of foodstuff can be carried out on the different color models: RGB, CIELab и XYZ.

Description of the color according to RGB model is based on fact that any color consists of the sum of three linearly independent colors – red R, green – G and blue – B. The white color has the values of coordinates: R=255, G=255 and B=255, and black R=0, G=0 and B=0.

CIELab color model has the separate brightness coordinate – L (0…100 units), color area is defined by the values «a» and «b». These values change: «a» – from green «–128» to purple «+127» and «b» – from blue «–128» to yellow «+127».

XYZ color model is a unified system that determines color of object as three-dimensional vector coordinates.

It must be noted, that wide list of applied computer programs (for example, Colorlab, Microsoft Word 97-2003, Epson Scan – program that is attached to scanner, CorelDraw and others) has in its content functional possibility for reading color coordinates in one or another systems. The recalculation in several coordinate systems allows choose such coordinate system that is more sensitive to the change of studied product.

For analysis of the color of received digital images was applied program, written in MathCad environment, distributing every pixel of image in digital values of coordinates in RGB system. Synchronously it was carried out the recalculation of color from RGB model in CIELab and XYZ using CorelDraw and ColorLab programs respectively [11].

At that the pixels body or mean values of coordinates of selected part of image can be analyzed (**Fig. 2**).

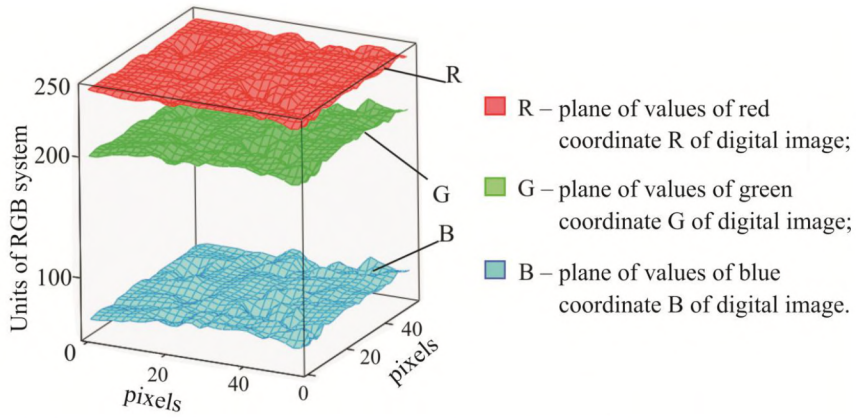

Fig. 2. Value of constituent coordinates of pixels body of digital image of studied sample

For assessment of color are also applied such parameters as saturation C_{ab} (1):

$$C_{ab} = \sqrt{(a)^2 + (b)^2} \text{ units,} \quad (1)$$

where a and b – values of coordinates in CIELab system, units; Y – yellowness index [12] (2):

$$Y = 100\frac{(1.28 \cdot x - 1.06 \cdot z)}{y} \text{ units,} \quad (2)$$

where x, y, z – color characteristics of studied object.

The aforesaid parameters give additional information about the color of image. For example, saturation characterizes intensity of coloring of the studied sample, yellowness index – rated parameter that is agreed with visual perception for samples, in which appeared the yellow (positive index) or blue (negative index) tint.

2. 1. Experimental procedures

At experimental procedures were studied the meat half-finished products, namely the dried beef. There were selected samples, received by the different methods of drying: with mixed heat supply and traditional [13] (for Ukrainian territory) convective drying (**Fig. 3**). After assessment of color of powders there was carried out their restoration with water: to the one share of dry meat were added 3 shares of water of 20 °C and their color was measured in 30 minutes.

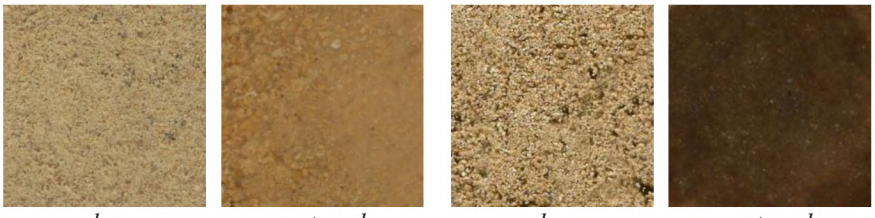

Fig. 3. Digital images of meat samples: *a* – sample received by drying with mixed heat supply and *b* – sample received by convective drying

The meat dried at mixed heat supply is realized on market in granulated form as opposite to the friable state of meat of convective drying. That is why there was carried out the study of different variants of sample preparation of dried meat. It was established, that with increase of size of fragments of meat powder the standard deviation (deviation from the mean value shows how large are the limits of changes of brightness values of image) increases: thus for fragment with mean size Ø=4,5 mm the standard deviation is ~42 %, for fragments Ø=3,0 mm – 38 % and for powder

with Ø=0,25 mm – 18 %. That is why it was offered for redpoducibility of the method of computer colorimetry to carry out the reduction of analyzed sample to the powder state. Such sample preparation allows get the real values of color of the sample.

3. Results of research

The received digital images of the meat half-finished product in native and restored with water states, assessed on coordinate values in RGB, CIELab and XYZ systems and also the rate values of saturation and yellowness index are presented in **Table 1.**

Table 1

Characteristics of the samples of meat half-finished materials in native and restored state in RGB, CIELab and XYZ color models

Samples	Color coordinates, units									Saturation, C_{ab} units	Yellowness index, Y units
	RGB			CIELab			XYZ				
	R	G	B	L	a	B	X	Y	Z		
Dry powders											
Meat with mixed heat supply	169	145	103	62	5	26	30,64	30,40	13,16	701,00	**83,12**
Meat of convective drying	170	142	98	61	6	28	29,27	29,25	11,85	820,00	**85,14**
Restored powders											
Meat with mixed heat supply	153	112	62	51	12	35	20,99	19,27	5,38	1369,0	109,83
Meat of convective drying	67	48	27	22	7	17	3,48	3,52	1,18	338,0	104,10
Control – boiled meat	198	177	154	74	5	15	46,80	46,70	28,40	250,00	63,81

Experimentally received data (**Table 1**) of the meat powders indicate identity of their color in dry state. According to this, it can be recommended to control the quality of this raw material on parameters of color of dried meat in set limits: R=165…175 units, G=140…150 units and B=95…105 units; L=60…63 units, a=4…7 units and b=25…30 units and X=28…31 units, Y=28…31 units and Z=11…14 units in correspondent color systems. At that the yellowness index is ~84 units. The yellowness index that complexly includes the values of color coordinates can be selected as the main parameter of color of dry meat powder.

The color of meat is conditioned by myoglobin pigment that changes under the influence of several factors and as a result changes the color of meat products.

The different processes of pigments changes flows depending of method of production of meat half-finished product. That is why at comparison of values of coordinates of color of restored and boiled (analyzed as control sample) meat samples took place the clearly observed difference. The yellow index for boiled beef was ~64 units unlike the restored samples with more than 100 units.

The color of restored meat gives possibility to assess the method of its drying. Analysis of color of restored meat powders allows made conclusion that the difference of processing method influences the change of meat pigments, because the values of color coordinates are differ. Thus, the meat powder, received by convective drying has significantly more dark color than the other sample (dried by the method with mixed heat supply) that is proved by the less values of RGB coordinates and L brightness.

In further it is planned to carry out the study of influence of the factor of meat processing on kinetics of change of its pigments at getting the meat half-finished products and their use in preparation of ready production.

4. Conclusions

The offered method of computer colorimetry gives possibility to control the half-finished products on color parameter. The color value of dry meat must be normalized by the value of yellowness index in limits Y=84±1,5 units. This parameter gives a possibility to take into account the change of all color coordinates for dry meat half-finished product. For granulated products must be carried out the preliminary reduction to the size of fragments less than 0,2 mm. Such preliminary

stage allows assess the color of product by analysis of the digital image with the least value of standard deviation.

For identification of meat, received by the different methods of drying, it must be studied the kinetics of pigments change depending on such factors: temperature, air presence and effect duration.

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THE STUDY OF QUALITY AND SAFETY PARAMETERS OF THE SPECIAL VODKA OF NATIVE PRODUCTION

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Abstract

Insofar as country is in unstable situation, many goods and products of the low quality and falsified ones appeared on the native market. Excise alcohol production is the most beneficial for falsification, because its profitability is very high.

Among alcohol drinks vodka stays the most popular one that is produced in large scales. Last time the consumption of alcohol drinks increased by 22 %, so, the efforts of consumption policy must be directed on the rise of culture of drinking behavior and prophylaxis strategy.

The parameters of quality and safety of the special vodka of TM "Home rye pervak" are studied. The normative documents that regulate quality of the special vodka in Ukraine are analyzed. There were studied organoleptic, physical-chemical parameters and safety of the special vodka of TM "Home rye pervak" made by LTD "UDK" (Poltava, Ukraine).

It was established, that special vodka of TM "Home rye pervak" made by Ukrainian producer "UDK" corresponds to all requirements of the national standard of Ukraine as to physical-chemical parameters and the ones of safety.

Keywords: vodka, quality, safety, strength, alkalinity, aldehydes, fusel oils, esters, alcohol.

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1. Introduction

For today there is a possibility to create the civilized goods market that would develop the economy of Ukraine. The internal Ukrainian market is filled with wide spectrum of goods of the native and foreign production that leads to decrease of pressure of consumer demand. In these conditions the need to improve the quality of production, to require safe and harmless production for consumers increases.

These scientists studied the parameters of safety and quality of vodka in Ukraine [1–7].

The problem of quality and safety of food products is certainly the one most important for consumers. According to the article 1 of the Law of Ukraine "On the main principles and requirements to the quality and safety of food products" [8] food product is considered as unacceptable for consumption by human, if it, among the other, does not correspond to the obligatory minimal specifications of quality.

The producers of alcoholic products in Ukraine try to improve the quality of their production by the different ways: use different components that soften taste; purify both the ready product and its components; prepare water by the different ways and so on. But vodka is assigned to the most often falsified group of alcoholic products, because it is easy in production and is in demand among consumers.

Falsification of vodka quality is attained by the spread and specific ways by adding water; introduction of substances, not provided by recipe; full or partial replacement of ethanol by technical alcohol; use of the water that does not fit for preparation of alcoholic products. That is why the study of parameters of quality and safety of such food product as special vodka is timely and urgent.

The object of research is the special vodka of TM "Home rye pervak" of the first distillation made by "UDK" LTD (Poltava). Characteristics of the object of research: volume – 0,5 L, strength – 40 %.

The realized researches were aimed at comprehensive, complex study and determination of the main parameters of quality of special vodka of TM "Home rye pervak" for determination of the level of its quality and safety and also the correspondence of requirements of normative documentation [9].

2. Materials and methods of research

The assessment of physical-chemical quality parameters of the special vodka of TM "Home rye pervak" was realized by the standard methods according to SSTU "Vodkas and special vodkas. Rules of taking and methods of testing" [10].

Content of heavy metals was determined by voltammetric method.

2. 1. Experimental procedures

For assessment of physical-chemical quality parameters of the special vodka of TM "Home rye pervak", made of alcohol "Lux", were chosen such parameters as strength, alkalinity, mass concentration of aldehydes, mass concentration of fusel oil, mass concentration of esters, volume part of methyl alcohol.

The content of alcohol is determined by dependence of its concentration from the relative density of solution that is determined by aerometric method using the glass alcoholmeter (**Fig. 1**).

Fig. 1. Determination of strength of vodka of TM "Pervak" with help of glass alcoholmeter

Alkalinity of vodka was determined in such a way – sample of vodka of 100 cm^3 was placed in conical flask of 250 cm^3 and was titrated in solution of methyl red by solution of hydrochloric acid with concentration 0,1 mol/dm^3 up to coloration of yellow tint of solution in orange rose one (the start of coloration) (**Fig. 2**).

The final result of analysis was considered as arithmetical mean of the results of two parallel values that are approximated to the first decimal digit.

Mass concentration of aldehydes in recalculation on acetic aldehyde in absolute alcohol in vodka was determined by the method that is grounded on reaction of alehydes, present in studied vodka, with fuchsin-sulfuric reagent (**Fig. 3**).

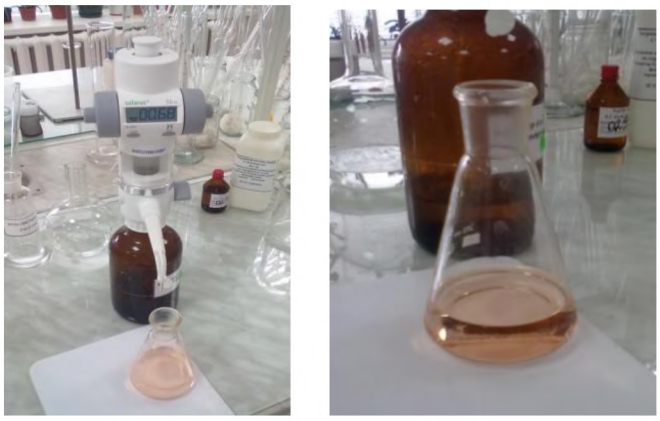


Fig. 2. Determination of alkalinity of special vodka of TM "Pervak"

Fig. 3. Determination of mass concentration of aldehydes in special vodka of TM "Pervak"

Mass concentration of fusel oil in recalculation on mixture of isoamyl and isobutyl alcohols (1:1) in absolute alcohol was determined by reaction of fusel oil with salicylic aldehyde at presence of concentrated sulfuric acid using photoelectrocolorimeter.

Mass concentration of esters in recalculation on acetic-ethyl ester in absolute alcohol was determined with help of photoelectrocolorimetric method that is grounded on determination of intensity of coloration after reaction of ferric chloride (III) hexahydrate with hydroxamic acid, formed as a result of contact of esters of studied vodka with muriatic hydroxylamine in alkaline medium, and also gas chromatographic method.

The volume part of methyl alcohol in recalculation on absolute alcohol in vodka was determined by photoelectrocolorimetrc method that is grounded on measurement of intensity of coloration as a result of contact of disodium salt of chromotropic acid (1,8-dioxy-naphthalene-3,6-disulfonic acid) with formaldehyde that is formed as a result of acidation of methyl alcohol, contained in studied vodka, by potassium permanganate.

The content of heavy metals was determined with the help of voltammetric method that is grounded on registration and study of dependence of voltage that flows through electrolytic focus from external superimposed voltage.

Graphic presentation of this dependence (voltammetrogram) shows peaks of voltage, which place on axis of potentials is a quality characteristics and height of peak, proportional to ions concentration in solution, is a quantity characteristics.

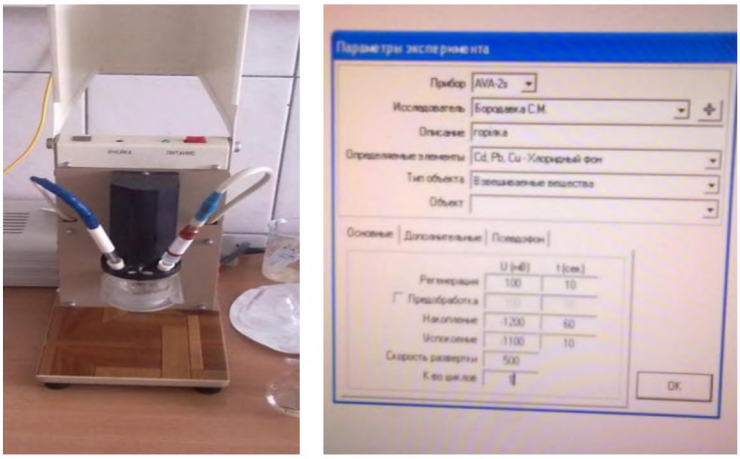


Fig. 4. Determination of content of heavy metals in special vodka of TM "Pervak"

3. Results of research

The results of research of physical-chemical quality parameters of the special vodka of TM "Home rye pervak" by the standard methods are presented in the **Table 1.**

Table 1

Results of research of physical-chemical quality parameters of the special vodka of TM "Home rye pervak"

Name of parameter	Requirements according to SSTU 4256:2003	Value of received results
Strength, %	37,5–56,0	39,8
Alkalinity, cm^3, not more than	3,5	0,68
Mass concentration of aldehydes in recalculation on acetic aldehyde in absolute alcohol, mg/dm^3, not more than	6,0	2,7
Mass concentration of fusel oil in recalculation on mixture of isoamyl and isobutyl alcohols (1:1) in absolute acid, mg/dm^3, not more than	3,0	0,7
Mass concentration of esters in recalculation on acetic-ethyl ester in absolute alcohol, mg/dm^3, not more than	7,0	1,0
Volume part of methyl alcohol in recalculation on absolute alcohol, %, not more than	0,01	0,005

Analysis of voltammerograms of the sample of special vodka of TM "Home rye pervak" gives information about qualitative and quantitative content of analyzed solution (**Fig. 5**).

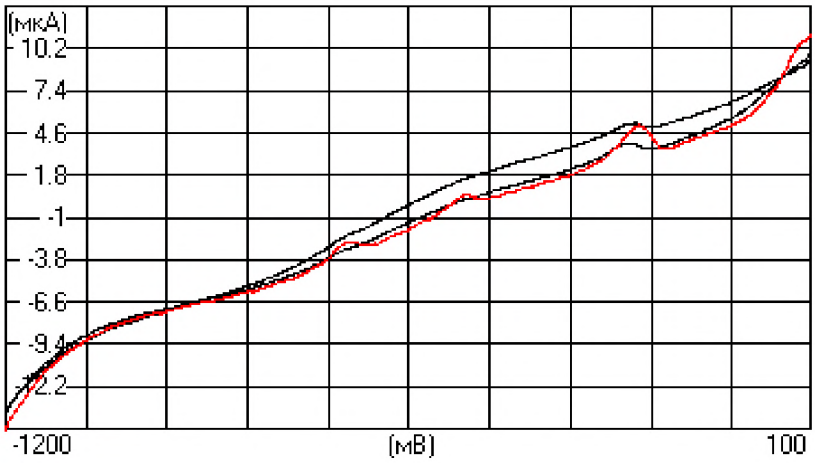
Results of measurements are given in the **Table 2.**

Table 2

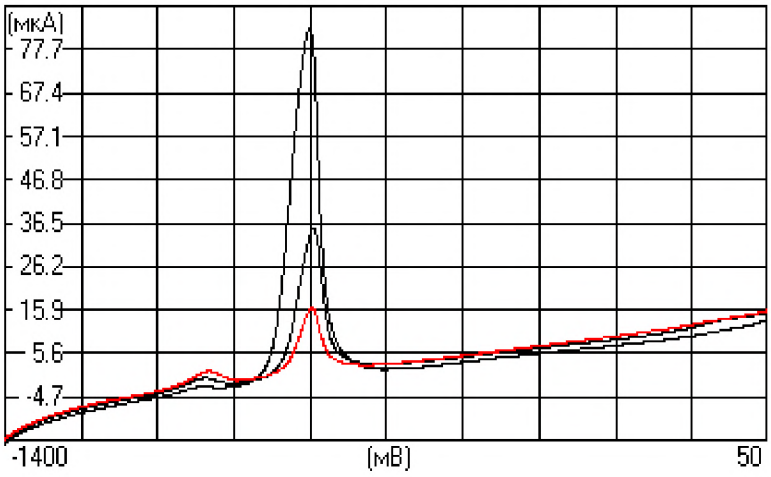
Heavy metals content in special vodka of TM "Home rye pervak"

Heavy metals	Allowable level, mg/kg, not more than	Values of received results, mg/kg
Cadmium	0,03	**0,0134**
Copper	5,0	**0,0539**
Lead	0,3	**0,0298**
Zinc	10,0	**0,8540**

The special vodka of TM "Home rye pervak" corresponds to the requirements of SSTU 4256:2003 as to the heavy metals content [9].



a



b

Fig. 5. Voltammetrograms of the heavy metals content in special vodka of TM "Home rye pervak": *a* – cadmium, lead, copper; *b* – zinc

4. Conclusions

1. It was established, that Ukrainian producer "UDK" LTD of the special vodka of TM "Home rye pervak" corresponds to all accepted requirements as to packaging and marking, provided by SSTU 4256:2003 [9].

2. The researches elucidated that the special vodka of TM "Home rye pervak" made by "UDK" LTD corresponds to requirements, provided by SSTU 4256:2003 by physical-chemical quality parameters (strength, alkalinity, mass concentration of aldehydes, mass concentration of fusel oils, mass concentration of esters, volume part of methyl alcohol) and by safety parameters (cadmium, copper, lead, zinc content) [9].

It can be stated, that this product, chosen as object of research, is high-quality and safe for consumption.

Acknowledgment

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STABILITY AND MORPHOLOGICAL CHARACTERISTICS OF LIPID-MAGNETITE SUSPENSIONS

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Abstract

The study of stability of lipid-magnetite suspensions (LMS) was carried out using photometry and electronic microscopy. All suspensions are rather stable in time. The best results in stability were demonstrated by suspensions with ratio Fe_3O_4:SAS=0,02:0,35 g or 0,04 mass %:0,70 mass % and 0,025:0,35 g or 0,05 mass %:0,70 mass %. The sizes of magnetite particles from SAS were determined as – <d>~76 nm.

It was established, that with time (0–48,0 hours) and growth of wave length (210–1000 nm) is observed the gradual increase of transmission coefficient from 25 % (210 nm) to 71,9 % (1000 nm) at 0 hours of suspension ageing; from 27,5 % (210 nm) to 81,2 % (1000 nm) at maximal time of suspension ageing (48 hours).

There parameters of LMS were determined: concentration of particles – $N=1,43\cdot10^{12}$ cm^{-3}, in 48 hours concentration decreased by 20 % ($N=1,19\cdot10^{12}$ cm^{-3}); r=38 nm, n=1,48, κ=0,01. The function of particles distribution by sizes is rather narrow and symmetric that certifies the system of synthesized nanoparticles as homogenous with low degree of polydispersity.

Ultraviolet spectrums of LMS and their components were fixed and analyzed. Comparison of transmission spectrums of suspensions with different degree of dilution testifies to the chemical identity of samples.

There were studied kinetic dependencies of transmission coefficient for suspensions with different magnetite concentration (Fe_{gen}), on which base was calculated the effective radius of particles of stabilized magnetite: 76–168 nm. The mean radius of particles in lipid suspension of magnetite without stabilizer (r_{eff})=400 nm. Visually LMS manifested the high aggregative stability with high sedimentation time 48 hours.

It was established, that LMS can be used as biologically active and feed additives with complex effect: manifest antioxidant activity, are the source of easily assimilated iron, improve quality and increase storage terms of fat-containing products. Thus, introduction of LMS in foodstuff improves its quality, nutritive and biological value.

Keywords: magnetite, photometry, lipid-magnetite suspension, morphology, effective mean radius, function of particles distribution by sizes, surface active substance (SAS), aggregative and sedimentation stability.

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1. Introduction

The important problem, solved by food industry, is the widening of assortment of production with raised nutritive value and long storage term and also economy of deficient types of raw material [1].

As biologically active additive that has antioxidant effect and is a source of easily assimilated iron [2] the offered magnetite – double oxide of bi- and trivalent ferum ($FeO \cdot Fe_2O_3$) [3].

The uniqueness of magnetite properties allows recommend Fe_3O_4 as feed additive of complex effect in lipid-magnetite suspensions (LMS) [4–7].

That is why creation of LMS stable in time; analysis of process of sedimentation and determination of their morphologic characteristics is a topical and important problem.

2. Materials and methods of research

At getting suspensions was used the ultra-thin magnetite (with particles size 30–60 nm), synthesized according to the method of co-precipitation of salts of bi- and trivalent ferum in alkaline medium [8]. According to this method, magnetite is received at mixing of water solutions of iron salts (II) and (III) with concentrated water solution of hydroxide ammonium (25 %) with further washing by water.

In the study was used the sunflower oil, refined and deodorized according to SSTU 4492:2005; unrefined corn oil SSTU 8808-2003 "Corn oil. Technical conditions (SSTU 8808-2000. IDT)"; Soy unrefined oil SSTU 4534:2006 "Soy oil. Technical conditions"; pig fat of SSTU 25292-82; beef fat, SSTU 1288-41; unrefined salomas for margarine industry TC 9145-181-00334534-96, TC 15.4-13304871-005:2005; surrogate of milk fat "Vioil – milk fat 3" TC 15.4-13304871-005:2005, SSTU 53796-2010; cakes fat "Shortening" TC U 15.4-00373758:022-2006; SAS (monoacylglycerol) Dimodan HP.

On the **Fig. 1** are given the following lipids: oils (soy, corn, sunflower); salomas; fats (pig, beef and cakes: "Vioil – milk fat 3" and "Shortening"), **Fig. 1.**

Fig. 1. Studied lipids: in glass bottles – oils (soy, corn, sunflower); in plastic package – salomas and cakes fats "Vioil – milk fat3" and "Shortening"); unpackaged – animal fats (pig and beef)

Lipid-magnetite suspensions (LMS) were received by technology [6].

The study of stability and concentration of suspensions, morphological features of particles was carried out using spectrophotometry (spectrometer Spekol 11) ("Milaform" production-service center of trial laboratory equipment, Russia), PE-5400 UV ("Ecochem" Company, Russia) and electronic microscopy (transmission electric microscope (TEM) JSM-820 (JEOL firm, Japan).

2. 1. Experimental procedures

The method of determination of stability and morphological characteristics of lipid-magnetite suspensions is based on analysis of weakening spectrum of suspension with nanoparticles. There is measured the dependence of transmission coefficient T of cell with suspension from the wave length λ of optic radiation that passes through the cell. Spectrophotometric method is based on the Buger-Lambert-Beer law:

$$I = I_0 e^{-\alpha l}, \quad (1)$$

where I_0 – intensity of incident light, I – intensity of light, passed through the cell, l – thickness of suspension layer in cell (1,0 cm), α – coefficient of light weakening.

Transmission coefficient T is defined by the formula:

$$T = \frac{I}{I_0}, \quad (2)$$

where I_0 – intensity of incident light, I – intensity of light, passed through the cell, T – transmission coefficient.

Weakening coefficient α is connected with transmission coefficient T by the next formula:

$$\alpha = -\frac{\ln T}{l}, \quad (3)$$

where l – thickness of suspension layer in cell (1,0 cm), T – transmission coefficient.

If the unit of medium volume includes N equal particles, weakening coefficient can be determined as following (4):

$$\alpha(N, r, m, \lambda) = N\pi r^2 Q(r, m, \lambda), \quad (4)$$

where r – particle radius, m=n–iκ, n – refraction index, κ – absorption index, λ – wave length in medium that surrounds particle, Q – weakening effectiveness factor. The last parameter indicates what part of energy is emitted (diffused and absorbed) by the unitary particle from the radiation beam incident on medium.

If medium contains particles of the different sizes, the formula (4) is transformed into (5):

$$\alpha(N, r, m, \lambda) = N\int_0^\infty Q(r, m, \lambda)\pi r^2 f(r)d(r), \quad (5)$$

where f (r) – function that describes the particles distribution by sizes.

At solving such tasks it is usually thought, that particles are spherical. In many cases it is true – for example, in emulsions. If particles have incorrect form, the characteristics of light, diffused with a large number of chaotically oriented particles do not essentially differ from the ones of light, diffused with spherical particles.

The spherical weakening effectiveness factor can be calculated by formulas, known from diffraction theory [9, 10]:

$$Q = \frac{2}{\rho^2}\sum_{l=1}^{\infty}(2l+1)\mathrm{Re}\,(a_l + b_l), \quad (6)$$

where

$$a_l = \frac{m\psi_l(m\rho)\psi_l'(\rho) - \psi_l'(m\rho)\psi_l(\rho)}{m\psi_l(m\rho)\zeta_l'(\rho) - \psi_l'(m\rho)\zeta_l(\rho)}, \quad (7)$$

$$b_l = \frac{m\psi_l'(m\rho)\psi_l(\rho) - \psi_l(m\rho)\psi_l'(\rho)}{m\psi_l'(m\rho)\zeta_l(\rho) - \psi_l(m\rho)\zeta_l'(\rho)}, \quad (8)$$

where $\psi_l(\rho)$ and $\zeta_l(\rho)$ Bessel-Riccati functions, $\rho=2\pi r/\lambda$.

After experimental determination of the spectrum of light weakening by the medium with particles and solution of integral equation (5), the function of particles distribution by sizes f(r), their complex refraction index m and concentration N can be found.

The object of research was the soy-magnetite suspension with refraction index 1,48. The cell with studied suspension was placed in spectrometer Spekol 11 ("Milaform" production-service center of trial laboratory equipment, Russia), PE-5400 UV ("Ecochem" Company, Russia).

The transmission spectrums of diluted suspensions (concentration 4,85–38,9 mg/l, diluter ethanol or isooctane were analyzed in regime of spectrum measurement (210–1000 nm) and kinetic measurements on the same wave length (600 nm) and duration of suspension ageing 6000 s. For assessment of time of suspension sedimentation t_{sed} the received kinetic dependences of transmission coefficient from time (or area of dependences) were linearly approximated. The mean effective radius of particles was determined by the following equation [11]:

$$r_{eff} = \sqrt{9\eta\upsilon_{sed} / 2(\rho - \rho_0)g}, \quad (9)$$

where η – viscosity of disperse medium $1510\cdot10^{-3}$ Pa·s (for water $1\cdot10^{-3}$ Pa·s), ρ – mean actual density of particles, consisted of magnetite and monoacylglycerol (near 4,15 g/cm^3), ρ_0 – density of disperse medium (in our case soy oil – 0,925 g/cm^3), υ_{sed} – sedimentation speed, found as $\upsilon_{sed}=H/t_{sed}$. Here H – height of liquid column in cell is equal 2 cm, g=9,8 m/s^2 – gravitation acceleration of free fall.

Weakening coefficient was calculated by formula (3). Numerous mathematical methods allow solve integral equation (5) and find function f(r) and parameters r, n, κ, N. But at the same time it is necessary to solve the problem of search of the minimum of function of the four variables. As far as such function can have many minimums, the absolutely incorrect result can be found. At the same time the weakening effectiveness factor is described by the bulky expressions (6)–(8), so the time, necessary for solution of equation (5) using the modern computers is very long (tens of minutes). That is why some simplifications are used in setting and solution of the problem.

– It was thought, that particles distribution by sizes is described by the following formula:

$$f(r) = \frac{\beta^{\mu}}{G(\mu+1)} r^{\mu} e^{-\beta r}, \quad (10)$$

where f (r) – gamma – function, μ and β – parameters of function.

In the works [12–14] it was noted, that this function well describes the distribution of micro- and nanoparticles by sizes in emulsions and suspensions. The values of μ and β parameters are determined by the position of function maximum r_{max} and its width Δr by equation (10):

$$\mu = \left(\frac{2{,}48 r_{max}}{\Delta r}\right)^2, \ \beta = \left(\frac{2{,}48}{\Delta r}\right)^2 r_{max}.$$

In such case the task is reduced to determination of such values of μ and β parameters, at which the equation (5) is correct.

– To decrease the time of calculations it was used the approximated expression for the weakening effectiveness factor. There is a series of mathematical expressions [12–14], each of which is correct for the certain conditions – very big or very little (comparing with wave length) particles,

ideally reflecting particles or ones with a small refraction index. For nanoparticles ($\rho<<1$) it is expedient to use expansion of the expression (6) in series by degrees ρ [9, 11]:

$$Q = -\mathrm{Im}\left[4\rho\frac{m^2-1}{m^2+2}+\frac{4}{15}\rho^3\left(\frac{m^2-1}{m^2+2}\right)^2\times\frac{m^4+27m^2+38}{2m^2+3}\right]+\mathrm{Re}\left[\frac{8}{3}\rho^4\left(\frac{m^2-1}{m^2+2}\right)^2\right].$$

At $\rho<0,6$, n=1.2 ... 2, $\kappa<0,75$ error of this series does not exceed 2 %.

– Integral (5) is substituted by sum:

$$\alpha(N,r,m,\lambda) = N\pi\delta r\sum_j Q(r,m,\lambda)r_j^2 f\left(r_j\right).$$

Index j in this expression changes from null to j_{max} that determines the number of node points on the integration area. The distance between node points is equal:

$$\delta_r = \frac{r_{max}-r_{min}}{j_{max}},$$

where r_{min}=0, r_{max}=0,05 mcm (50 nm) – diapason of possible values of radiuses of particles, measured in experiment. It also shortens the calculations time by 20–30 %.

Processing of experimental data was realized in two stages:

1. With the help of equation (4) was determined the mean particles radius r and parameters n, κ and N. The function was formed for it:

$$S(r,n,\kappa,N) = \sum_{i=0}^{i_{max}}\left[N\pi r^2 Q(r,n,\kappa,\lambda_i)-\alpha_i\right]^2,$$

where λ_i – wave lengths, at which was measured weakening coefficient α_i, and with the help of the least square method were determined the values of parameters r, n, κ, N, at which function (r, n, κ, N) has minimum.

The found values of these parameters essentially depend on initial approximations that are used to find minimum. That is why the additional control was realized over the form of graphs with experimental points α_i and curve α (r, n, κ, N, λ), that must passes near these points. The value of function S (r, n, κ, N) was also controlled; it also depends on the initial approximation and must be the least.

2. The received data were used in Mathcad program for determination of parameters β and μ in function of particles distribution by sizes. The studied function was:

$$S(r_{max},\Delta r) = \sum_{i=0}^{i_{max}}\left[N\pi\delta r\sum_j Q(r,m,\lambda_i)r_j^2 f(r_{max},\Delta r,r_j)-\alpha_i\right]^2$$

and the values of parameters r_{max} and r, at which it is minimal, were determined.

For calculations and analysis of experimental data are also needed the values α_i and λ_i, determined by formulas (11), (12):

$$\alpha_i = -\ln(T_i/100)/l, \quad (11)$$

$$\lambda_i = \lambda_0/n_0, \quad (12)$$

where λ_0 – wave length in air, mcm (nm); λ_i – wave length in fat (oil), mcm, (nm); l – size parameter (thickness) of cell (1 cm or 10^{-2} m); T – transmission coefficient, %; n_0=1,48 – refraction index of disperse medium (soy oil), determined experimentally.

Determination of size of the system of synthesized magnetite particles, stabilized by the surface active substance (momoacylglycerol) was carried out by transmission electric microscope (TEM) JSM-820 (JEOL firm, Japan) with possible magnification up to 150000 times. Electronic microscopy it is a direct method of the study of powder particles system. It not only allows recognize the separate particles in their totality and determine their morphological features but also gives idea about the state of surface particles.

The examples for electronic-microscopic studies were prepared by suspension method. In this method of humid preparation of particles the sample is created directly from the studied powder. The films, received by spreading of drop of collodion solution in amylacetate on water surface, were used as backing. The particles of magnetite material, added in composition, were dispersed using ultrasound dispersant USD ("Eco", Ukraine) (ν=35 kHz, t~20 min). Such method of samples preparation does not influence the particle surface – does not remove it that allows receive with the help of microdiffraction the necessary information about crystal structure of the separate particles. In the result of studies were received electronic microphotos, processed by AutoCad 2014 and MathCad 2014 programs.

3. Results of research

The results of measurement of transmission coefficient (T, %) depending on light wave length (λ, nm) in time (ratio Fe_3O_4:SAS=0,05:0,70 mass %; suspension concentration 29,25 mg/l) are given in the **Table 1**

Table 1

Results of measurement of transmission coefficient (T, %) depending on light wave length (λ, nm) in time for soy-magnetite suspension

λ, nm	Transmission coefficient T, % Suspension ageing time τ, hours					ΔT, %
	0	0,5	1,0	24,0	48,0	
210	25	25,6	26,3	26,9	27,5	10,0
250	23	24,1	25,2	26,7	27,2	18,3
300	26	26,5	27,3	28,5	29,9	15,0
350	28,2	29,7	31,4	32,9	34,4	21,9
400	29	30,6	31,9	33,8	35,7	23,1
450	33,1	34,4	35,7	37,3	39,5	19,3
500	31,5	33,8	34,5	35,6	38	20,6
550	30,5	32,6	33,3	34,5	36,8	20,6
600	48,6	50,7	52,8	58,2	63,5	30,7
650	54,6	55,8	58,4	63,5	68,7	25,8
700	57,8	59,6	62,5	66,7	71,3	23,4
750	58,5	60,3	64,6	68,3	72	23,1
800	61,2	62,9	66,5	70,3	74,6	21,9
850	64,5	66,2	68,6	72,5	76,1	18,0
900	69,6	70,9	73,4	76,3	80	14,9
950	71,6	72,3	73,9	76,9	80,9	13,0
1000	71,9	72,5	73,7	77	81, 2	12,9

The typical form of experimental dependence α(λ) for soy-magnetite suspension is given on the **Fig. 2.** At that α_i and λ_i were determined by formula (11), (12) n_0=1,48 – experimentally determined index of disperse medium (soy oil) refraction.

Theoretical curve is built by approximation of experimental data of weakening coefficient dependence from the wave length.

Using equation (4) the mean radius of particles r and parameters n, κ and N were determined. For that the function was formed:

$$S(r,n,\kappa,N)=\sum_{i=0}^{i_{max}}\left[N\pi r^2 Q(r,n,\kappa,\lambda_i)-\alpha_i\right]^2,$$

where λ_i – length of waves, at which the weakening coefficient α_i was measured.

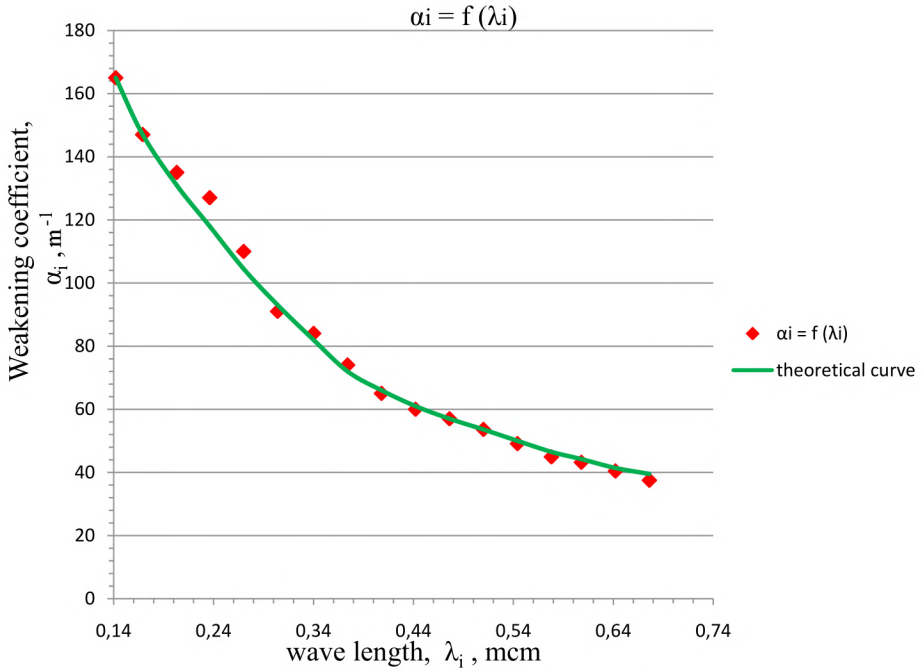

Fig. 2. Dependence of light weakening coefficient (α, m^{-1}) in soy-magnetite suspension from wave length (λ, mcm)

The value of parameters, n, κ, N, at which the function S (r, n, κ, N) has minimum was determined by the least squares method. Calculation of minimization function was carried out using Mathcad.

Then the additional control was realized over the form of graphs with experimental points α_i and curve α (r, n, κ, N, λ), that must pass near these points **Fig. 1**. The value of function S (r, n, κ, N) was also controlled; it also depends on the initial approximation and must be the least.

The following values were received for the studied soy-magnetite suspension: r=38 nm, n=1,48, κ=0,01, $N=1,43\times10^{12}$ m^{-3}.

The values of refraction and absorption indices are satisfactorily agreed with additional data for magnetite: in wave length diapason from 0,4 to 0,8 mcm its refraction index changes from 1,9 to 1,7, and absorption index – from 0,1 to 0,01.

The received data were used in MathCAD for determination of parameters β and μ in function of particles distribution by sizes.

The **Fig. 3** is presented the graph of normalized function of particles distribution f(r) by size.

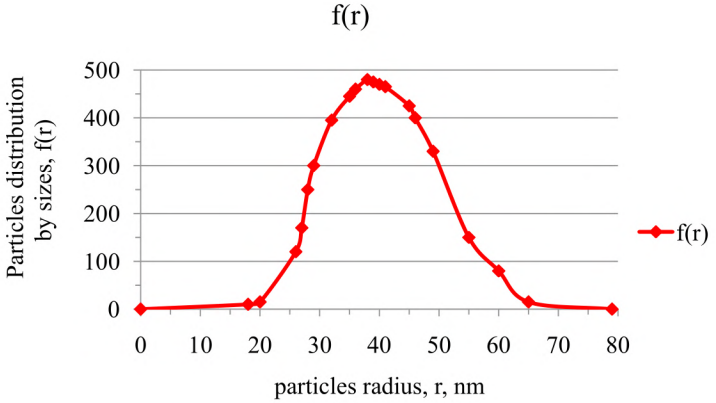

Fig. 3. Particles distribution in soy-magnetite suspension SMS) by sizes, measured by optical method

For comparison on the **Fig. 4** is given histogram of magnetite particles distribution in soy-magnetite suspension (SMS) by size, received in the result of processing of observations using electronic microscope, that demonstrates that the results of both methods are agreed.

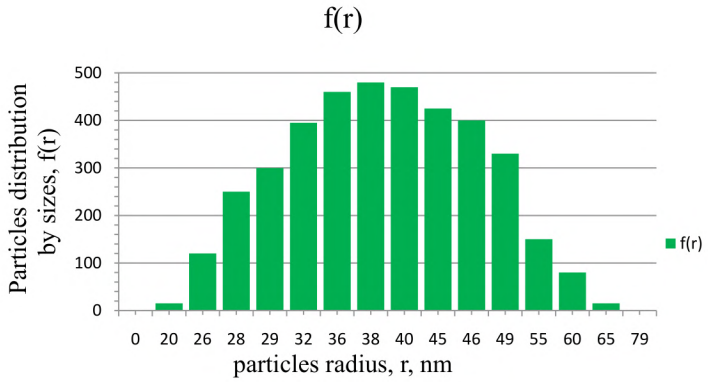

Fig. 4. Histogram of magnetite particles distribution in soy-magnetite suspension (SMS) by size, received in the result of processing of observations using electronic microscope

Knowing the particles size, found their concentration in suspension were found. In the **Table 2** are given the results of study of changes of particles number (concentration) in 1 cm³ of suspension during 45 days.

Table 2

Number of particles in 1cm³ of soy-magnetite suspension (SMS)

SMS ageing time, τ, hour	Number of magnetite particles in 1 cm³ of suspension
0	$1{,}43 \cdot 10^{12}$
0,5	$1{,}42 \cdot 10^{12}$
1,0	$1{,}40 \cdot 10^{12}$
24,0	$1{,}34 \cdot 10^{12}$
48,0	$1{,}23 \cdot 10^{12}$
1080,0	$1{,}19 \cdot 10^{12}$

Concentration (particles number in 1 cm³) at preparation of suspension is equal $N=1{,}43 \cdot 10^{12}$ cm^{-3} (**Table 2**).

According to experimental data, given in the **Table 2**, it is possible to make conclusion as to sedimentation, aggregative stability and dispersity of LMS (on example of SMS). LMS are stable in time – for 1080 hours particles concentration in suspension decreases by 16,8 %; and for 48 hours by 14 % – from $1{,}43 \cdot 10^{12}$ to $1{,}19 \cdot 10^{12}$ cm^{-3} (**Table 2**).

The best stability results were demonstrated by suspensions with ratio Fe_3O_4:SAS=0,02 g:0,35 g or 0,04 mass %:0,70 mass % and 0,025:0,35 g or 0,05 mass %:0,70 mass %.

The following values for soy-magnetite suspension (SMS) were determined: diameter of magnetite particles from SAS – 76 nm, n=1,48, $\kappa = 0{,}01$.

It was established, that with time (0–1080,0 hour) and growth of wave length (210–1000 nm) was observed the gradual increase of transmission coefficient from 25 % (210 nm) to 71,9 % (1000 nm) at 0 hours of suspension ageing; from 41,8 % (210 nm) to 88,7 % (1000 nm) at maximal suspension ageing time (1080 hours) (**Tables 3, 4**).

Experimental data on dependence of transmission coefficient (T,%) from the light wave length (λ, nm) for the soy-magnetite suspensions (SMS) of the different composition with different concentration of $Fe_{(gen.)}$ are given in **Tables 3, 4.**

The assessment of aggregative stability was carried out using kinetic measurements.

On the **Fig. 5** are demonstrated kinetic dependencies of transmission coefficient for suspensions with different magnetite concentrations ($Fe_{gen.}$).

Table 3

Dependence of transmission coefficient (T, %) from the light wave length (λ, nm) for the soy-magnetite suspensions (SMS) of the different composition (suspension concentration 4,85 mg/l)

Light wave length (λ, nm)	Fe_3O_4	Monoacylglycerol (MA)	Soy oil, (SO)	Fe_3O_4+MA	Fe_3O_4+SO	MA+SO	Fe_3O_4+MA+SO
200	13	9	5	9	7	10	10
205	22	9	6	11	9	12	10
225	24	10	6	14	13	16	12
230	23	22	9	20	18	19	14
250	25	28	16	26	23	25	20
275	26	31	27	29	27	28	30
300	28	34	30	35	31	32	33
310	29	37	33	39	35	36	36
350	27	42	38	43	39	39	37
360	28	46	42	40	36	44	38
375	27	51	47	44	40	48	42
400	29	56	52	50	48	52	43
450	26	71	65	47	46	54	44
490	25	77	73	43	44	62	42
500	24	80	76	42	43	66	41
540	23	84	80	41	42	71	40
550	34	86	82	47	49	78	45
600	50	89	85	56	58	82	57
650	60	90	86	64	66	85	67
700	65	91	87	72	70	87	72
750	68	92	88	78	76	90	73
800	70	92	89	82	80	92	74
850	71	92	90	82	80	92	75
900	72	92	90	81	79	92	75
950	72	92	90	80	79	91	75
1000	72	92	90	80	79	91	75

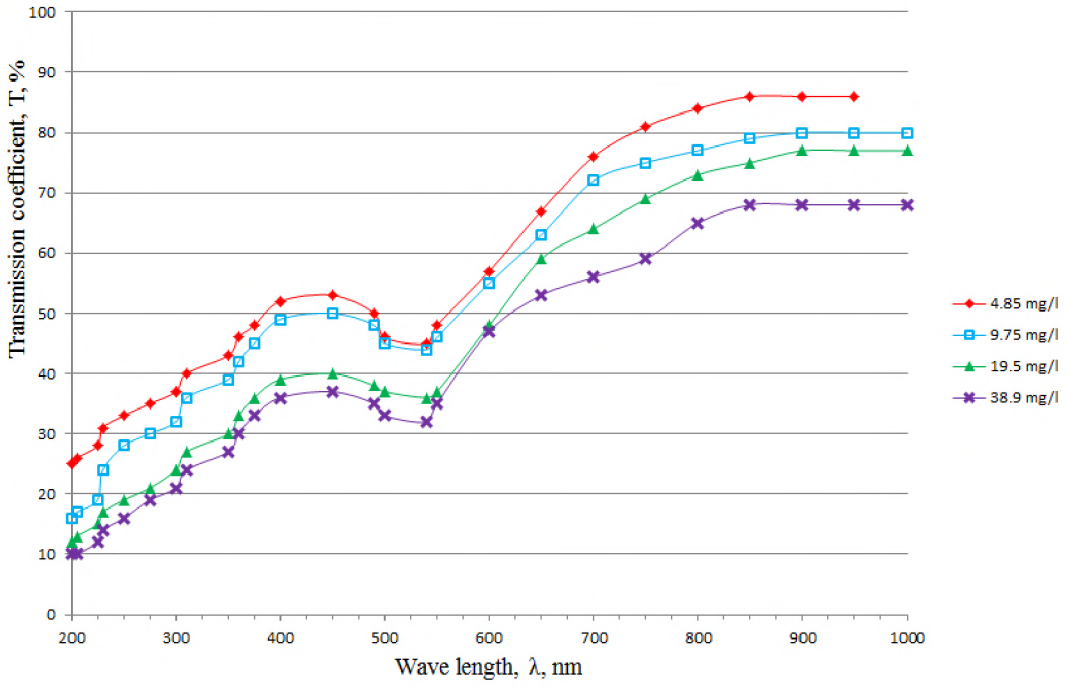

Fig. 5. Dependence of transmission coefficient (T, %) from light wave length (λ, nm) of soy-magnetite suspensions (SMS) of the different concentration

Table 4

Dependence of transmission coefficient (T, %) from the light wave length (λ, nm) for the soy-magnetite suspensions (SMS) of the different concentration

Light wave length, λ, nm	Transmission coefficient T, %			
	$Fe_{gen.}$ In suspension, mg/l			
	4, 85 mg/l	9,75 mg/l	19,5 mg/l	38,9 mg/l
200	25	16	12	10
205	26	17	13	10
225	28	19	15	12
230	31	24	17	14
250	33	28	19	16
275	35	30	21	19
300	37	32	24	21
310	40	36	27	24
350	43	39	30	27
360	46	42	33	30
375	48	45	36	33
400	52	49	39	36
450	53	50	40	37
490	50	48	38	35
500	46	45	37	33
540	45	44	36	32
550	48	46	37	35
600	57	55	48	47
650	67	63	59	53
700	76	72	64	56
750	81	75	69	59
800	84	77	73	65
850	86	79	75	68
900	86	80	77	68
950	86	80	77	68
1000	86	80	77	68

In UV-spectrums (**Tables 3, 4** and **Fig. 5**) are the weak strips of transfer n→π* at 200–210 nm, typical for saturated radicals (monoacylglycerol– MA) and more intense strips of transfer π→π* at 210–230 nm, typical for α, β-unsaturated acyls (soy oil – SO). In magnetite spectrum are observed the wide strips of absorption within 490 and 540 nm, associated with lattice fluctuations of Fe–O–connections in tetra- and octahedral positions of Fe_3O_4. Comparing these curves with dependence of transmission coefficient from the wave length for LMS, can be seen the presence of spectrum features, typical for magnetite, monoacyglycerol and oil (lipid). Comparison of the transmission spectrums of suspensions with the different dilution degree testifies to the chemical identity of samples.

Analysis of kinetic dependences of transmission coefficient for LMS indicates the nonlinear law of change of transmission coefficient for suspensions without stabilizer or with the high content of magnetite (38,9 mg/l), that can be explained by existence of different fractions of magnetite particles and their aggregation. In UV-area of spectrum at the low concentrations is observed the direct proportionality between transmission coefficient and concentration of Fe(gen.), that is absorbing centers Fe_3O_4. The assessment of effective mean radius of particles by sedimentation kinetics gives values 76–168 nm, moreover up to concentration 38,9 mg/l the dependence of (r_{eff}) from C (Fe_{gen}) is nonlinear.

Approximating the received dependence by the straight lines and extrapolating them to T=100 %, the mean effective radius of particles can be assessed. In the **Table 5** are given the temporary dependences of transmission coefficient of studied suspensions on the wave length 600 nm. The received values of sedimentation time and effective mean radius are given in the **Table 6.**

Table 5

Temporary dependences of transmission coefficient (T, %) of soy-magnetite suspensions (SMS) of the different concentration on the light wave length (λ=600 nm)

Suspension ageing time, τ, hours	Transmission coefficient T, %				
	Fe gen. concentration in suspension, mg/l				
	4,85 mg/l	9,75 mg/l	19,5 mg/l	38,9 mg/l	4, 85 mg/l without SAS
0	67	63	59	53	58
1800	68,4	64,8	61,3	56,9	72,7
3600	69,2	66	63,2	64,5	82,7
6000	71,7	67,3	66,9	68,9	89,8

Table 6

Results of calculation of sedimentation time t_{sed} and mean effectice radius of particles r_{eff} at the different suspension concentration

Parameter	$Fe_{gen.}$ concentration, mg/l			
	4,85	9,75	19,5	38,9
$t_{sed,}$ hour	454	228	168	147
$r_{eff,}$ nm	76	92	146	168

According to the data of the **Table 6** can be assessed the mean effective radius of particles in LMS of the different concentration and also aggregative stability of suspensions.

4. Conclusions

All LMS are stable in time – up to 1080 hours. The best stability results were shown by suspensions with ratio Fe_3O_4:SASP=0,02 g:0,35 g or 0,04 mass %:0,70 mass % and 0,025:0,35 g or 0,05 mass %:0,70 mass %. The diameter of magnetite particles with SAS was determined – 76 nm. It was established, that with time (0–48,0 hours) and growth of the wave length (210–1000 nm) was observed the gradual increase of transmission coefficient from 25 % (210 nm) to 71,9 % (1000 nm) at 0 hours of suspension ageing; from 27,5 % (210 nm) to 81,2 % (1000 nm) at maximal time of suspension ageing (48 hours).

There was determined concentration of magnetite particles, stabilized with surface active substance – concentration (number of particles in 1 cm^3) at preparation of suspension is equal $N=1,43 \cdot 10^{12}$ cm^{-3}. It was established the decrease in time of the number of magnetite particles with SAS in 1 cm^3 soy-magnetite suspension: for 48 hours concentration in 1 cm^3 decreased by 20 % – from $1,43 \cdot 10^{12}$ to $1,19 \cdot 10^{12}$ cm^{-3}. The following values were determined for soy-magnetite suspension (SMS): r=38 nm, n=1,48, κ=0,01. The established order of the mean size of particles is <r>~38 nm.

In UV-spectrums are the weak strips of transfer n→π* at 200–210 nm, typical for saturated radicals (monoacylglycerol – MA) and more intense strips of transfer π→π* at 210–230 nm, typical for α, β-unsaturated acyls (soy oil – SO). In magnetite spectrum are observed the wife strips of absorption within 490 and 540 nm, associated with lattice fluctuations of Fe–O– connections in tetra- and octahedral positions of Fe_3O_4.

Comparing these curves with dependence of transmission coefficient from the wave length for LMS, can be seen the presence of spectrum features, typical for magnetite, monoacyglycerol and oil (lipid). Comparison of the transmission spectrums of suspensions with the different dilution degree testifies to the chemical identity of samples.

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and their aggregation. In UV-area of spectrum at the low concentrations is observed the direct proportionality between transmission coefficient and concentration of Fe(gen.), that is absorbing centers Fe_3O_4. The assessment of effective mean radius of particles on sedimentation kinetics gives values 76–168 nm, moreover up to concentration 38,9 mg/l the dependence of (r_{eff}) from C (Fe_{gen}) is nonlinear.

Last decades there are actively created the new nanomaterials, elaborated nanotechnologies that find the wide use in the different industrial branches. The modern level of nanotechnologies allows elaborate on the base of magnetite nanoparticles the unique means for pharmacy, medicine, biology, food industry. Their introduction in practice is a base of the modern progress in fields of creation of biologically active, deictic additives; therapeutic and preventive nutrition; diagnostics and therapy, including cellular and gene levels.

So, creation of LMS, stable in time with magnetite nanoparticles; analysis of their sedimentation process; determination of aggregative and sedimentation stability of magnitive suspensions, sizes of stabilized particles Fe_3O_4, functions of distribution by sizes is a topical and important task.

Magnetite has magnetic properties, so the further study of magnetic properties of magnetite nanoparticles in lipid-magnetite suspensions is interesting.

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THE STUDY OF PRODUCTION REGIMES AND QUALITY PARAMETERS OF EXTRUDED FEED ADDITIVE BASED ON CORN SEED AND SUBSTANDARD EGG MASS

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Abstract

On the base of practical studies were established the rational parameters of technological processes of production of extruded feed additive. There was determined an expedience of mixture of substandard chicken egg mass and the crushed corn seed in two stages in frame (during 18 s) and blade (during 120…180 s) mixers. There were determined the optimal regimes of mixture extruding: pressure in working zone of extruder 2…3 mPa, consumed force of electric motor 4,0…4,5 kW, temperature on outcome of extruder 110…120 °C, duration of process 60…120 s, diameter of matrix port 10 mm.

There were given the results of study of parameters of quality and nutritive value of extruded feed additive. It was established, that in the process of extruding the quality parameters of food additive are improved at the expense of dextrinization and gelatinization of starch, decrease of bacterial and fungal pollution, disinfection of product.

There was proved a possibility to solve problem of utilization of defective eggs at feeding poultry.

Keywords: extruded feed additive; rational parameters of processes; substandard egg mass; technological processes of extruding and mixing.

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1. Introduction

Last 5 years in mixed fodder industry of the world was marked the course on the rise of requirements to the quality and safety of mixed fodder production [1–3].

At the same time there was observed the decrease of nutritive value of the raw material for production of the ready goods [4]. In this connection scientists and practicians throughout the world search for possibility to use the new fodder means that would lead to reduction of prices of mixed fodders and cattle-breeding production.

In Ukraine are produced near 100000 tones of substandard egg mass annually [5, 6], that is often missed because of significant cost of its processing [7, 8]. There is a possibility to use substandard chicken eggs without shell as a source of animal protein in composition of mixed fodders for poultry, namely for production of extruded feed additive (EFA). Technological method of EFA production provides getting of homogenous mixture of crushed corn seed and substandard egg mass and extruding of mixture [9].

The studies were aimed at establishing of the optimal parameters of processes of mixing and extruding of corn seed and substandard egg mass under conditions of the best quality parameters of EFA.

2. Materials and methods of research

Theoretical and practical studies on the topic were carried out in Odessa national academy of nutritive technologies (Ukraine). Experimental studies were carried out on the base of departments of mixed fodders and biofuels, biochemistry, microbiology and physiology of nutrition and also laboratory of biochemistry of Odessa selection-genetic institute of National center of seed and sort studies of NAAS of Ukraine.

The process of mixing egg mass without shell and crushed seed raw material for getting highly homogenous feed additive enriched with protein was carried out in frame mixer (**Fig. 1**) and in mixer of periodic action with blade mixing device (**Fig. 2, 3**) [10].

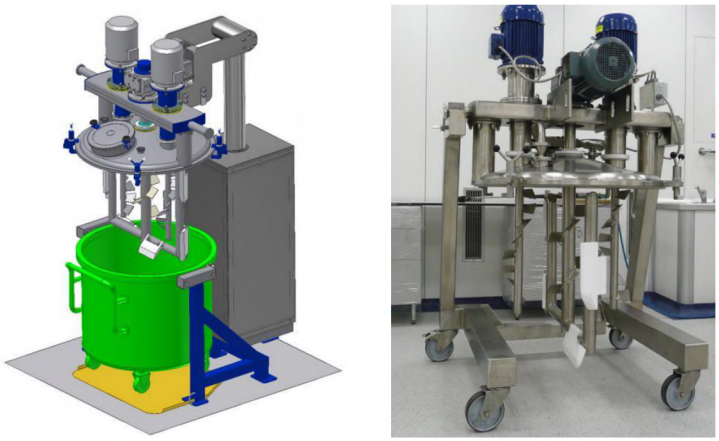

Fig. 1. Frame mixer with scraper (Kates, Poland)

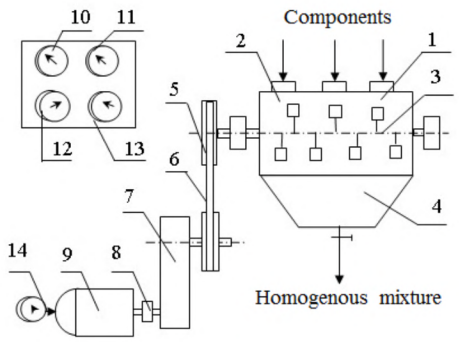

Fig. 2. Scheme of experimental stand for the study of technological mixing process:
1 – bath of mixer, 2 – loading port, 3 – shaft of mixing device, 4 – bunker, 5 – pulley on shaft of mixing device, 6 – wedge-belt transmission, 7 – worm reducer, 8 – coupling box, 9 – electric motor, 10 – voltmeter, 11 – ammeter, 12 – LATR, 13 – timer, 14 – tachometer TC-45

Fig. 3. Laboratory stand for study of technological mixing process: 1 – mixer, 2 – loading pipes, 3 – unloading tray, 4 – control desk, 5 – electricity cable

The part of crushed seed raw material and homogenous egg mass without shell was dosed and mixed in frame mixer during 180 s in 1:1 ratio for even distribution of liquid raw material in mixture.

Preliminary prepared components were loaded in bath of the 1 mixer through the loading ports starting from the main part of crushed seed raw material that is included in the content of feed additive in maximal amount and finishing with preliminary mixture that is included in the content of feed additive in minimal amount. The components were mixed in laboratory mixer during 60…360 s at the equal frequency of rotation of mixer working organ n=1,33 s^{-1}. After finishing of process the hatch was open for unloading the mixture components in bunker 4. The homogeneity of components distribution in mixture content was assessed by the node component (beta-carotene) that is included in the content in minimal amount. The assessment of efficiency of the mixing process was carried out by heterogeneity coefficient (V_c) of distribution of egg mass without shell in mixture depending on time of mixing (1) [11]:

$$V_c = \frac{1}{\bar{x}}\sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})^2}{n-1}} \cdot 100, \% \qquad (1)$$

where $\bar{x}$ – mean arithmetical observation of values that is the mean content of node component in samples; x_i – random value in в i-th experience; n – number of selected samples.

Technological process of extruding was carried out on extruder of EX-150 (Bronto, "Cherkaselevmotormach", Ukraine) (**Fig. 4**) [12].

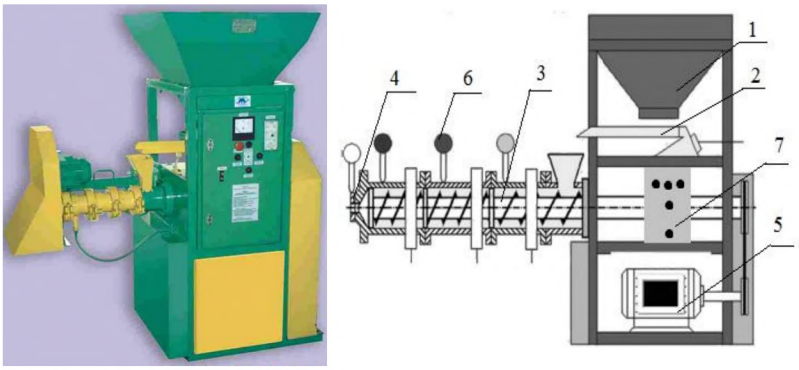

Fig. 4. Seed extruder EZ-150: 1 – reception bunker, 2 – vibrofeeder, 3 – screw, 4 – pressing annular matrix, 5 – motor, 6 – thermocouples, 7 – control desk

Extruder works in the following way. Product comes to bunker 1 from external supply system. After switching on the electric motor 5 and then vibrofeeder 2, mixture is supplied from bunker 1 by vibrofeeder in the working zone of screw part through the reception funnel with magnet-catcher. During the movement on tract of the screw working zone 3, made by spiral channels and glasses ribs, mixture is crushed and pressed out through the central port of outcome screw bush 3. Heating up of the mixture takes place at the expense of force internal friction and at the expense of friction between mixture and screws and basic parts. Ready product comes out through the central port of outcome bush as jet or braid. Extruder is completed with the short spinnerets that are not cooled that allows receive products of porous macrostructure. If appears a necessity in crushing product, extruder is completed with cutter.

For acceleration of extruder starting the matrix was preliminary heated up to the temperature 90...100 °C. Regulation of the process temperature and "explosion" coefficient is realized by the change of axis position of outcome bush that is displaced on thread. The change of bush position leads to increase or decrease of clearance between tip and port of outcome bush of the screw part 3. At that the decrease of clearance leads to increase of the product temperature, increase of product "explosion" coefficient and vice versa.

Before the start of the work ammeter and wattmeter were connected to the set for determination of energy-power characteristics. The indications of these devices were fixed at idling and under load.

Determination was carried out by the way of weighing mass that came out from the outcome port of extruder screw part during 180 s. By the way of recalculation was received the hour set productivity. For reducing productivity to the conventional density 750 kg/m^3 the received productivity value was multiplied by coefficient that was determined by division of conventional density by the actual one.

The power of electric motor at idling and under load was determined by formulas (2), (3):

$$N_{idling} = I_{idling} \cdot U \cdot \cos\varphi \cdot 10^{-3}, \text{kW} \quad (2)$$

$$N_{load} = I_{load} \cdot U \cdot \cos\varphi \cdot 10^{-3}, \text{kW} \quad (3)$$

where I_{idling}, I_{load} – power of current at idling and under load, A; cosφ – coefficient of phases displacement; U – tension of current in nets (380 V).

Electric power consumption was determined by formula (3):

$$N_{specific} = \frac{N_{load} - N_{idling}}{Q}, \text{kW} \quad (4)$$

where N_{idling}, N_{load} – power of electric motor at idling and under load, kW; Q – productivity, kg/year.

After starting up extruder was taken to regime when its productivity, process temperature and power of electric motor current corresponded to the nominal values. Only after attaining this regime the indication of ammeter and wattmeter under load were fixed. Indications were registered with periodicity, accepted depending on mass of outcome raw material and its quality (during 120…300 s). The set productivity was determined under conditions when the consumed power of the main electric motor is 100 %, quality of extruded product is satisfactory and temperature corresponds to the specified one [10, 12, 13].

For determination of technological properties the complex of standard laboratory equipment was used: drying cabinet (EDC) (**Fig. 5**), dry-air thermostat DT-80M (**Fig. 6**), purka PX-1 (**Fig. 7**), dessicator (**Fig. 8**), densimeter DM2 (**Fig. 9**), device for determination of the natural slope angle (**Fig. 10**), sower SL-5M and the set of sieves with round ports with diameter ∅3, ∅2, ∅1 mm, wire net № 080 and № 056 (**Fig. 11**), electric ScoutSC 2020-EU1 (**Fig. 12**) and analytic BLE-200 (**Fig. 13**) balance. The content of nutritive and biologically active substances was determined using the following devices: Kamovsky electrovacuum pump with dilution 13 Pa (**Fig. 14**), photoelectrocolorimeter KPC-2MP (**Fig. 15**), and also laboratory crockery and reagents according to accepted methods [14].

Fig. 5. Electric drying cabinet (EDC-3M (PE SumyCDDandA, Sumy, Ukraine)

Fig. 6. Dry-air thermostat DT-80M (NPE Podgornaya A. A., Kyiv, Ukraine)

Fig. 7. Liter purka PX-1 (NPE Pashkov, V. A., Dnipro, Ukraine)

Fig. 8. Dessicator (Parmmedtech COMPANY, Ukraine)

Fig. 9. Densimeter PZ2 (Standard-M, SPF COMPANY, Zaporizhia, Ukraine)

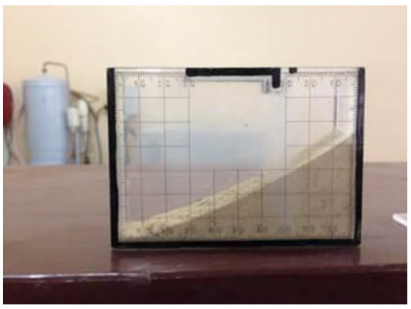

Fig. 10. Device for determination of natural slope angle

Fig. 11. Sower SL-5M and set of sieves

Fig. 12. Electric balances ScoutSC 2020-EU1

Fig. 13. Analytic balance BLE-200

Fig. 14. Kamovsky electrovacuum pump with dilution 13 Pa

Fig. 15. Photoelectrocolorimeter KPC-2MP ("ZOMF", Russia)

3. Results of research

To get the highly homogenous mixture of crushed corn seed and substandard egg mass it is expedient to carry out two-phased mixing (in frame mixer during 180 s was received preliminary mixture of components in 1:1 ratio and in mixer with blade mixing device during 120…180 s was realized the main mixing of preliminary mixture of components and crushed corn seed that remained).

Experimental production of EFA samples was carried out on mechanical extruder EZ-150. In extruder was set the matrix with port of diameter 10 mm. In extruding process the pressure in extruder working zone, consumed power of electric motor, temperature of product at outcome of extruder were fixed 2…3 mPa, 4,0…4,5 kW, 110…120 °C respectively. The process duration was 60…120 s.

As a result of research it was determined, that at introduction in the content of feed additive of 10 % of egg mass without shell the extruding process passes at minimal energy consumption, and the quality parameters of feed additive are the best.

In studied samples of feed additive were determined the changes of physical properties (**Table 1**), chemical composition (**Table 2**), amino acid composition of proteins (**Table 3**) and qualitative-quantitative composition of microflora (**Table 4**) in extruding process.

Table 1

Influence of extruding on physical properties of feed additive (n=3, P ≥ 0,95)

Parameters	Feed additive	
	Before extruding	After extruding
Mass part of humidity, %	17,1	**12,8**
Natural slope angle, degree	35,0	38,0
Friableness, cm/s	8,6	4,6
Volume mass, kg/m^3	625,0	480,0
Size module, mm	1,8	1,1
Starch dextrinization degree, %	0	**58,0**
Extrudate extension index	**2,1**	
Electrical energy consumption, kW×hour	17,0	

Analysis of data, given the **Table 1** testifies that extruding process positively influences the physical properties of final product.

Table 2

Changes of chemical composition of feed additive in extruding process (in calculation for the dry substance) (n=3, P ≥ 0,95)

Parameters	Feed additive	
	Before extruding	After extruding
Mass part of dry substances, %:	82,90	87,20
Crude protein	12,90	12,50
Crude fat	7,60	7,50
Water-soluble carbohydrates	3,90	**23,70**
starch	66,40	**48,60**
crude cellulose	2,20	2,10
Crude ash	1,90	1,85
calcium, mg%	53,00	54,00
phosphorus, mg%	348,00	340,00
Digestibility of protein, %	61,70	**85,50**

As it can be seen from the data of **Table 2** the starch content decreases in extruding process. It is connected with deep gelatinization of seed starch at processing. At that takes place the destruction of starch macromolecules with creation of dextrins and sugars that significantly increases assimilability of the final product. Nutritive properties of protein essentially depend on the duration of thermal processing of product. In the case of short-term process the high result is provided – nutritive value of protein practically does not decrease [15, 16].

Extruding was carried out at temperature 110…120 °C during 60…120 s that caused interest of the study of change of amino acid composition of proteins at extruding.

Table 3

Amino acid composition of proteins of feed additive before and after extruding, % of N×6,25 crude protein (in calculation for dry substance) (n=3, P ≥ 0,95)

Amino acid	Feed additive	
	Before extruding	After extruding
Irreplaceable		
Valine	0,68	0,62
Isoleucine	0,52	0,47
Leucine	1,28	1,18
Lysine	0,56	0,50
Methionine+cystine	0,55	0,51
Threonine	0,48	0,43
Tryptophan	0,12	0,11
Phenylalanine	0,62	0,61
Together	**4,81**	**4,43**
Replaceable		
Alanine	0,89	0,83
Aspartic acid	1,00	0,92
Glycine	0,46	0,45
Glutamic acid	2,08	2,06
Prolin	0,95	0,86
Serine	0,73	0,66
Arginine	0,67	0,61
Histidine	0,33	0,31
Tyrosine	0,40	0,36
Together	**7,51**	**7,06**

As in can be seen from the results of the study (**Table 3**) extruding influences the biological value of protein in feed additive, especially the general content of amino acids in EFA decreased by 6,5 %. Moreover the content of irreplaceable amino acids in extruding process decreased by 7,9 %, and of replaceable – by 6 %.

Table 4

Change of sanitary quality of feed additive in the process of processing and storage in unregulated conditions

Sample	GBS, CCU/g	Mycelial fungi, CCU/g	Leaven CCU /g	CB titer, g	Salmonella
Mixture of crushed corn and egg mass without shell	**250000**	120	90	0,1	Was not revealed
Extruded Mixture of crushed corn and egg mass without shell	1340	10	Was not revealed	Was not revealed	Was not revealed
Extruded mixture of crushed corn and egg mass without shell (storage 1 month)	730	Was not revealed	Was not revealed	Was not revealed	Was not revealed
Extruded mixture of crushed corn and egg mass without shell (storage 2 months)	460	Was not revealed	Was not revealed	Was not revealed	Was not revealed
Extruded mixture of crushed corn and egg mass without shell (storage 3 months)	**200**	Was not revealed	Was not revealed	Was not revealed	Was not revealed

The results of research, given in the **Table 4,** indicate that under the complex effect of high temperatures and pressure in extruder working zone takes place disinfection of feed additive. The decrease of general bacterial seeding in the process of storage is connected with low humidity of the studied samples.

4. Conclusions

1. The grounded materials and methods of research are modern and correspond to the requirements of state standards of Ukraine and ISO standards, technical conditions and normative acts [17–21].

2. The study of physical-technological properties of feed additive for poultry testifies that in extruding process is observed insignificant losses of crude protein, starch content decreases by 26,8 % at the expense of increase of its digestibility, namely increase of water-soluble carbohydrate content.

3. In the process of EFA storage in unregulated conditions during three months the level of sample seeding abruptly shortens. EFA must be stored in dry, well ventilated accommodations without humidification and compression. In such case the stable quality parameters and satisfactory sanitary state of product can be guaranteed and this product can be used for feeding poultry during the whole storage term.

4. It was proved, that due to EFA use such valuable and easily assimilated product as egg mass of substandard chicken eggs is used at feeding poultry instead of being missed. The additive can be used in the content of mixed fodder in amount of 15…25 % or independently at farms.

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THE DEVELOPMENT OF CRYOGENIC METHOD OF DEEP TREATMENT OF INULIN-CONTAINING VEGETABLES (TOPINAMBOUR) AND OBTAINING OF PREBIOTICS IN THE NANOPOWDERS FORM

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Abstract

The aim of the work is elaboration of the principally new cryogenic method of deep processing of inulin-containing vegetables (topinambour) using cryogenic "shock" freezing and fine-dispersed comminution and getting of it nanopowders (prebiotics).

There was elaborated principally new cryogenic method of deep processing of topinambour for getting nanopowders – prebiotics. This method differs from traditional ones by the full exclusion of thermal processing of the raw material. Method is based on the use of complex effect of cryogenic "shock" freezing on the raw material using liquid nitrogen, fine-dispersed comminution and sublimation drying. It allows not only preserve biological potential of vegetables but also reveal it more fully and extract the hidden (associated) forms of the low molecular biologically active substances and polymers and transform them into soluble, easily assimilated nanoform.

It was established, that cryogenic method allows more fully extract the low molecular biologically active substances from the state associated with biopolymers in nanocomplexes into free one (1,8…2,3 times more than in initial raw material). There was revealed mechanism of process, connected with cryomechanodestruction, non-enzymatic catalysis and mechanocracking.

It was revealed, that cryogenic methods allows more fully extract heteropulysaccharides – pectin substances, cellulose and proteins from the form associated in nanocomplexes with other biopolymers (1,3…3 times more).

It was established, that cryogenic method of topinambour processing allows partially (by 45…55 %) destruct the difficultly soluble biopolymers such as inulin, pectin substances, cellulose and proteins to their separate monomers in soluble nanoform. There were also revealed conformational changes of molecules of topinambour proteins. It was demonstrated, that form changes and the protein molecule, size of its kernel, coat and ratio of hydrophobic and hydrophilic amino acids remains decrease.

It was demonstrated, that topinambour nanopowders outgo the known analogues of traditional topinambour powders by chemical and disperse composition. It was established that their assimilability is 3 times higher than in traditional ones.

Keywords: cryogenic method, inulin, prebiotics, fine-dispersed, cryogenic freezing, nanopowders, nanocomplexes.

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1. Introduction

The aim of the work is elaboration of the principally new cryogenic method of deep processing of inulin-containing vegetables (topinambour) using cryogenic "shock" freezing and fine-dispersed comminution and getting of it nanopowders (prebiotics).

In Kharkov state university of food technology and trade (Kharkov, Ukraine) at the department of technology processing of fruits and vegetables in laboratory of innovative cryo- and nanotechnologies of vegetable additives and wellness products together with Kharkov trade and economic Institute of Kyiv national university of trade and economics (Kharkov, Ukraine) was elaborated cryogenic method of the deep processing of topinambour and getting of it nanopowders – prebiotics.

This method differs from traditional ones by the full exclusion of thermal processing of the raw material [1–5]. Method is based on the use of complex effect of cryogenic "shock" freezing on the raw material using liquid nitrogen, fine-dispersed comminution and sublimation drying [6]. It allows not only preserve biological potential of vegetables but also reveal it more fully and extract the hidden (associated) forms of both the low molecular biologically active substances (BAS) and polymers and transform them into soluble, easily assimilated nanoform.

2. Materials and methods of the study of the low molecular BAS and biopolymers content at elaboration of cryogenic method of deep processing of inulin-containing vegetables

2. 1. Studied material and equipment used in experimental procedures

The study was carried out in Kharkov state university of food technology and trade at the department of technology processing of fruits and vegetables and milk (Kharkov, Ukraine).

Cryogenic "shock" freezing was carried out using the modern experimental equipment, especially, cryogenic program freezer with computer support (**Fig. 1**) that functions using both coolant and inert medium of gaseous nitrogen. Cryogenic program freezer was elaborated in National aerospace university of M. E. Zhukovsky "KAI" (Kharkov, Ukraine) together with joint authors of the article.

Fig. 1. Cryogenic program freezer with computer support

Cryogenic processing of topinambour samples was carried out at temperature – 60 ˚C in the chamber of fast freezing. Topinambour samples were frozen with different speeds (2, 5, 10, 20 ˚C/min) to the final temperature in product –35…–40 ˚C. At that, for freezing of 1 kg of vegetables were used from 0,5 to 1,0 l of liquid nitrogen depending on thickness of frozen product. The volume of working chamber on the raw material load was up to 10 kg.

Sublimation vacuum drying was carried out in vacuum sublimation dryer (**Fig. 2**), produced at the experimental factory of Institute of problems of cryobiology and cryomedicine of National academy of sciences of Ukraine (Kharkov city, Ukraine) and was created for drying of medical preparations, living microorganisms, foodstuff and other biological objects. The drying of samples was carried out at temperature –20 ˚C…–22 ˚C, pressure $-10^{-3}…8{\cdot}10^{-4}$ Pa and additional drying at +50…+55 ˚C (during 30…40 min). Drying was carried out to the final humidity 5 %.

Fine-dispersed comminution was carried out in comminutors (especially, in bedded, vibration-bedded mills, attritors of Ukrainian production and cutter-activator (France)) at temperature not higher than –10 ˚C to the particles size in dozens times less than at traditional comminution.

As objects of the study were used topinambour tubers (**Fig. 3**) and nanopowders of sublimation drying of them (**Fig. 4**).

Fig. 2. Vacuum sublimation dryer

Fig. 3. Initial raw material (topinambour tubers)

Fig. 4. Nanopowder of topinambour sublimation drying

2. 2. Methodologies of determination of parameters of studied samples

Criteria of assessment of cryomechanodestruction processes at elaboration of cryogenic method of topinambour processing into the form of topinambour nanopowders were used at determination of chemical substances in vegetable raw material and ready additives, especially:

– protein of associated and free amino acids, hydrophilic and hydrophobic remains of amino acids, inulin, fructose, general pectin, protopectin, soluble pectin substances, cellulose, organic acids and other;

– L-ascorbic acid, low molecular phenol compounds (oxycinnamic acids), flavonol glycosides, catechins, tanning substances.

At the same time the influence of cryomechanodestruction processes was controlled by determination of conformational changes of protein molecules (especially, radius, volume of kernel

and coat, form of protein molecules and so on) and assimilation degree of additives using bio-testing express-method.

For solving the set problems alongside with commonly used chemical [7–13], physical-chemical [14], spectroscopic [15], chromatographic methods of research [15], were used the original ones, namely: the method of protein structure and conformational changes determination by E. G. Fisher [16, 17] and express-method of biological activity (or assimilability) determination by L. N. Brayenes [18].

As a control sample was used fresh, ripe, washed topinambour of Interest sort, planted in Kharkov region and harvested in autumn (October), stored in the vegetable store house at temperature +2…+4 ˚C. The mean size of topinambour tubers by the largest transversal diameter was 30 mm, and mass – 150 g (tubers). Experimental procedures were carried out with fivefold repetition. The received results are given in units of CI international system.

Mass fraction of the general nitrogen was controlled by Kjeldahl method [7].

Mass fraction of free and associated amino acids was controlled using chromatographic methods of research (ion-exchanged chromatography) on automatic analyzer AAA 339 (Microtechna-Prague-CSSR) on the base of laboratory of assessment of the of forage and animal production quality in Institute of cattle breeding of National academy of agrarian sciences of Ukraine (Kharkov, Ukraine).

Method of determination of protein structure and conformational changes. The structure of initial raw material proteins and their conformational changes at getting nanoadditives were determined using method, elaborated by Nobel prizewinner Fisher E. G. [16, 17]. This method allows by the known ratio of polar and non-polar remains of amino acids in protein molecule calculate its radius, volume and form and also radius of its kernel and index of kernel filling with hydrophobic remains. Method is based on the fact that all amino acid remains, included in polypeptide chain of protein molecule, can be conventionally divided in two groups: non-polar (hydrophobic) and polar (hydrophilic) ones. In water the flexible molecules curls up in globule. Sphere has a minimal area of surface at given volume. Non-polar remains create within protein fraction the certain likeness of spherical drop and the polar ones are concentrated on its surface. It leads to creation of compact body – globule with hydrophobic kernel and hydrophilic coat.

Method allows determine the molecule form by the general number of amino acid remains in kernel and polar and non-polar remains ratio. Using the method at work the forms of protein molecules of the fresh raw material and topinambour nanoadditives were determined. Methodology of determination of the protein structure and conformational changes of studied samples is presented in the works [16, 17].

Biological activity (or assimilability) of samples was determined by original express-method of L. N. Brayenes. The assessment of substances (or product) biological activity was carried out by generative activity (or increase of young forms) of biological test-objects (unicellular infusoria Paramecium caudatum), that is by stimulation of reproduction [9]. The essence of method of control of biological activity (or assimilability) of the different products and substances using infusoria is based on straightening of absorbing and digestive ability of elementary organism – infusoria and activation of their reproduction in the case if studied product includes substances that stimulate their growth and development. At presence of toxic or other harmful substances in tested product there is observed deceleration of development or death of infusoria. Methodology of determination of biological activity of studied samples is presented in the work [18].

Inulin content was determined according to methodical instructions of biochemical analysis. Method is based on inulin property to hydrolyze at presence of hydrochloric or oxalic acid with creation of fructose and also on inulin ability to be dissolved in hot water and not to be dissolved in alcohol. After conducting reaction of neutralization by alkali hydroxide to slightly acid reaction the sugar determination is carried out by the method of Bertran [8]. The difference between percent content of sugars, found after hot extraction with water and 82-percent alcohol will be the sugar, received of inulin.

Mass fraction of pectin substances (general, soluble and protopectin) was measured by the standard weight calcium-pectate method (SSTU 8756.11-70), based on determination of pectin acid content by the mass of calcium pectate, created at interaction of calcium chloride with pectin acid [13].

Mass fraction of cellulose was determined by the standard method, based on creation of furfurol of pentosans at cellulose processing by the solution with 13 % mass fraction of hydrochloric acid at heating and determination of skimmed furfurol by spectrofotometric method (SSTU 10820-75) [9].

Vitamin C content was determined by iodometric method, based on oxidizing-renewing reaction that takes place between ascorbic acid and indicator 2,6 – dichlorphenollindophenol (Tillmans paint) (SSTU 24556-89) [10].

Phenol substances content was determined by the method of Folin-Denis in recalculation on chlorogenic acid (SSTU 4373:2005). Method is based on creation of blue complexes at renewal of tungsten acid under effect of polyphenols with Folin-Denis reagent in alkali medium [11].

Polyphenol (tanning substances) content was determined by titrimetic method by tannin (SSTU 24027.2-80). Method is based on the property of tanning substances to oxidize at presence of indigo carmine indicator [12].

Mass fraction of titrated (organic) acids was determined by the method of volume titration (SSTU 25555.0-82). Method is based on neutralization of acids extracts of the studied sample by the alkali solution to the appearance of pink coloration that testifies to the end of reaction [14].

3. Results of research

At elaboration of cryogenic method of topinambour processing and getting nanopowders of it using cryogenic "shock" freezing and fine-dispersed comminution it was important to increase the degree of extraction of the hidden forms of BAS associated with biopolymers into free state from the raw material. At the same time it was necessary to partially transform the difficultly soluble polysaccharides, oligosaccharides and proteins into soluble form. It becomes possible at the expense of cryodestruction and cryomechamodestruction and also mechanolysis. It was also important to reveal mechanisms of aforesaid processes and assimilability by the living organisms.

For the first time in international practice authors revealed and demonstrated that at complex action of cryogenic "shock" freezing and fine-dispersed low-temperature comminution on the raw material takes place not also the full preservation of all BAS but also their more full extraction from the raw material. It was demonstrated, that they are in hidden associated forms with biopolymers (proteins, heteropolysaccharides), nanocomplexes and nanoassociates. It was established, that extraction and transformation of BAS into the free state (1,8…2,3 times more than in the raw material) is connected with mechanocracking. In parallel it was revealed, that at cryoprocessing and fine-dispersed comminution of topinambour takes place destruction of inulin into the separate monomers – fructose by 45…55 %, protein – into free acids, cellulose in sugars – by 43…55 % at the expense of non-enzymatic biocatalysis – cryomechanolysis [19, 20]. So, there takes place destruction of the difficultly soluble biopolymers and their transformation in easily assimilated nanosized form. The conformational changes of proteins globules were studied. It was shown, that the forms of protein molecule changes, the size of its kernel, coat and ratio of hydrophobic and hydrophilic remains of amino acids and so on decrease. There was also studied the transformation of difficultly soluble heteropolysaccharides, their nanocomplexes together with proteins into soluble easily assimilated form.

It is well-known, that in vegetable raw material (including topinambour) pectin substances are in non-active form and that is why they have the low jelly and absorptive properties [21, 22]. In this connection were carried out scientific researches when topinambour was frozen using high (2, 5, 10, 20 ˚C/min) and low (0,1; 0,2; 0,5 ˚C/min) freezing speeds. The cut tubers were frozen to the different final temperatures in product (especially –18…–20 ˚C) and to the lower temperatures in product (–32…–35 ˚C) and sublimation drying and fine-dispersed comminution were carried out. In the process of freezing and comminution take place cryomechanodestruction and cryomechanoactivation. It was established, that at complex effect of aforesaid processes on topinambour takes place the more full extraction of pectin from associated state with other biopolymers and nanocomplexes into free active (soluble) form. It was revealed, that there takes place essential degradation and cryodestruction of protopectin and its transformation from non-active form into active (soluble) one. Thus, it was established, that at getting nanopowders of tominambour takes place the more full extraction of pectin substances mass fraction from nano-

complexes, 3,0…3,4 times more that in initial raw material, including protopectin (2 times) and its destruction to the soluble pectin (4,5 times more). In general in topinambour nanopowders 70 % of pectin substances are in soluble form. Mechanism of the more full extraction of pectin substances from nanocomplexes and nanoassociates of the vegetable raw material is connected with their cryomechanocracking (destruction) and non-enzymatic biocatalysis – cryomechanolysis.

Using the method of biotesting of infusoria test-cultures (by generative activity of unicellular organisms) was shown that in comparison with coarsely dispersed topinambour the assimilability of its nanopowders is 2,7…3,0 times higher. It is connected with the higher extraction from the raw material of soluble biologically active and food substances that are in nanosoluble form at fine-dispersed comminution.

It was established, that topinambour additives – nanopowders by chemical composition, BAS content and dispense state exceed the known world analogues, received by traditional technologies. Such technologies are realized at thermal drying at temperature +65…+130 ˚C and higher, especially, by convective, convective-vacuum, convective-impulse, conductive, vacuum, spraying and other drying methods [23–25]. The significant part of substances (especially, inulin, protein, cellulose, pectin substances) and BAS (phenol compounds, flavonol glycosides, tanning substances) in 60…70 % are in nanosized form (**Table 1**). Thus, for example, difficultly soluble biopolymers (proteins, inulin, cellulose, pectin substances) of topinambour in 45,0…55,0 % were transformed into soluble form as separate monomers (fructose, free α-amino acids, glucose, galacturonic acids) that have nanosoluble form. It is known, that the last ones have molecules size from 0,8…1,4 nm [26, 27]. Nanopowders differ from analogues by the high fructose content (up to 25,0 %) and fructooligosaccharides [23–25]. At the same time they differ by the high content of low molecular phenol compounds (by chlorogenic acid) (up to 2800 mg in 100 g, flavonol glycosides (by rutin) (up to 1800 mg in 100 g), tanning substances (up to 2160,0 mg in 100 g) (**Table 1**). The cited compounds have potential immune-modeling, antioxidant, detoxifying and anti-tumor properties [29].

Table 1

Content of biologically active and prebiotic substances in topinambour nanopowders comparing with analogues (n=3)

Parameter name	Fresh topinambour	topinambour nanopowder	Analogue – topinambour powder of convective vacuum-impulse (CVI) drying	Analog – topinambour powder of convective drying
Inulin, %	12,8±0,5	25,6±1,5	9,75±0,1	7,46±1,3
Fructose, %	–	25,6±1,5	0,0	0,0
Protein, %	1,2±0,01	9,1±0,2	8,9±0,1	8,7±0,1
Associated amino acids of protein, mg in 100 g	1664,0	3698,0±0,2	–	–
Free amino acids of protein, mg in 100 g	350,0	5415,0±0,2	–	–
General pectin, %	1,9	30,0	9,3±0,1	8,4±0,1
Protopectin, %	1,2	10,4	–	–
Soluble pectin, %	0,7	23,0	–	–
General sugar, %	4,4±0,1	23,7±1,4	70,25±0,2	71, 33±0,2
Vitamin C, mg100 g	10,3±0,1	78,2±2,4	16,4±1,1	12,2±0,3
Phenol compounds (by chlorogenic acid), mg in 100 g	350,0±5,7	2800,0±12,4	–	–
Flavonol glycosides (by rutin), mg in 100 g	240,0±4,8	1800,0±12,4	–	–
Tanning substances, mg in 100 g	300,0±6,4	2160,0±14,0	–	–
Ash content, %	1,6±0,1	6,8±0,2	6,0±0,2	5,9±0,1
Organic acids, %	0,3±0,01	2,0±0,1	0,8±0,1	0,65±0,1
Humidity, %	76,4±1,2	5,5±0,1	7,9±0,1	7,3±0,1

4. Conclusions

Thus, the use of cryomechanodestruction (cryogenic freezing and fine-dispersed comminution) allows get the qualitatively new feed additives in the form of topinambour nanopowders with record BAS and biopolymers content in easily assimilated nanoform that are impossible to be gotten using traditional methods (convective, convective-vacuum, convective-impulse, conductive, vacuum, spraying and other) of the raw material drying. According to the chemical composition, new feed additives (nanopowders) of topinambour have potential perbiotic, immune-modeling, anti-tumor and detoxifying effects [30]. It is knows, that inulin, pectin substances, cellulose, protein are the indigestive food components, contained in topinambour nanopowders and have prebiotic properties [30]. They stimulate in human organism development and metabolic and biological activity of one or several groups of own bacteria that form intestinal human micriflora, have a positive influence on composition of microbiocenosis. It is also known, that phenol compounds (by chlorogenic acid), flavonol glycosides (by rutin) and tanning substances, contained in topinambour nanopowreds, have potential immune-modeling, antioxidant, detoxifying and anti-tumor effect [28, 30]. In this connection there are reasons to think that nanopowders have the same properties because of containing significant part of these substances.

Experimental data, presented in the article, are the base of elaboration of the cryogenic nanotechnology of topinambour as nanopowders.

New technologies were probated in production conditions of SPE “CRIAS” (Kharkov, Ukraine) and SPE “FIPAR” (Kharkov, Ukraine), the normative documentation was elaborated (TC U 15.3-01566330-304 and TI). On their base were elaborated the new types of wellness products (dry fast soluble fruit nanodrinks «Instant»m dry juices, pastry, new types of nanoicecream, biokefirs, bioyoghurt with prebiotic properties and so on).

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THE NEW METHOD OF PROCESSING OF CAROTENE-CONTAINING VEGETABLES FOR THE PRODUCTION OF NANOPRODUCTS USING COMBI-STEAMERS AND FINE-DISPERSED COMMINUTION

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Abstract

The aim of the work is elaboration of the principally new method of deep processing of carotene-containing vegetables (CCV). For attaining this aim was used the complex effect of steam-thermal processing and fine-dispersed comminution for preservation and extraction of biologically active substances from the raw material and getting products of nanosized form. There was also used the new generation of equipment: combi-steamer and dine-dispersed comminutor.

There was elaborated the new method of deep processing, alternative to cryogenic one. This method is based on the complex effect of steam-thermal processing and fine-disperse comminution using the modern equipment (combi-steamer and fine-dispersed comminutor) that is used at enterprises of restaurant business. This method allows use biological potential of the raw material more fully (2…3 times more) and get the foodstuff in nanoform.

It was shown, that at steam-thermal processing of vegetables (carrot, pumpkin) in combi-steam antioxidant enzymatic processes flow with less intensity (3…4 times less) than at blanching.

It was established, that at the steam-thermal processing in combi-steamer in 10 minutes in carotene-containing vegetables takes place not only conservation of β-carotene but also increase of its mass fraction in 2…2,5 times (comparing with initial raw material). Mechanism of this process is connected with fact that carotenoids are transformed from the hidden state (frms associated with biopolymers) into free form that is fixed by chemical methods.

It was also established, that after steam-thermal processing and fine-dispersed comminution of carotene-containing vegetables at preparation of puree takes place the significant increase of extraction of ascorbic acid and β-carotene comparing with initial raw material that is for pumpkin 2 and 3 times more and for carrot 1,7 and 2,5 times more, respectively.

It was established, that complex use of the new equipment at steam-thermal processing of vegetable raw material in combi-steamer with fine-dispersed comminution gives a possibility to get puree, which quality is approximated to the one of puree, received using cryogenic processing of product (especially, by the content of β-carotene and other biologically active substances (BAS).

Keywords: carotene-containing vegetables, steam-thermal processing, fine-dispersed comminution, products in nanoform.

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1. Introduction

The aim of the work is elaboration of the principally new method of deep processing of carotene-containing vegetables (CCV). For attaining this aim was used the complex effect of steam-thermal processing and fine-dispersed comminution for preservation and extraction of biologically active substances from the raw material and getting products of nanosized form.The was also used the new generation of equipment: combi-steamer and dine-dispersed comminutor.

Kharkov state university of food technology and trade (KSUFTT, Kharkov, Ukraine) together with Kharkov Trade-Economic Colledge of Kyiv National University of Trade and Economics, Municipal enterprise "Combine of child food" (Kharkov, Ukraine) and Academy of hospitality and catering in Poznan city (Poland) elaborated principally new method of the deep processing of vegetable raw material without using cold. The new method, alternative to cryogenic processing, allows not only maximally preserve, but also more fully use biological potential of vegetable raw material and transform BAS and polymers from the associated state in nanoform. This method is based on the process of non-enzymatic catalysis-mechanolysis (destruction of nanocomplexes that contain biologically active substances in hidden form) in steam-thermally processed vegetable raw material that leads to getting product in nanosized form.

As innovation in the work it was offered to use the complex effect on carotene-containing vegetables at steam-thermal processing and fine-dispersed comminution using the new generation of highly effective modern equipment – combi-steamer and activator – homogenizer-comminutor [1–4].

2. Materials and methods of research

2. 1. Studied materials and equipment used in experiments

The study was carried out at the department of technology processing of fruits, vegetables and milk of KSUFTT (Kharkov, Ukraine) in laboratory of "Innovative cryo- and nanotechnologies of vegetable additives and wellness products". The steam-thermal processing was carried out in combi-steamer UNOX SPA of XVC series (Italy) that has 70 programs that differ by temperature regimes, intensity of steam supply, circulation or blowing by air (**Fig. 1**).

As objects of research there was used carotene-containing raw material – carrot (**Fig. 2**) and pumpkin (**Fig. 3**) and fine-dispersed puree of carrot and pumpkin in nanosized form (**Fig. 4**).

Fig. 1. Combi-steamer UNOX SPA of XVC series (Italy)

Fig. 2. Initial raw material (carrot)

Fig. 3. Initial raw material (pumpkin)

Fig. 4. Nanoproduct of carrot after steam-thermal processing and fine-dispersed comminution

At elaboration of principally new method of vegetables processing there was carried out comparison of effect of the different types of steam-thermal processing in combi-steamer and blanching on traditional equipment (blancher) on carotene-containing raw material (carrot and pumpkin) on the basic enzymatic, biochemical and mechanochemical processes. The steam-thermal processing of CCV samples (carrot, pumpkin) was carried out at such regimes: temperature in combi-steamer – 105 ºC, in product – 70…75 ºC, regime of steam creation – 100 % (that corresponds to the maximal amount of steam). In parallel there was carried out the thermal processing of raw material by blanching on traditional equipment (blancher – double boiler Kaiserhoff KH-8000, Germany). Blanching was carried out by immersion in boiling water at t=100 ºC during 10 min, 20 min and 30 min. The steam-thermal processing was carried out during 30 minutes with samples collection each 5 minutes. The fine-dispersed comminution was carried out in activator – homogenizer-comminutor.

2. 2. Methodologies of determination of parameters of studied samples

The comparison of quality of initial vegetable raw material and products of it was carried out by enzymatic activity of oxidant enzymes (peroxidase, polyphenol oxidase), content of β-carotene mass fraction, low molecular phenol compounds and L-ascorbic acid. The content of aforesaid substances is the one of assessment criteria of the raw material quality, accepted in international practice [1, 2, 5, 6]. For assessment of samples quality there were used standard methods (especially, the methods of determination of mass fraction of β-carotene, L-ascorbic acid, phenol compounds, flavonol glycoside) excluding the method of enzymatic activity determination. The methods of determination of aforesaid substances are given below.

Determination of carotene-content (especially β-carotene) was controlled by colorimetric Muri method after exclusion of carotene from product by organic solvent and purification of carotene from concomitant color substances using column chromatograpy.

Determination of L-ascorbic acid was carried out by the method of visual and potentiometric titration by solution of 2,6-Na dichloroindorphenol.

Determination of the general quality of low molecular phenol compounds was carried out by colorimetric method of Folin-Denis.

Determination of the sum of flavonol glycosides was carried out by colorimetric method, based on the flavonols property to change the absorption spectrum at presence of aluminum salts and at pH change. Maximal flavonol absorption is within 350…390 nm. In alkaline medium or at presence of aluminum salts the light absorption displaces by 20 nm and more to the longer waves. This ability is used at determination of flavonol glycosides by Muri method by reaction of 2 % $AlCl_3$. The calculation of flavonol glycosides was carried out by rutin.

Determination of enzymatic activity (peroxidase and polyphenol oxidase) was carried out by the conventional method of M. Mikhlin and Z. S. Bronovitska, based on the quinone ability to oxidize ascorbic acid.

3. Results of research

It was established, that at the steam-thermal processing of carotene-containing vegetables in combi-steamer (at aforesaid regimes) in 10 minutes takes place not only conservation of β-carotene but also increase of its mass fraction in 2…2,5 times comparing with initial raw material. It takes place at the expense of carotene release from the hidden state (forms associated with biopolymers) into free form that is fixed by chemical methods of research. The same regularities are established also at blanching. It is also established, that the losses of vitamin C at thermal processing of carotene-containing vegetables in combi-steamer are 2 times less that at blanching. Thus, after 20 minutes of thermal processing in combi-steamer the mass fraction of L-ascorbic acid was preserved in 65…80 %, whereas after blanching – in 40…50 %.

It was also revealed, that after steam-thermal processing and fine-dispersed comminution of carotene-containing vegetables at preparation of puree takes place the significant increase of L-ascorbic acid and β-carotene extraction that is comparing with the raw material: for pumpkin – 2 and 3 times more, for carrot – 1,7 and 2,5 times more. It was elucidated the mechanism of this process, connected with mechanical destruction and mechanical cracking (destruction) of nanocomplexes of biopolymer-carotenoid, biopolymer ascorbic acid. At the same time there takes place the release of hidden associated forms of carotene and L-ascorbic acid of nanoassciates and nanocomplexes with proteins, polysaccharides, tanning substances and other in free form. These substances are controlled by the chemical methods of research [7, 8].

It was established, that complex use of the new equipment at steam-thermal processing of vegetable raw material in combi-steamer with fine-dispersed comminution gives a possibility to get puree, which quality is approximated to the one of puree, received using cryogenic processing of product, by the biologically active substances (BAS) content (**Table 1**).

Thus, for example, the mass fraction of β-carotene in 100 g of fresh pumpkin is 8,5 mg, in fine-dispersed puree – 26,5 mg in cyopuree – 32,2 mg. Mass fraction of β-carotene in 100 g of fresh carrot and fine-disperse puree of it is 9,2 mg and 24,6 mg, respectively, in cryopuree – 28,8 mg in 100g.

Thus, it was established, that after steam-thermal processing and fine-dispersed comminution of carotene-containing vegetables at preparation of puree takes place the significant increase of extraction of L-ascorbic acid and β-carotene that is for pumpkin 2 and 3 times more and for carrot 1,7 and 2,5 times more, respectively. The results of researches demonstrated the high effectiveness of the use of new generation of equipment for steam-thermal processing and fine-disperse comminution of carotene-containing vegetables that allowed get the half-finished products and ready products in nanosized form with unique BAS content characteristics that were earlier impossible to be gotten using traditional methods of the vegetable raw material processing and existing equipment [9, 10].

Table 1

Comparative characteristic of carotene of other BAS content in fresh, steam-thermally processed carotene-containing vegetables, fine-dispersed steam-thermally processed puree and nanostructured cryopuree of them (≥3)

Product	Mass fraction (mg in 100 g)			
	β-carotene	L-ascorbic acid	Phenol compounds (by chlorogenic acid)	Flavonol glycosides (by rutin)
Fresh carrot	9,5±0,3	8,2±0,2	146±1,5	50,2±1,8
Carrot steam-thermally processed in combi-steamer	19,4±1,8	7,0±0,3	120,4±1,4	40,2±0,9
Fine-dispersed steam-thermally processed carrot puree	24,6±2,0	15,2±0,9	200,6±3,2	85,4±2,4
Nanostructured carrot cryopuree	28,8±2,5	29,7±1,5	262,6±2,8	105,8±2,8
Fresh pumpkin	8,5±0,3	9,8±0,2	128,4±1,8	45,4±1,2
Pumpkin steam-thermally processed in combi-steamer	20,0±3,4	8,2±0,2	95,8±2,0	39,2±0,5
Fine-dispersed steam-thermally processed pumpkin puree	26,5±4,2	16,5±1,8	210,6±3,5	78,8±1,6
Nanostructired pumpkin cryopuree	32,2±2,6	19,7±1,0	210,6±2,8	98,6±1,8

4. Conclusions

It was established, that complex use of the new equipment at steam-thermal processing of vegetable raw material in combi-steamer with fine-dispersed comminution gives a possibility to get puree, which quality is approximated to the one of puree, received using cryogenic processing of product (especially, by the content of β-carotene and other BAS).

The probation in production conditions of ME "CCF", SPF "KPC", "CRYOS PLUS" (Kharkov, Ukraine) and production of experimental samples of nanoproducts of carotene-containing vegetables prove the expediency of using the new method of deep processing at getting nanoproducts using the new generation of equipment at enterprises of restaurant business and trade. Thus, the aforesaid method of the deep processing of vegetable raw material allows reveal more fully the biological potential of carotene-containing vegetables that can be useful not only in food production but also at getting the natural carotenoid pharmpreparations and additives for immunoprophylaxis of population and so on.

Among the aforesaid methods the most laborious and expensive are traditional methods of the vegetable raw material processing (blanching, boiling, frying and other). It is known, that at their use at the vegetable raw material processing take place the significant wastes (15…30 %) and losses of biological potential of vegetable raw material, not used by people. At that almost half of vegetables harvest is lost at its processing and production of different foodstuff.

The new method of deep processing of carotene-containing vegetables is principally new (unique, cheaper, less laborious), it not only preserves all valuable biologically active and food substances but also allows reveal the biological potential more fully, extract its hidden BAS, associated with biopolymers, into free soluble form. At the same time this method gives a possibility to transform the part of difficultly soluble biopolymers in soluble form – nanoform that is better assimilated by human organism (2,5…3 times better) [1, 2, 4].

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THE STUDY OF MAIN PHYSICAL-CHEMICAL PARAMETERS OF CHAENOMELES AND PRODUCTS OF ITS PROCESSING

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Abstract

In the article were considered the topical problems, connected with health worsening and human existence. The use of vegetable raw material as a source of biologically active components is prospective in production foodstuff. There were offered the rational methods of processing of chaenomeles for getting juice and puree. There were carried out an analysis of expedience of using chaenomeles and products of its processing for enrichment foodstuff. It was established, that maximal amount of phenol substances is contained in fruit peel and L-ascorbic acid – in flesh. It was determined, that apple acid prevails among organic ones, fructose – among sugars and phenol substances are mainly presented by procyanidins. Using chromotographic analysis in the products of chaenomeles processing were identified 48 names of aromatic compounds, alcohols, acids, ethers and unsaturated carbohydrates prevail among them. There were studied the physical-chemical parameters of fruit sauces and flour products with addition of chaenomeles processing products. The received results prove that the ready foodstuff that contain puree and juice of chaemomeles have the high organoleptic, physical-chemical parameters and also heightened biological value.

Keywords: chaenomeles, aromatic substances, biologically active substances, phenol substances, enzymolysis.

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1. Introduction

The problem of modernity is an essential health worsening and population life shortening, caused by unfavorable ecological situation, low quality of foodstuff, use of artificial feed additives and consumption of significant amount of refined products [1].

The result of influence of these factors is a disorder of the normal physical state of human organism, increase of quantity of oncologic and other professional diseases. The problem of children health is most urgent, because each second child is born already with certain types of allergic diseases, innate pathologies and other disorders of normal development [1].

The topical problem is creation of food products with directed biological effect at the expense of using natural ingredients of the raw material with antioxidant and adaptogenic properties.

In this connection the great social importance is gained by elaboration of producing foodstuff with improved consumer properties that provides lowering of their energetic value and rising of the food one, improvement of organoleptic parameters.

2. Materials and methods of research

2. 1. Standardized methods of study of physical-chemical parameters of chaenomeles and products of its processing

The mixture of species of chaenomeles fruits, harvested in Ukraine, In Poltava region, was used for studies.

The object of studies was chaenomeles, juice and puree of it and also fruit sauces and flour products using products of chaenomeles processing.

For determination of the main physical-chemical parameters the standard methods were used: dry substances were determined by the method of arbitral drying, acidity – by the method of volume titration, vitamin C – by iodometric method, phenol substances – by Folin-Chiocolteu method in recalculation on gallic acid [2].

2. 2. Method of chromatographic study for identification of phenol substances, organic acids, sugars and volatile compounds

For identification of phenol substances, contained in chaenomeles and products of its processing were used chromatographic studies, carried out on chromatograph of Agilent Technologies (model 1100) (USA), completed with running vacuum decontaminator G1379A, four-channel pump of low pressure gradient G13111A, automatic injector G1313A, column thermostat G13116A, diode matrix detector G1316A. For analysis was used chromatographic column with size 2,1×150 mm, filled with octadecylsilyl sorbent, granulations 3,5 mcm «ZORBAX-SB C-18».

For analysis was set the following regime of chromatography: supply speed of mobile phase 0,25 ml/min; eluent working pressure 240–300 kPa; temperature of column thermostat 35 °C; sample volume 2 mcl. Detecting parameters were set as following: measurement scale 1,0; scanning time 0,5 s. Parameters of spectrum removal: each peak 190–400 nm. Waves lengths: 280, 313, 350, 371, 254 nm.

Identification of phenol substances was determined by the time of standards content and spectral characteristics.

For analysis were used the extracts of vegetable raw material (1:10), filtered through the membrane Teflon filter with pores size 0,45 mcm Vial for analysis.

Determination of content of organic acids and sugars was carried out on chromatograph of Agilent Technologies (model 1100), completed with running vacuum decontaminator G1379A, four-channel pump of low pressure gradient G13111A, automatic injector G1313A, column thermostat G13116A, diode matrix detector G1316A, refractometric detector G1362A. For analysis was used carbohydrate chromatographic column with size 7,8×300 mm, «Supelcogel-C610H».

For analysis was set the following regime of chromatography: supply speed of mobile phase 0,5 ml/min; eluent 0,1 % water solution of H3PO4; eluent working pressure 33–36 kPa; temperature of column thermostat 30 °C; sample volume 5 mcl.

Parameters of refractometric detecting: measurement scale 0,5 s.

Detecting parameters of diode matrix detector: measurement scale 0,5 s; wave length – 210/8, comparison – 360/80 nm.

Identification of organic acids and sugars was determined by time of standards retention.

The content of volatile (aromatic) substances was determined on chromatograph Agilent Technologies 6890 (USA) with mass-spectrometric detector 5973. Chromatographic column – cap-

illary DB-5 internal diameter 0,25 mm and length 30 m. Speed of carrier gas (helium) 1.2 ml/min. Temperature of heater of sample input – 250 °C. Temperature of thermostat is programmed from 50 to 320 °C with speed 4 °C /min.

For identification of components the library of mass-spectrums NIST07 and WILEY 2007 on the general number of spectrums more than 470000 in combination with programs for identification AMDIS and NIST was used. For quantitative calculations was used the method of internal standard.

3. Experimental procedures

For analysis of organoleptic parameters was chosen chaenomeles in stage of consumer ripeness, harvested in the middle of September on the territory of Ukraine, in Poltava region. The fruits differed by color from light yellow to the yellow (**Fig. 1**), had the typical sour, slightly tart flavor and rich scent corresponding to their botanical characteristics [3].

Fig. 1. Organoleptic characteristic chaenomeles fruits

Analysis of studies [3] on determination of components of chanomeles fruits and their biological value testifies that 60 % of fruit is flesh containing organic acids (6,33 %), pectin substances (1,82 %), L-ascorbic acid (248 mg/100 g) and phenol substances (920 mg/100 g). Nevertheless the fruit peel (17 % of fruit mass) and seed cell (9 % of fruit mass) containing phenol substances (1400 mg/100 g) are also valuable.

The use of enzymatic preparations is the most effective method of preliminary processing of fruits and berries raw material [4]. Their use accelerates technological processes, increase juice output of the raw material and raises its nutritive value at the expense of enrichment with phenol compounds. This processing method allows except the rise of juice output, maximally extract BAS of fruits peel and flesh, although for restaurant enterprises the method of pressing is more rational [3].

The experimental studies [5] established that the high puree output and minimal amount of wastes are reached at blanching of chaenomeles fruits in water. Such method of preliminary processing is most available in conditions of restaurant [5].

In chaenomeles fruits and products of their processing (juice, puree) were determined the physical-chemical quality parameters, which results are presented in the **Table 1.**

Table 1

Physical-chemical quality parameters of chaenomeles and products of its processing (n=3, p≤0,05)

Raw material name	Quality parameters				
	Mass fraction, %			Content, mg/100 g of dry substances	
	Dry substances	Titrated acids	Pectin substances	L-ascorbic acid	Phenol substances
Chaenomeles	18,44	6,36	1,62	248,00	885,00
Juice	11,44	5,63	0,82	144,32	410,00
Puree	13,55	4,77	1,74	98,56	560,00

The results, given in the **Table 1**, prove that products of chaenomeles processing contain pectin substances, phenol compounds and L-ascorbic acid.

For determination of biological value of products of chaenomeles processing the composition of organic acids and sugars composition was studied **(Table 2).**

Table 2

Composition of organic acids and sugars in products of chaenomeles processing (n=3, p≤0,05)

raw material name	Mass concentration, g/100 g						
	Organic acids				Sugars		
	lemon	apple	succinic	cinchona	sucrose	glucose	fructose
Juice	0,15	3,40	0,11	1,64	0,64	0,36	2,69
Puree	0,09	2,85	0,07	0,82	0,43	0,41	1,72

The results of the studies demonstrate **(Table 3)** that the main part of soluble dry substances is sugars, namely hexoses – glucose and sucrose. Fructose is a sugar, easily assimilated by organism that is why the products of chaenomeles processing can be used in technology of foodstuff of dietary and special direction.

The studies of fraction composition of phenol substances, contained in products of chaenomeles processing (**Table 3**), demonstrate the significant content of procyanidins with antioxidant activity 20 times more than ascorbic acid and 50 times more that vitamin E.

Table 3

Composition of phenol substances in chaenomeles products processing (n=3, p≤0,05)

sample name	Groups of phenol substances	Content, mg/100 g	% of PS* content	Dominating representative	Content, mg/100g	% of content
Juice	Procyanidins and their derivatives	276,27	69,20	Procyanidin trimer	87,59	31,70
Puree		322,09	58,16		157,79	5,83
Juice	Flavan-3-oils and their derivatives	116,52	29,19	Epicatechins	64,08	54,99
Puree		218,59	39,47		197,94	7,31
Juice	Oxycinnamic acids and their derivatives	5,89	1,48	Chlorogenic acid	5,89	1,48
Puree		11,02	1,99		11,02	1,99
Juice	Flavons and their derivatives	0,54	0,14	Rutin	0,54	0,14
Puree		2,07	0,37		2,07	0,37

Taking into account the fact that half-finished products of chaenomeles have powerful antioxidant properties, it can be talked about the high biological value of foodstuff, prepared with them.

The study of fraction composition of volatile substances (**Table 4**) in products of chaenomeles processing prove its significant biological value.

The received data (**Table 4**) prove that the scent of juice and puree is formed by aromatic alcohols, acids, aldehydes, ketons, ethers, carbohydrates that are present in the raw material. Significant amount of volatile aromatic substances are contained in puree because the whole fruit is used at preparation, including peel – the main source of aromatic substances.

Because of significant acidity of chaenomeles puree, it is not expedient to use it in the pure form. That is why at elaboration of sauces receipts it was blended with other pectin-containing raw material: apple, pumpkin, sunroot [5].

As a result of blending of apple and chaenomeles puree in set proportions it was elaborated the receipt of sauce "Nasoloda". In the sauces samples were studied the structural-mechanical properties and physical-chemical parameters. The received sauces have the high biological value, thermal stability, viscosity comparing with control **(Table 5).**

The positive factor is also that the use of half-finished products of chanomeles decreases their total microbiological pollution, provides prophylaxis of potato disease development [9].

Physical-chemical quality parameters are presented in the **Table 5, 6.**

Table 4

Content of volatile aromatic compounds in juice and puree of chaenomeles (n=3, p≤0,05)

compounds groups	raw material name					
	Puree			Juice		
	Number of names	Content, mg/dm³	% of total content	Number of names	Content, mg/dm³	% of total content
Alcohols	9	7,49	11,77	9	4,37	18,45
Acids	12	36,24	56,93	12	7,67	32,39
Aldehydes	2	0,60	0,94	2	0,56	2,36
Ketones	4	0,98	1,54	4	1,89	7,98
Terpenes	4	3,61	5,67	4	1,04	4,39
Ethers	9	4,95	7,78	9	2,88	12,16
Unsaturated carbohydrates	8	7,45	11,70	8	2,92	12,33
Unidentified	3	2,34	3,68	3	2,35	9,92
Total content of volatile compound	51			51		

Table 5

Physical-chemical quality parameters of sweet sauces with product of chaenomeles processing (n=3, p≤0,05)

Sauce name	Mass fraction, % mass			Content, mg/100 g		pH
	Dry substances	Pectin substances	Titrated acids	L-ascorbic acid	Phenol substances	
Apple sauce (control)	48,00	0,42	0,13	13,45	80,00	3,70
Sauce "Nasoloda"	53,00	0,81	1,61	61,60	260,00	3,50
Sauce "TopiHen"	55,00	1,49	1,68	61,18	262,00	3,50
Chaenomeles-pumpkin sauce	58,00	1,12	2,56	62,19	262,00	3,40

Table 6

Physical-chemical quality parameters of ready products of yeast dough with products of chaenomeles processing (n=3, p≤0,05)

Parameters	Control	Studied samples	
		With juice	With puree
Specific volume, cm³/g	2,80	3,30	3,30
Form stability, H/D	0,60	0,70	0,70
Acidity, degrees	2,50	2,60	3,00
Humidity, %	38,00	40,10	41,00
Porosity, %	68,00	75,00	75,00

The results of the studies **(Table 5**) prove that the use of products of chaenomeles processing in the sweet sauces technology raises their biological value at the expense of increase of L-ascorbic acid, pectin and phenol substances content comparing with control.

Taking into account that chaenomeles puree contains high percentage of pectin substances and organic acids, it can be used as natural structure-creator in technology of fruit juices and pastry.

There was determined an expedience of using chaenomeles puree in technology of flour products of yeast dough and of flour with weak gluten. Introduction of chaenomeles juice or puree in receipt of yeast dough at the mix stage favors the strengthening of dough structure and rise of hardness of gluten proteins structure that can be explained by proteins oxidation under influence of L-ascorbic acid, organic acids and complex-creation with polyphenols, contained in puree in sufficient amount [9].

Introduction of chaenomeles processing products in receipts of flour products of yeast dough (**Table 6**) raises porosity of ready products and improves assimilation. The humidity and acidity growth in experimental samples comparing with control allows prolong the storage terms of ready products and prevent the potato disease development.

4. Results of research

The results of the study (**Table 4**) testify to the predominance of alcohols, acids, ethers and carbohydrates among volatile compounds, presented in products of chaenomeles processing.

Alcohols are presented by unsaturated, saturated and aromatic alcohols. Combination of α-terpineol (lilac), β-terpeniol (hyacinth), β-ionone (violet), α-farnesene (green apple), estragole (estagon), lianol (may lily), evdesmol (rose, eucalyptus) and ethyl caprylate (flower scent) form the unique stable scent in the products of chaenomeles processing.

The special attention must be paid to squalene (representative of unsaturated carbohydrates) in amount 2,11 mg/kg in juice and 6,43 mg/kg in puree that is considered as "oxygen vitamin" and is a unique component of lipids of human skin.

Having analyzed the data of the **Table 4**, we established that almost 60 % of the total content in puree and 30 % in juice are acids. The group of acids is generally presented by carboxylic ones that have antimicrobial, antiseptic properties, immune-raising effect, help to fight against diabetes and high blood pressure. There are also linoleic and oleic acids, known as ω-6 and ω-9 unsaturated fatty acids that have positive influence on human organism and are used for prevention of diseases of different etiology [10].

Antimicrobial and antibacterial properties of products of chaenomeles processing allow assume the decrease of microbiologic contamination in foodstuff with chaenomeles.

Taking into account the high nutritive and biological value of products of chaenomeles processing, it is rational to use them in technologies of sweet sauces and flour pastry to improve organoleptic, structural-mechanical and physical-chemical parameters of ready products.

5. Conclusions

The studies of chemical composition of chaenomeles established that the raw material and products of chaenomeles processing contain organic acids, mainly apple, cinchona, lemon and succinic ones. Sugars are presented mainly by monosaccharides with predominant fructose and glucose that allow offer it in technology of foodstuff of medical-prophylactic direction. Determination of fraction composition of phenol substances demonstrated that raw material contains procyanidins, catechins, chlorogenic acid and rutin, the positive influence of these substances on human organism is proved by the medical-biological studies.

There was established the positive influence of products of chaenomeles processing on organoleptic and physical-chemical parameters of sweet sauces and yeast dough products.

Thus, chaenomeles it is a raw material that can be used in production of foodstuff with improved nutritive value and heightened antioxidant properties.

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THE STUDY OF METHODS OF PRELIMINARY COOLING OF FRUITS

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Abstract

The studies were aimed at scientific grounding of expedience of combination of preliminary cooling of apples, pears and plums and their processing by antioxidant compositions before the long storage and also at establishing of the optimal regimes and methods of this technological operation. The objects of studies were apple, pear and plums fruits of the different pomological species. As a result of studies was offered the combined method that provides preliminary cooling of apple fruits firstly by hydro-cooling in solutions of antioxidant compositions during 1 hour to the temperature in fruit center 8,5 °C, then additional cooling in AOC solutions during 1,5 hours to the temperature in fruit center 9 °C, additional cooling in chamber of intensive cooling during 50 minutes to the temperature in fruit center 1 °C. For plum: hydro-cooling in AOC solutions during 40 minutes to the temperature in fruit center 9 °C, additional cooling in chamber of intensive cooling during 30 minutes to the temperature in fruit center 1 °C. The use of such method of preliminary cooling provides the fast decrease of intensity of breath and thermal flux of fruits and essentially decreases the lost of their mass. It favors the prolongation of term of storage of fruit raw material with maximal preservation of quality and biological value. The received data and their scientific grounding give a possibility to recommend producers to use the offered method of preliminary cooling in production conditions.

Keywords: preliminary cooling, distinol, lecithin, ascorutinum, fruit thermal flux.

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1. Introduction

The use of artificial cold is one of the main methods of keeping quality and biological value of fruit production. But the advantages of this storage method are not fully used. It concerns the first stage of using low temperatures – preliminary cooling [1, 2].

Preliminary cooling is a technological process of fast temperature lowering from the initial one to the temperature of further storage of fruits [3].

After harvest the complete physiological-biochemical and physical processes take place in fruit raw material. The main ones are evaporation of humidity, breath and ripening [4].

The result of excessive humidity evaporation is the losses of fruit mass that are visually manifested in the loss of tissues turgor and withering [5].

Breath is considered as the main physiological process after harvest period that realizes three functions in organism. At first, the energy, released at substrates oxidation is transformed into converted forms of cellular energy and used at the support of living functions and further development of fruits. The second one it is provision of cells with metabolites that are created at substrates oxidation and used in diverse biosyntheses. As a result of balanced flowing of biochemical processes the ripening processes take place and fruits gain the best consumer properties. The third function is connected with thermogenesis that is energy dissipation as heat. As a result the fruits with high breath intensity evolve in chamber space the large amount of heat that needs the significantly more cooling productiveness of equipment [6].

The breath intensity of fruit raw material depends on type, specie, ripeness degree. But the most influential factor is temperature. Thus, at temperature 20 °C fruits breath flows almost 5 times more actively that at 0 °C [7].

The timely preliminary cooling decreases intensity of breath and thermal flux of fruits, decelerates the tempos of accumulation and expenditures of energetic substrates for living processes of vegetative tissues that significantly detains the ripening process [8].

But only the use of artificial cold does not provide the stable decrease of breathe intensity during the whole period of fruits storage. In addition to artificial cold the regulated and modified gas medium, ozonization, ionization, processing by 1-methylcyclopropene are used [9].

In Tavria state agrotechnological university (Melitopol, Ukraine) since 1994 are carried out the researches on the use of antioxidant compositions for processing of fruits before storage. The use of this technology gives a possibility to stabilize the breath intensity at the low level during the whole period of fruits storage, to decrease their thermal flux and mass losses.

The processing by antioxidant compositions can be realized by the different methods: the spraying in garden or on the line of fruits preparation to storage, irrigation or immersion [10]. At the further scientific studies authors faced the question as to possibility to combine technological operations of fruits processing with antioxidant compositions and preliminary cooling. The research is dedicated to the solution of this question.

Taking it into account, the authors' researches were aimed at scientific grounding of expedience of combination of preliminary cooling of fruits and their processing with antioxidant compositions before the long storage and also establishing of the optimal regimes and methods of this technological operation.

2. Materials and methods of research

The researches were carried out in Tavria state agrotechnological university (Melitopol, Ukraine). The objects of research were apple fruits of species Aidared. Golden, Delicious, Renet Simirenko, Florina, Starcrimson, pear fruits of species Crimea Raison and Conference, plum fruits Voloshka and Stanley, entered to the State list of species of plants, suitable for spreading in Ukraine.

Preliminary cooling was carried out by the following methods:

Variant 1. Apples and pears of the first, plums of the higher commodity sort, packaged in boxes, were sent for preliminary cooling. At that fruits were processed with cold air in experimental chambers of the slow cooling with temperature 2…5 °C, speed of the air movement 0,5 m/s, air exchange ratio 30 volumes for hour. Relative humidity of the air in chambers 90…95 %.

Variant 2. Apples and pears of the first, plums of the higher commodity sort, packaged in boxes, were sent for preliminary cooling. Fruits were processed with cold air in chambers of intensive cooling. The process was carried out in following regime parameters: temperature –2…–4 °C, speed of the air movement 3 m/s, air exchange ratio 90 volumes for hour. Relative humidity of the air in chambers was kept within90…95 %.

Variant 3. Hydro-cooling: apples and pears of the first, plums of the higher commodity sort were cooled in bathes, filled with cooling medium. The solutions of antioxidant compositions (SAO) were used as cooling medium. Among them composition including ionol, dimethyl sulfoxide and lecithin (DL), composition including ascorbic acid, rutin, lecithin (AARL) and also composition including ionol, dimethyl sulfoxide and polyethylene glycol mixture (DPM).

The frequency of variant is fivefold.

The breath intensity of fruits was determined by the method of I. P. Tolmachev, by the mass losses before and after cooling – method of fixed trials [11]. At analysis and processing of experimental data were used the methods of variation statistics [12], with the help of computer programs «MS Office Excel 2007», «Statistica 6» package.

3. Results of research

In experimental chambers of the slow cooling the temperature decrease of consignment of apple fruits with mean diameter 65 mm was 8 hours, of consignment of pear fruits with mean diameter 70 mm – 11 hours, plum fruits with mean diameter 38 mm – 5 hours.

The general term of temperature decrease by intensive method of apple and pear fruits to the 0 °C was 2 hours, and plum – 1,33 hours.

At the study of regimes of fruits preliminary cooling by the method of hydro-cooling the AOC solutions were used as cooling medium. For establishing of the optimal temperatures of working AOC solutions during fruits cooling their cryoscopic temperatures were determined. Thus, the ice-creating process of DPM composition takes place in temperature diapason from 0,7 to – 0,9 °C, Dl composition – from 0,6 to 0,1 °C and AARL – at 0,3 °C. The duration of crystallization of all working solutions of antioxidant compositions is 2 hours. So, for preliminary cooling of fruits can be recommended the temperature of working solutions 1,5±0,5 °C. The general duration of cooling apple and pear fruits to the 0 °C is near 3,5 hours, plum fruits – 1,5 hours.

So, the most intensive method of preliminary cooling is cooling by air at the temperature –2…–4 °C and at the speed of air movement 3 m/s.

The intensity of fruits breath before and after preliminary cooling and also thermal flux intensity at breath are given in the **Table 1.**

Table 1

Intensity of breath and thermal flux at cooling

Fruit specie	Cooling method	Breath intensity, mg CO_2/kg·hour		Thermal flux intensity, kJ/kg·°C	
		1*	2**	1	2
Apple fruits (mean 2005–2006)	slow	19,622±0,893	11,314±0,580	209,763	120,949
	intensive		4,792±0,406		51,227
	DL		5,815±0,438		62,157
	AARL		5,805±0,327		62,059
	DPM		5,712±0,445		61,059
	Combined		4,881±0,456		52,178
Pear fruits (mean 2002–2003)	slow	25,227±1,249	14,484±0,852	269,679	154,837
	intensive		7,529±0,535		80,490
	DL		8,602±0,195		91,957
	AARL		8,102±0,272		86,607
	DPM		8,442±0,316		90,247
	Combined		7,415±0,484		79,261
Plum fruits (mean 2010–2011)	slow	27,785±0,706	7,219±0,424	297,023	77,180
	intensive		4,385±0,522		46,879
	DL		4,582±0,176		48,977
	AARL		4,782±0,128		51,114
	DPM		5,057±0,249		54,057
	Combined		4,389±0,376		46,917

Note: 1 – before cooling, 2** – after cooling*

At that the thermal flux intensity of fruits was calculated by the following formula:

$$Q = q_{sp} I, \quad (1)$$

where q_{sp} – specific breath warmth, 10,69 kJ for 1 g of CO_2; I – fruits breath intensity, mg of CO_2/kg for year.

Specific breath warmth was determined by the following way, the process of aerobic breath can be described by equation:

$$C_6H_{12}O_6+6O_2 \rightarrow 6H_2O+6CO_2+2824, \text{ kJ}.$$

Since molecular mass of CO_2 is 44, according to equation of breath process is evolved 44·6=264 g of CO_2. So, for 264 g of CO_2 will be evolved 2824 kJ of heat and at evolution of 1 g of CO_2 will be evolved 10,69 kJ of heat.

The received data state the dependence of intensity of fruits breath at harvest from their specific features. The most breath intensity was inherent to plum fruits, the less – to pear fruits and the minimal one – to apple fruits. The mean coefficient of changeability of this parameter was 24 %, with variation depending on specie and sort of fruits within 13 % (plum fruits of Italian Ugorka sort) up to 39 % (pear fruits of Cure sort).

According to that the thermal flux intensity of plum fruits at harvest was maximal almost 300 kJ/kg·°C, pear fruits – 270 kJ/kg·°C, apple fruits – 210 kJ/kg·°C.

Along with it the speed constant of decrease of plum fruits breath was 2,3 and 2,8 times higher than in apple and pear fruits respectively **(Table 2)**. It means that at cooling of plum fruits the additional thermal load from their breath decreases significantly faster.

Table 2

Speed constants of decrease of breath intensity of fruits at cooling

Fruit species	Speed constants at methods of preliminary cooling, k min^{-1}				
	slow	intense	Dl	AARL	DPM
Apple fruits	–0,0043	–0,0229	–0,0131	–0,0134	–0,0132
Pear fruits	–0,0036	–0,0238	–0,0129	–0,0154	–0,0150
Plum fruits	–0,0101	–0,0438	–0,0361	–0,0387	–0,0355

Maximal value of speed constant was at intense cooling of all fruit types, with exceeding of speed constant of slow cooling in 6,6 times for pear fruits, 5,3 times – for apple fruits and in 4,3 times – for plum fruits. At hydro-cooling in AOC solutions the speed of breath intensity decrease was lower comparing with intensive one in 1,6, 1,5 and 1,2 times respectively.

So, preliminary cooling by intensive method favors maximally fast decrease of breath intensity and thermal flux of fruits.

Along with it the losses of fruit mass at intensive cooling were maximal and varied from 0,56 % in pear fruits to 0,44 % in plump fruits. At decrease of the temperature in experimental chambers of the slow cooling the mass losses were less for apples in 1,97 times and pear and plum fruits – in 3 times.

Thus, the high speed of air movement intensifies the process of cooling fruits. The result is more fast and effective braking of breathing process. But at that the natural losses of fruit mass increase.

At fruits cooling in AOC solutions the losses of fruit mass were absent at all and the speed and degree of braking of breathing processes was not essentially less than at intensive method.

Taking it into account, there was considered the combined method that provided preliminary fruits cooling firstly in working AOC solutions, then additional cooling in chambers of intensive cooling. At additional cooling the drying process also takes place. At that from the fruits surface is excreted the excessive humidity that remains after previous stage of technological processing instead of the natural one.

Duration of 1 and 2 stages of combined preliminary cooling was determined based on the speed of intensive and hydro-cooling processes. The speed of processes of temperature decrease was determined by the formula (2):

$$\vartheta = \tan\alpha = \frac{\Delta t}{\Delta \tau}, \quad (2)$$

where ϑ – the speed of cooling process, °C/min, $\tan\alpha$ – tangent of tilt angle of straight line or the first derivative of equation $t = a\tau + b$, Δt – difference between initial and final temperatures, °C, $\Delta\tau$ – time difference, min.

The speed of intensive cooling of apples was 0,15 °C/min, pear fruits – 0,16 °C/min, plum – 0,26 °C/min. The speed of hydro-cooling was equal 0,099, 0,106 and 0,220 °C/min, respectively.

According to that, the following regimes of stages of combined cooling were established:

For apple fruitsi: 1 stage – hydro-cooling in AOC solutions during 1 hour to the temperature in fruit center 8,5 °C, 2 stage – additional cooling in the chamber of intensive cooling during 50 minutes to the temperature in fruit center 1°C;

For pear fruitsi: 1 stage – hydro-cooling in AOC solutions during 1,5 hour to the temperature in fruit center 9 °C, 2 stage – additional cooling in the chamber of intensive cooling during 50 minutes to the temperature in fruit center 1°C;

For plum fruits: 1 stage – hydro-cooling in AOC solutions during 40 minutes to the temperature in fruit center 9 °C, 2 stage – additional cooling in the chamber of intensive cooling during 30 minutes to the temperature in fruit center 1°C.

The losses of fruit mass at combined cooling method varied from 0,005 % for plum fruits to 0,014 % – for apple and pear fruits. The constant of speed of decrease of breath intensity for apple fruits was 0,0245 min^{-1}, for pear fruits – 0,0215 min^{-1} and for plum fruits – 0,045 min^{-1}, that is did not essentially differ from the constant at intensive cooling.

Thus, combined method of preliminary cooling is the most acceptable by both regime parameters and technological indices of fruits quality.

4. Conclusions

It was established, that combined method that provides firstly preliminary cooling in the working solutions of antioxidant compositions and the further cooling by intensive method was characterized with the high constant of the speed of decrease of breath intensity and thermal flux of fruits and the low level of natural mass losses. At that the quantitative value of mass losses varied from 0,005 % for the plum fruits to 0,014 % – for pears and apples.

The received data and their scientific grounding give a possibility to recommend producers to carry out simultaneously the preliminary cooling and processing of fruits with antioxidant compositions before their further storage. At that it is necessary to carry out the following technological operations gradually: harvest of fruits, inspection, sorting, calibration, packaging in boxes, transportation to the place of storage, processing with antioxidant compositions and preliminary cooling by combined method: 1 stage – temperature of solutions 1,5±0,5 °C, duration 40 min …1,5 hour, 2 stage: temperature of cooling air – 2…–5 °C, relative humidity of the air 95 %, movement speed 3 m/s, duration 30…50 min.

Unfortunately the modern lines of fruits preparation to storage are absent in Ukraine. So, the further studies will be devoted to the selection of technological equipment for the line of fruits preparation to storage using antioxidant compositions.

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