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Contents

Induced effects by oxidation with potassium permanganate on the thermal, morphological, colorimetric and pasting properties of corn starch

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Abstract

Introduction. Native starches are the most consumed polysaccharides in human diet. They are used in several industries as food, textile, pharmaceutic, etc. However due to some limitations starches should be modified chemically.

Materials and methods. Corn starch modified with standard solutions of potassium permanganate ($KMnO_4$) was analysed by simultaneous thermogravimetry-differential thermal analysis, differential scanning calorimetry, rapid viscoamylographic analysis, field emission gun-scanning electron microscopy/energy dispersive spectroscopy, X-ray powder diffraction and colorimetric analysis.

Results and discussion. Corn starch was oxidised with $KMnO_4$ at different concentrations (0.01; 0.02 and 0.05 mol L^{-1}) at pH = 6.0 for 1 hour. After filtered, washed and dried at 40 °C by 24 hours, the properties of the samples were investigated. Thermogravimetric curves showed an endothermic peak attributed to evaporation of water and two exothermic peaks, which refer to the decomposition and oxidation of organic matter until the formation of ash. A period of stability was observed, which decrease after modification. The gelatinisation of oxidised starch occurred at higher peak temperatures and also required higher gelatinisation enthalpy. The viscosity of the samples was significantly reduced and the relative crystallinity increased in proportion to the oxidant concentration used. Manganese and potassium content increased with the modification. There were no morphological changes after oxidation; however a darkening of the samples was identified due to the presence of potassium and manganese observed by energy dispersive spectroscopy (EDS).

Conclusions. The obtained fluid paste with low retrogradation tendency suggests the application of oxidised starch in the paper industry.

Introduction

Due to the high productivity and its nutritional importance, corn has become the most cultivated and consumed cereal. It plays an important role as a staple food, especially in less developed countries. Corn flour has a high starch content which can be used in various food and non-food products, such as papers, textiles and pharmaceutical excipients. In the food industry the starch is used to optimize the technological properties, performing functions such as gelling agent, stabilizer, thickener and absorbent [1, 2, 3].

Numerous researches about starches from different sources have been conducted in order to evaluate its properties and to define its best application. Thus, modifications can be made to suppress limitations and to expand its industrial use, such as the chemical modification by oxidation using potassium permanganate [4].

The main use of oxidised starches is concentrated in the paper industry. This type of modification occurs through the addition of an oxidising agent in the starch in appropriate amounts, under a controlled time, temperature and pH. During the oxidation process, the hydroxyl groups present at C-1, C-2 and C-3 of the starch molecules are initially oxidised to carbonyl groups and then to carboxyl groups, which indicate the degree of oxidation. Parallel to this, there is the breaking of glycoside bonds with partial depolymerisation of starch [5].

The major oxidising agent employed is sodium hypochlorite, but its use is associated with the formation of toxic chlorinated by-products. However, hydrogen peroxide, ammonium persulfate, sodium bromate and potassium permanganate also can be used. The oxidation reaction using permanganate is very complex because it produces free radicals (reduction of Mn^{4+} to both Mn^{3+} or Mn^{2+}) and/or direct oxidation [3,6].

Many tools are used to evaluate thermal behaviour of starches, as well as thermal analysis [7,8]. Thermogravimetry (TG) is a technique that evaluates the mass variation of a sample in function of temperature or time. Differential scanning calorimetry (DSC) measures the heat flow between a sample and a reference material subjected to a temperature change. Through these and some others techniques such as morphological, structural and rheological analysis can be identified changes in the behaviour of the modified starches [9].

Therefore, this study aims the modification of corn starch by oxidation using potassium permanganate (KMnO4) at different concentrations (0.01; 0.02 and 0.05 mol L^{-1}). The samples were characterised by thermogravimetry and differential thermal analysis (TG-DTA), differential scanning calorimetry (DSC); rapid viscoamylographic analysis (RVA); field emission gun/scanning electron microscopy with energy dispersive spectroscopy (FEG-SEM/EDS), X-ray powder diffraction (XRD) and colorimetric analysis.

Materials and methods

Starch modification

The native maize starch was bought in Colombo, PR, Brazil and it was divided into four parts of 20 g (dry basis). One sample (a) was maintained in the native form. The modification was performed according to literature with some modifications [10]. The samples were treated at pH 6.0, for 1 h with standard potassium permanganate ($KMnO_4$) at concentrations of 0.01 mol L^{-1} (b), 0.02 mol L^{-1} (c) 0.05 mol L^{-1} (d). Then the samples were

washed and filtered until the complete elimination of the oxidising agent. After this, the modified samples were dried in an oven with forced air circulation at 35 °C for 24 h.

Thermogravimetric study (TG-DTA)

The TG-DTA curves were obtained using a thermal analysis system (Shimadzu, model DTG-60H). Approximately 6.0–8.0 mg of the samples were heated from 30 °C to 600 °C in an open alumina crucibles under a synthetic air flow of 50 mL min^{-1} and a heating rate of 10 °C min^{-1}. The instrument was previously calibrated with standard weight and monohydrated calcium oxalate standard. All the mass loss percentages were determined using TA-60WS software [11].

Differential scanning calorimetry (DSC)

The DSC curves were obtained using a thermal analysis system (TA-Instruments, model DSC-Q200, USA). The DSC curves were recorded under an air flow of 50 mL min^{-1} and heating rate of 10 °C min^{-1}. A suspension with 2.5 mg of the samples in a proportion of 4:1 (water:starch w/w) was prepared in aluminium crucibles which were sealed and left for 1 h to equilibrate the moisture content. The instrument was previously calibrated with 99.99% purity Indium, mp = 156.6 °C, ΔH = 28.56 J g^{-1} [12].

Rapid viscoamylographic analysis (RVA)

The pasting properties of the samples were obtained using a viscometer (Newport Scientific, model RVA-4, Australia). Suspensions of 3.0 g of starch in 25.0 g of distilled water were submitted to a controlled process of heating and cooling under constant stirring, where the samples were held at 50 °C for two min, heated from 50 to 95 °C at 6 °C min^{-1}, held at 95 °C for 5 min, cooled to 50 °C at 6 °C min^{-1} and held at 50 °C for 2 min [13].

Field emission gun-scanning electron microscopy/Energy dispersive spectroscopy (FEG-SEM/EDS)

The micro-images of the native and modified samples were obtained using field emission gun-scanning electron microscopy (FEG-SEM) (MIRA 3, Tescan, Czech Republic). The samples were placed on a carbon tape and pulverised with gold and palladium to promote the electrons conductivity. A tension of 20 kV was generated by a lamp with tungsten filament [14]. The chemicals elements present in the samples were identified by EDS, which is based on the released energy measurement when an excited atom (due to electron beam that focuses on the sample) returns to its normal state.

X-ray diffractometry (XRD)

The X-ray diffraction patterns were obtained using an X-ray diffractometer (Rigaku, model Ultima, Japan), employing Cu Kα radiation (λ = 1.541 Å) and settings of 40 kV and 20 mA. An angular range of 5–50° (2θ) with a scanning speed of 8° min^{-1} and a step of 0.06° was used in order to detect the scattered radiation. The degree of relative crystallinity was quantitatively estimated using Eq. 1 and according to the literature [15].

$$Xc = \frac{A_p}{A_p + A_b} \cdot 100 \quad (1)$$

where Xc = relative crystallinity; A_p = peak area; A_b = basis area which refers to amorphous area of diffractogram.

Colorimetric analysis

Colour parameters of the starch samples were determined using a reflectance spectrophotometer, model MiniScan XE 45/0-L Plus (Hunter Inc., USA). This technique consists in the evaluation of three colour components: L*, a* and b*. The L* parameter correspond to the lightness (from 0, black to 100, white); a* indicates the tendency to red (+) and green (-), and b* indicates the tendency to yellow (+) or blue (-) [11].

Statistical analysis

The analyses were performed in triplicate. All the averages of the samples were analysed by variance analysis (ANOVA) and Tukey's test with a 95% confidence interval ($p<0.05$), using STATISTICA 7.0 software (StatSoft, Inc., Tulsa, OK, USA).

Results and discussion

Thermogravimetry-Differential thermal analysis (TG–DTA)

The thermogravimetric curves of the native and treated samples (TG-DTA), Figure 1, presented three main events of mass loss. The first event, which corresponds to the endothermic peak shown by DTA curve, was attributed to evaporation of water and volatile compounds. After this, a period of stability was observed, registering the highest thermal stability for the native sample. The second and third exothermic events refer to the decomposition and oxidation of organic matter until the formation of ash. Similar results were found in the literature [16, 17].

The values obtained by TG-DTA curves are shown in Table 1. The dehydration of the samples occurred in a temperature range from 30 to 150 ºC, as reported by Liu *et al.* [18]. Compared with the centesimal composition analysis, the thermogravimetric method has advantages such as lower mass and time required [19]. The modification by $KMnO_4$ decreased the thermal stability of corn starch to temperatures between 215–249 ºC. This may be related to the presence of mono and divalent metal ions complexed with starch granules from anionic groups, such as carboxyl groups formed after the oxidation [20].

The final temperature of decomposition was similar for all the samples (592–599 ºC), resulting in 0.7% ash for native sample and 1.8; 3.3 and 3.5% for the modified samples (b-d), respectively. The increase in the ash content was attributed to the presence of manganese and potassium in the samples due to modification, which was confirmed with EDS analysis.

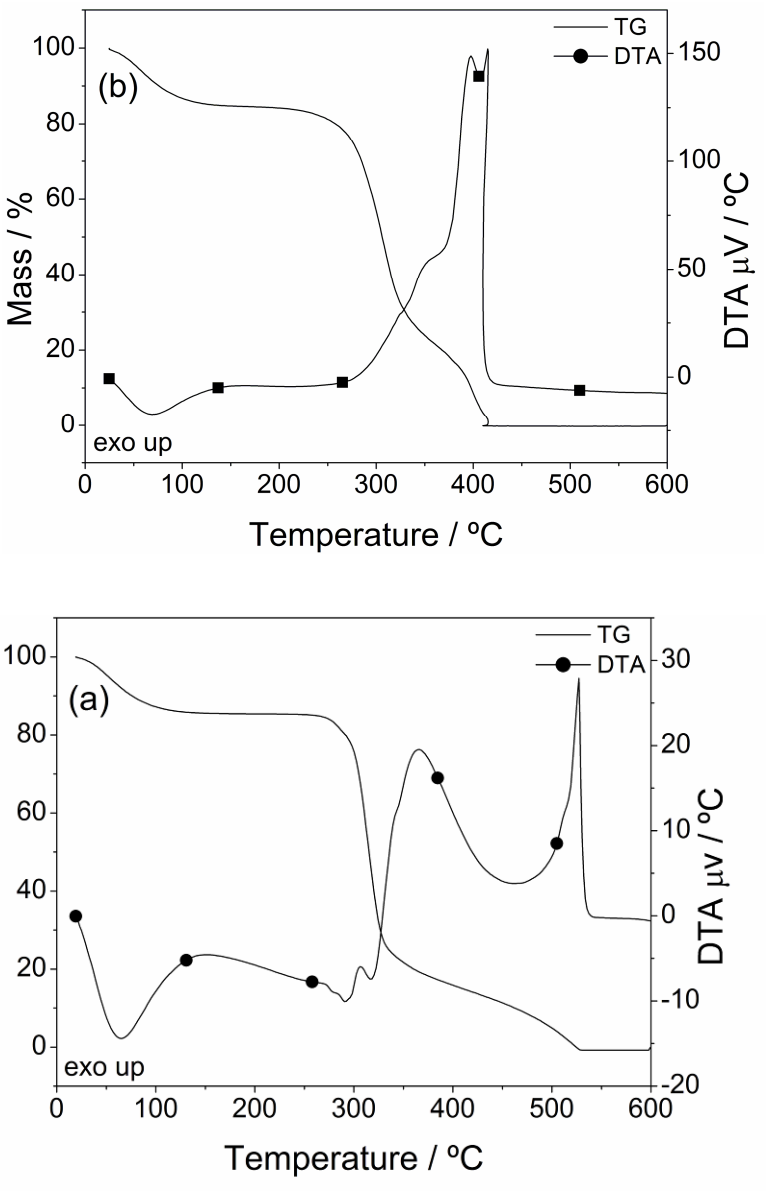

Figure 1. TG-DTA curves for native (a) and modified corn starch with standard $KMnO_4$ at 0.01 mol L^{-1} (b); 0.02 mol L^{-1} (c) and 0.05 mol L^{-1} (d)

(Continuation of Figure 1 see on next page)

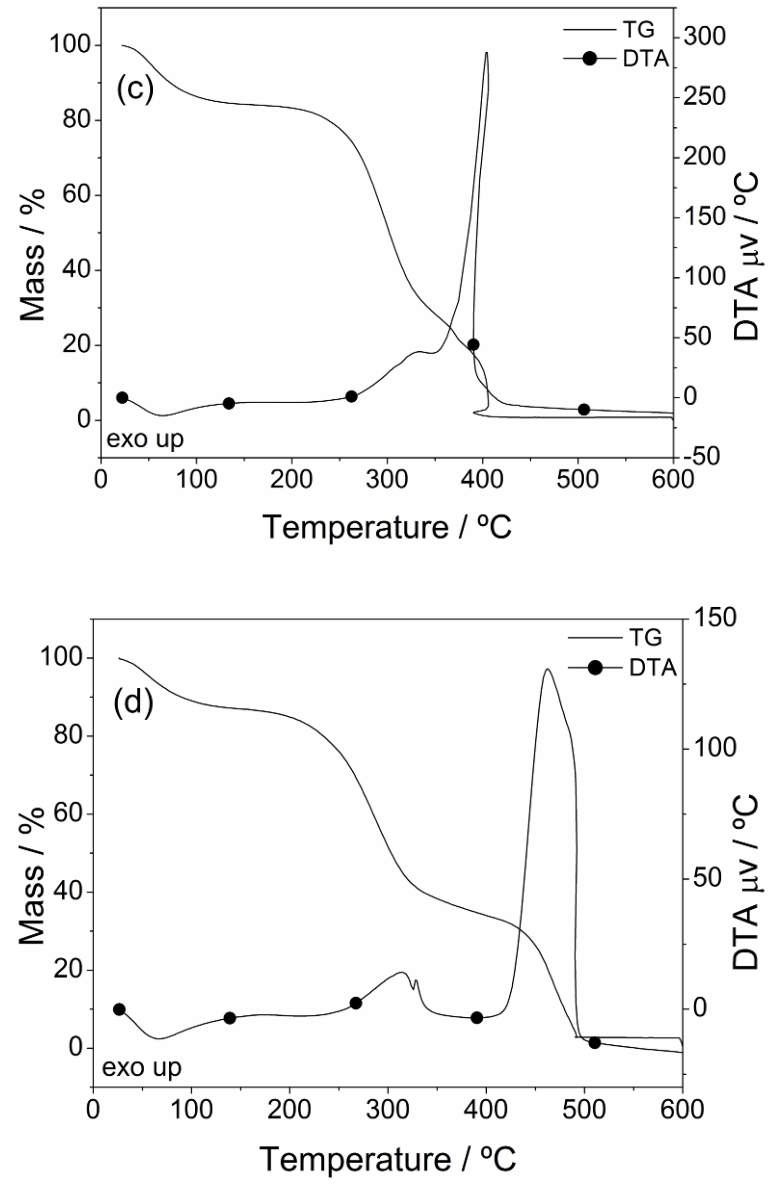

Figure 1 *(continuation)*. TG-DTA curves for native (a) and modified corn starch with standard $KMnO_4$ at 0.01 mol L^{-1} (b); 0.02 mol L^{-1} (c) and 0.05 mol L^{-1} (d)

Table 1

TG-DTA results for native (a) and modified corn starch with standard $KMnO_4$ at 0.01 mol L^{-1} (b); 0.02 mol L^{-1} (c) and 0.05 mol L^{-1} (d)

Sample	TG Results		DTA Results	
	Step	*Δm* (%)	*ΔT* (°C)	*Tp* (°C)
(a)	1st	13.3	30–158	58.7 (Endo)
	Stability	-	158–249	-
	2nd	71.9	249–431	316.3 (Exo)
	3rd	14.1	431–592	512.2 (Exo)
(b)	1st	14.5	30–159	62.2 (Endo)
	Stability	-	159–224	-
	2nd	61.4	224–360	308.6 (Exo)
	3rd	22.3	360–592	397.7 (Exo)
(c)	1st	15.00	30–136	67.1 (Endo)
	Stability	-	136–215	-
	2nd	52.8	215–346	315.2 (Exo)
	3rd	28.9	346–594	479.2 (Exo)
(d)	1st	12.1	30–146	67.5 (Endo)
	Stability	-	146–237	-
	2nd	52.1	237–406	313.9 (Exo)
	3rd	32.3	406–59	462.3 (Exo)

Δm, mass loss (%); ΔT, temperature range (°C); Tp, peak temperature (°C).

Gelatinisation study

DSC was used to evaluate the gelatinisation of native and oxidised samples. The transition in the curves (Figure 2) corresponds to the dissociation of the amylose and amylopectin molecules within the starch granules and leaching out of amylose to the continuous phase, characteristic of gelatinisation process [21]. There was a slight shift to the right in the endothermic event for the samples (b) and (c) in relation to the sample (a).

The results in Table 2 of native and oxidised starches were similar to those obtained by Liu *et al.* [22]. The oxidised samples (b) and (c) had a higher onset temperature (T_o) than the native sample (a). The sample modified with the highest concentration of $KMnO_4$ presented the lowest value for the onset temperature (T_o). The peak temperatures of modified starches were higher than the native sample, as well as the gelatinisation enthalpy (ΔH_{gel}) values. It was suggested that this occur due to hydrolysis in the amorphous lamella, resulting in the increased of

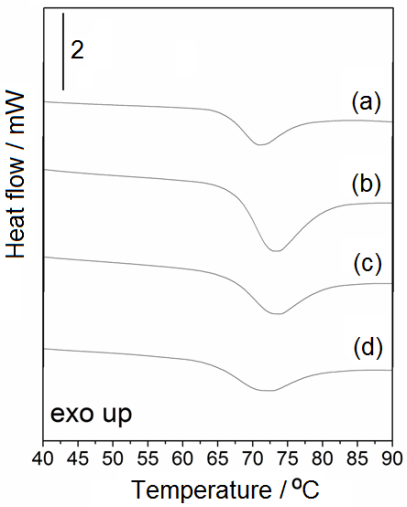

Figure 2. DSC curves to the gelatinisation phenomenon for native (a) and modified corn starch with standard $KMnO_4$ at 0.01 mol L^{-1} (b); 0.02 mol L^{-1} (c) and 0.05 mol L^{-1} (d)

the hydration and swelling of starch crystallites, disrupting the crystalline lamella. Thus, a highest temperature was necessary to oxidised starch gelatinisation [23]. Conclusion temperature (T_c) decreased significantly for the samples (a, b, c).

Table 2

DSC gelatinisation results for native (a) and modified corn starch with standard $KMnO_4$ at 0.01 mol L^{-1} (b); 0.02 mol L^{-1} (c) and 0.05 mol L^{-1} (d)

Sample	DSC gelatinisation			
	T_o (°C)[a]	T_p (°C)	T_c (°C)	ΔH_{gel} (J g^{-1})
(a)	66.1 ± 0.15[b]	70.8 ± 0.05[c]	83.2 ± 1.96[a]	7.3 ± 0.33[c]
(b)	67.7 ± 0.03[a]	73.0 ± 0.14[a]	79.7 ± 1.11[b]	13.1 ± 0.17[a]
(c)	66.4 ± 0.41[b]	73.0 ± 0.04[a]	79.7 ± 1.46[b]	10.4 ± 1.61[b]
(d)	63.8 ± 0.33[c]	71.0 ± 0.04[b]	79.3 ± 1.00[b]	9.4 ± 0.80[b]

T_o "onset" initial temperature, *Tp* peak temperature, T_c "endset" conclusion temperature, ΔH_{gel} gelatinisation enthalpy. Values followed by the same letter in the same column are not significantly different by Tukey's test ($p<0.05$).

Pasting properties (RVA)

The RVA curves are shown in Figure 3. Oxidation of starch with potassium permanganate caused a reduction in the viscosity peak of the samples. This reduction can be attributed to degradation of the starch chains caused by oxidation, with consequent reduction of the molecular weight [24]. This type of starch can be used in the batter applications because it promotes a higher binding and stability[23].

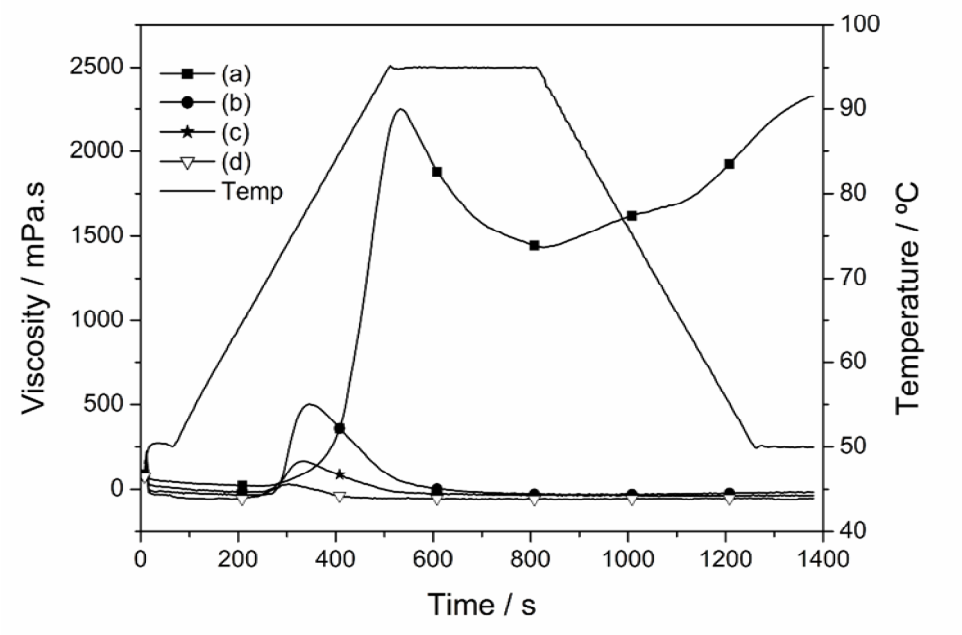

Figure 3. RVA curves for native (a) and modified corn starch with standard $KMnO_4$ at 0.01 mol L^{-1} (b); 0.02 mol L^{-1} (c) and 0.05 mol L^{-1} (d)

There was significant difference between the samples for all the parameters. The lowest value for the peak viscosity (Table 3) was observed to the sample (d), modified with the highest concentration of $KMnO_4$. It was not possible to determine the pasting temperature for the sample (d), probably due to the low peak viscosity value. The sample (b) presented a significant reduction in this parameter.

Since there was a major disruption of the starch chains by the modification, there was no reassociation of amylose chains during cooling the starch slurry (setback), which can also be confirmed by the low values of final viscosity recorded.

Table 3

RVA results for native (a) and modified corn starch with standard $KMnO_4$ at 0.01 mol L^{-1} (b); 0.02 mol L^{-1} (c) and 0.05 mol L^{-1} (d)

Sample	Pasting temperature (ºC)	Viscosity peak (mPa.s)	Setback (mPa.s)	Breakdown (mPa.s)	Final viscosity (mPa.s)	Peak time (s)
(a)	82.5 ± 0.02^{a}	2246.3 ± 1.53^{a}	889.8 ± 0.38^{a}	814.9 ± 0.15^{a}	2323.7 ± 0.58^{a}	82.5 ± 0.02^{a}
(b)	71.8 ± 0.02^{c}	499.7 ± 1.53^{b}	15.0 ± 0.01^{b}	533.2 ± 0.21^{b}	-17.0 ± 0.01^{b}	71.8 ± 0.02^{c}
(c)	73.6 ± 0.01^{b}	165.7 ± 1.15^{c}	5.0 ± 0.02^{d}	205.2 ± 0.15^{c}	-35.4 ± 0.53^{c}	73.6 ± 0.01^{b}
(d)	-	28.3 ± 1.53^{d}	7.0 ± 0.01^{c}	90.0 ± 0.20^{d}	-53.9 ± 1.00^{d}	-

mPa s "millipascal-second", s "second". Values followed by the same letter in the same column are not significantly different by Tukey's test ($p<0.05$).

Morphology and determination of metallic ions

The micro-images of the starch granules obtained using field emission gun-scanning electron microscopy are showed in Figure 4. A polyhedral and irregular shape with flat surface was observed for corn starch, as found in the literature [9]. There was no change in the morphology of the granules after modification, as obtained by Zhou *et al.* [25] after oxidation of potato starch at low concentrations of sodium hypochlorite. Other studies reported the appearance of pores on the surface of the starch granules after the oxidation under alkaline conditions, which was not observed in this study [26].

The average diameter of the untreated and treated maize starch granules was calculated and its results are presented in Table 4. There was no significant difference between the average diameter values, although a decrease can be observed with increasing concentration of the oxidising agent.

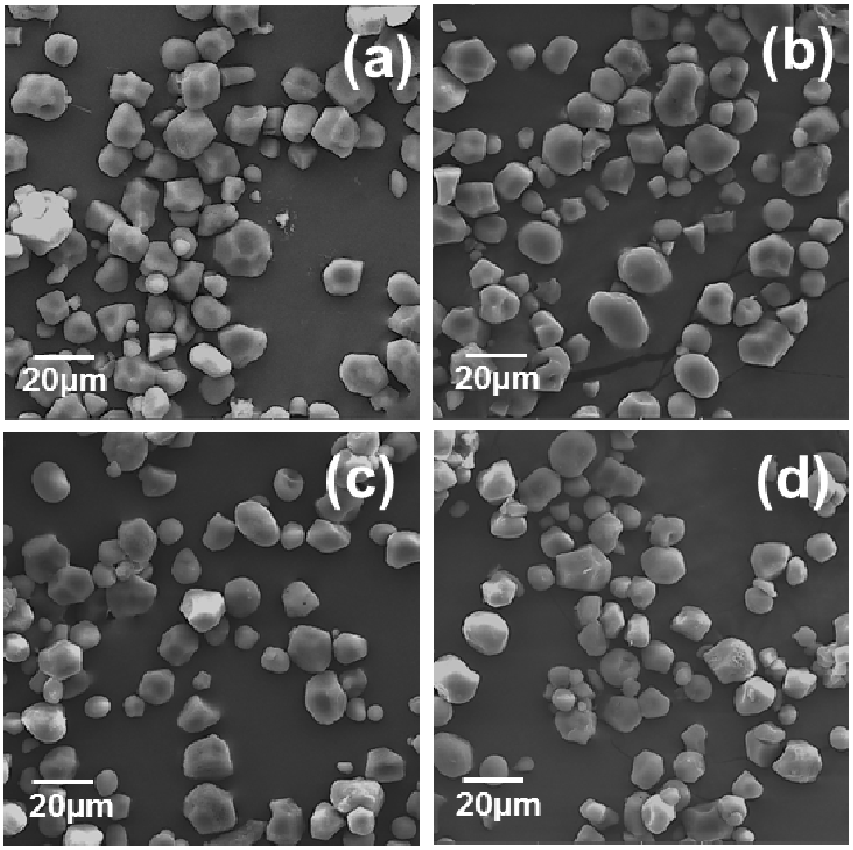

Figure 4. FEG images for native (a) and modified corn starch with standard $KMnO_4$ at 0.01 mol L^{-1} (b); 0.02 mol L^{-1} (c) and 0.05 mol L^{-1} (d)

Table 4

FEG-EDS and XRD results and Colour parameters for native (a) and modified corn starch with standard $KMnO_4$ at 0.01 mol L^{-1} (b); 0.02 mol L^{-1} (c) and 0.05 mol L^{-1} (d)

Samples	FEG-EDS			Colour parameters		
	K/Pd (wt%)	Mn/Pd (wt%)	d_a (μm)	L*	a*	b*
(a)	N. D.	N. D.	13.9 ± 0.77^{a}	93.2 ± 3.0^{a}	-0.8 ± 0.1^{d}	3.3 ± 0.8^{d}
(b)	27.8 ± 0.12^{a}	53.4 ± 6.18^{a}	13.1 ± 0.49^{ab}	54.6 ± 0.19^{b}	6.0 ± 0.07^{c}	26.0 ± 0.30^{b}
(c)	30.6 ± 1.82^{b}	57.5 ± 0.24^{a}	12.6 ± 0.54^{ab}	43.2 ± 0.15^{c}	8.2 ± 0.02^{b}	28.3 ± 0.19^{a}
(d)	33.7 ± 0.86^{b}	61.6 ± 4.46^{a}	12.1 ± 0.34^{b}	27.7 ± 0.21^{d}	9.4 ± 0.11^{a}	22.7 ± 0.43^{c}

FEG-EDS: weight ratio of potassium and manganese; d_a: average diameter. Values followed by different letters in the same column present significant difference according to Tukey's test ($p<0.05$).

Through EDS it was possible to measure some chemical elements present in the samples (Figure 4). The identified elements were manganese and potassium, which were derived from the oxidation of starch with potassium permanganate. The palladium was added by the metallisation process that is required for FEG analysis. As the metallisation time was similar for all the samples, it was considered as a constant the palladium content and it was calculated the relative presence of manganese and potassium on the modified samples, since there was no presence of these elements in the native sample. The concentrations are presented in Table 4. With increasing of $KMnO_4$ concentration it were observed an increase of the manganese and potassium concentration in the oxidised samples.

X-ray powder diffraction (XRD)

X-ray diffractograms for each sample are shown in Figure 5. According to the literature [27], starch diffraction patterns are related with the main peaks obtained by XRD. Therefore, when the starch presents peaks at 15; 17; 18 and 23º (2θ), it can be classified as A-type. B-type presents peaks at 5.6; 15; 17; 18 and 23º, and C-type shows peaks at 5.5; 15; 17; 22 and 23º, which is considered a mixture of A and B types. The native and modified corn starches presented the most intense peaks at 15º; 17º; 18º and 23º (2Θ); therefore, the diffraction pattern was classified as A-type, which is characteristic for starches derived of cereals [28].

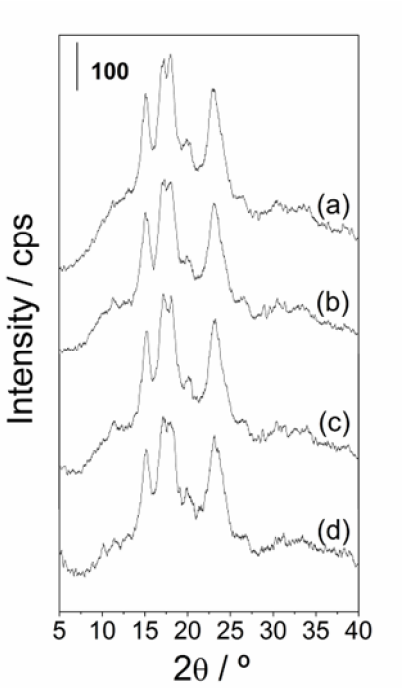

Figure 5. X-ray diffraction for native (a) and modified corn starch with standard $KMnO_4$ at 0.01 mol L^{-1} (b); 0.02 mol L^{-1} (c) and 0.05 mol L^{-1} (d)

The relative crystallinity values calculated for the samples were: (a) 30.68 ± 0.36^c; (b) 36.56 ± 0.24^b; (c) 36.92 ± 0.66^b and (d) 42.62 ± 0.17^a. Analysing these values, an increase in this parameter was observed for the modified samples, with significant difference

between themselves, except between the samples (b) and (c). Similar results were reported by Zhou *et al*. [25] for potato starch treated with sodium hypochlorite at low concentrations, suggesting that oxidation reactions occur mainly in the amorphous regions of the granule.

Colorimetric parameters

The colorimetric parameters are shown in Table 4. The results corroborate the changes that can be observed visually in the modified starch samples. A significant decrease was identified in the L* parameter for the oxidised starches (b-d) in relation to the native (a), which showed a greater tendency to black proportionally to concentration of potassium permanganate used.

When the samples were treated, a tendency to red and to yellow was observed by the a* and b* parameters, respectively. This darkening of the samples can be attributed to the action of the oxidising agent in the starch structure. Similar results were reported by Pietrzyk *et al*. [20].

Conclusions

Corn starch was investigated after oxidation with potassium permanganate at different concentrations.

The TG-DTA analysis showed a highest thermal stability for the native sample. DSC curves presented higher peak temperature and the gelatinisation enthalpy (ΔH_{gel}) values for the modified samples.

There was a considerable reduction in peak viscosity of the oxidised samples with potassium permanganate proportional to the concentration used.

It was detected an increase in the manganese and potassium content for the modified starches by EDS.

All the samples showed A-type diffraction pattern and the degree of relative crystallinity was lower for the native sample.

A decrease in the L parameter and a higher tendency to red and yellow were identified for the oxidised corn starches, resulting in the darkening of them.

Therefore, the modification with potassium permanganate promoted strong changes in the properties of corn starch. This process can be used to modified the characteristics of native corn starch as alternative for others oxidising agents, such as sodium hypochlorite which is associated with the formation of toxic compounds. Besides, the obtained fluid paste with low retrogradation tendency suggests the application of oxidised starch in the paper industry.

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Methodology for accelerated monitoring and assurance of sanitary quality and food safety

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Abstract

Introduction. The microbiological criteria that ensure sanitary quality and safety of food products, methods for identifying regulated microorganisms, and the urgency of accelerated microbiological control of food safety are characterized.

Materials and methods. The methodology for assessing the safety of products and the classical and accelerated methods for determining regulated microbiological indicators that identify the presence of heat-resistant pathogens of food diseases are studied. Analytical studies are based on modern literary sources and some of own results.

Results and discussion. The characteristics of microbiological criteria and requirements for microbiological safety of food products were given. Analysis of modern requirements for the sanitary safety of food has shown the need for microbiological control for the presence of heat-resistant microorganisms, which are potential pathogens of foodborne diseases. Microbial species traditionally the main assessment of their health status such as *Clostridium botulinum, Bacillus cereus, Clostridium perfringens, Staphylococcus aureus* were given. Characteristics of the phenotypes and genotypic properties of criterial microorganisms – potential causative agents of foodborne infections and poisonings are given. The study methodology and methods of control of regulated microorganisms showed failure and inaccuracy of their phenotypic diagnosis due to the similarity of morphological and tinctorial properties within the individual groups, the variability of a number of biochemical parameters, weak antigenicity for the immunological diagnosis, the advent of new metabolic features associated with the ability to synthesize genes toxicity by microorganisms, which were traditionally considered to be non-pathogenic, labor-consuming and durable analysis. Genotypic diagnostics of microorganisms using modern molecular genetic methods and methodologies, in contrast to the phenotypic one, ensures the accuracy of identification, the ability to monitor and predict the behavior of pathogens of foodborne infections and toxic infections in products in assessing microbiological risk, allows accelerated microbiological control of food safety, taking into account their specific features of composition and properties, is a reliable method of sanitary control.

Conclusions. Molecular genetic diagnosis of pathogens is a promising accelerated method for determining food safety and is relevant especially in the Ukrainian region.

Introduction

The characteristics of microorganisms that are criterial in assessing the microbiological safety of food, of the methodology and methods for identifying biological pollutants occurring in food products – agents of foodborne infections and poisoning, identifying a potential danger to the consumer with accelerated and reliable methods for controlling food safety, are relevant.

The *aim of the research* is to investigate the criteria indicators of sanitary quality and food safety, methodology and methods for accelerated control of thermally stable regulated microorganisms – potential causative agents of food poisoning.

Microbiological criteria for food safety. Biological hazards are the main ones in assessing the degree of risk if they are caused by the presence of microorganisms in foodstuffs such as bacteria or products of their vital activity, toxigenic molds, viruses; parasites – helminths and protozoa, as well as insects that are potential carriers of pathogenic microorganisms [1, 2, 3]. According to statistics, annual economic losses due to diseases caused by several pathogenic microorganisms in the US amount to 35 billion dollars, in Australia – up to 2.6 billion Australian dollars, and social losses are irreplaceable [4, 5].

The reason for increasing the level of biological hazards is the modern fashion for the consumption of raw or minimally cooked food, the increase in the share of products of animal origin, improperly prepared or stored long before consumption, through the expansion of international trade in new types of food raw materials that have changed the overall a picture of microbiological hazards, a modification of the microorganisms themselves [5–7].

The Codex Alimentarius Commission has developed guidance documents CAC/GL 21, «Principles for the Establishment and Application of Microbiological Criteria for Food Products», CAC/GL-30 «Principles and Guidelines for Microbiological Risk Assessment», where requirements for microbiological safety of food are set out, as well as microbiological criteria establishing general risk assessment rules that can be used are indicated [8–10]:

- to check the conformity of the technological process with the requirements of good hygiene practice (GHP) and GMP (good manufacturing practice) – good manufacturing practices and hygiene practices;
- to determine the suitability or unsuitability of the product or batch of products presented for delivery to the market or already in the sphere of trade;
- to determine the acceptability or unacceptability of new products and new technology in terms of ensuring microbiological safety;
- to develop trade agreements between the supplier and the recipient of the products.

General considerations regarding the principles for the development and application of microbiological criteria for different types of food are given in the Codex Alimentarius CAC/GL 21 document and other EU policy documents, for example, in the report of the EU Commission «On the strategy for selecting microbiological criteria for food in the EU food legislation», in the EU Guidelines 2073 «On Microbiological Criteria for Food», as well as in the guidelines of the Federal Food and Drug Administration (USA) [1, 4, 11–13]:

- if it is a question of products with a short shelf life or products of increased demand that are not delayed in the trade network, the method used must be fast enough so that the time taken to obtain information about the safety of the product does not exceed the period of storage or shelf life;

- microbiological criteria should be established only when there is a need for them (for example, in connection with a special epidemiological situation);
- when determining the criteria, such circumstances as the actual or potential health hazard, the microbiological status of the raw material, the influence of technological methods on the microbiological status of the finished product, the possibility of recontamination of the finished product or the possibility of microorganisms developing in it at subsequent stages of the technological or life cycle, category of consumers, for which the product is intended, the way in which the product is used, the ratio between the costs of control and profit;
- both pathogenic and indicator organisms can be used as controlled microorganisms; Instead of microorganisms, their toxins can be controlled;
- in cases where the pathogens themselves can be isolated reliably, preference should be given to their direct control, and not to indirect monitoring by indicator microorganisms;
- as for the choice of analytical methods, it should be borne in mind that for carrying out comparative tests in different laboratories only those methods can be used whose reliability is as far as possible estimated, i.e., statistical indicators of the accuracy of the results obtained, convergence and reproducibility of the analysis results, In different laboratories of comparative trials can only be used;
- test methods intended for use in controversial situations should have greater selectivity and reproducibility of results than the methods used in the production environment (which, in return for these qualities, should have other advantages, such as speed and ease of obtaining the necessary information);
- the limits should be established not for individual products but for groups of homogeneous products, and therefore should be based on the input data obtained for all such products manufactured under the operating conditions of the HACCP system and GMP-good manufacturing practices;
- when establishing microbiological criteria, consideration should be given to the possibility of changing the microflora of the product during its storage during the specified shelf life, as well as during its redistribution, taking into account the conditions for storage and transportation of the product, as well as the process of its preparation for use (if it is required);
- if the microbiological criterion requires a lack of a microorganism in the product, the mass or volume of the analytical sample and the number of analytical samples must be indicated.

Modern sources note [4, 7, 12] that selective control of finished products by microbiological indicators can not provide the required security guarantees. The necessary level of microbiological safety of food products can be achieved only through measures of a preventive nature and mainly through compliance with and control of sanitary norms and rules, and through the application of control procedures based on the principles of hazard analysis and control of critical points in the processing and redistribution processes food (implementation of the principles of the HACCP system) [12].

Requirements for the biological safety of food products. The focus of attention of hygienists are currently following bacteria, which become sources of food poisoning and infections: microorganisms of the genus *Salmonella, Clostridium botulinum, Clostridium perfringens, Staphylococcus aureus, Campilobacter jejuni, Yersinia enterocolitica and Yersinia pseudotuberculosis, Listeria monocytogenes, Vibrio cholerae O and non- O-1, Vibrio parahaemolyticus, Vibrio vulnificus* and other representatives of the genus *Vibrio,*

Aeromonas hidrophila, Plesiomonas shigelloides, Shigella, bacteria group Miscellaneous enterics, Streptococcus, and Escherichia coli [2, 12, 14, 15].

The risk of alimentary diseases make their share as viruses – *Hepatitisvirus, Rotavirus, Norvalk virus* etc., as well as parasites such as *Helminths* and intestinal pathogenic protozoa, whose source can be water, shellfish, sick animals and humans. Among the viruses that cause nutritional disorders, it should be noted *Hepatitis (A and E)* virus, *Rotavirus, Norwalk*, and among this organisms infesting and worms [1, 2].

The subject of constant supervision should not be absolutely all the listed microorganisms, viruses and parasites. Modern food safety systems require control only over the most dangerous sources of risk, different for different types of food products. Therefore, one of the key stages in the development of a security management system, including HACCP systems for each specific type of food, is to assess the magnitude of the risk and to decide whether or not a particular control effort is appropriate.

Particular attention from these positions should be given to long-term storage products – to various types of canned, dried foods, semi-canned foods. Depending on the type of heat treatment – sterilization, sub-sterilization, pasteurization or hot packing, the residual microflora can be represented by different types of microorganisms [16, 17]. The causative agents of food poisoning, found among the residual and secondary microflora of full canned food, are sporiferous microorganisms (*Clostridium botulinum, Bacillus cereus, Clostridium perfringens*), and in semis – also *staphylococci (Staphylococcus aureus)*.

Materials and methods

The methodology and methods for assessing the safety of products with the use of classical methods for determining phenotypic indicators of regulated microorganisms were investigated. There were such parameters of regulated microorganisms studied as morphological, tinctorial, cultural, biochemical, physiological, some chemotaxonomic properties (some of them listed in Table 1) [5, 12, 17–19, 21–23, 25–26, 36] and others. Methods for rapid determination of regulated microbiological parameters that identify the presence of heat-resistant food pathogens diseases are based on the determination of molecular genetic features [24, 31–32, 37–38, 44–52]. The analytical studies are performed on the basis of modern literary sources and some of own results [27, 34, 35, 39–42].

Results and discussion

1. Characteristics and traditional methods of diagnosis of regulated microorganisms, which are the causative agents of food poisoning

A brief generalized phenotypic characteristic of the causative agents of food poisoning that occur in the residual and secondary microflora of products of long-term storage, as well as their effect on the properties of food products, are given in Table 1 [5, 12, 17–19, etc].

Table 1

The main characteristics of the causative agents of food poisoning from the residual and secondary microflora of long-term storage products

Microorganism type, Determination method	Morphology and tinctorial features	Physiological and some biochemical properties	Impact on product quality, toxigenicity
Clostridium botulinum, ISO/TS 17919: 2013, [19, 26]	Spore-forming large rod-shaped bacterium with rounded ends measuring (0.3–4.3) x (3.4–8.6) mkm, at young age is mobile, gram positive. Spores oval, subterminal, a cell with a spike resembles a tennis racket	Mesophilus, severe anaerobic. Catalazo-negative, splits gelatin. Lactose, sucrose, mannitol does not ferment, nitrates do not reduce, indole does not form. The fermentation of glucose, maltose and salicin varies. Proteolytic strains A, B decompose casein, non-proteolytic B, E, F – do not decompose milk casein. There are eight types of botulinum toxins differentiated in neutralization reactions with type-specific diagnostic antibotulinum sera. Thermostability at pH 7.0 for *C. botulinum* A and B corresponds to D_{121} = 0.2 min, for type E D_{80} =1.8 min. The toxin formation and multiplication of *C. botulinum* is observed under strictly anaerobic conditions at a pH above 4.2 (usually in media with a pH of 4.5–8.0), with a NaCl concentration of not more than 10% and a sugar content of not more than 50%.	Botulinum toxin can accumulate without visible changes in the product. Human disease is usually associated with intoxication caused by *C. botulinum* types A, B, E, less often F. The disease caused by *C. botulinum* type A is most often very severe, lethality is 60-70% of cases. Diseases associated with types B and E are characterized by a lighter course (lethality 10–30%). The development of *C. botulinum* under favorable conditions (pH above 4.2, water activity (a_w) above 0.85) leads to the bombing of cans and packages, the product acquires a foreign smell, most o ften of butyric acid.

Table 1 (Continue)

Microorganism type, Determination method	Morphology and tinctorial features	Physiological and some biochemical properties	Impact on product quality, toxigenicity
Clostridium perfringens, ISO 7937:2004	Large, straight thick sticks with rounded or blunt ends with a size (0,9–1,3) x (4,0–8,0) mkm. The size of the cells depends on the strain of clostridia, age and substrate. The cells are arranged in groups parallel to each other, stacked in pairs, in pairs, singly, more rarely – by a chain. Can form a capsule. Gram-positive, in old cultures, mosaic staining is possible – cells appear that are repetitively gram-negative. The diagnostic sign is immobility of cells. Spores oval, central or subterminal. In contrast to causative agents of botulism, the cell does not swell during sporulation	Mesophilic anaerobes (the optimum temperature is 37 °C, but *C. perfringens* can grow over a wide range of temperatures – from 16 to 50 °C). The optimum pH value is 6.7–7.6, but they develop well in products with pH ≥ 5.3, in some canned foods with a pH of 3.5–5.3. The optimum value of a_w for the growth of *C. perfringens* is 0.95–0.96, the minimum value is 0.93. Limit the development and toxin formation in *C. perfringens* table salt at a concentration 7.4–12% and carbohydrates 7–15%. They have a sulphite-reducing ability, cause a rapid fermentation of milk with the formation of a spongy bunch, as a rule, decompose gelatin, form lecithinase, hemolysins, collagenase, and carry out haemolysis. Six types of *C. perfringens* are known: A, B, C, D, E and F, which are distinguished by the antigenic structure and antigenic properties of the toxins they produce. Spores thermostability D_{90} = 5–145 min.	Widespread in soils and water. Food poisoning is associated with the formation and sprouting of *C. perfringens* spores in the gastrointestinal tract. Food poisoning is caused mainly by strains A and D. Food poisoning of people is associated with A-toxin, the production of enterotoxin and a number of enzymes with toxic properties. As an exception, with massive contamination of *C.perfringens* product, a bombing is possible.

Table 1 (Continue)

Microorganism type, Determination method	Microorganism type, Determination method	Microorganism type, Determination method	Microorganism type, Determination method
Bacillus cereus, ISO 7932:2004	Large movable rods with straight or rounded ends, gram-positive. Dimensions (1.0–1.2)x(3.0–5.0) mkm are located. In the form of stacker-like clusters, chains, occasionally singly. Can form long threads. Spores cylindrical, ellipsoidal, are located centrally or eccentrically, the cell is not inflated. Capsule does not form	Mesophilic aerobes or facultative anaerobes. Catalase-positive. Grow in at temperatures from 8 to 50 °C, the optimum temperature is 30–32 °C, at pH≥4.0, 8% concentration of NaCl. *B. cereus* form acetoin acetylmethylcarbinol, most strains form lecithinase, do not form acid from mannitol.	Widespread in the environment, in soil, in products. Causes food-borne diseases of diarrhea and emetic types. Accumulation in the product of a large number of cells (10^6–10^7 or more in 1 g) usually leads to minor changes in the appearance of the product. When developing in crushed and homogenized products (minced meat, cutlets, cream, sausage), their organoleptic properties can change significantly – a grayish film forms on the surface, the color changes and an odor appears, rancidity and souring of the product can be observed. The development of *B. cereus* in canned food is accompanied by the formation of a wall ring at the border of the product and packaging and the precipitation of a white precipitate at the bottom of the container.

Table 1 (Continue)

Microorganism type, Determination method	Microorganism type, Determination method	Microorganism type, Determination method	Microorganism type, Determination method
Staphylococcus aureus, ISO 6888-3:2003	Cells are spherical and gram-positive, non-spore forming in diameter 0,5–1,5 mkm. Can form clusters of irregular shape, immovable, do not form a spore; When viewed microscopically, they are seen as short chains, pairs of cells or clusters similar to grape clusters.	Metabolism is respiratory and fermentative, form a catalase, use carbohydrates to form lactic acid under anaerobic conditions, acetic and CO_2 to aerobic. The main diagnostic test to identify *S. aureus*, is the ability to coagulate blood plasma by the enzyme coagulase. Distinguish six serotypes of entero-toxins A, B, C, D, E and F. The most common enterotoxin A which is synthesi-zed by the cells in exponential growth phase. Pathogenicity staphylococci determine their ability to produce a number of toxins. Hemolysins, dermatoxin, eucocidin, enterotoxin, as well as enzymes – plasmo-coagulase, hyaluronidase, deoxyribonuclease, etc. Facultative anaerobes develop at pH≥4,2, sensitive to heat $D_{60} \approx 3$ min.	Foods contaminated with staphylococci usually do not have external and organoleptic signs of spoilage. Staphylococci can develop and produce enterotoxin in canned foods, especially low-acid foods. Reproduction of pathogenic staphylo-cocci and accumulation of enterotoxin occurs under aerobic conditions at room temperature without visible organoleptic changes in the product for several hours.

Morphology and tinctorial features, which are given in Table 1, a number of physiological and some biochemical properties of regulated microorganisms that are the causative agents of food poisoning, as well as the classical methods for their determination, indicate a sufficiently profound study of these microorganisms. However, despite the popularity and standardization of methods, their disadvantage was low compared to the required promptness to obtain the necessary information (7 days for the identification of *C. botulinum* and when using the fastest biological test with mice, 48 hours). Standardized

methods of analysis of *C. perfringens* (ISO 7937) provide for bacteriological culture, and serological analysis is used to detect enterotoxin. The duration of the procedure is 3 days. In determining trace amounts, for example, of staphylococcal enterotoxin in food products, the toxin should be isolated and concentrated before its serological identification. Currently, express methods based on the use of monoclonal antibodies, which have high efficiency, are being developed, since it is possible to detect toxin concentrations of the order of 1 nanogram per gram of food product.

Identification of pure cultures (up to the species of microorganism) is carried out taking into account the morphological, tinctorial, cultural, biochemical, toxigenic and antigenic properties of the microorganism [20–22]. The used (classical) *B. cereus* identification method is based on the isolation of pure culture on the MYP medium of the Mossel-yolk agar with mannitol, polymyxin and phenol red, and subsequent biochemical testing of the isolated culture [23], which requires of a considerable time [24]. In this regard, the question of developing an accelerated reliable method of identification of *B. cereus* is still relevant.

To identify individual species, immunological methods are often used. They are the agglutination reaction, immunoelectrophoretic analysis of antigenic components, immunofluorescence methods [1, 2, 23]. Most studies involve the determination of susceptibility to antimicrobial agents in the isolated pathogen. For the epidemiological assessment of the role of the microorganism, an intraspecific identification is carried out by the definition of phage, biovars, resistants, etc. Such studies are material and labor-intensive, long-lasting, often do not correspond to the shelf-life of food products and, as we noted in studies, do not always allow the microorganism to be accurately established.

The need to improve methodological approaches to the diagnosis of these microorganisms is necessary, and among the methods of microbiological control of food production a special place should be taken by precise, relatively rapid molecular genetic methods.

2. Molecular genetic methods of microbiological control of regulated microorganisms

The use of molecular genetic methods for the sanitary control of food safety is a relatively new approach in the genotypic diagnosis of regulated microorganisms. Foreign and domestic scientists developed DNA analysis technologies that include DNA methods, in particular, polymerase chain reaction (PCR), multiplex PCR, reverse transcription PCR, qualitative or quantitative real-time PCR with various fluorescent systems. TagMan probes, SYBR Green et al., DNA hybridization methods, in particular FISH, as well as isothermal amplification (RSA, SDA) [24–27]. Such methods can be used in practice in the sanitary control of food products in establishing their safety by identifying pathogenic and opportunistic pathogens of foodborne infections and toxic infections, monitoring the quality of raw materials and the technological process of its processing. Molecular genetic methods can be used in scientific forecasting when studying regulated microorganisms and evaluating microbiological risks, as well as for identifying nucleotide sequences-toxicity genes responsible for the pathogenic properties of microorganisms [28–29].

There are test systems for the microbiological analysis of clostridia and other anaerobes [30]: F5110 SureFast® *Clostridium botulinum* Screening PLUS, F5123 SureFast® *C. perfringens* Screening PLUS, based on DNA determination by PCR, which, according to the developer, are the most accurate way to determine Microorganisms.

Currently, seven serologically different types of neurotoxins (A, B, C, D, E, F and G) are known to be produced by the corresponding strains of *C. botulinum*, which have similar sizes and molecular organization. These are large enough proteins, consisting of two polypeptide chains – light (50-59 kDa) and heavy (85-105 kDa), which block the release of the mediator – acetylcholine. Despite the fact that botulism has been known for more than 200 years, at present the detailed mechanism of neurotoxins at the molecular level has not been sufficiently studied. It is believed that the neuroparalytic effect of the toxin is achieved as a result of the passage of 3 stages: the binding of a toxic molecule to the membrane surface, the energy-dependent penetration of a part of the molecule into the cell and the inhibitory stage. Medicines against botulism do not exist now [31]. It is believed that human botulism is caused by four types of neurotoxins A, B, E and F. In addition to the classic strains of *C. botulinum*, it has been found that other microorganisms, for example *C. butyricum*, producing the type E neurotoxin, may be the cause of botulism and *C. barati*, producing neurotoxin type F.

As noted in [31], a PCR method for the identification of *C. botulinum* types A and B has been developed, which has high specificity and sensitivity (1 pg DNA), which can be used in diagnostic laboratories to identify these microorganisms. The PCR method is simple in execution, it ensures quickness of the results (less than 5 hours from the beginning of the study) and is especially convenient in cases when it is necessary to test a large number of samples.

As is known, *C. perfringens* is the causative agent of food-borne diseases, necrotic enteritis, gas gangrene [32, 33]. Strains B and D produce Ɛ-toxin, which leads to edema of the organs due to the formation in the cells of the channels through which the potassium ions emerge. Strain A causes food-borne diseases. There is a priority method for the PCR determination of *C. perfringens* [34], as well as the methodology for conducting research [35].

In addition, in the literature, there is sufficient information on the pathogenic properties and methods of determining *Staphylococcus aureus* [36–38].

Particular attention is currently being paid to bacillary pathogens of foodborne diseases, because, thanks to the development of molecular genetic methods, it has become known that not only microorganisms of the *Bacillus cereus* group (including 6 representatives), but a number of other bacilli are capable of producing toxicity genes [1, 2]. As noted in [23], during the study of 114 samples of raw milk for the presence of bacilli, it was found that the bacilli (*B. cereus, B. subtilis*) were preserved even after heating for 10 minutes at 80 °C, in 21% of samples from pasteurized ham samples microorganisms of the genus *Bacillus* (the most common were *B. cereus, B. subtilis, B. licheniformis*), and spore-forming *B. cereus* were isolated from boiled sausages. It is indicated that 95 strains of bacilli were isolated and identified from wheat flour. Among the 53 strains isolated from the cooled dough, 24 strains were *B. subtilis*, 17 were *B. cereus*, 10 were *B. pumilis*, 2 were *B. licheniformis*. Our studies also show an abundance of bacillary contamination of plant [39, 40] and animal products [41, 42].

The presence of *B. cereus* or its toxins in food products is identified by morphological, biochemical, serological (ELISA), chemo-taxonomic and molecular genetic (PCR) methods [43]. It is possible to detect a toxin that causes vomiting, with the help of animal models (cats, monkeys) and cellular ones. The most common classical method of *B. cereus* identification is based on the isolation of pure culture on the MYP medium (the Mosell-yolk agar), and subsequent biochemical testing of the isolated culture [23]. However, the instability of *B. cereus* enzymatic reactions hampers the interspecies differentiation of the bacteria of the first morphological group of the genus *Bacillus* and, in addition, requires

considerable time-consuming [44]. In this regard, the question of developing an accelerated reliable method of identification of *B. cereus* is still relevant. Under experimental administration, the subcutaneous method of *B. cereus* is caused by disorders of the function of the gastrointestinal tract, lethargy, inhibition of movements. With the introduction of large doses of these microorganisms, the disease develops sharply, with a rapidly advancing (10 – 16 h) lethal outcome. At morphological research in organs of the fallen animals hemorrhages, inflammatory and necrotic changes are observed. To the greatest extent these lesions are recorded in the intestines, liver, heart muscle and in the brain. The authors [23] based on the traditional method developed a new scheme for isolating *B. cereus*, dividing the objects of the study into 2 groups, depending on the form in which the causative agent (vegetative or spore) is located. This scheme allows typing of *B. cereus* pathogen within 4–5 days due to expansion by additional biological tests (Fig. 1) [23].

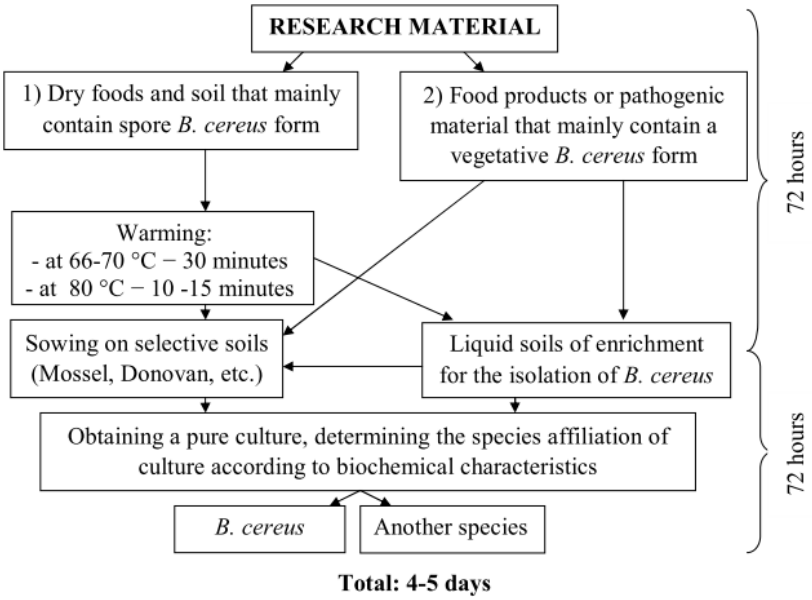

Figure 1. Scheme of identification of the causative agent *B. cereus*

The scheme shown in Figure 1, despite the length and laboriousness, does not make it possible to diagnose the presence of all bacillary representatives-carriers of toxicity genes capable of producing the corresponding toxins and confirms the need for an improved microbiological control methodology.

Modern works of a number of foreign researchers have shown that bacillary microorganisms synthesize genes that cause the ability of *B. cereus* to cause diarrheal and emetic syndromes [44–47]. *B. cereus* causes diarrhea and emetic syndromes, producing various extracellular toxins, including the three main types of enterotoxins, namely hemolysin BL (*hbl*), nonhemolytic enterotoxin (*nhe*) and cytotoxin K (*cyt K*) [48]. Eight new pairs of PCR primers were developed and effectively detected eight toxin genes – *hblC, hblD, hblA, nheA, nheB, nheC, cytK* and *entFM*) in 411 strains of *B. cereus* (121 and 290 isolated from food and soil) and 205 strains *B. thuringiensis*.

The presence of *hblACD* genes in all 70 tested isolates from ready-to-eat vegetables in South Korea, detection of one or more *hbl* genes in 23.5–70.6% of *B. cereus* group isolates from food products in Brazil, detection of *hblA* in all 57 *B. cereus* isolates from raw vegetable samples collected in Mexico City, detection of *hblA* and *hblD* in 72% of *B. cereus* isolates from retail spices in the USA, *hblC* in 71% of these isolates are noted in the literature and testify to the relevance of such studies [45, 47–50].

Recently, scientific works on the differentiation of living and dead cells of bacillary pathogens of food poisoning have appeared [51, 52].

Among the strains of *B. cereus*, enterotoxigenic genes *hbl A, nhe A, cyt K* and *Fm* (enterotoxin FM) were widely spread. However, we selected only the *nhe A* gene for PCR, given its greatest prevalence and detectable visual toxicity, which is associated with a major role in food poisoning [39, 41, 42]. The PCR with specific primers *nhe A*F and *nhe A*R, matched to the site of the *nhe A* gene, confirmed the belonging of all tested collection strains of *B. cereus* to the enterotoxigenic species of *B. cereus*, whereas in PCR analysis of the DNA of the collection species *G. stearothermophilus* and *Paenibacillus polymyxa* and in negative control (PCR mixture without DNA), no amplification products were detected.

Thus, the substantiation of the methodology and the development of accelerated molecular genetic methods of microbiological control are relevant in improving the control of food safety.

Conclusions

Analysis of modern requirements for the sanitary safety of food has shown the need for microbiological control for the presence of heat-resistant microorganisms, which are potential pathogens of foodborne diseases.

Investigation of the control criterion microbiological indicators regulated types of microorganisms such as *Clostridium botulinum, Bacillus cereus, Clostridium perfringens, Staphylococcus aureus* showed failure phenotypic diagnosis due to the similarity of morphological and tinctorial properties within the individual groups, the variability of a number of biochemical parameters, weak antigenicity of a number of toxins, The emergence of new metabolic features associated with the ability to synthesize the toxicity genes by microorganisms, which are traditionally considered to be non-pathogenic, laborious and lengthy analysis.

Genotypic diagnostics of microorganisms using modern molecular genetic methods and methodologies that allow for accelerated microbiological control of food safety taking into account the characteristics of their composition and properties, the accuracy of identification, the ability to monitor and predict the behavior of infectious agents of foodborne infections and toxic infections in products in assessing microbiological risk are relevant, especially in the Ukrainian region.

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Comparison of biological value and technological properties of oil seed proteins

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Abstract

Introduction. The objective of this work was comparative analysis of protein properties of main oil seeds, cultivated in Ukraine, notably rape, sunflower and soy..

Materials and methods. *Tetrachimena piriformis* (WH–14 strain) cultures were used for the determination of relative nutritive value and toxicity of the protein products. The emulsifying capacity of seed proteins were determined as maximum volumes of emulsified oil relatively to 1 g of proteins and foaming capacity as volume of foam, obtained at standard conditions relative to volume of protein suspension.

Results and discussion. According to our data biological value of soy proteins were limited by sulfur containing amino acid methionin and cystin (2,1% from common amino acid content). There total content was only about 60% of FAO/WHO scale. Biological value of sunflower proteins was limited by three amino acids – sulfur containing amino acids (1,6% of methionine and cysteine) and lysine (3,0% from common amino acid content). The contents of majority of indispensable amino acids in rape proteins are 8–57% higher than FAO/WHO scale. The exception are valin and isoleycin with 80–85% content. Score of sulfur containing amino acid was 157,1% from FAO/WHO scale. Isolated rape proteins had highest technological properties, their solubilities were 16,4 to 38,6% at different pH, water holding capacity − 211 %, oil binding capacity − 130 %, emulsifying capacity − 140 ml/g, and foaming capacity – 122 %.

Conclusions. Investigated protein isolates of oil seeds (soy, sunflower and rape) had no toxicity. Rape proteins isolate had the highest relative biological value and technological properties.

Introduction

Oil seeds are cultivated as raw material for vegetable oils production, but their chemical compositions are unique as to content of lipids, proteins and numerous biological active substances. Protein content of oilseeds is on the level or even exceeds their content in cereals. Special place belongs to soy beans as they contain about twice time higher proteins than lipids. Therefore soy beans are cultivated first of all for feed and food proteins production.

Thus the main products of soy bean processing are soy meal and soy oil. Protein content of soy meal varies from 40 to 45 %, about 80% of which are storage proteins [1]. The main soy storage proteins are glycinin and β-conglycinin, which belong to the legumin (11S globulins) and vicilin (7S globulins) families of proteins, respectively. These two globulins have different polypeptide composition and technological properties [2-4] and they were precipitated at different pH, notably 11 S globulins − at pH 5,8 and 7 S – at pH 4,5 [5].

Soy meal is using as a source of different protein products. Removal of seed coats and preserving of high PDI (protein dispersion index) are necessary for edible soy meal production. The high PDI of soy meal generates suitable technological properties of proteins. Soy meal with a high PDI is a raw material for soy protein isolates and with a lower PDI – for protein concentrates. When PDI of soy meal is very low such meal can be used for soy meat production, biscuits etc. Thus the technological properties of proteins are very important for vegetable proteins production particularly of edible range.

Traditional technology of edible soy meal, protein concentrates, isolates, extruded and fermented soy products are described in detail in [6]. But Nazareth *et al.* [7] have shown that soy protein isolates obtained from gas-supported screw-pressed soybean meal had more than 90% protein content and had exhibited the high water solubility, water-, oil holding and emulsifying capacities and viscosity of suspensions.

Technological properties of isolated seed proteins first of all depend from degree of their denaturation, which in turn is determined by technology of their obtaining and seeds processing. Conformational changes of soy proteins were observed as at 105 °C and at 23 °C [8]. It was shown [9] that denaturation degree of soy proteins depends on hydrophobicity of organic solvents and water content, hydrophobic solvents have a low denaturing capacity even at high temperatures, the degree of denaturation of proteins increased with the addition of water. Lower alcohols have the highest denaturing ability among the studied solvents. At the same time Lhocine *et al.* [10] have shown that technological properties of protein isolates, obtained after defatting of soy flour by ethanol or water, were comparable with protein isolates from soy meal extracted by hexane.

Structure, chemical composition and properties of other oil seeds were studied too. Proteins account for about 20% of sunflower seeds dry weight. The main storage protein of sunflower seeds heliantin as well as soy globulin consist of two fraction – hexamer 11S globulins and threemer 7S globulins with a denaturation temperature 65 and 90 °C, respectively [11]. But heliantin has low water solubility and thermo-induced jellification capacity, which complicates using of such proteins in food systems. Nevertheless heliantin has higher thermal stability compare with globulins of other seeds [12]. Detailed analysis of physicochemical, structural and functional properties of sunflower storage proteins was made by Gonzalez-Perez and Vereijken [13]. Thus it was demonstrated increase of solubility of nondenaturated heliantin even at isoelectric point under high ionic strength of solution (2 M NaCl). At the same time decrease of solubility in a pH range from 2 to 8,5

under increase of ionic strength of solution to 0,25 M NaCl was detected for sunflower protein isolates, obtained from industrial sunflower meal [14].

The main storage protein of Cruciferous seeds is 11S globulin – cruciferin account for about 60% of seed protein content and content of albumin is about 20% [15, 16]. Using of rape seeds as source of food and feed proteins is associated with glucosinolates content. The different methods were proposed to avoid content of these substances in rapeseed meal. To decrease glucosinolates content in rapeseed and canola meal Diosady *et al.* had used two stage extractions of oils from seeds using polar and nonpolar solvent [17–19]. In spite of this method did not promote complete oil recovery from seeds, protein isolates and concentrates obtained from such meal did not contain glucosinolates [20–24]. In addition steam explosion was used for detoxification of rapeseed meals [25] and it was shown that enzyme treatment could be used to decrease of glucosinolates content in meal [26] .

The biological value of oil seed proteins measured as indispensable amino acid content depends first of all from plant species, variety and climate conditions of their growing. Therefore the data about these values varied in different source. The objective of our work was comparative study of biological value and technological properties of proteins of three main oil seed crop notably soy, sunflower and rape.

Materials and methods

Materials

Soybeans variety NK25D3 and sunflower seeds variety KP11B were received from Institute of oil crops of National Academy of Agrarian Science (Zaporizhia, Ukraine). Rape (*Brassica napus)* seeds of winter (*Artus*, Lembke KG, Germany) variety were collected from local oil market. The chemical composition of soy beans: 11.3% moisture, 39.2% (dry basis) protein, 29.8% (dry basis) lipids, and 5.9% (dry basis) ash. Sunflower KP11B is a linoleic variety (62.5% of total content of fatty acids). The sunflower seeds contained 6.7% moisture, 48.2% (dry basis) lipids, 16.7% (dry basis) proteins, and 7.3% (dry basis) ash. The rape seeds contained 4.2% moisture, 43.6% (dry basis) lipids, 23.7% (dry basis) proteins, 5.6% (dry basis) ash, and 0.8% (dry basis) glucosinolates.

Proximate analyses

Moisture content of seeds was determined using the gravimetric method. Fat content of seeds was measured according to Soxhlet's method. For this purpose 2 g of sample were extracted for 24 hrs using hexane as a solvent. Crude protein (Nx6.25) was determined by the Kjeldahl method according to AOAC Method [27]. Content of total soluble proteins in seeds were determined suspending 5 g of defatted meal in water solution at pH 10, adjusted with 1N NaOH. Suspensions were mixed by agitation during 90 min. Suspensions were centrifuged for 15 min at 3,500 rpm/min. Concentration of soluble proteins in supernatants were determined by Biuret method [28] using bovine serum albumin as standard.

Ash content was determined by igniting the samples at 550 °C in a muffle furnace until light grey ash resulted. Glucosinolate content was measured as glucose released from glucosinolates in stoichiometric amounts under hydrolysis by the endogenous enzyme myrosinase using GLUCOTEST paper according to Interstate Standard [29]. For glucosinolate hydrolysis 0.5 g of crushed seeds were mixed with 5 mL of distilled water and incubated in the presence of activated carbon during 2 min.

Determination of toxicity and relative nutritive value of protein products

Tetrachimena piriformis (WH–14 strain) cultures were used for the determination of relative nutritive value and toxicity of the protein products. The dead cells, changed shapes, characteristic of movement and growth depression of infusoria were measure of toxicity. 50 mg of protein samples, 2 mL of sea salt solution (5.6 mg/mL, pH 7.0) and 0.04 mL of 3-days *Tetrachimena piriformis* cultures were placed in vials, mixed and incubated in thermostat at 25 °C during 24 and 72 h. For better aeration the vials were periodically shake during incubation. After incubation infusoria cells were fixed in iodine solution in ethanol (50 g/kg) and analyzed under light microscope. Cell quantity was determined using counting chamber. The control samples contained casein instead of seed protein products. Relative nutritive values of investigated samples were represented as a number of cells grown per sample, compared with the control.

Protein isolation

Proteins were extracted from defatted seeds by sodium chloride solution (70 g/L, pH 7.0) under constant stirring and temperature 50-55 °C during 40-50 min, meal: solution ratio was 1:10 (w:v). After this insoluble residues were precipitated by centrifugation (1 000g, 15 min). The supernatant (protein extract) was used for isoelectric protein precipitation at pH 4.5. After protein coagulation pellet was separated from whey by centrifugation (3 000g, 15 min), washed with distilled water at pH 4.5, collected and dried at 55–60 °C to 6–8% moisture.

Determination of amino acid composition of protein isolates

The direct acid hydrolysis of protein isolates was used to obtain hydrolysates suitable for determination of all amino acid except cysteine and tryptophan. Hydrolysis was carried out in test tubes by adding of 1 mL HCl to dry sample, corresponding to 2 mg of protein. The mixture was frozen in a bath at - 80°C, evacuated, sealed and then samples were exposed at 106 °C for 24 h in a thermostat. After hydrolysis samples were cooled and HCl was removed from them by evacuating in dessicator containing NaOH pellet. After drying of samples 4 mL of deionized water was added and drying procedure was repeated. Dry samples were dissolved in citrate buffers (0.3 M/L, pH 2.2) and used for amino acid analyses.

Amino acid analyzer T 339 (Czech Republic) was used for amino acid content analysis. Standard amino acid mixture containing 0.5 μM of the 17 commonly occurring amino acid was used to calculate the amount of amino acids in the samples.

Determination of proteins functional properties

Determination of protein products solubility were performed according to [30] using solutions with pH values from 2 to 10, adjusted with 1 N HCl or 1 N NaOH, and protein concentration 1 mg/1 ml. Prepared protein suspensions were mixed by shaker during 1 h. Suspensions were centrifuged for 30 min at 3,500g. Concentration of soluble proteins were determined in the supernatant by Biuret method [28] using bovine serum albumin as standard.

The water holding capacities (WHC) of the extracted seed proteins were measured as described by Ashraf *et al.* [31] taking 1 g of protein extract and resuspended in 10 mL of

distilled water and mixed vigorously for 2 minutes, the supernatants obtained after centrifugation at 3 000 x g for 20 min, were decanted and the weights of the sediments were determined, the WHC values expressed as gram of water absorbed per 100 g of protein extracted.

The oil binding capacities (OBCs) of the extracted seed proteins were measured using the method of Ashraf *et al.* [31] taking 1g of protein, deposited and reweighed in 50 mL centrifuge tubes and thoroughly mixed for 3 min with 10 mL of vegetable oil. Samples were allowed to stand for 30 min and the mixtures were centrifuged at 3 000xg for 20 min, the supernatants were carefully poured immediately after the centrifugation and tubes with the sediments were weighted. The OBC values expressed as gram of oil absorbed per 100 g of protein isolates.

The emulsifying capacity (EC) of the extracted seed proteins were determined according to Karki *et al.* [32] taking 8.5 g of each sample and mixed with 50 mL of distilled water for 2 min using a blender and vegetable oil was adding slowly with continuous blending. The process was stopped after every 2 min to check for emulsion breakage. The maximum volumes of oil that was emulsified were measured and emulsifying capacity was determined as volume of oil relatively to 1 g of protein isolates.

The foaming capacity (FC, %) of the extracted seed proteins was determined according to Makri *et al.* [33] taking 1% of the protein extracted and resuspended in deionized water, pH was adjusted to 7.4 with 0.1N NaOH and 0.1N HCl. 100 mL of solution were blended for 3 minutes and poured into a 500 mL graduated cylinder. The volume of foam (V_f) and liquid (V_l) were immediately recorded and FC was calculated using the following equation:

$$FC = \frac{V_f}{V_l} \cdot 100$$

Foam stabilities of proteins suspensions (%) were determined as ratio of undestroyed foam volume after 5 min to initial volume of foam.

Statistical analysis

Samples were analyzed by triplicate. Statistical analysis was performed using Microsoft Excel 2007 (Microsoft, City of Redmond, USA). The results were reported as mean ± SD. Differences were considered to be significant at validity α=0.95.

Results and discussion

Biological value and safety of oil seed protein products

Measuring of oil seed protein products toxicity was carried out using *Tetrachimena piriformis* (WH–14 strain) cultures and neither dead cells, nor changed shapes of cells or their movement, nor growth depression of infusoria were detected. Infusoria cells had usual shape, were active, fissionable in the presence of every studied meal – soy, sunflower and low glucosinolate rape.

Relative nutritive values of defatted oil seeds and isolated proteins were calculated on the basis of nutritive value of casein (control). Defatted oil seeds meal had high nutritive value, varying from 92% (for rape meal) to 98% (for soybean meal) comparing with casein (Figure 1). Slight decrease of rape meal value probably was caused slight glucosinolates content. In spite of this isolated rape proteins had even higher nutritive value than rape seed

meal that evidently caused by reduction of glucosinolates content. Indeed, isolated proteins contained about half of glucosinolates meal content. At the same time insoluble residue of rape meal had the highest glucosinolates content (Figure 2).

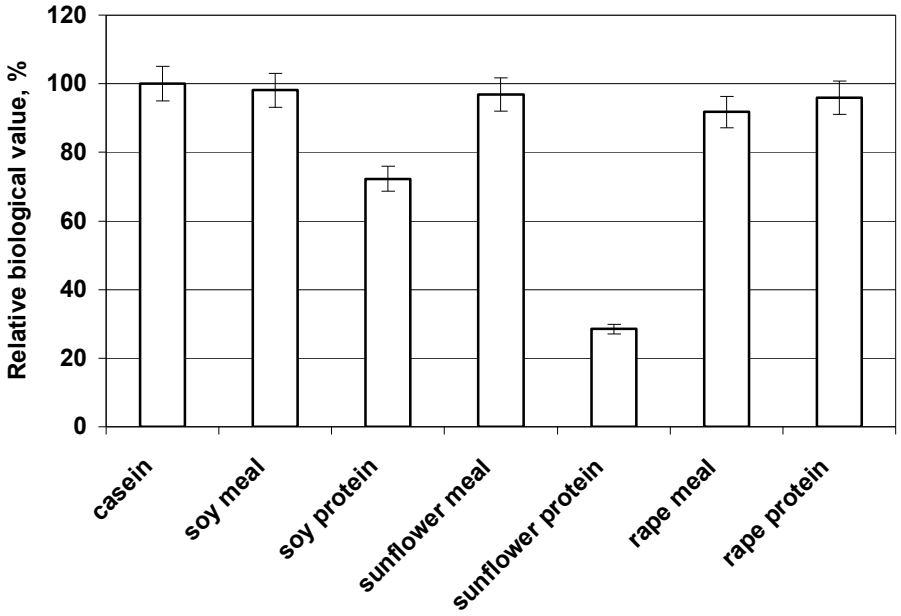

Figure 1. Relative nutritive values of protein products.

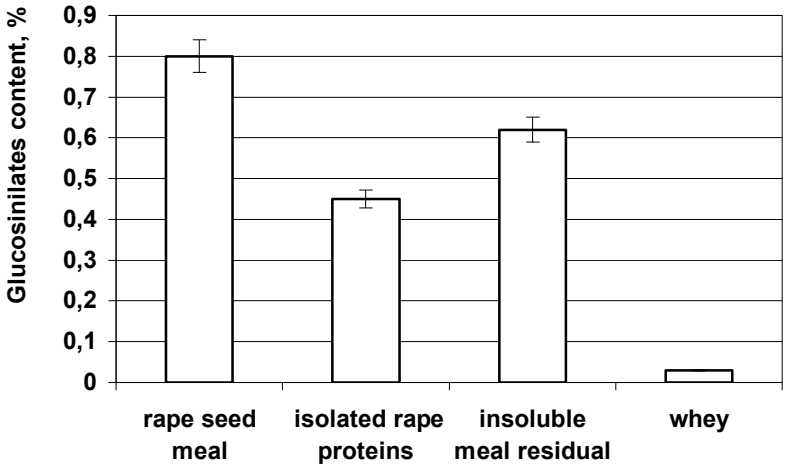

Figure 2. Glucosinolates content in rape seeds and their derivatives (glucosinolates content is given on the dry basis)

The relative biological value of isolated soy proteins had decreased to 72.3% that was about 74% of soy meal value. The value of sunflower isolated proteins had decreased most drastically and was only 28.5% comparing with casein. Such decline of nutritive values probably was resulted by loosing of high biological value proteins which retaining in whey water. As it is known, this fraction of proteins is albumins, which are not precipitated at pH 3.8–4.5, corresponding isoelectric point of globulins [34]. Content of albumin fractions were 5.7, 6.8 and 36.2% in soybeans, sunflower and rape seeds respectively. Rape seeds albumin fraction is most abundant, but it was shown in early works the biological value of rape albumin napin had been limited by content of tyrosine, which is only 23% of FAO/WHO scale protein [35].

The main characteristic of proteins biological value is content of indispensable amino acids and their score to FAO/WHO scale protein. The protein isolate from rape seeds had highest biological value (Table 1), valine and isoleucine were limited amino acids with their score to scale protein 80 and 85 %, respectively. Scores of other essential amino acids were higher than 100 %.

Content of sulfur containing amino acids methionine and cystine had limited value of soy seeds protein isolates, their score was only 60 %, the threonine score was about 100% and content of other essential amino acids was higher their content in scale protein.

The sunflower seeds protein isolates were of lowest quality. Their value was limited by the content of sulfur containing amino acids, which was less than 50% of scale protein. The lysine was the second limiting amino acid, its score was only a negligible higher of methionine and cystine score. Content of other amino acids exceeded that of scale protein.

It is known that biological value of protein isolates depend from number of factors such as genetic properties of plants, climate conditions of seeds growing, and most of all from the parameters of seeds processing. The chemical composition and quality of proteins can be changed significantly as result of seeds processing (drying, heating, pressing, extraction and desolvation of meal) and protein recovery from meal, their precipitation from solution and drying. Therefore the published data about indispensable amino acids content of seed proteins and protein isolates are not identical. Usually content of all essential amino acids in soy protein isolates are higher [37].

Table 1

Content of main indispensable amino acids in soy and rape protein isolates relative to FAO/WHO scale protein.

Amino acid	FAO/WHO protein, mg/100mg of protein [36]	Soybean protein isolate		Sunflower seeds protein isolate		Rape protein isolate	
		mg/100 mg of protein	% to FAO/WHO protein	mg/100 mg of protein	% to FAO/WHO protein	mg/100 mg of protein	% to FAO/WHO protein
Lysine	5.5	6.1±0.18	110.9	3.0±0.17	54.2	6.5±0.20	118.2
Methionine+ Cystine	3.5	2.1±0.06	60.0	1.6±0.16	45.7	5.5±0.17	157.1
Valine	5.0	5.4±0.16	108.0	6.2±0.11	123.8	4.0±0.12	80.0
Threonine	4.0	3.9±0.12	97.5	4.4±0.14	109.3	4.3±0.13	107.5
Leucine	7.0	7.9±0.24	112.9	7.8±0.22	110.9	7.0±0.21	100.0
Isoleucine	4.0	4.1±0.12	102.5	5.5±0.10	138.5	3.4±0.10	85.0
Pheyilalanine + Tyrosine	6.0	8.0±0.23	133.3	8.6±0.23	143.5	7.5±0.23	125.0

Technological properties of oil seeds proteins

Technological properties of proteins determine their using in food processing, influencing the rheological properties, emulsion or foam stability, plasticity, appearance and taste of food. The main technological properties are water solubility, capacities to stabilize emulsion and foam, water and oil binding capacities etc.

The water soluble protein fraction content in soy, sunflower and rape seeds were mention above. Content of total soluble proteins were 85.2, 84.3 and 70.8% of protein content in rape, soy and sunflower seeds respectively. Mass of total soluble proteins, which were determined in alkaline medium, was lowest in sunflower seeds. Apart from genetic peculiarities of protein fraction composition, using of alkaline medium under protein extraction from defatted sunflower seeds had resulted changing of isolated proteins color and water solubility due to creation of complexes between proteins and products of chlorogenic acid oxidation [38]. Colors of these isolated proteins were from bright green to dark green. On the contrary, it was shown that protein recovery in salt solution maintained their native state [39].

After protein recovery in neutral solution (sodium chloride), isoelectric precipitation and protein drying, water solubility of isolated proteins was not as high at every pH, the maximal solubility was determined to be only about 38% for rape proteins (Figure 3).

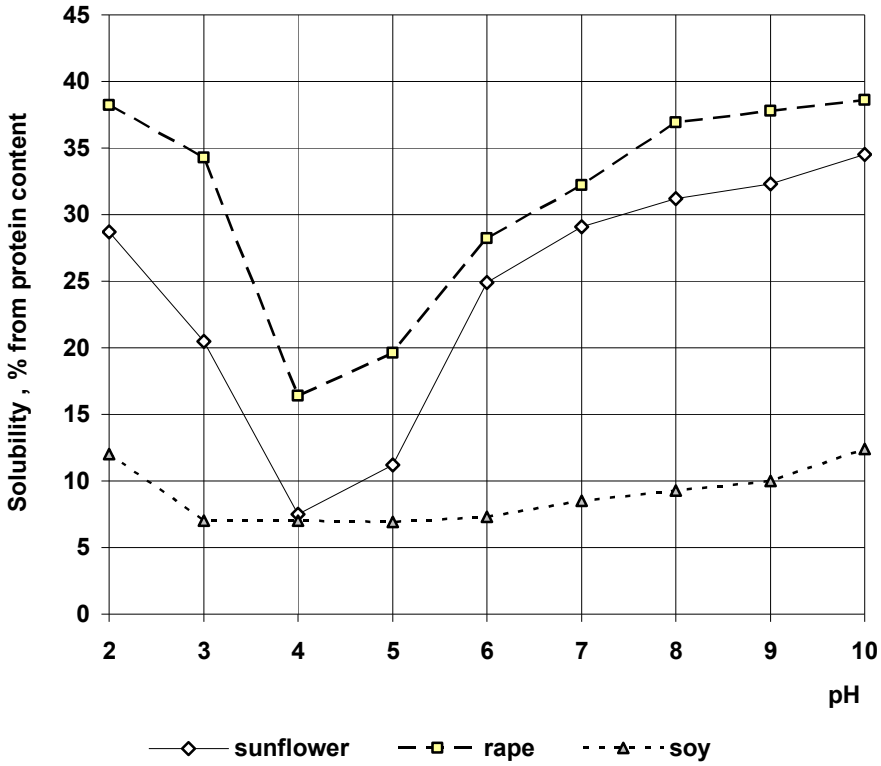

Figure 3. Solubility of protein isolates from oil seeds at different pH values

Evedently, that this is the result of solubility changes of primary soluble seed proteins under isolation procedure. Lowest protein solubility was at pH 4–5 and highest – in alkaline medium. Additional water washing of isoelectric precipitated protein pellets had increased protein solubility by 10–15% at pH 7–8 (data not shown). Rape proteins isolate had higher solubility relatively soy and sunflower isolates at all pH range. High rape proteins isolate solubility in water solutions probably caused by high albumin content in rape seeds. It is known, that rape proteins solubility is determined by their isolation procedure. Protein isolates, prepared by isoelectric precipitation, consist of 7S globulins and have a poor solubility [40], but a good solubility of isolates, precipitated with acid were reported too [41].

Solubility of isolated sunflower proteins had dropped drastically at pH range 4–5 and was highest (about 35 %) at pH 10. At the same time it was shown that protein isolates, prepared from sunflower oil cake, had very high solubility (above 80% at pH 8) [30]. For this purpose authors had suspended isoelectric protein pellet in water at pH 9 and suspension was dried lyophilization.

Isolated soy proteins had very low solubility in studied pH range. It could be resulted by presence of polypeptides with higher molecular weight in soy protein isolates, which abounded by polypeptides with molecular weight from 30 to 76 kDa [42], whereas sunflower protein isolates − by polypeptides with molecular weight from 20 to 45 kDa [34, 43,44] and rape protein isolates − by polypeptides with molecular weight 12–50 kDa [45]. Similar values of soy proteins isolate solubility were obtained by Molina Ortiz and Cristina An [46].

As the result of high molecular weight of soy protein isolates their water holding capacity was very high (385%), that was the highest value compare with sunflower and rape protein isolates (Figure 4, a). The sunflower protein isolate had lowest degree of hydrophility, it was about 160%. The highest oil binding capacity was detected for rape proteins isolate (Figure 4, a). Probably this is due to high content of hydrophobic sulfur containing amino acids in rape proteins. The sunflower and soy protein isolates still had high capacity to oil absorption.

The rape protein isolate had also highest foam and emulsifying capacities comparing with sunflower and soy protein isolates (Figure 4, b), though most rape protein isolates were reported to have poor foaming capacity [47, 48]. At the same time foam of rape protein suspension was unstable. It is known, that foam and emulsifying capacities are depended from hydrophobicity of proteins. Thus isolated rape proteins having relative high water solubility had demonstrated higher hydrophobic properties too. In spite of this the opposite data about relationship between rape protein isolates solubility and their emulsifying capacity were reported [40].

Salgado et al. [30] had proposed that protein aggregation had resulted in decrease of surface hydrophobicity. On the contrary, it is possible, that high solubility and surface hydrophobicity of isolated rape proteins were associated with their disaggregation.

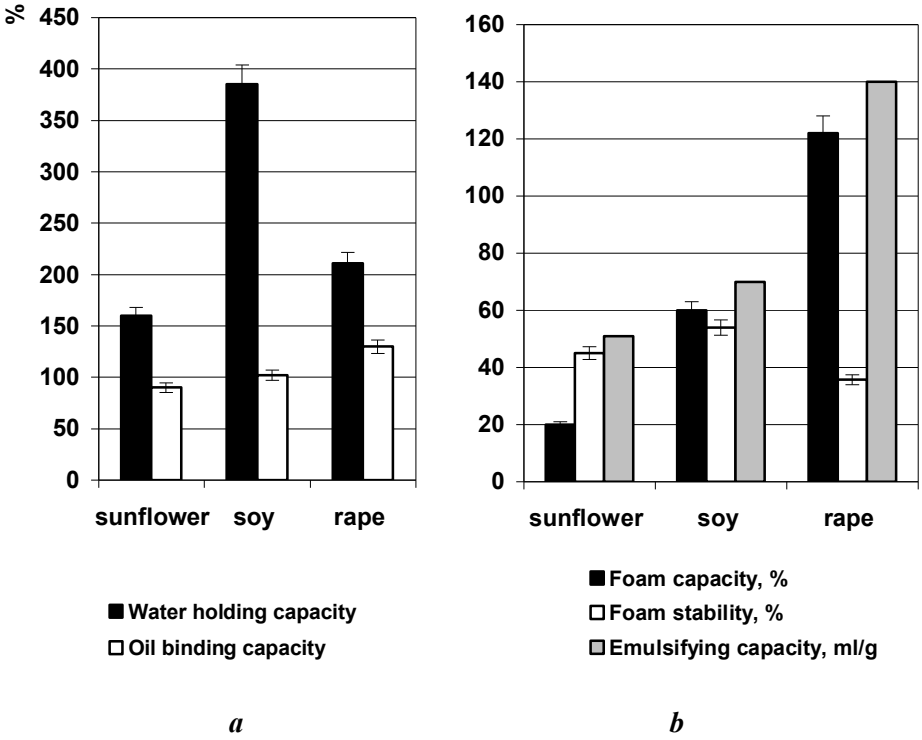

Figure 4. Technological properties of protein isolates from oil seeds

Conclusion

Investigated protein isolates of oil seeds (soy, sunflower and rape) had no toxicity according to test with *Tetrachimena piriformis*. Rape proteins isolate had the highest relative biological values comparing with soy and sunflower isolated proteins. Relative biological value of sunflower isolated proteins was poor. Rape protein isolate had also the highest value on the basis of indispensable amino acids content. This value was districted only by valine score (80% of scale FAO/WHO protein) and isoleucine (85% of scale protein). Soy and sunflower isolated proteins were diminished by sulfur containing amino acids. The water solubility, oil binding, foam and emulsifying capacities of rape proteins isolate were also higher comparing with soy and sunflower isolated proteins.

Thus isolated proteins of low glucosinolate rape seeds are promising source of edible proteins, which have enhanced technological properties. The technological properties of soy and sunflower isolated proteins can be modified by limited enzymatic hydrolyses or other treatment.

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Effects of the water desalting by reverse osmosis on the process of formation of water-alcohol mixtures. ^{1}H NMR spectroscopy studies

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Abstract

Introduction. The aim of the publication is to study the effect of demineralising of the water by reverse osmosis on the drift of protons of ethanol and water, as well as the stabilization these systems by *^{1}H NMR* spectroscopy.

Materials and methods. *^{1}H NMR* analysis was conducted with the usage of the following: *FT-NMR* Bruker Avance II spectrometer (400 MHz); specially shaped capillary with acetone-d_6; high accuracy ampoules № 507–HP; dispenser; ethyl rectified spirit (ERS); demineralized water by reverse osmosis; water-alcohol mixtures (WAM) from ERS and demineralized water.

Results and discussion. In this paper, we have established some new features in the process of creating WAM that are directly dependent on the demineralization of water by reverse osmosis. The drift of protons of ethanol and water in the process of creating WAM indicates the complex dynamic of the system stabilization processes. A «restoration» of location of hydroxyl proton's signal (*OH*) of ethanol is not observed during the time interval of 0 to 432 h after the mixing, with a constant alcohol concentration (WAM's strength – 39,92 % vol.) and system's temperature control (t=23,5 ºC). A characteristic feature of ethanol (*EtOH*) and water (H_2O) hydroxyl protons in the WAM during the interval of τ=12–432 h is that the signals (δ_{EtOH}=4,93–5,01 ppm; δ_{H2O}=4,33–4,41 ppm.) located separately from each other with a difference in a chemical shifts of $\Delta\delta$=0,59–0,61 ppm. Division of the signals related to the process of reconstruction of water structure that was destroyed by demineralization by reverse osmosis and to set an equilibrated structure of new system. The low exchange rate (separately observed signals of hydroxyl and water) can be related to a significant microheterogeneity of the system and the corresponding barrier effect that reduces the effective rate of protons' exchange.

Conclusion. Experimentally, using the method of *^{1}H NMR* spectroscopy, the influence of the use of reverse osmosis of water treatment on the spectral characteristics of mobile protons of ethanol and water, as well as the stabilization of the system in the process of creation of water-alcohol mixtures, was established. It is shown that for such systems, the stabilization process of the water-alcohol mixture is simultaneously with the restoration of a network of hydrogen bonds in the aqueous phase of the microheterogeneous medium.

Introduction

NMR spectroscopy is widely used in physics research, industry, agriculture and other industries. *NMR* plays a particularly important role in food chemistry where it used in the study of both simple organic molecules and complex macromolecular structures and their complexes (Minoja, Napoli, 2014; Singh, Blümich, 2016; Hore, 2017) [1, 13, 16]. A large number of articles discuss the use of *NMR* for research of food products; meat, fish, dairy products, vegetables, fruits, juices, pastry, cheese, starch, honey and alcohol products (Minoja, Napoli, 2014; Zuriarrain et al, 2015; Youssouf et al, 2017; Campo et al, 2016; Zhu, 2017; Yuan et al, 2017; Diop et al 2012; Tian et al, 2017, Sucupira et al, 2017, Li et al, 2017; Shumilina et al, 2016; Okaru et al, 2017) [1, 2, 11, 12, 14, 15, 17–22]. This method provides comprehensive information with relatively simple obtaining spectra, thus greatly facilitating and accelerating chemical research (Nose et al, 2005; Richards, Hollerton, 2011; Roberts, 2002; Hu et al, 2010) [5–8].

NMR spectroscopy is most commonly applied to the nuclei of lightest isotope of hydrogen ^1H (protium, ^1H isotope) proton. The first ^1H *NMR* spectra of ethanol C_2H_5OH was obtained in 1951 (Arnold et al. 1951) [3]. The first ^1H *NMR* spectra of H_2O were obtained in 1946 (Bloch et al. 1946) [4]. At the first glance, it may seem that these are fairly simple organic molecules, at the same time *NMR* spectras exhibits greate variety (Nose et al, 2005; Richards, Hollerton, 2011; Roberts, 2002; Hu et al, 2010) [5–8] in such characteristics as chemical shift, spin-spin interactions and the effect of chemical exchange (Matsugami et al, 2016; Jora et al, 2017) [9, 10].

An ethanol molecule consists of 6 protons located in a 3 proton-containing groups: methyl (CH_3), methylene (CH_2) and hydroxyl (OH) with a relative intensity characteristic CH_3:CH_2:OH – 3:2:1. Nuclear spin-spin interaction is observed between the three proton-containing groups of ethanol, all of which have different resonant frequencies (Roberts, 2002) [7]. "N" number of equivalent protons of one group split the signal of the nearest group into (n+1) lines with the intensity of a Pascal triangle (Richards, Hollerton, 2011) [6]. The ability to observe spin-spin interactions depends on the rate of the intermolecular proton exchange (Jora et al, 2017) [10]. Wherein the hydroxyl proton (OH) of ethanol can interchange with free hydrogen ions (Matsugami et al, 2016) [9]. The hydrogen ions are generated due to self-dissociation of water or traces of acids, alkalis or dissociated ethanol (Jora et al, 2017) [10]. The concentration of free protons is characterized by pH level.

Vodka – is an alcoholic drink with strength from 37,5% to 56%, obtained by special mixing ERS with water, with addition of non-volatile ingredients or without them.

In the opinion Hu et al. (2010) [8] vodka is a fairly simple physicochemical system: a mixture of alcohol and water. However, each brand has its own distinctive taste and features on the molecular level. Research conducted by Hu et al. (2010) [8] confirm that these differences are significant both during the stage of creating WAM, and in the final product – the commercial vodka. The major differences are associated with hydrogen bonds, in particular their strength, as confirmed by various research methods such as ^1H *NMR* spectroscopy, *FTIR* spectroscopy, Raman spectroscopy. ^1H *NMR* and *FTIR* spectroscopy demonstrates the presence of water in the hydrate structure $EtOH{\cdot}(5{,}3{\pm}0{,}1)H_2O$. Water can also be observed in WAM as well as in vodka. The authors (Hu et al, 2010) [8] attribute this value with the perception of organoleptic characteristics of vodka.

Lots of attention in the work of Hu et al, 2010 [8] has been given to ^1H *NMR* spectra of hydroxyl proton of OH water and alcohol. Water protons are represented as narrow singlets with δ_{OH}=5 ppm. The spectra of some samples are represented by the appearance of a second broadened OH signal of ethanol at a level of δ_{OH}=5,5 ppm. The presence in the samples of a single signal of OH ethanol (Hu et al, 2010) [8] is attributed to the weak hydrogen bonds of ethanol.

In their paper, the authors (Hu et al, 2010) [8] introduced the concept of «structurability» – defined as the ability to maintain structure – a parameter that determines the ability of vodka (alcohol) to streamline its structure.

The effect of impurities (such as salts, acids, phenols) strengthening the hydrogen bonds in WAM as well as in the finished product such as sake, has been studied by Nose et al (2005) [5]. Hu et al [8] have identified that the impurity of compounds has an effect on the molecular dynamics in ethanol's hydration process.

Previously, we have conducted primary research of *^1H NMR* WAM, which were described in the work of Kuzmin et al, 2013–2015 [23–26]. The obtained results give grounds to assert a fundamental difference in the behavior of the WAM prepared from the alcohol and water passing through various processes. This may indicate the presence of such features as separate signals of *OH*-protons of H_2O and *EtOH*. Also abnormal waveforms of CH_3 and CH_2 characterize a product with a lower tasting properties. The presence of the combined signal of H_2O+*(EtOH)* and a "clear" form of CH_3 and CH_2 signals (triplet – for CH_3, quartet – for CH_2) – characterizes the WAM with the best tasting properties.

Thus, in the work of Kuzmin O., Sujkov S. et al, 2013 [23] established experimental evidence of instalment nature / (non- instalment) of thermodynamic balance, taking into account the organoleptic characteristics of WAM in dependence on water treatment method and time of system's functioning. However, the questions related to internal mechanism's specification and the rate of establishment of thermodynamic balance depending on type of water used in the process of creating the WAM are remain unsolved.

Therefore, the additional research is required for a detailed study of internal mechanism of thermodynamic balance and insurance in obtaining high quality vodka products – for each type of water separately.

Therefore, the aim of this work is study of drift of ethanol protons (ERS) and water (demineralized by reverse osmosis) in the process of WAM creation.

Materials and methods

Materials: demineralized water by reverse osmosis water; ERS; WAM from ERS and water demineralized by means of reverse osmosis.

The following characteristics were determined for water demineralized by reverse osmosis: solid residual – 15 mg/dm^3; electrical conductivity – 20,7 μS/cm; pH – 5,05; ORP – "+" 393 mV; total hardness – <0,05 mM/dm^3; permanganate oxidability – 0,46 mg O_2/dm^3; mass concentration (MC) of sodium – 11,60 mg/dm^3; MC of potassium – <2,0 mg/dm^3; MC of ammonium – <2,0 mg/dm^3; MC of calcium – <2,0 mg/dm^3; MC of magnesium – <2,0 mg/dm^3; total alkalinity – 0,15 mM/dm^3.

Characteristics of ERS: volume part of ethanol – 96,37 %, volume part of water – 3,63%; content of aldehydes in anhydrous alcohol, in recalculation on acetic aldehyde – 1,3 mg/dm^3; content of fusel oils in anhydrous alcohol: propyl, isopropyl, butyl, isobutyl and isoamyl – 1,5 mg/dm^3; content of esters in anhydrous alcohol, in recalculation on acetic-ethyl ether – 1,3 mg/dm^3; content of methanol in anhydrous alcohol – 0,0022 % vol.

WAM made of ERS and process water – demineralized by the reverse osmosis has the following characteristics: alcoholic strength – 39,92 % vol.; electrical conductivity – 3,5 μS/cm; ORP – "-" 98 mV; pH level – 7,60; content of aldehydes in anhydrous alcohol, in recalculation on acetic aldehyde – 1,8 mg/dm^3; content of fusel oils in anhydrous alcohol: propyl, isopropyl, butyl, isobutyl and isoamyl – 1,4 mg/dm^3; content of esters in anhydrous alcohol, in recalculation on acetic-ethyl ether – 1,4 mg/dm^3; content of methanol in anhydrous alcohol – 0,0021 % vol.; alkalinity – 0,4 cm^3 0,1 M of hydrochloric acid for titration of 100 cm^3 sorting; oxidability test – 9 min.; taste evaluation – 9,30 pointa (appearance – colourless liquid without sediment; odor – strong alcoholic; taste – sour and bitter, pungent).

^1H NMR analysis of WAM was conducted with the usage of the following: *FT-NMR* Bruker Avance II spectrometer (400 MHz) with operating frequency at ^1H – 400 MHz; specially shaped capillary with acetone-d_6; high accuracy ampoules № 507–HP for high resolution *NMR*'s spectroscopy (400 MHz); dispenser.

Work methodology (Kuzmin et al, 2013–2015) [23–26]:

1. 0,3 ml of a WAM prepared with a volumetric pipette with a predetermined strength (40,0 ± 0,2)% vol.
2. External standard which is required for LOCK's system operation is added into an ampoule of special form capillary.
3. *^1H NMR* spectra records and data processing were performed according to the manuals of *FT-NMR* Bruker Avance II (400 MHz) spectrometer.

Results and discussions

Spectrum of water – H_2O (figure 1), ERS (figure 2), WAM (figures 3–23), made of demineralized water prepared by means of osmosis and ERS at a different lifetimes (h) is characterized by a unitary signal of hydroxyl group of H_2O (figure 1). The sygnal of H_2O protons – singlet (*s*), located at δ_{H2O}=4,63 ppm. Waveform of H_2O protons – is distorted Gaussian curve, with a broadened base and a slight asymmetry of apex, which is offset from the centerline.

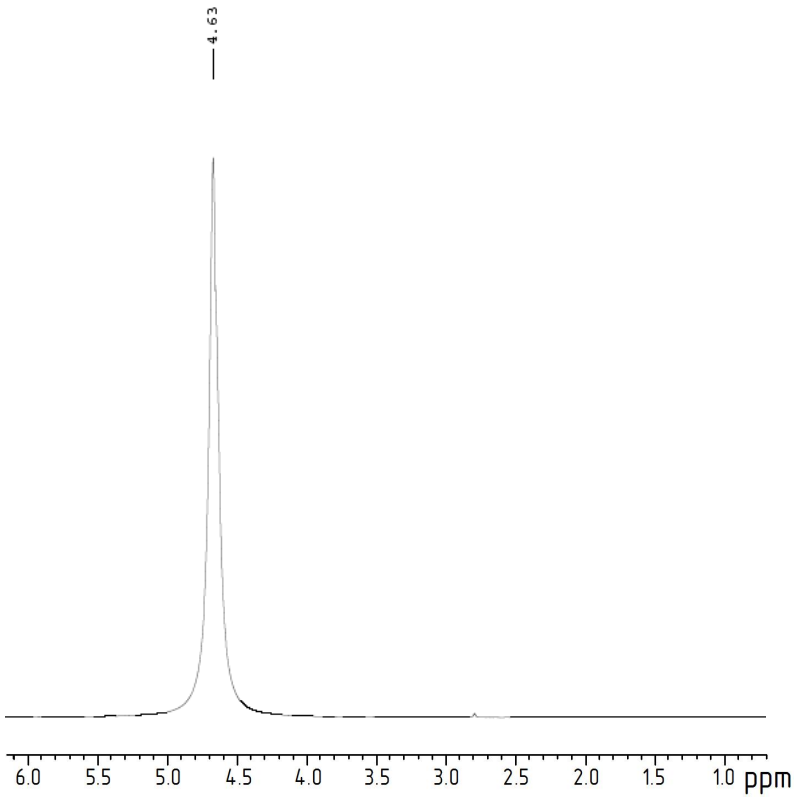

Figure 1. *^1H NMR* spectra of *H_2O*-proton of water, prepared in demineralized by reverse osmosis

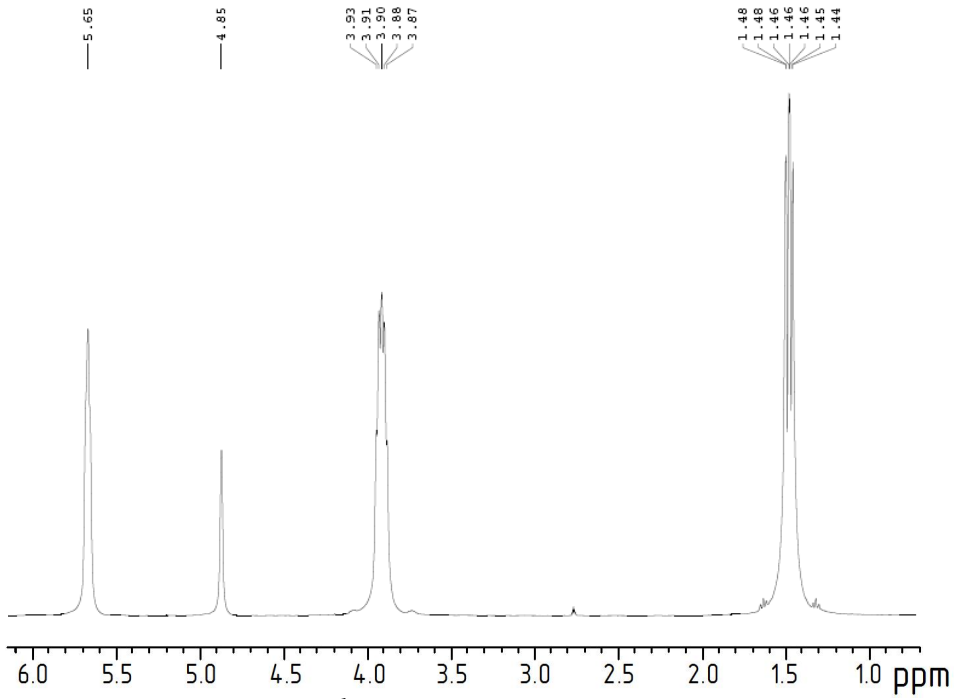

Figure 2. *^{1}H NMR* spectra of proton groups ERS: *CH_3; CH_2; H_2O; EtOH*

We will analyze the spectra of ERS (figure 2). Hydroxyl group of protons of ERS are represented by two separate peaks. A component of ethanol is represented as a single broad singlet, located in a «low field» with the chemical shift δ_{EtOH}=5,65 ppm. A component of water proton is represented as singlet with a chemical shift of δ_{H2O}=4,85 ppm. The form of H_2O protons' signal is a distorted Gaussian curve, with a broadened base and a certain asymmetry. The difference between the *OH*-proton of ethanol (*EtOH*) and the proton of water (H_2O) in the chemical shifts – $\Delta\delta$ = 0,80 ppm.

The analysis of the ^1H *NMR*-spectra of protons methyl group of ethanol (CH_3) allows us to state the following. The protons' methyl group is represented as a septet (*sp*) with a relative intensity (1:6:15:20:15:6:1). This is abnormity as according to Pascal's triangle and on the assumption of protons' methyl group spin-spin interactions, methylene group's (CH_3) signal has to be split by an adjacent protons' group (CH_2) as a triplet (*t*) with intensity ratio (1:2:1). Besides the methylene group (CH_2), no other group of protons can have observable an effect on the active spectrum of the methyl group (CH_3).

The analysis of methylene group's (CH_2) ^1H *NMR*'s protons shows the following. The methylene group's protons (CH_2) are represented as quintet (*qi*) with the intensity (1:4:6:4:1). This is an abnormity. Protons of methyl (CH_3) groups must split the signal of methylene group (CH_2) into four components and form a quartet (*q*) with an intensity ratio of 1:3:3:1, as based on the spin-spin interaction. In turn, protons of hydroxyl (*OH*) groups should split each quartet's component of methylene (CH_2) group into two components to form a double quartet. The signal of methylene (CH_2) groups should remain as quartet. This happens due to the absence of observable spin-spin interaction between the hydroxyl (*OH*) and methylene (CH_2) groups by the chemical exchange.

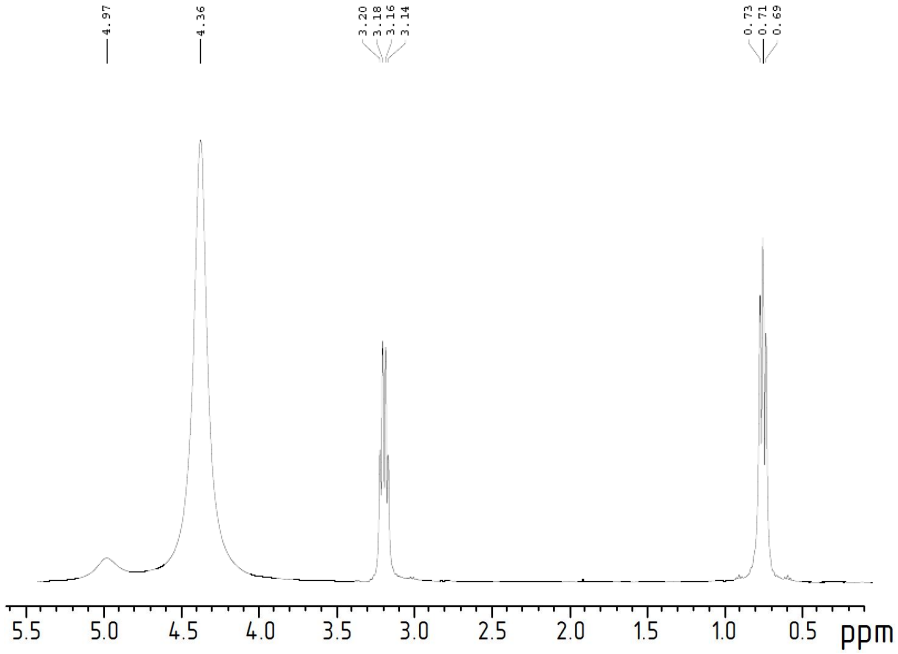

Figure 3. *^{1}H NMR* spectra of proton groups of WAM, prepared in demineralized by reverse osmosis water and ERS: *CH_3*; *CH_2*; *H_2O; EtOH*, dependent from system's functioning time (0 h)

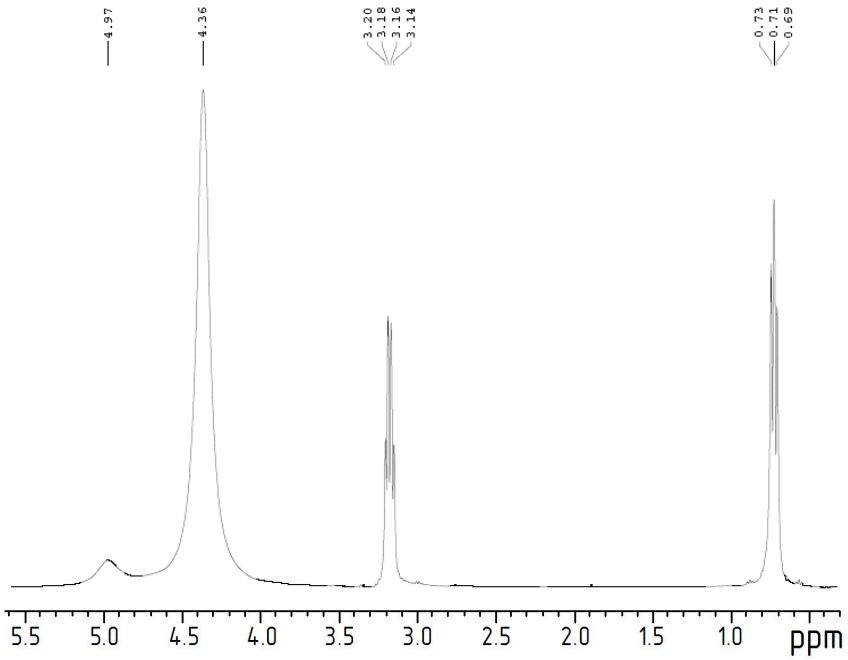

Figure 4. *^{1}H NMR* spectra of proton groups of WAM, prepared in demineralized by reverse osmosis water and ERS: *CH_3*; *CH_2*; *H_2O; EtOH*, dependent from system's functioning time(12h)

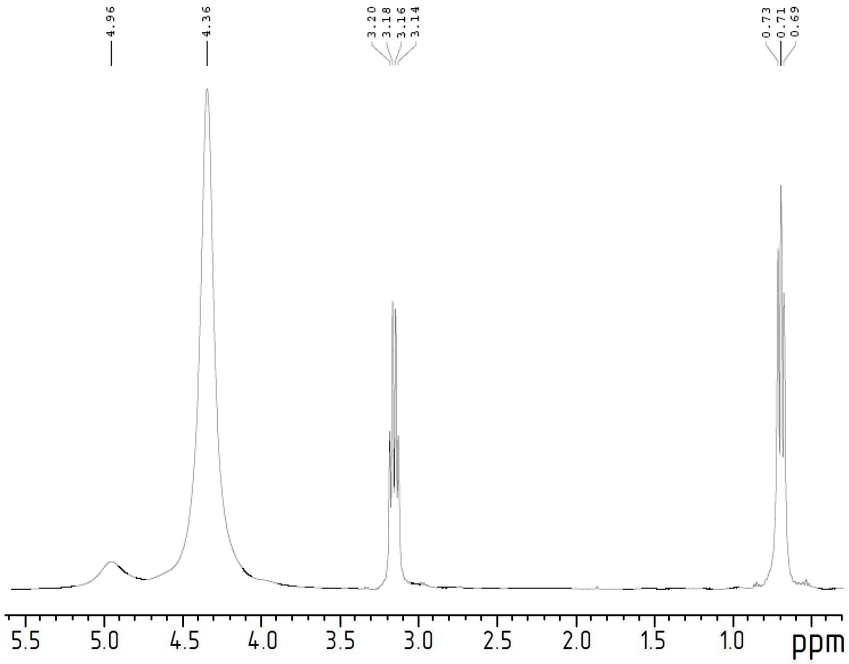

Figure 5. ^{1}***H NMR*** **spectra of proton groups of WAM, prepared in demineralized by reverse osmosis water and ERS: *CH_3*; *CH_2*; *H_2O*; *EtOH*, dependent from system's functioning time (24 h)**

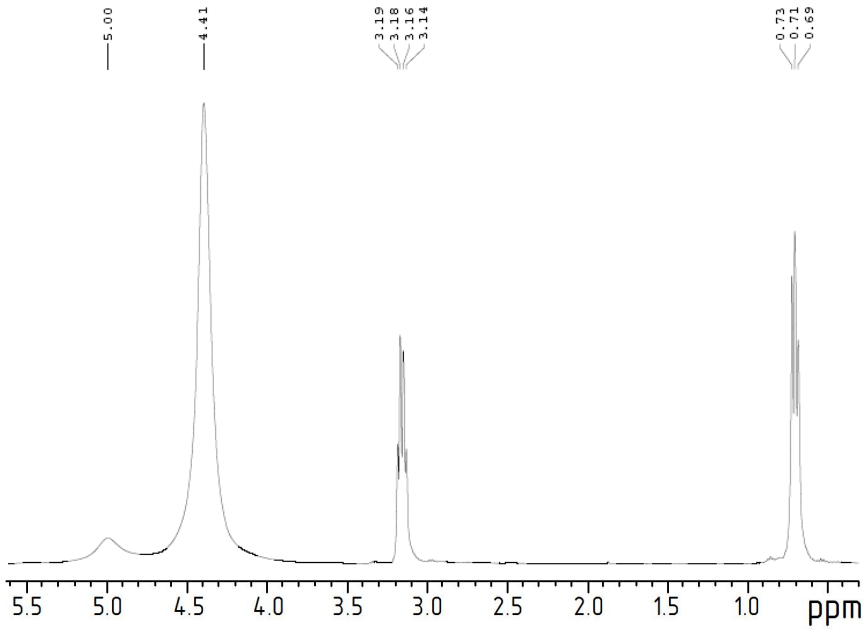

Figure 6. ^{1}***H NMR*** **spectra of proton groups of WAM, prepared in demineralized by reverse osmosis water and ERS: *CH_3*; *CH_2*; *H_2O*; *EtOH*, dependent from system's functioning time (36 h)**

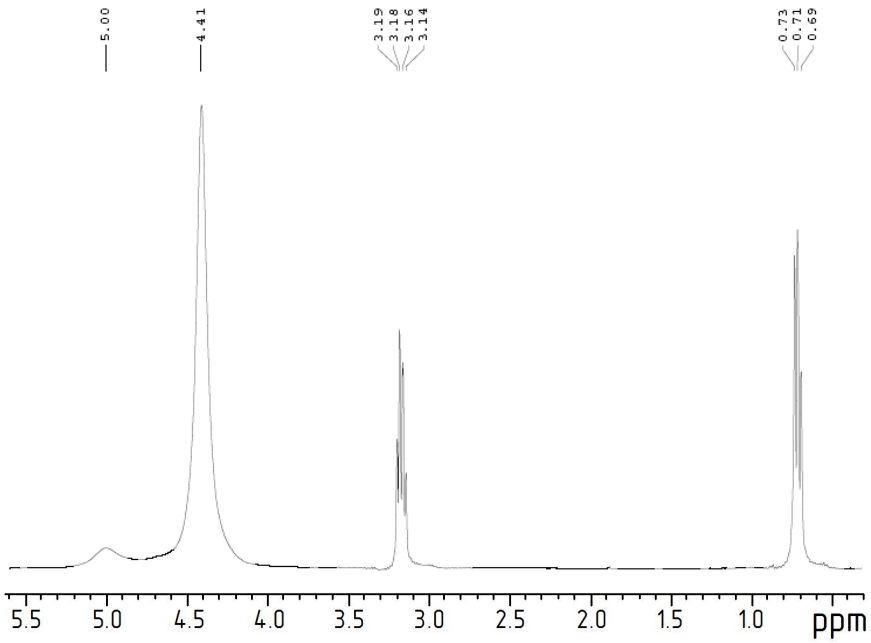

Figure 7. *^{1}H NMR* spectra of proton groups of WAM, prepared in demineralized by reverse osmosis water and ERS: *CH_3*; *CH_2*; *H_2O; EtOH*, dependent from system's functioning time (48 h)

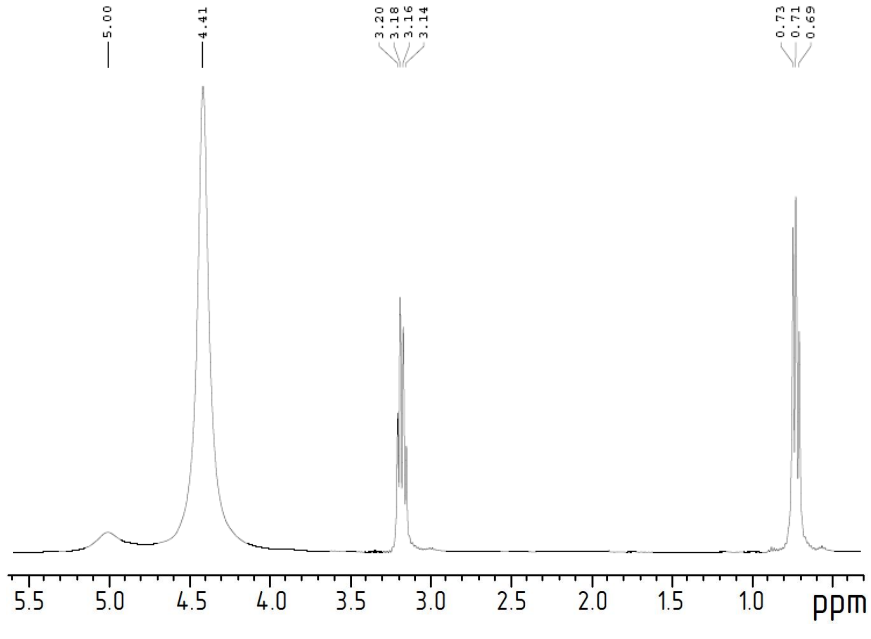

Figure 8. *^{1}H NMR* spectra of proton groups of WAM, prepared in demineralized by reverse osmosis water and ERS: *CH_3*; *CH_2*; *H_2O; EtOH*, dependent from system's functioning time (60 h)

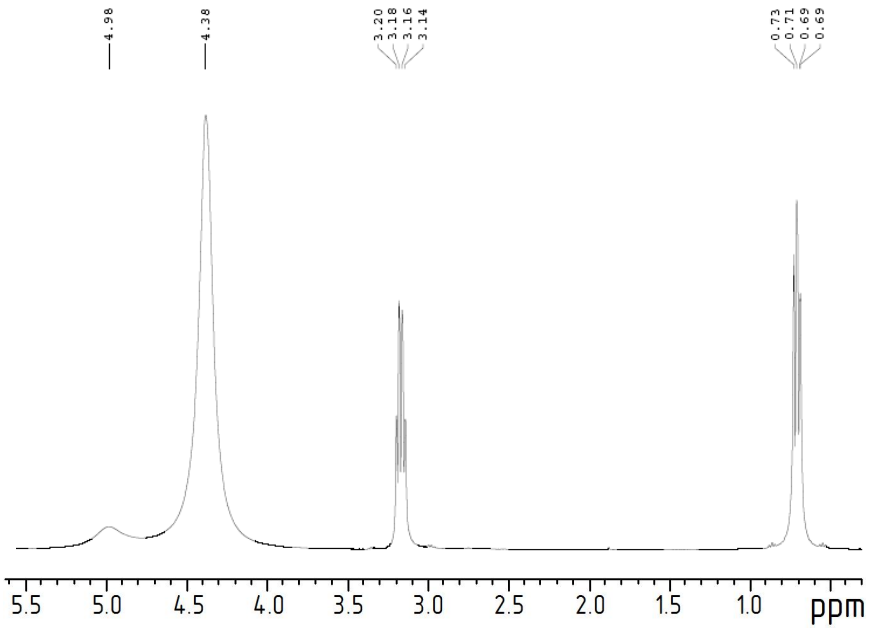

Figure 9. *^{1}H NMR* spectra of proton groups of WAM, prepared in demineralized by reverse osmosis water and ERS: *CH_3*; *CH_2*; *H_2O; EtOH*, dependent from system's functioning time (108 h)

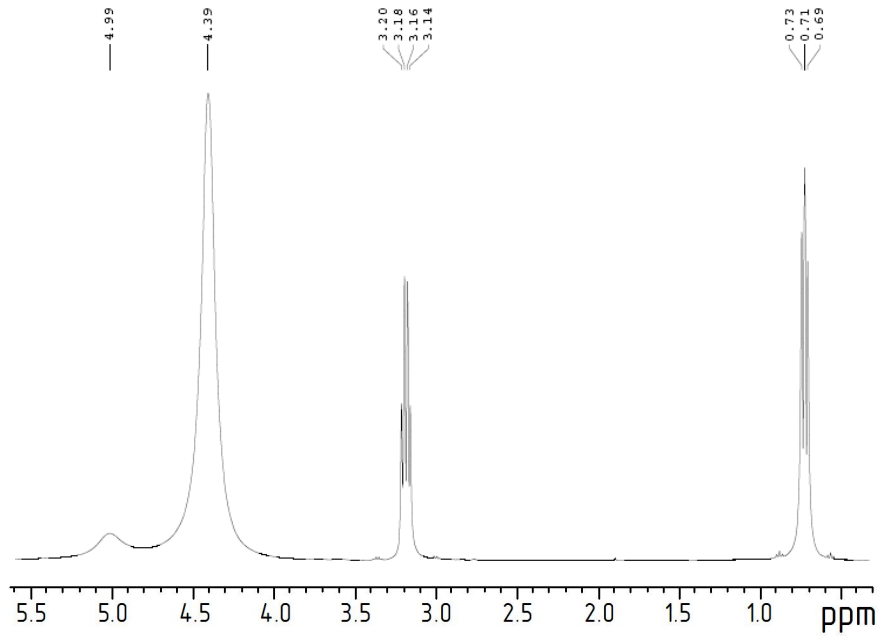

Figure 10. *^{1}H NMR* spectra of proton groups of WAM, prepared in demineralized by reverse osmosis water and ERS: *CH_3*; *CH_2*; *H_2O; EtOH*, dependent from system's functioning time (132 h)

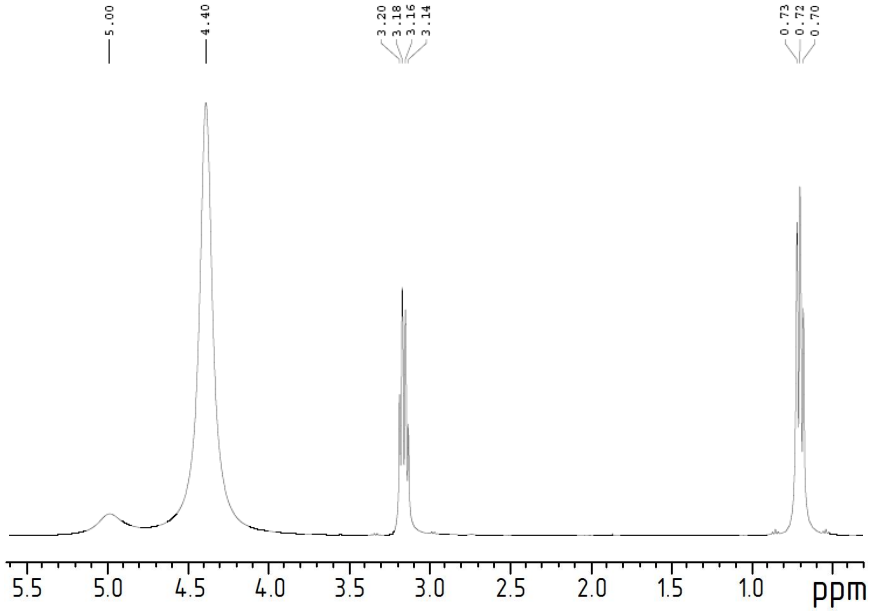

Figure 11. *^{1}H NMR* **spectra of proton groups of WAM, prepared in demineralized by reverse osmosis water and ERS:** *CH_3*; *CH_2*; *H_2O; EtOH*, **dependent from system's functioning time (144 h)**

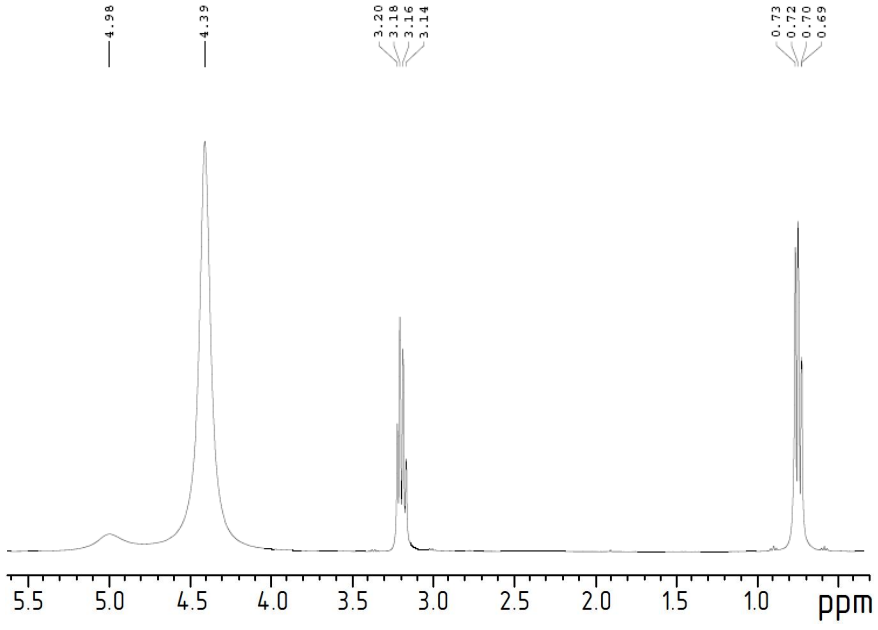

Figure 12. *^{1}H NMR* **spectra of proton groups of WAM, prepared in demineralized by reverse osmosis water and ERS:** *CH_3*; *CH_2*; *H_2O; EtOH*, **dependent from system's functioning time (156 h)**

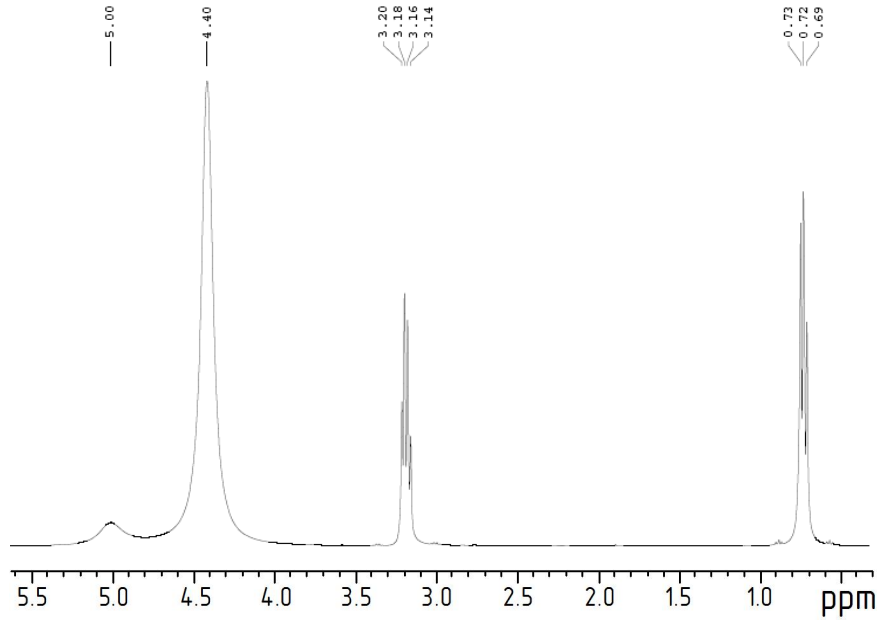

Figure 13. *^{1}H NMR* **spectra of proton groups of WAM, prepared in demineralized by reverse osmosis water and ERS:** *CH_3*; *CH_2*; *H_2O; EtOH*, **dependent from system's functioning time (168 h)**

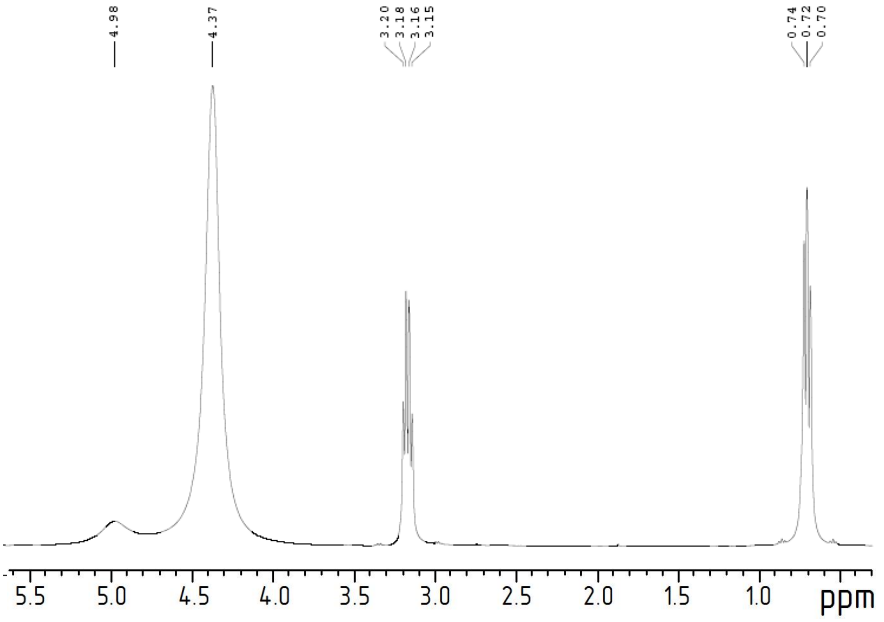

Figure 14. *^{1}H NMR* **spectra of proton groups of WAM, prepared in demineralized by reverse osmosis water and ERS:** *CH_3*; *CH_2*; *H_2O; EtOH*, **dependent from system's functioning time (180 h)**

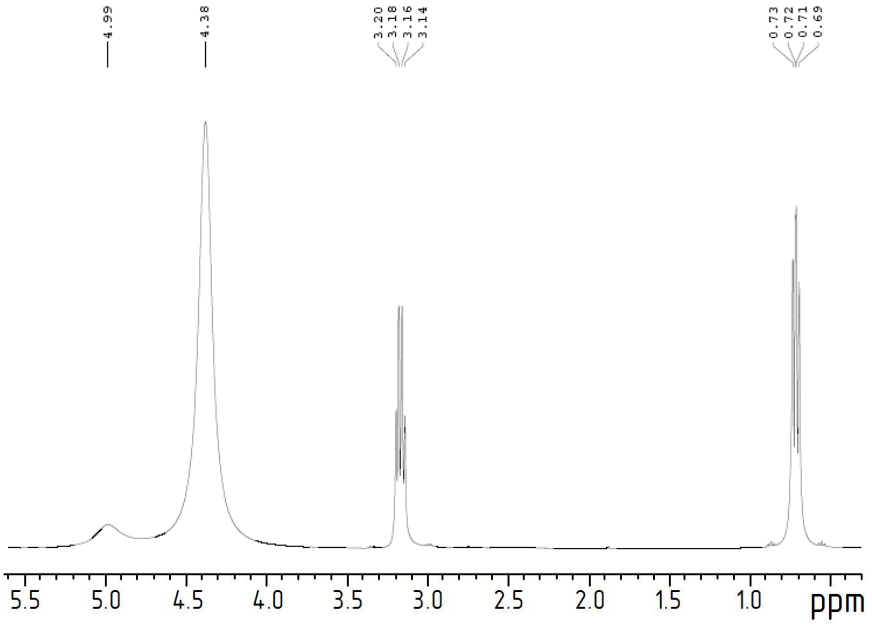

Figure 15. *^{1}H NMR* **spectra of proton groups of WAM, prepared in demineralized by reverse osmosis water and ERS:** *CH_3; CH_2; H_2O; EtOH*, **dependent from system's functioning time (192 h)**

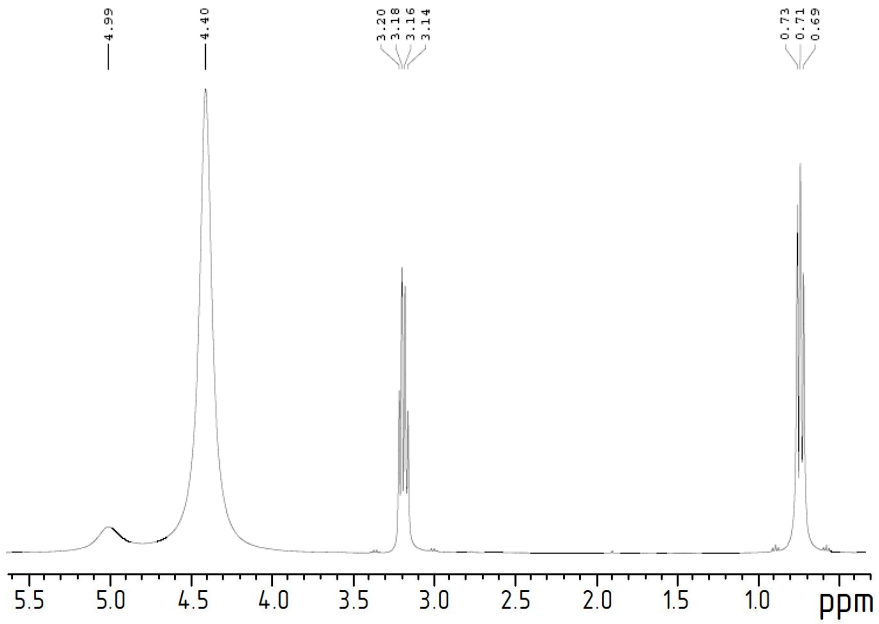

Figure 16. *^{1}H NMR* **spectra of proton groups of WAM, prepared in demineralized by reverse osmosis water and ERS:** *CH_3; CH_2; H_2O; EtOH*, **dependent from system's functioning time (204 h)**

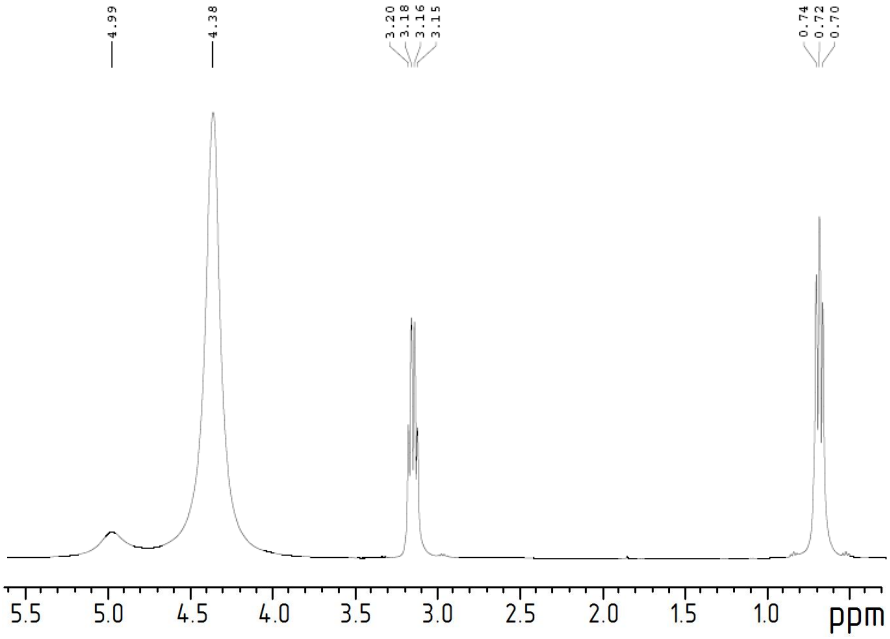

Figure 17. *^{1}H NMR* **spectra of proton groups of WAM, prepared in demineralized by reverse osmosis water and ERS:** *CH_3; CH_2; H_2O; EtOH*, **dependent from system's functioning time (216 h)**

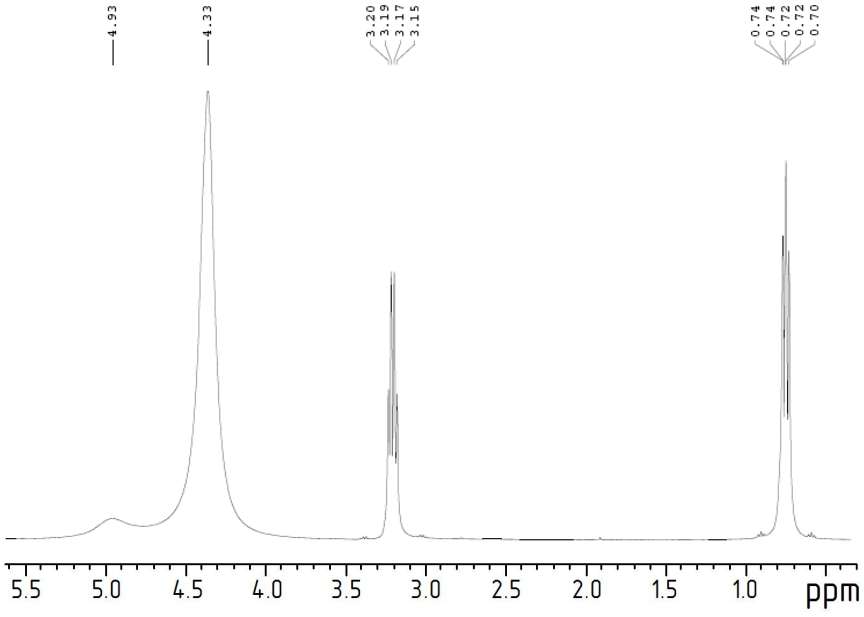

Figure 18. *^{1}H NMR* **spectra of proton groups of WAM, prepared in demineralized by reverse osmosis water and ERS:** *CH_3; CH_2; H_2O; EtOH*, **dependent from system's functioning time (288 h)**

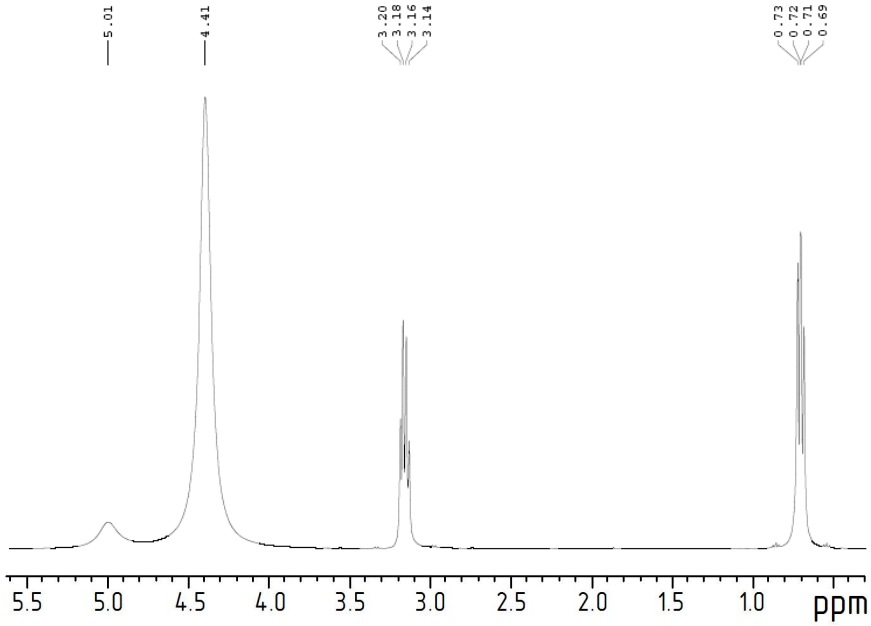

Figure 19. ^{1}H ***NMR*** **spectra of proton groups of WAM, prepared in demineralized by reverse osmosis water and ERS:** CH_3; CH_2; H_2O; ***EtOH*****, dependent from system's functioning time (300 h)**

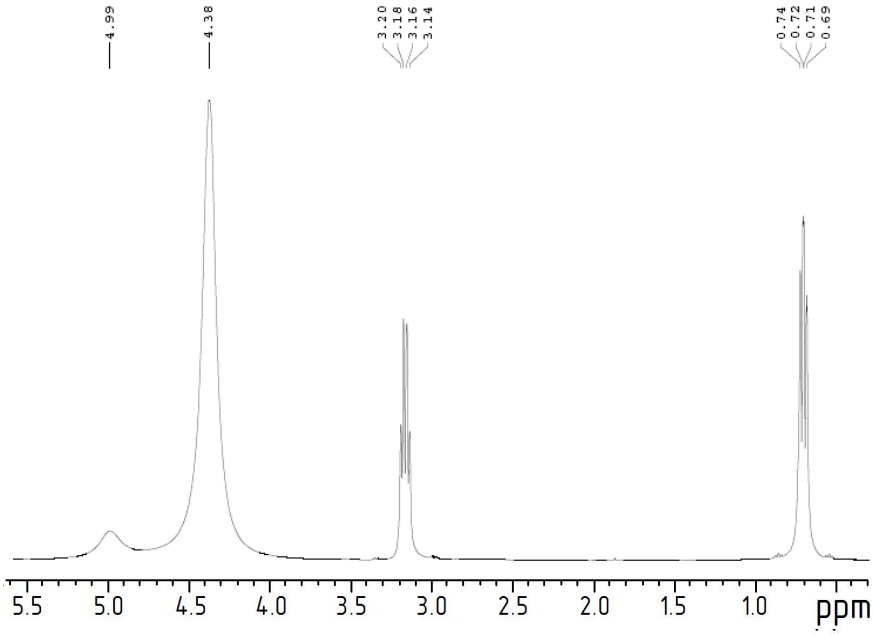

Figure 20. ^{1}H ***NMR*** **spectra of proton groups of WAM, prepared in demineralized by reverse osmosis water and ERS:** CH_3; CH_2; H_2O; ***EtOH*****, dependent from system's functioning time (312 h)**

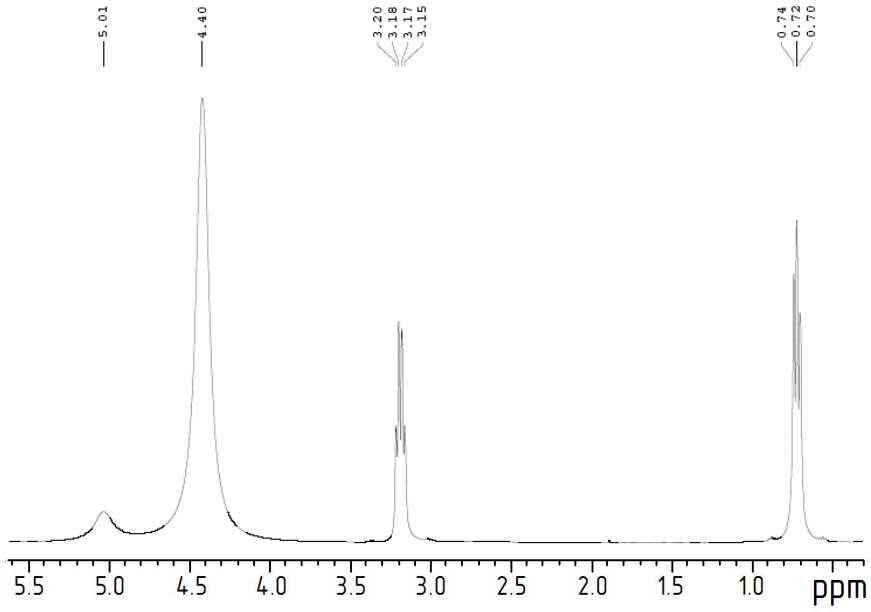

Figure 21. *^1H NMR* **spectra of proton groups of WAM, prepared in demineralized by reverse osmosis water and ERS:** *CH_3; CH_2; H_2O; EtOH*, **dependent from system's functioning time (324 h)**

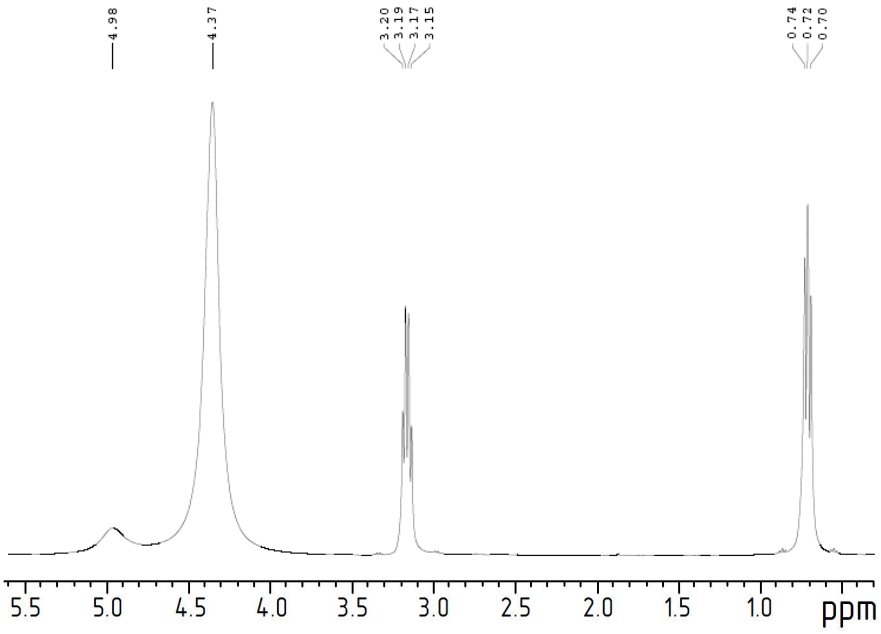

Figure 22. *^1H NMR* **spectra of proton groups of WAM, prepared in demineralized by reverse osmosis water and ERS:** *CH_3; CH_2; H_2O; EtOH*, **dependent from system's functioning time (336 h)**

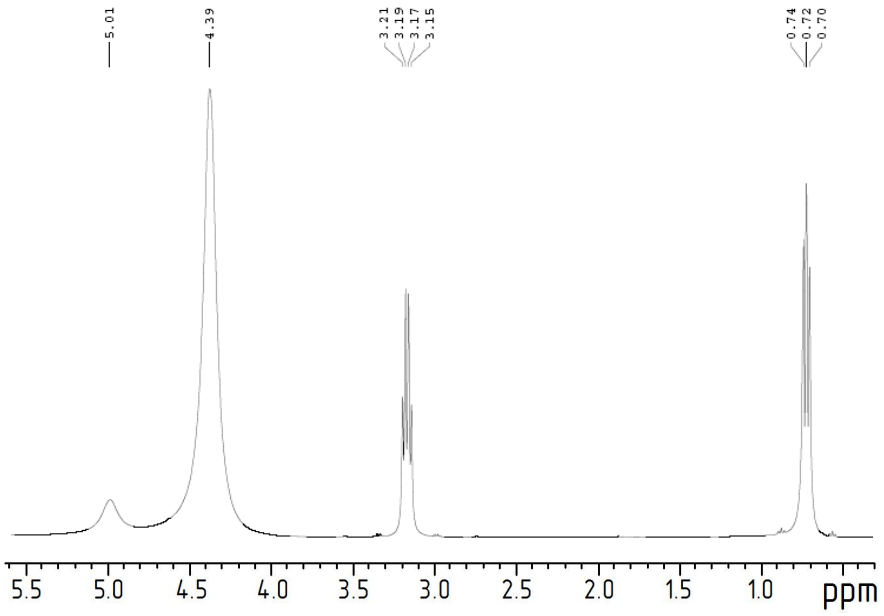

Figure 23. *^{1}H NMR* spectra of proton groups of WAM, prepared in demineralized by reverse osmosis water and ERS: *CH_3*; *CH_2*; *H_2O; EtOH*, dependent from system's functioning time (432 h)

The figures 3–23 shows the proton group's *^{1}H NMR* spectras of freshly prepared WAM sample (0 h) and a sample taken after few days, with an interval of 12–72 h with indication of chemical shift.

At the initial instant of WAM formation – τ=0 h (figure 3) the presents of two separate signals – *OH* of ethanol (*C_2H_5OH*) and water *H_2O* is observed in the area of hydroxyl protons of ethanol and water. Signal of hydroxyl (*OH*) proton of ethanol (*C_2H_5OH*) is presented in a form of bulge. The bulge is found in a weak field with a chemical shift of δ_{EtOH}=4,97 ppm. Signal of water (*H_2O*) protons is presented as an elongated singlet of symmetrical shape with a broad base which is located at δ_{H2O}=4,36 ppm. The difference in chemical shifts of *OH* proton (*C_2H_5OH*) and *H_2O* proton at this stage (τ=0 h) is $\Delta\delta_{OH}$=0,61 ppm.

A characteristic feature of hydroxyl proton of ethanol (*EtOH*) and water (*H_2O*) during the interval of τ=12–432 h (figures 4–23) is that the spectra (δ_{EtOH}=4,93–5,01 ppm; δ_{H2O}=4,33–4,41 ppm.) located separately from each other with a difference in a chemical shifts of $\Delta\delta$=0,59–0,61 ppm. This may indicate that there were no conditions created to form a water composition with hydroxyl proton of alcohol. Therefore, it proves that the state of thermodynamic equilibrium is absent up to τ<432 h.

The analysis of *^{1}H NMR* spectra of WAM methyl group's protons (*CH_3*) states the following. τ=0. Methyl group of protons (*CH_3*) is represented as a triplet (*t*) in the initial time of system's operation. Triplet is formed by the spin-spin interaction with protons of adjacent methylene group (*CH_2*). The intensity ratio is (1:2:1) according to the Pascal triangle. Not a single group of protons can affect methyl group's spectrum (*CH_3*) besides the methylene group (*CH_2*). Thus, the methyl group of protons (*CH_3*) is located in a strong field with an average value of the chemical shift as δ_{CH3}=0,71 ppm.

τ=12–432 h. The methyl group of protons (CH_3) did change its position comparatively to the initial position (τ=0 h), and also changed the waveform – from the triplet (*t*) to the quintet (*qi*) and back. The following initial conclusion can be made: the range (12–432 h) is not characterized by a complete structuring of signal of methyl group (CH_3) as a triplet (t) as its form and by the middle positioning of a chemical shift – δ_{CH3}=0,70–0,72 ppm. There is abnormal change in the spectra's structure during this period of time.

The analysis of ^1H *NMR* spectra of methylene group (CH_2) reveals the following. At the beginning of the formation of WAM (τ=0 h) methylene group of protons (CH_2) is presented as a quartet (*q*), which is confirmed by the spin-spin interaction of protons of methyl (CH_3) groups, that should split signal of the methylene group (CH_2) into four components, form a quartet (*q*) with intensity ratio of 1:3:3:1.

In turn, protons of hydroxyl (*OH*) group should cleave every component of methylene (CH_2) group's quartet into two components to form a double quartet. The absence of spin-spin interaction between hydroxyl (*OH*) and methylene (CH_2) groups due to chemical exchange would have to ascertain that the signal of the methylene (CH_2) group must remain as quartet.

Methylene group of protons (CH_2) has an average value of a chemical shift as δ_{CH2}=3,17 ppm, distance between each peak of quartet (spin-spin coupling constant) is 8 Hz.

τ=12–432 h. Methylene spectrum with an average value of chemical shift δ_{CH2}=3,17–3,18 ppm is shifted to a weak field by 0,01 ppm relatively to its initial position (τ=0 h). Waveform – quartet (*q*), which is typical for the above proton group, on the assumption of spin-spin interaction with protons of the methyl (CH_3) group and chemical exchange between the hydroxyl (*OH*) and methylene (CH_2) groups.

The following initial conclusion can be made: the range (0–432 h) is characterized by a complete structuring signal of the methylene group (CH_2) as quartet (*q*) in its form and by the middle positioning of the chemical shift – δ_{CH2}=3,17–3,18 ppm, which remains unchanged. There is no abnormal change in the spectra's structure during this period of time. Its position can be described as stable. The distance between the peaks also remain unchanged – 0,02 ppm.

Conclusions

As a results we have evidence of a complex dynamic of achievement processes of solution equilibrium for WAM prepared in demineralized by reverse osmosis water with *pH* = 5,05 and ERS. At the same time *pH* of obtained WAM is *pH* = 7,60 i.e. alkalescent medium. A «restoration» of location of hydroxyl proton's signal (*OH*) of ethanol is not observed during the time interval of 0 to 432 h after the mixing, with a constant alcohol concentration (WAM's strength – 39,92 % vol.) and system's temperature control (t=23,5 ºC). It can be assumed that division of the signals related to the process of reconstruction of water structure that was destroyed by demineralization by reverse osmosis. The low exchange rate (separately observed signals of hydroxyl and water) can be related to a significant microheterogeneity of the system and relevant barrier effect that reduces the effective rate of protons' exchange.

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Assessment of the nutritional potentials of *Theobroma cacao* L. and *Coffee liberica* W. Bull.

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Abstract

Introduction. Consumption of cocoa and coffee had been on increase due to a number of beneficial health properties attributed to the cash crops. The study of the phytochemical constituents and nutritional potentials of these valuable crops would further reveal their nutritional and phytomedicinal importance in human diet.

Materials and methods. Cocoa and coffee beans were harvested from a farm in Ado-Ekiti, Ekiti State, Nigeria and were studied for their proximate, mineral and phytochemical constituents using standard analytical procedures. The harvested cocoa and coffee were sundried for a week and later air dried, de-shelled, and ground into powder and then sent to the laboratory for phytochemical and proximate analysis.

Results and discussion. The results obtained showed that both plant samples contained alkaloids, tannins, saponins, flavonoids, phenol and cardiac glycosides. However, steroids, phlobatannin and terpenoids were present in *C. liberica* but absent in *T. cacao*. The proximate analysis revealed moisture content (12.16 and 10.84%), carbohydrate (57.19 and 62.51%), crude protein (4.08 and 3.75%), crude fiber (18.95 and 16.72%) and ash (6.82 and 5.58%) in the *C. liberica* and *T. cacao* respectively. The vital minerals (mg/100g) present in the coffee and cocoa were found to be Na (1050.14 and 1133.11), K (305.12 and 719.36), Ca (407.86 and 65.33), Mg (41.83 and 35.28), P (43.69 and 37.37), Mn (12.62 and 5.86), Fe (28.86 and 32.40) and Zn (2.41 and 3.61). Nickel contents were within the permissive level. No Pb and Cd were detected in the plant samples.

Conclusion. Cocoa and Coffee beans investigated could be considered as rich in bioactive secondary metabolites which justify their widely acclaimed health benefits.

Introduction

Since time immemorial, the importance of plants is well known irrespective of the era and area throughout the world. The beneficial roles of plants which include nutritional, aesthetic, cultural, religious and human health have been documented by several authors over the years. Almost all parts of plants have played significant roles in maintaining the health and promoting the well being of human life. Plant products which can be derived from roots, barks, gum, leaves, fruits, flowers, seeds and seed oil have been parts of phytomedicine. Cocoa and Coffee were the major export crops in the early 60's through 1970's and they provided highest foreign exchange in Nigeria [1]. However, evidence has shown that there is downward trend in the production and exportation of these cash crops due to oil boom that now account for the larger percentage of Nigeria foreign exchange [2].

Cocoa **(***T. cacao***)** discovery could be dated back to 1502 by Columbus on his fourth voyage to America [3] and introduced cocoa into Nigeria in 1874 by the Portuguese trade through Equatorial Guinea [4]. The seed of cocoa tree when further processed yields chocolate amidst other products. The plant is grown in different parts of the world like Brazil, Ghana, Ivory Coast, Malaysia, Nigeria, Venezuela and Indonesia [5]. *T. cacao* (Cocoa tree) is an evergreen tree of the family Sterculiaceae. It grows between 4–8m and preferred the shade of other layered trees. The leaves are dark green, shinning, leathery, elliptical in shape, alternate and unlobed. The leaf surfaces are hairless. The flowers are small, yellowish, white to pale pink, non-scented and clustered. The fruits (Cocoa pods) ovoid, 15–30cm long and 8–10cm wide, cauliflower, when ripe, yellow to orange pods.

Cocoa is mainly consumed as chocolate and used beverages, cosmetics and pharmaceuticals [6]. Numerous researchers have documented various health beneficial effects associated with the consumption of cocoa products [7]. Consumption of cocoa and chocolate has been reported to combating diseases like cancer and cardiovascular diseases [8], diabetes mellitus [9] and in immune system boosting. Cocoa pod husk are used traditionally as medicine to treat the pains of pregnancy, fever and coughs [10].

Coffe (*C. liberica* W. Bull ex) is an evergreen shrub or tree up to 20 m tall, branchlets and glaborous. *C. liberica* is native to tropical West and Central Africa. Nowadays, it is fairly widely cultivated in Liberia, Malaysia and lesser extent in Sierra Leone, Nigeria, Sri Lanka and Taiwan. Leaves are opposite, stipules interpetiolar, triangular ovate to almost truncate, 2–4.5mm long, obtuse, petiole 0.8–2cm long. Flowers are in auxillary clusters, 4–30 per axil. Fruits are oblong-ellipsoid drupe, red or yellow, mesocarp fleshy and endocarp fibrous. Seeds (commonly referred to as 'beans'), 0.7–1.15cm long, grey brown-green with a groove on the inner surface. Coffee has been used traditionally in the treatment of several diseases and ailments such as ashma, fever, headache jaundice, malaria, sores and vertigo [11].

Coffee is known to possess a number of beneficial health properties among them are diuretic, antimicrobial and antioxidant activities. Coffee served as the most consumed beverages in the world. It can be drink naturally, as a stimulant and painkiller. Coffee contains some biochemical compounds like chlorogenic acid and its derivatives that help in preventing different chronic degenerative disease [12]. Also caffeine is commonly found in coffee and its values vary widely with differences in species as well as within species [13]. Consuming high concentration of caffeine has adverse physiological [14] and psychological effects on man. As a result of this there is an increase demand for de-caffeination of coffee.

Considering the health potentials and economic importance of these crops, there is needs to renew research work which will provide information on the health promoting constituents of *Theobroma cacao* and *Coffee liberica* in Nigeria. More importantly and

pathetically, *C. liberica* have been abandoned for crops that are readily marketable locally. This important cash crop may go into extinction in Nigeria if adequate measures are not taken. Hence, this work was carried out to provide information on the nutritional potentials of *T. cacao* and *C. liberica* in Ekiti State, Nigeria.

Materials and methods

Collection of materials

The cocoa beans and coffee fruits were collected from a cocoa farmer in Ado Ekiti, Ekiti State. They were authenticated in the Department of Plant Science and Biotechnology, Ekiti State University, Ado Ekiti. The harvested coffee fruits were sorted out and cleaned by floatation in a washing basin using distilled water. The materials were put in a large tray and spread in the sun for a week and were later air dried for 5 days. The cocoa beans and coffee beans were de-shelled, then separated from the chaffs, ground into powder using electric blender (Binatone BLG-450). The powdered samples were tightly packed into separate plastic containers and taken to the Department of Biochemistry, University of Lagos, Lagos State for phytochemical, proximate and mineral analyses.

Preparation of plant extract

A portion (200g) of each of the powdered sample was extracted separately using distilled water for 48hours. The extract was filtered using Whatman filter paper and kept for further use.

Phytochemical analyses

Qualitative screening. Qualitative phytochemical screenings were carried out using standard procedures of [15, 16].

Test for alkaloids. Alkaloid was detected by taking about 1g of each plant sample and stirred with 5 ml of 1% HCl on a steam bath and filtered. 1ml of the filtrate was treated with a few drops of Dragendorff's reagent (Bismult nitrate + conc HCl). A change in the colour of the sample to black indicates alkaloid's presence.

Test for tannins. A portion (1g) of the plant sample each was taken and boiled in 10ml of distilled water in a test tube and filtered. A few drops of 5% ferric chloride were added. Black or blue-green colouration or precipitate shows the presence of tannins [17].

Test for saponins. One gram of each plant powdered sample was heated in 5 ml of distilled water in a test tube. The mixture was shaken vigorously by hand for about 15minutes and heated to boil. Persistent frothing shows the presence of saponins [18].

Test for phenols. A portion (1g) of the sample each was soaked in 25 ml of 2% HCl for 1hour and then filtered. 5 ml of each plant extract was then mixed with 1ml of 0.30% Ammonium thiocyanate solution and few drops of ferric chloride solution. A brownish yellow colour indicates the presence of phenol.

Test for flavonoids. A few drops of diluted NaOH solution were added to 0.5 ml of an aqueous extract of each plant sample. Intense yellow coloration which became colourless upon the addition of few drops of diluted H_2SO_4 acid shows the presence of flavonoids [19].

Test for steroids. Two milliliters of acetic anhydride was added to 0.5 g of the plant sample each with 2 ml of conc. H_2SO_4 acid. Presence of steroids is noted by the changing of colour from violet to blue [20, 21].

Test for terpenoids. One gram of each plant sample was mixed with 2 ml of chloroform and 3 ml of conc. H_2SO_4 were carefully added to form layer. A reddish brown colouration of the interface indicates the presence of terpenoids.

Test for cardiac glycosides (Keller-Killiani test). One gram of plant sample each shaken with 5 ml of distilled water in a tube and 2 ml of glacial acetic acid containing a few drops of ferric chloride was added slowly along the side of the test tube. Formation of brown ring at the interface gives positive indication for cardiac glycoside. A violet ring may also appear below the brown ring [22].

Test for anthraquinance (Bontrager's test). One gram of the plant sample was weighed and 1ml of 5% H_2SO_4 was added, boiled in a water bath and filtered. The filtrate was shaken with the equal volume of chloroform was then taken and shaken with half of its volume with dilute ammonia. Formation of rose pink to red colour of the ammonical layer shows the presence of anthraquinone [23].

Test for phlobatanins. A portion (2g) of the powdered sample each was boiled with 1% aqueous HCl. Presence of phlobatanins is noted by the formation of red precipitate [15, 19].

Quantitative phytochemical estimation

The phytochemicals which are present in the *C. liberica* and *T. cacao* powdered samples were determined and quantified by standard procedures of [15, 24, 25].

Proximate analyses

Moisture content for each sample was determined by weighing 5grams of each of the sample into a crucible and heated at 105°C until a constant weight was attained [26]. Total ash was determined by taking 5g of each of the sample in a crucible and ignited in a muffle furnace at 550°C for 6hours, cooled and weighed at room + temperature [27].

Total nitrogen was analyzed using Kjeldal digestion method followed by distillation and titration. The percentage nitrogen was calculated and multiplied by 6.25 to obtain the value of the crude protein [27]. Crude lipid estimation was carried out using the Soxhlet extraction method. N-hexane was used to extract the lipid [27]. Caffeine was determined by boiling 5g of each sample, filtered, washed with chloroform, evaporated, dried in an oven and weighed as outlined by the Kjeldal method [26]. The carbohydrate content was determined by subtracting the summed up percentage compositions of moisture, protein, lipid, fiber and ash contents from 100 [28].

Determination of minerals

For mineral determination, wet digestion of the two samples was carried out according to the method of [29]. Zinc, Manganese, Calcium, Magnesium and Iron were determined by atomic absorption spectrophotometer while Sodium, Potassium and Calcium were measured through flame photometer.

Results and discussion

Results

The results of the phytochemical constituents of *C. liberica* and *T. cacao* revealed the presence of alkaloids, tannins, saponins, phenols, flavonoids and cardiac glycosides. Steroids, phlobatannins and terpenoids were found in coffee but absent in cocoa while anthraquinones were detected in cocoa but absent in coffee (Table 1).The quantitative estimation (mg/100g) of the phytochemicals showed that *C. liberica* and *T. cacao* contained flavonoids (55.74 and 80.78), phenols (42.98 and 51.70), tannins (24.47and 18.09), saponins (19.45 and 26.11), alkaloids (19.16 and 22.31) and cardiac glycosides (16.67 and 18.14) respectively (Table 2).

Table 1

Phytochemicals present in the seeds of *C. liberica* and *T. cacao* inmEkiti State, Nigeria

Phytochemicals/ Samples	Alk.	Tan.	Sap.	Phen.	Flav.	Ster.	Phlob.	Terp.	Car. Glyc.	Anth.
C. liberica	+	+	+	+	+	+	+	+	+	-
T. cocoa	+	+	+	+	+	-	-	-	+	+

Alk. – Alkanoids, Tan. – Tannins, Sap. – Saponins, Phen. – Phenols, Flav. – Flavonoids, Ster. – Steroids, Phlob. – Phlobatanins, Terp. – Terpenoids, Car. Glyc. – Cardiac Glycosides and Anth. – Anthraquinone.

+ indicates presence, – indicates absence

Table 2

Quantitave phytochemical estimation of the seeds of *C. liberica* and *T. cacao* in Ekiti State, Nigeria

Phytchemicals/ Samples	Flavonoids	Phenols	Tannins	Saponins	Alkanoids	Cardiac Glycosides
C. liberica	55.74±0.23	42.98±0.43	24.47±0.26	19.45±0.40	19.16±0.78	16.67±0.31
T. cocoa	80.78±0.23	51.70±0.24	18.09±0.15	26.11±0.75	22.31±0.28	18.14±0.18

Values are the mean of triplicates ± S.D

The percentage proximate content of coffee and cocoa beans investigated (Table 3) contained carbohydrate (57.19 and 62.51), crude protein (4.08 and 3.75), crude fat (0.80 and 0.61), crude fiber (18.95 and 16.72), ash content (6.82 and 5.58), moisture content (12.16 and 10.84) and caffeine (0.04 and 0.03) respectively.

The results of the mineral compositions (mg/100g) revealed coffee and cocoa to contain Na (1051 and 1133), K (305.12 and 719.36), Ca (407.86 and 65.33), Mg (41.83 and 32.28), P (43.69 and 37.37), Mn (12.62 and 3.61), Cu (0.15 and 0.04), Zn (2.41 and 3.61), Fe (28.86 and 32.40) and Ni (0.03 and 0.07) respectively. Pb and Cd were not found in the two samples investigated (Table 4).

Table 3

Proximate composition of the seeds of *C. liberica* and *T. cacao* in Ekiti State, Nigeria

Parameters (%)	*C. liberica*	*T. cacao*
Carbohydrate	57.19±0.32	62.51±0.25
Crude Protein	4.08±0.04	3.75±0.09
Crude Fiber	18.95±0.28	16.72±0.18
Crude Fat	0.08±0.04	0.61±0.02
Ash Content	6.82±0.03	5.58±0.22
Caffeine	0.04±0.00	0.03±0.00
Moisture Content	12.16±0.34	10.84±0.09

Values are the mean of triplicates ± S.D

Table 4

Mineral compositions of the seeds of *C. liberica* and *T. cacao* in Ekiti State, Nigeria

Mineral Element (g/mg)	*C. liberica*	*T. cacao*
Sodium	1051.04±2.35	1133.11±1.27
Potassium	305.12±1.25	719.36±1.79
Calcium	407.86±0.43	65.33±0.66
Magnesium	41.83±0.62	35.28±0.83
Phosphorus	43.69±0.62	37.37±0.16
Manganese	12.62±0.09	5.86±0.35
Copper	0.15±0.00	0.04±0.01
Zinc	2.41±0.24	3.61±0.10
Iron	28.86±0.44	32.40±0.48
Nickel	0.03±0.00	0.07±0.01
Lead	ND	ND
Cadmium	ND	ND

Values are the mean of triplicates ± S.D and ND means not detected.

Discussion

The phytochemicals found in the coffee and cocoa seeds in this study play diverse roles in these plants as well as various biochemical and pharmacological actions when ingested by animals [30]. The presence of these bioactive secondary metabolites in the seeds investigated suggests their importance as health promoting cash crops. Several authors such as [31, 17, 32, 33] had previously reported the therapeutic properties of these phytochemicals in various plant parts.

The phytochemical profile obtained in this study for *T. cacao* was similar to the reports of [34]. The result of the phytochemical estimation revealed that *T. Cacao* had higher concentration of flavonoids, phenols, saponins, alkaloids and cardiac glycosides when compared to *C. liberica*. However, qualitatively, *C. liberica* contained more phytochemical constituents. Alkaloid in coffee and cocoa in this study are found in considerable quantity which makes them biologically active and equally suggests their potential for disease resistance and stress [35]. Alkaloids offer a wide range of health benefits which ranges from anti-inflammatory [36], antimalarial [37], antimicrobial and antisparmodic [38].

High quantity of flavonoids in both beans suggests that they perform some biological functions. Our finding is similar to the reports of [39] and [40] who reported higher concentrations of flavonoids in cocoa than coffee. Lee *et al.* [39] reported that cocoa have higher contents of phenolic and flavonoids than any other phytochemical-rich foods. Flavonoids are effective antioxidant and have strong anti cancer activities [41, 42]. The presences of flavonoids in the two seeds lead to their antioxidant effects which may influence insulin resistance hence reduce the risk for diabetes [43]. Tannins contents in *C. liberica* were higher than that of *T. cacao.* Tannins according to several researchers are known to have anti-inflammatory and antibacterial properties [44], wound healing properties [45], as well as in treatment of intestinal disorders. Plant extracts containing saponins have been reported to exhibit a wide spectrum of biological activity such as inhibitory effect on inflammation [46], antifungal and antibacterial agents, lowering of blood cholesterol and adding bitter taste [47]. In the previous work of Okwu and Okwu [48], it was reported that saponins and steroids have relationships with sex hormones like oxytocin which stimulates contractions during labour in pregnant women and followed by the release of milk. The palatability characteristics of these beverages revealed that they are bitter and this might be due to the high levels of saponins.

Several beneficial health effects that have been attributed to these cash crops may be largely explained by their rich bioactive phytoconstituents. Consumption of cocoa rich in phytochemicals may confer its effectiveness in maintaining skin health and phytoprotection. The presence of these constituents in coffee buttresses its uses traditionally in the treatment of fever, headache, malaria, sores and vertigo. The proximate composition results revealed that *C. liberica* contained higher crude protein, fiber and ash contents while carbohydrate obtained is higher in *T. cacao* than *C. liberica.* The crude protein content in the coffee is higher than 1.43 mean distribution of total nitrogen content reported by [49] for some brands of tea in Nigeria. The crude protein content of the cocoa beans is lower compared to the values range of 6.11% to 9.25% [50]. The crude protein in *C. liberica and T. cacao* may contribute to their health potential as it supports growth and development in infant and children as well as constant replacement and turnover of protein in adult [51].

Fiber content in our cocoa is comparatively higher than value of 1.80% reported by [52]. The fiber content of the coffee is in agreement with reports of [53]. Several researchers have documented the health benefits of fiber to include; lowering the risk of diabetes and heart disease, as well as preventing constipation [54]. Crude fat content in the two plants are relatively low and quite reasonable as excess fat consumption has health implications such as cardiovascular diseases [55]. Considerable amount of crude fiber and low crude fat in the cocoa and coffee studied suggest that the beverage may help to protect against the aetiology of certain coronary heart and cardiovascular diseases. The products could also be recommended as good drinks for people who suffer from high cholesterol level.

The percentage ash content value is an indication of its mineral contents. The two samples compare favorably with the value range of 5.32 to 6.31% and Carbohydrate values are low when compared with the value range of 67.24% to 73.00% reported by [50]) for cocoa beans The carbohydrate contents of *T. cacao and C. liberica* are high, an indication that this beverage could serve as a good source of energy for human being.

The caffeine content in *C. liberica* is comparatively higher than the value obtained for *T. cacao*. Interestingly, the values of our findings are comparatively low to 0.07% caffeine reported in Ethiopian coffee designated as naturally decaffeinated varieties [12]. The caffeine content in our study falls within the range of 0.036 to 0.041% reported by [56] for decaffeinated coffee. Caffeine is found in various kinds of foods and drinks that we

consume every day. Several researchers had reported various physiological and psychological effects of consuming high concentration of this compound [57, 58]. Caffeine concentration evaluation have been used as an additional tool for assessing beverage (such as cocoa and coffee) quality. Farah *et al*. [59, 60] reported that higher caffeine content is associated with less quality samples. Hence, the two beverage samples evaluated are good for human consumption.

The cocoa and coffee beans investigated in our study are very rich source of many macro and micro elements that are needed in normal human metabolism. These essential minerals include Sodium, Potassium, Calcium, Magnesium, Phosphorus, Manganese and Iron. Comparing with other results previously documented, our result for cocoa beans is similar to the reports of [61] and [43]. Our work disagrees with dominant magnesium in the reports of the former and low potassium in the reports of the latter.

Also the result of the mineral content for coffee in this study is in line with previous work of [56]. Determination of these minerals in cocoa and coffee is of great interest and will help immensely in improving their nutritional effects. Minerals play vital roles in physiological functions. Lead and Cadmium were not detected which suggest that the beverage under investigation cannot pose any health risk for consumers. Sodium in moderate quantity plays a role in nervous and muscular body function. Calcium is necessary for the development of bones and teeth. Magnesium is an anti arrhythmic and hypertensive agent [62]. Copper helps in glucose metabolism and brain development [63].

Conclusion

Several health promoting effects have been attributed to these cash crops. These may be largely explained by their rich bioactive phytoconstituents and nutritional compositions as revealed in this study. *C. liberica* and *T. cacao* investigated are rich in health promoting chemicals and their consumption should be encouraged. They also contain very low caffeine which makes them to be considered as good for human well being. Nigeria government needs to look at how to boost the production of these important cash crops more importantly *C. liberica* which is more nutritious and contain very little amount of caffeine. Its seeds do not need laborious and expensive chemical decaffeination.

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Investigation of viscous characteristics of ice cream mixtures with starch syrup

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Abstract

Introduction. Starch syrup is widely used as a sweetener for the production of ice cream, but its structuring ability is not sufficiently studied and requires additional research. Revealing patterns of structuring mixtures with the syrup of different degrees of saccharification allows to reduce the need for structural stabilizers and to achieve a technological effect in the process of ice cream production at the expense of only natural ingredients.

Materials and methods. Rheological characteristics of mixtures of ice cream and aromatic ice cream with glucose-fructose syrup (HFCS-96), glucose syrup (HFCS-42) and carotene syrup (HFCS-30) have been investigated by using a rotary viscometer.

Results and discussions. With complete replacement of sugar for starch syrup HFCS-30 and HFCS-42, the initial effective viscosity of ice cream mixtures increases by 22,1% and 2,5% respectively, compared to the control sample with sugar. as compared to the control sample with sugar. At the same time, complete replacement of sugar on the syrup HFCS-96 contributes to a decrease in the initial effective viscosity of the ice cream mixture by 15,3%. Initial effective viscosity of aromatic ice cream mixtures at full replacement of sugar by HFCS-30 and HFCS-42 increased by 27,1% and 14,8% respectively, and decreased by 11,6% at full replacement of sugar for HFCS-96 syrup.

Starch syrups HFCS-42 and HFCS-96 provide mixtures of thixotropic properties. Instead, systems with syrup HFCS-30 can not only completely restore the structure, but also show weak reopectic properties. Due to this, in the mode of inverse reduction of the shear rate, the effective viscosity of the mixtures of ice cream of cream and aromatic, in case of complete replacement of sugar, increases by 12,7% and 18, 8%, respectively, compared with the initial values. In mixtures containing a mixture of HFCS-96 and HFCS-30 patches at a ratio of 30:70, the effective viscosity increases in reverse slip rate by 9,5% and 12,5% for ice cream and aromatic ice cream, respectively, compared to Initial values.

Conclusions. The structuring ability of starch syrup decreases with increasing its degree of saccharification. The revealed pattern of the effect of starch syrup with different dextrose equivalent on viscosity characteristics of mixtures of different chemical compositions makes it possible to purposefully form indicators of ice cream quality.

Introduction

The viscosity characteristics of ice cream mixtures change during the technological process under the influence of certain types of thermal and mechanical processing (mixing, pasteurization, homogenization, cooling, maturation, freezing) [1-6]. Thus, scientists at the University of Manchester (UK) have confirmed that the viscosity of ice cream mixtures is volatile and depends, first of all, on the temperature of the samples under study and the rate of shear [2]. Scientists at the Department of Food Science, Faculty of Agriculture, University of Udine (Udine, Italy) have proved the dependence of the viscosity characteristics of ice cream mixtures on the process of homogenization [3].

Existing recommendations on the regulation of structural and mechanical properties of ice cream mixtures chiefly take into account only the effective viscosity of the virtually undamaged structure of mixtures. Thus, for mixtures of ice cream of classical species (milk, cream, plombir) at a temperature of 20 ºC at a shear rate $\gamma = 3$ this figure should be about 200, 600 and 1200 mPa·s respectively. For the aromatic mixtures, effective viscosity is much lower and can reach 250 mPa·s [5].

In the process of ice cream production, in the period between two technological operations, "freezing" and "quenching", when the structure of a complex food system varies from liquid (mixture) to a practically solid (hardened ice cream), it is equally important that the ability of ice cream mixes to collapse significantly under the action of the external shearing forces of the blades of the stirrer in the frieze and to quickly and effectively restore the structure in a static state after the formation of portions before the quenching process. The structure of the mixture must be partially or completely restored in the formed portion of the finished product, which significantly improves its quality [2, 5]. Proper viscosity of the mixtures and the ability to restore it contributes to the formation of a solid structure of ice crystals and the formation of a hard ice cream consistency [1, 2, 4, 5, 18]. Instead, scientists almost do not pay attention to the ability of mixtures to restructure the structure, in spite of the fact that in ice cream technology this particular characteristic is one of the most important.

Initial relative viscosity of the finished mixtures and its change in the production of ice cream, primarily, are determined by the physical and chemical characteristics of the formulation components [4]. Hydrocolloids and surfactants (stabilizers, emulsifiers and stabilization systems) are essential in the structuring of mixtures for the production of ice cream [5]. Equally important is the content of the fatty component, with the increase in the viscosity of the mixtures also rises [1-7], as well as its chemical composition and degree of conscientiousness. In the course of the latest developments, so-called "low-fat" milk fat substitutes such as starch, starch-lipid compositions, serum protein isolates (WPI), maltodextrins, etc. are becoming increasingly popular. [6-9], whose influence on the organoleptic and structural-mechanical properties of ice cream is still not sufficiently studied.

Sugar and sugar-containing components, in particular starch syrup, also influence the process of forming the rheological characteristics of the mixtures and the finished product [4, 9-14]. The content of reducing agents in the starch syrup is designated as dextrose equivalent (DE): low conversion DE 28-38, intermediate DE 49-58, and high conversion DE 59-96. Ice cream makers usually use liquid or dry corn syrups from DE 28-42 [4, 14]. With a decrease in DE, the sweetness of the molasses decreases, and the structuring ability increases [5, 10, 15], which should be taken into account when used as part of food systems. At the same time, there is no information on the possibility of complete

replacement of sugar by starch syrup and its influence on the viscosity characteristics of mixtures for the production of ice cream.

Consequently, taking into account the above, the study of the effect of starch syrup of different degrees of saccharification on the viscosity characteristics of dessert mixtures is a promising scientific direction in ice cream technology.

In view of the above, the purpose of scientific research is to determine the patterns of the influence of starch syrup of varying degrees of saccharification on the effective viscosity of mixtures for the production of ice cream.

Materials and methods

Materials

For the comparison of the rheological characteristics of milk-based mixtures for control, the typical formula of ice cream is selected: with a mass fraction of fat – 10%, dry skim milk residue – 10%, sugar –14%, stabilizing system Cremodan SE 709 – 0,5%. For the study of ice cream on the basis of sugar syrups, a flavor mixture with a mass fraction of sugar of 28% and a classical stabilizer (gelatin) in the amount of 0,5% of the total mass of the mixture was selected as the Control sample.

As a sweetener and a structuring component, molybdenum-fructose syrup (HFCS-96), glucose syrup (HFCS-42), carotene molasses (HFCS-30) and glucose-fructose syrup were used as a syrup of starch dry.

The following designations were adopted.

Mixtures of ice cream:

- Control 1 (14% of sugar);
- Sample No. 1 (7% sugar + 7% HFCS-42);
- Sample No. 2 (14% HFCS-42);
- Sample No. 3 (7% sugar + 7% HFCS-96);
- Sample No. 4 (14% HFCS-96);
- Sample No. 5 (7% sugar + 7% HFCS-30);
- Sample No.6 (14% HFCS-30);
- Sample No. 7 (4.2% HFCS-96 + 9.8% HFCS-30);

Mixtures of aromatic ice cream:

- Control 2 (28% of sugar);
- Sample No. 8 (14% sugar + 14% HFCS-42);
- Sample No. 9 (28% HFCS-42);
- Sample No. 10 (14% sugar + 14% HFCS-96);
- Sample No. 11 (28% HFCS-96);
- Sample No. 12 (14% sugar + 14% HFCS-30);
- Sample No. 13 (28% HFCS-30);
- Sample No. 14 (8.4% HFCS-96 + 19.6% HFCS-30).

Preparation of mixture for ice cream samples with starch syrups

Mixture for ice cream production was prepared according to the classical technological scheme and typical recipes (pasteurization at a temperature of 85 ± 2 ºC for 2-3 minutes, cooling to 4 ± 2 ºC, maturity for 12 hours).

In the samples under study, 50 and 100% of the sugar replacement was performed on starch syrup with different DE and composition (HFCS-96:HFCS-30 = 30:70), the feasibility of which was confirmed by the authors earlier [11].

Research of rheological characteristics of ice cream mixtures

The viscosity characteristics of the ice cream mixtures were determined by removing the curves of the kinetics of deformation (flow), using a rotary viscometer with a measuring system, cylinder-cylinder. Measurements were performed at a temperature of 20 °C. The measuring cylinder (rotor) S1 was selected in such a way that the gradient layer was distributed over the entire thickness of the product layer located in the annular gap of the viscometer gauge. The measurement of shear stress was carried out in twelve values of shear rate γ in the range from 3 to 1312,2 s^{-1} in series with a gradual increase in shear rates at the highest speed for reverse gradual reduction of velocities [12].

Results and discussions

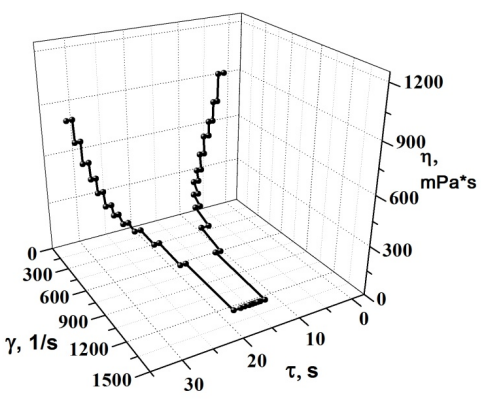
The dynamics of changes in the effective viscosity of ice cream mixtures of different types for the gradient of the shear rate γ in the range from 3 to 1312,2 s^{-1} in the direct and reverse is determined (Table 2).

Table 2

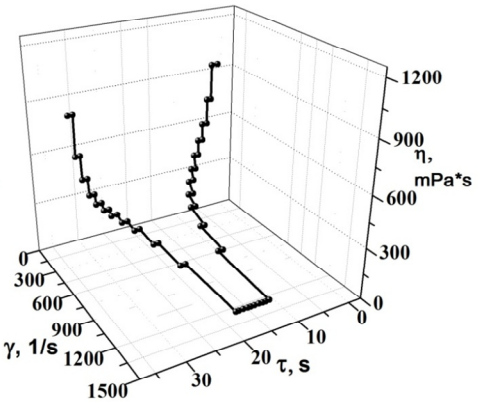
Rheological characteristics of the studied systems

Sample name	η_1 (γ=3), mПа·с	η_2 (γ=1312,2), mПа·с	η_3 (γ=3), mПа·с	τ (γ=1312,2), с
Mixtures of ice cream				
Control 1	896,92	51,35	782,11	336
Sample No. 1	907,64	51,72	808,42	318
Sample No. 2	919,12	51,55	829,53	304
Sample No. 3	793,56	48,12	674,46	267
Sample No. 4	759,91	47,51	628,93	200
Sample No. 5	967,63	60,63	1050,19	425
Sample No. 6	1095,34	64,50	1234,31	440
Sample No. 7	1001,71	57,24	1097,26	370
Mixtures of aromatic ice cream				
Control 2	252,30	6,21	204,54	152
Sample No. 8	269,82	6,66	208,96	141
Sample No. 9	288,61	6,91	217,57	139
Sample No. 10	206,43	5,73	182,32	99
Sample No. 11	191,55	4,84	160,45	83
Зразок No. 12	299,11	7,92	342,03	181
Sample No. 13	323,67	9,42	384,51	197
Sample No. 14	291,61	7,81	327,95	185

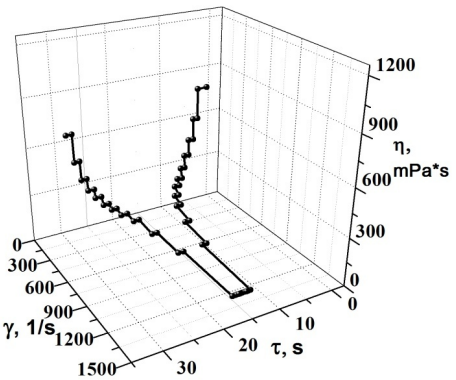
The nature of the structure destruction of the studied food systems in the process of m easuring the effective viscosity is shown in Figure 1 and 2 on the example of a mixture of ice cream and aromatic cream with a complete replacement of sugar on the starch syrup.



Control 1



Sample No. 2



Sample No.4

Figure 1. Dynamics of changes in the viscosity characteristics of ice cream cream (Control 1) and samples with 100% sugar substitution on HFCS-42 (sample No.2) and 100% sugar substitution

According to the results of the study, it is evident that samples of mixtures of control and mixtures with HFCS-42 and HFCS-96 have thixotropic properties. In the process of rheological research the gradual destruction of the initial structure and the corresponding reduction of the effective viscosity (η_3) by 10,8% and 17,2% respectively for ice cream cream and 11,9% and 16,23% for aromatic ice cream per 100%-substitutes of sugar compared to their initial values (η_1) are characteristic for them. At the same time, food systems containing HFCS-30, are able not only to almost completely restore the structure, but also to show weak reopectic properties. The latter are manifested in increasing the effective viscosity in reverse shear rate (η_3) by 12,7% for ice cream and 18,8% for aromatic ice cream at full sugar replacement compared to the initial values (η_1). For comparison, in control samples of ice cream and aromatic ice cream with sugar, effective viscosity decreases by 12,1% and 18,7% respectively.

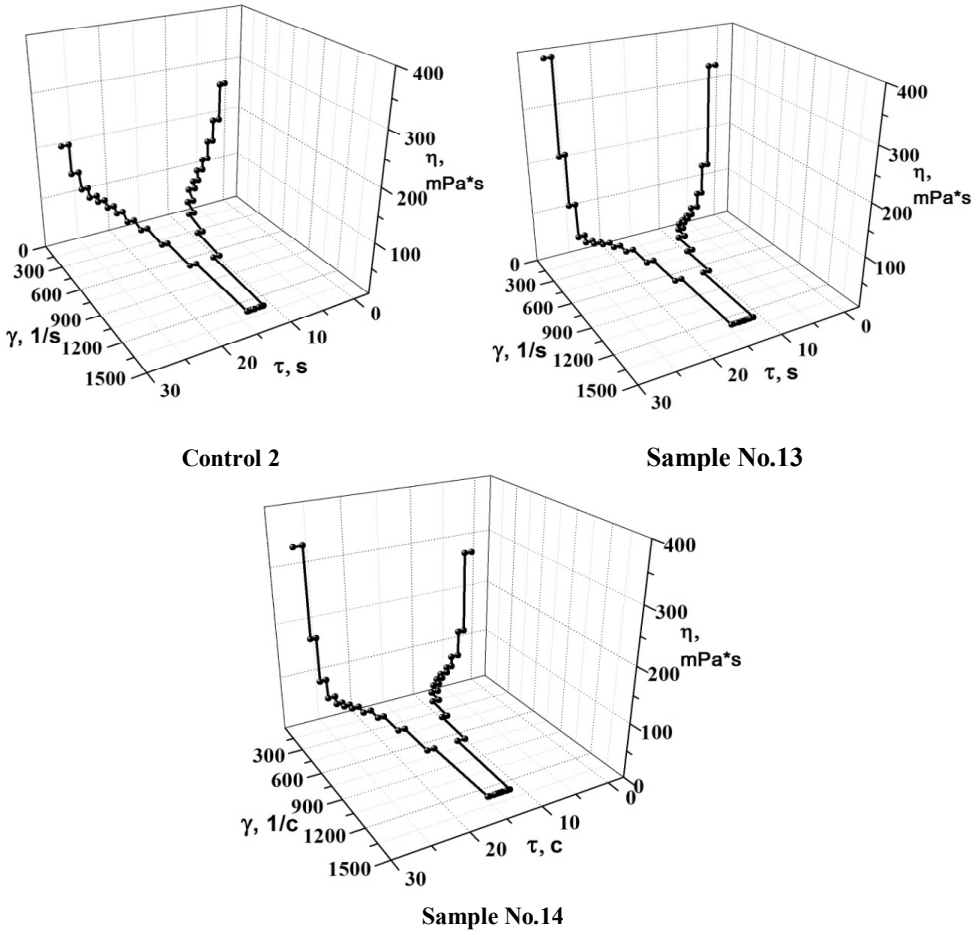


Figure 2. Dynamic of change of viscosity characteristics of aromatic ice cream (Control 2) and samples with 100% sugar substitution on HFCS-30 (Sample No.13) and 100% sugar substitution for a mixture of HFCS-96: HFCS-30 = 30:70 (Sample No.14)

It should also be noted, that in the event of an increase in the degree of saccharification and an increase in the content of mono-sugars in the syrupsmolasses, the time for which the systems under study are transferred to a state of equilibrium (τ) is reduced.

The use of HFCS-30 at the expense of increased content of polysaccharides not only structures the mixture, but also improves the ability to restore the structure of the formed portions of soft ice cream before quenching. At the same time, the effective viscosity of such mixtures is too high, which can lead to a decrease in the loss of the finished product and the formation of an overly dense structure and coarse consistency of the product [1, 2, 4, 5, 18]. Therefore, the complete replacement of sugar by HFCS-30, taking into account its significant effect on the rheological properties of the mixture for ice cream of various species, is not appropriate.

The partial and complete replacement of the traditional sweetener by HFCS-96, in turn, contributes to reducing the viscosity of the mixture and the ability to restore its structure, compared with the control sample. Considering the chemical composition of HFCS-96, the effect is due to the predominant content of monosaccharides in its composition [13]. That is, the surplus or lack of polysaccharides does not ensure the proper formation and stabilization of the structure of ice cream.

The food system, which has an overwhelming number of HFCS-30 polysaccharides, compared to HFCS-96 samples, does not provide sufficient structuring, while the use of HFCS-96 alone will provide ice cream with excessive sweetness and low resistance to dandruff [15, 16]. Therefore, in order to create a structure characteristic for a soft ice-cream, to balance the taste and consistency of the finished product, it is expedient to use a mixture of starch syrup with a low and high DE for a ratio that ensures the formation of the given physicochemical and organoleptic parameters of ice cream mixtures of different species, in comparison with control samples.

For mixtures with HFCS-96 + HFCS-30 syrup composition for 100% sugar replacement, an increase in effective viscosity is observed in reverse slope reduction (η_3) by 9,5% for ice cream and 12,5% for aromatic ice cream compared to the initial values (η_1). It should be noted that the use of the specified starch syrup composition also fully provides the degree of sweetness typical of the classic ice cream. While the replacement of sugar by HFCS-42 slightly affects the rheological parameters of mixtures, but significantly reduces the sense of sweetness.

Similar studies were carried out by the Atatürk University Department of Food Sciences by Cihat Ozdemir, using mixtures for the production of 5% fat dairy ice cream and a mass fraction of the sweetening component of 18%. As sweeteners in the samples studied, HFCS maltodextrin, HFCS low-soluble molasses, HFCS mixture of medium sugary sugar with a 1:1 ratio, HFCS low-sugar molasses mixture ratio of 1:1 were used in the samples studied. The results of the study showed an increase in the effective viscosity of HFCS low-octane samples and HFCS with an average degree of sacharification of 17,6% and 2,2%, respectively, for complete replacement of sugar [15]. According to the results of our study, the effective viscosity of ice cream mixtures with HFCS-30 and HFCS-42 increases by 22,1% and 2,5%, respectively in the case of complete replacement of sugar. Replacing sugar with molasses HFCS-96 contributes to lowering the initial effective viscosity of the cream mixture by 15,3%. Initial effective viscosity of aromatic ice cream mixtures at full replacement of sugar by HFCS-30 and HFCS-42 increased by 27,1% and 14,8% respectively, and decreased by 11,6% with full replacement of sugar for HFCS-96 starch syrup.

These results confirm the general tendency of the influence of the degree of saccharification of syrup on the structural and mechanical properties of the mixtures, but are more versatile due to the nature of the change in the viscosity characteristics of systems of different chemical compositions in the process of mechanical treatment.

The low viscosity of the mixture for aromatic ice cream, as compared with milk-based ice cream, is due to the use of gelatin as a stabilizer. Its macromolecules are not able to form a sufficiently dense framework, compared with the current stabilization system in the ice cream.

The revealed ability of mixtures with starch syrup and polysaccharides in its composition to restore the destroyed structure has practical significance, especially in the case of production of ice cream on the stream extrusion lines, which will improve the efficiency of the process of forming and dosage of ice cream portions.

In further researches it is planned to study the indexes of quality of ice cream with starch syrup taking into account the results of research of structural and mechanical properties of mixtures for its preparation.

Conclusions

1. Starch syrup in mixtures for ice cream, depending on the degree of saccharification, significantly affects their structural and mechanical characteristics. The content of higher sugars in the HFCS-30 syrup, unlike HFCS-96, contains the majority of monolysaccharides, contributes to the better structuring of mixtures, which directly affects the increase of their effective viscosity.
2. HFCS-96 and HFCS-42 mixtures are thixotropic, and mixtures with HFCS-30 have low reopectic properties, which allows to predict the dynamics of change in effective viscosity in the technological process of ice cream production.
3. It is expedient to use an HFCS-30 + HFCS-96 composite mixture at a ratio of 30:70 to produce ice cream with high whipping, proper melting resistance and a sufficient degree of sweetness.

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Sensory and chemical attributes of dessert wines made by different freezing methods of Marselan grapes

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Abstract

Introduction. The purpose of research was to determine the impact of different freezing methods of Marselan grapes on sensory and physicochemical compositions of obtained icewines.

Materials and methods. Sweet wines were obtained by two ways of freezing of Marselan grapes: naturally and alternative – cryogenic extraction. The production and physicochemical parameters of wines were conducted in agreement with the provisions of the International Organization of Vine and Wine relating to icewine technology. Quantitative and qualitative composition of aromatics in sweet wines were determined by gas chromatography. Sensory analysis consistent with ISO 8586-2 showed the organoleptic attributes of dessert wines.

Results and Discussion. According to the agricultural climatic resources of Northen Black Sea coast exactly in Odesa region red variety Marselan is suiTable for processing into dessert wine of premium sector. Freezing of grapes by cryogenic extraction was slower and at a lower temperature (-10°C) compare to natural method (harvesting at -7°C) for obtaining of must with a high sugar content.

The chemical composition of the wine grape Marselan, frozen in various ways were not significantly different. Positive correlations among the variables responsible for the content of sugar, ethanol and volumetric mass concentrations of volatile acids were observed in both samples. 35 and 37 aroma compounds were found in wines made by natural (NF) and alternative freezing (AF) respectively by gas chromatography. Concentrations of alcohols in both wines were the highest among aroma volatiles counting more than 60 % and 40 % in wines of NF and AF accordingly. Esters, higher alcohols, volatile acids differ in mass concentration, and C_6 compounds were found only in the wine produced from grapes frozen on the vine. Sensory analysis showed differences in intensity of fruit notes, hints of nuts and longitude of aftertaste.

Conclusions. The results of the research demonstrate the peculiarities in the formulation of unique aromatic and chemical profiles of icewines made from Marselan, as well as a way of freezing affects the defining characteristics of the wines.

Introduction

Using the new varieties in non-classic technologies impacts on developing of original wines whereby expanding of range inside market. Icewine is relatively new wine type for production of which particular conditions are required [1]. An agricultural climatic factors and cold resistant cultivars are the main aspects to obtain frozen grapes from vines. The white skinned varieties are widely applicable in atypical technology but recently winemakers have started to freeze dark grapes that also can withstand frosts [2].

To our knowledge icewine from Marselan grapes had not been produced in the world and its aromatic and chemical characteristics also had not been investigated in scientific literature [1], [2], [7], [8]. Marselan cultivar originated from cross-breeding of Cabernet Savingnoun and Grenache in France [3] was chosen due to characteristics appreciated for icewine grapes including thick skin, late maturing variety with a high natural acidity. A cold resistant of variety was determined through leaving grapes on vines after major of harvest had been picked for another wine types from vineyards of Shabo. Riesling is considered as king of icewine grapes in the world [4] but unfortunately due to the distribution of precipitation most of which was high in months of autumn cultivar was rotten in Northen Black Sea coast, Odesa region, Ukraine (Figure 1).

In order to avoid lost entire amount of grapes intended for icewine before temperatures will be cold producers use artificial methods of freezing. Place is especially important in wine grape production because soils and climate cannot be modified by humans, and thus geographic branding has become increasingly spatially specific [5].

The aim of current article was to determine the peculiarities of aromatic and chemical compositions of wines obtained by natural and alternative freezing of Marselan grapes. The main objectives of research were to compare chemical and sensory properties of dessert wines. The expected practical result was to produce the new premium wine possessing unique aroma and flavor due to atypical technology.

Materials and methods

Grape materials. In December of 2016 Marselan grapes from vineyards belonged to terroir of Shabo in Northen Black Sea coast, Odesa region, Ukraine were harvested and pressed at required level of temperature according to Definition of the vitivinicultural products by code sheet of OIV [6]: - 7°C. The sugar content of obtained must was over 300 mg/l that is accordance with international documentation about icewine production. Two month earlier another portion of Marselan grapes had been frozen using refrigerator during one week until statutory sugar level was reached in berries (until -10°C). The grapes had been picked while technological ripeness of variety was observed on October of 2016.

Fermentation. The intense advertence is devoted to choice of yeast strain that contributes to chemical and sensory attributes thereby question of optimal and suiTable yeast for icewine is still discussed by major of producers and researchers [7], [8], [9], [10], [11]. Before fermentation musts were clarified by Microcol bentonite alpha (Laffort CO., France) with concentration of 1g/l combined with Polylact (Laffort CO., France) for effective fining. The adding of Assotan (Esseco SRL, Italy) contributed to essential antioxidant protect. Both samples of must formerly heated to 18-20 °C were inoculated with Saccharomyces cerevisiae VIN 2000 hybrid (Anchor, South Africa) at rate of 5 g/dal. The yeast starter was prepared by such wise: 1) rehydration of yeast to intended concentration 5 g/dal, 2) after 15 minutes of rehydration equal volume of yeast and must previously heated to 28-30°C were mixed and then resulted started was left during 1 hour,

3) in this starter equal volume of sweet must was added and left at temperature of 25-30 °C stirring every 45 minutes. The yeast starter was appended triply: in 1st day of fermentation, after 2 days of fermentation and after one week in order to acclimatization and accumulation of yeast biomass. Also to reducing the fermentation time and increasing the rate of process simultaneously complete fermentation activator and yeast nutrient Maxaferm (DSM Food Specialties B.V, The Netherlands) with concentration of 2 g/dal and Booster Blanc (Lallemand, Canada) with concentration of 3 g/dal were added to both musts after 2 days of beginning of fermentation. The aforementioned nutrients were diluted in water 1:10 and supplemented one time.

Chemical methods. Chemical analysis was conducted according to prevailing laws in winemaking of Ukraine and international documentation regard to icewine production. The sugar content of must was measured by Digital Hand-Held "Pocket" Refractometer PAL1 (Atago CO., LTD, Japan) and then converted from Brix into g/l using Table giving the sugar content of musts and concentrated musts in grammes per liter recommended by OIV [12]. The pH was determined by pH- meter S220 (Mettler-Toledo International Inc., Switzerland). The concentration of titrated acid (TA) was determined in accordance with first method of GOST 14252-73. Concentrations of volatile acids (VA) were identified by analytical equipment Apparatus for the extraction of volatile acidity by direct distillation 116300 (Dujardin-Salleron Laboratory, France).

Determination of volatiles in the wines was carried out using of Gas chromatography Agilent Technology 7890A (Agilent Technologies, Inc., USA). The main characteristics of chromatograph utilized in ascertainment of volatiles are following Silica capillary column VF-WAXms 60 m, the carrier gas was helium at rate of 3 ml/min, column diameter – 0,33 mm, the temperature of the evaporator and the detector pointed 245 °C, the temperature of thermostat was from 450 to 245 °C with rate of 40 / min, sample volume – 1 mcl. The concentration was calculated according to the method of absolute calibration. A pentanol—standard solution (internal standard - 5 mg/l and 1 ml of methylene chloride) were added to 10 ml of wine base. After stirring for 2 hours on a magnetic stirrer methylene chloride layer was separated, which had been evaporated by pure nitrogen gas flow to a volume of 50 microliters. The extract was analyzed by a chromatograph mass spectrometry detector. The components were identified by comparing the mass spectra of the substances identified in the chromatogram and of the standard library of mass spectra. The concentration was calculated according to the ratio of the peak areas pentanol (5 mg / l) and the identified peaks of volatile substances without correction factors.

All methods of determination of wine and must compositions were conducted in producing laboratory of winery «Shabo» in triplicate. Data about amount of precipitation was obtained from meteocenter of territory where Shabo is located.

Sensory assessment. Analysis of organoleptic attributes of dessert wines were done in laboratory of sensory analysis of Odesa national academy of food technologies (ONAFT), Odesa, Ukraine by a panel of 10 judges who had trained according to ISO 8586-2 [13]. The most applicable descriptive terms had been selected during tasting to create own aromatic profile of dessert wines.

Statistical analysis. In order to determine differences in sensory and chemical attributes of obtained wines XLSTAT (Addinsoft; Paris, France) statistical software was performed. The diversity between chemical variables of grape musts and wines Factor analysis was utilized (Table 1, Table 2). LSD test showed the influence of temperatures on sugar contents of Marselan grapes frozen by refrigerator ($p \leq 0,05$) (Table 3). ANOVA (Assessor/Descriptors) was carried to calculate which descriptors had had the biggest influence on sensory parameters using grade scale with anchors at 0 to 7. Anchors for

parameters of length of aftertaste and color were labeled as low intensive and high intensive, for other attributes grades were characterized as low or high starting from 0. Using Descriptive analysis mean scores of descriptors defined by each judges were determined (Figure 2). Means and its standard deviations of volatiles of 2 dessert wines were calculated (Table 4). All Figure s were created using Excel software (Microsoft Office, USA).

Results and discussion

1. Natural and alternative freezing of Marselan grapes

Marselan originated from south of France and favored in hot climate withstood frequent precipitation especially during October in Northern Black Sea coast, Odesa region that also is important to produce rare wine without loses of grapes caused by high water status in ground before first frosts (**Figure 1**).

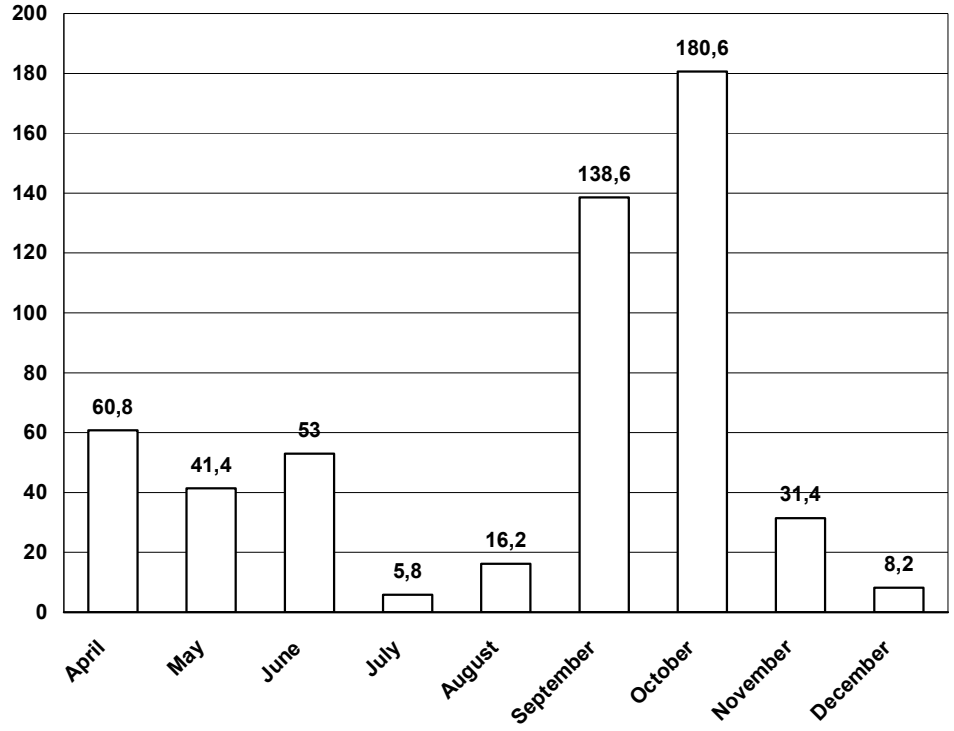

Figure 1. Precipitation from April to December of 2016 in Shabo, mm

The value of water for technological characteristics of grapes is essential: the more precipitation in the period of active vegetation of the plant, especially the berries growth, the higher the acid content in the grapes and aromatic substances [14].

In sequential decrease in temperature (-6 °C, -8 °C, -10 °C) for Marselan grapes harvested at the technological maturity in wine season 2016 have been frozen using the refrigerator working around the clock for seven days. The influence of different level of temperatures on sugar content of cultivar is represented in Table 3. Due to the the structure of thick peel variety achieved proper level of sugar needed for the production of dessert wines such as Icewine only under the lowest temperature -10 °C in refrigerator compared to natural freezing, when temperature was -7 °C.

Table 1

Pearson correlation matrix for Marselan musts made by natural and alternative freezing

Variables	Sugar content	TA	pH
Sugar content	**1**	**0,984**	-0,987
TA	**0,984**	**1**	-0,957
pH	-0,987	-0,957	**1**

Data based on 6 samples. Values in bold are different from 0 with a significance level alpha=0,05

Table 2

Pearson correlation matrix for wines produced by 2 different treatments

Variables	Sugar content	TA	pH	Ethanol	VA
Sugar content	**1**	**0,784**	0,000	0,983	**0,869**
TA	**0,784**	**1**	-0,032	**0,720**	**0,899**
pH	0,000	-0,032	**1**	-0,101	-0,348
Ethanol	**0,983**	**0,720**	-0,101	**1**	**0,861**
VA	**0,869**	**0,899**	-0,348	**0,861**	**1**

Data based on 6 samples. Values in bold are different from 0 with a significance level alpha=0,05

Regardless of freezing treatment both wine sample had the same correlations between variables – parameters (Table 2). Volatile acidity had positive association with sugar content due to activity of hyperosmotic stress of yeasts that had contributed to increasing of acetic acid. Also the higher sugariness the biggest concentration of ethanol was produced likely for reason of fermentation conversion into alcohol. The positive correlation between titraTable acidity and sugar content can be explained by freezing that concenters all substances of grapes passing into wine (Table 1, Table 2). Level of pH was independent from sugar content and negatively correlated with other attributes.

Table 3

Temperature, °C	(1) 318,23	(2) 306,90	(3) 287,33
-10		0,018164	0,000121
-8	0,018164		0,001436
-6	0,000121	0,001436	

The data of LSD test showed significant differences between the samples of grapes emphasizing the effect of temperature on the sugar content of berries (Table 3). The largest difference of sugar content was observed in grapes at -6°C sequential triple freezing, which is associated with activation of biochemical processes, due to a sharp decrease of temperature.

2. Sensory evaluation

According to descriptive analysis (Figure 2) wine produced by natural freezing is characterized by fruits notes including perceived nuances of pear, plum and apricots. The character of tropical fruits such as figs, banana of dessert wine made by alternative method was higher compared to first sample. The citrus aromas were more notable in wine grapes for which had been frozen in refrigerator but nutty tones were higher in experimental icewine. The lowest taste of spicy and caramel and approximately the same honey tins were presented in both wines. Length of aftertaste of wine obtained from naturally frozen Marselan was more intensive and deeply colored, than another sample.

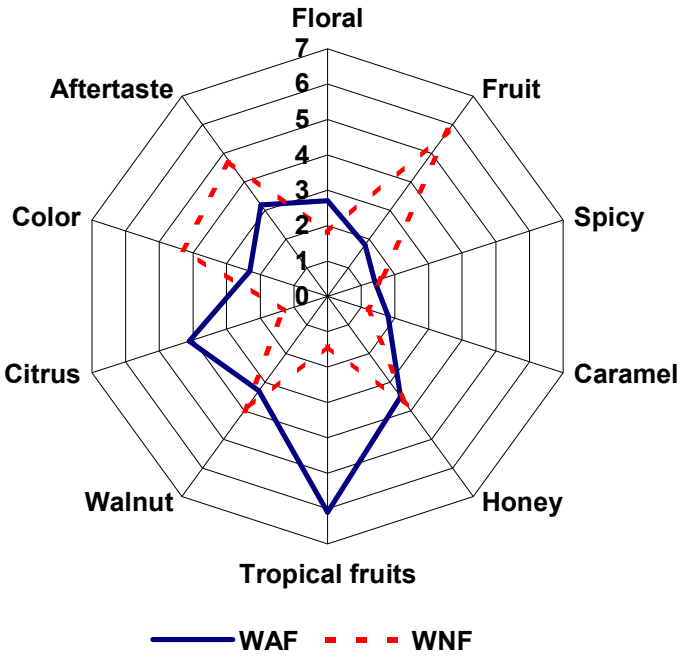

Figure 2. Biplot of sensory descriptors of dessert wines

Results of ANOVA shown that scores determined by each judges were different and distinguished significantly (F=18,883, p=0,051). The abovementioned descriptors were chosen by consensus. Each assessor proposed aroma characteristics according to own perception. Thus, terminology was ascertained for conducting of tasting. In general, the scores of all descriptors were not differed significantly estimated by judges. The most variation was presented in evaluation of intensity of caramel, walnut and citrus. The whole compliance was reached in determining of aromas of fruits, spicy and color.

3. Volatile compositions

In wine made by natural freezing (NF) 35 compounds were detected and 37 ones were found in wine of alternative freezing (AF). Means of volatiles and its standard deviations are represented in Table 4. Chemical standards, quantitative and qualitative ions for icewine and dessert wine from Marselan variety are shown in Table 5.

Table 4

Means and standard deviations of volatiles of 2 dessert wines

№	Volatiles	Wine of NF	Wine of AF
1	Phenylethyl Alcohol	74,85 ± 0,502	55,13 ± 0,0125
2	3-methyl- 1-Butanol	63,93 ± 0,562	53,60 ± 0,687
3	2-methyl-1-Propanol (isobutanol)	9,51 ± 0,044	7,52 ± 0,045
4	1-Propanol	8,37 ± 0,468	6,10 ± 0,358
5	2,3-Butanediol	5,17 ± 0,003	11,17 ± 0,001
6	3-ethoxy-1-Propanol	1,64 ± 0,302	0,46 ± 0,301
7	1-Butanol	0,63 ± 0,044	0,65 ± 0,047
8	3-methyl-1-Pentanol	0,22 ± 0,019	0,23 ± 0,017
9	3-(methylthio)-1-Propanol	0,21 ± 0,050	0,23 ± 0,058
10	1-Octen-3-ol	0,11 ± 0,004	
11	1-Hexanol	0,78 ± 0,273	0,63 ± 0,217
12	Cis-3-Hexen-1-ol	0,06 ± 0,001	
13	3-methyl-1-Butanol, (Isoamile acetato)	31,50 ± 2,109	32,72 ± 0,128
14	Ethyl Hexanoate	8,31 ± 1,639	9,25 ± 1,247
15	Ethyl butyrate	4,33 ± 0,804	3,87 ± 0,812
16	Ethyl hydrogen succinate (monoethyl ester)	3,02 ± 1,670	2,06 ± 1,238
17	Ethyl octanoate	4,44 ± 0,358	8,26 ± 1,647
18	2-Phenethyl acetate	2,28 ± 0,424	6,04 ± 0,547
19	Diethyl succinate	1,70 ± 0,071	0,71 ± 0,078
20	Ethyl decanoate	1,35 ± 0,164	3,45 ± 0,161
21	Ethyl lactate	0,95 ± 0,090	0,89 ± 0,07
22	Ethyl 3-hydroxybutyrate	0,27 ± 0,038	0,25 ± 0,09
23	3-Ethoxypropyl acetate	0,23 ± 0,036	0,10 ± 0,031
24	Hexyl acetate	0,19 ± 0,005	0,35 ± 0,001
25	1,3-propanedioldiacetate	0,19 ± 0,004	0,19 ± 0,005
26	Benzaldehyde	0,58 ± 0,014	
27	Benzeneacetaldehyde	0,43 ± 0,007	0,24 ± 0,007
28	Acetoin	0,15 ± 0,023	1,93 ± 0,067
29	N-(3-Methylbutyl) acetamide	0,11 ± 0,002	
30	Octanoic acid	17,44 ± 0,131	37,51 ± 0,147
31	Neodecanoic acid	8,18 ± 0,076	12,14 ± 0,029
32	Hexanoic acid	6,69 ± 0,432	10,94 ± 0,427
33	Acetic acid	5,22 ± 0,124	7,15 ± 0,143
34	n-Decanoic acid	4,80 ± 0,127	18,88 ± 0,125
35	Butanoic acid	0,32 ± 0,007	0,31 ± 0,09
36	3-methyl valeric acid		0,57 ± 0,001
37	2-Methoxy-4-vinylphenol		0,18 ± 0,001
38	Linalol		0,53 ± 0,125
39	Dihydro-2-methyl-3(2H)-Thiophenone		0,55 ± 0,05
40	Ethyl 5-Oxotetrahydrofuran-2-carboxylate		0,14 ± 0,078
41	Ethyl 4-hydroxy-3-methoxybenzoate		0,35 ± 0,097

Table 5

Chemical standards, quantitative and qualitative ions for Marselan icewine and dessert wine

Cas number	Compounds	Quanti-fication ions (m/z)	Qualitative ions (m/z)	Odor characteristics
60-12-8	Phenylethyl Alcohol	91	65, 51	Burnt, rose, oily
3391-86-4	1-Octen-3-ol	57	72,82	Mushroom
928-96-1	3-Hexen-1-ol	67	41,82	Green grass, resin
123-51-3	3-methyl- 1-Butanol (izoamyl alcohol)	55	70,42	Malt, rancid, pungent
78-83-1	2-methyl-1-Propanol	43	41,31	Fruity, floral
71-23-8	1-Propanol	31	59,42	Sweet, ripe fruit
513-85-9	2,3-Butanediol	45	57,89	Fruity, buttery, bitter[36]
111-35-3	3-ethoxy-1-Propanol	31	59,45	Not found
111-27-3	1-Hexanol	56	43,55	Leaf, grassy, resin, medicinal
71-36-3	1-Butanol	56	31,41	Medicinal, phenolic
589-35-5	3-methyl-1-Pentanol	56	69,41	vinous, herbaceous, cacao
505-10-2	3-(methylthio)-1-Propanol (Methionol)	106	41,53	VegeTable , boiled potato, and soup-like[36]
565-67-3	2-methyl-3-Pentanol	59	59,74	Fuel
626-89-1	4-methyl-1-Pentanol	56	69,41	Almond, toasted, nutty
98-55-5	alpha-Terpineol	59	75,63	Lilac, Citrus, Lime, sweet
100-51-6	Benzyl alcohol	79	85,93	Floral, fruity
123-92-2	3-methyl-1-Butanol, (Isoamile acetato)	43	55,70	Banana
123-66-0	Ethyl Hexanoate	88	99,43	Fruity, green, apple, banana
105-54-4	Ethyl butyrate	71	43,88	Apple
1070-34-4	Ethyl hydrogen succinate (monoethyl ester)	101	85,94	Herbaceous
106-32-1	Ethyl octanoate	88	101,127	Fruity, banana, pineapple, peach, sweet
103-45-7	2-Phenethyl acetate	104	42,47	ripe fruit, floral
110-38-3	Ethyl decanoate	88		Sweet, grass

Table 5 (continue)
Chemical standards, quantitative and qualitative ions for Marselan icewine and dessert wine

Cas number	Compounds	Quanti-fication ions (m/z)	Qualitative ions (m/z)	Odor characteristics
97-64-3	Ethyl lactate	45	29,75	Acid, medicine
5405-41-4	Ethyl 3-hydroxybutyrate	43	36,49	Apple
94825-54-4	3-Ethoxypropyl acetate	43	85,63	Sweet
142-62-1	Hexyl acetate	43	56,61	Fruity, apple, pear
628-66-0	1,3-propanedioldiacetate	43	44,87	Potato
1126-51-8	Ethyl 5-Oxotetrahydrofuran-2-carboxylate	85	51,39	Not found
617-05-0	Ethyl 4-hydroxy-3-methoxybenzoate	151	114,79	Not found
100-52-7	Benzaldehyde	106	111,56	bitter almond
122-78-1	Benzene acetaldehyde	91	58,74	Almond
513-86-0	Acetoin	45	75,98	Butter flavor
13434-12-3	N-(3-Methylbutyl) acetamide	30	44,68	Vinegar
124-07-2	Octanoic acid	60	78,81	Grass, rancid
26896-20-8	Neodecanoic acid	87	56,39	Strong odor
142-62-1	Hexanoic acid	60	45,68	Cheese
64-19-7	Acetic acid	43	69,81	Strong odor, Vinegar
334-48-5	n-Decanoic acid	73	78,63	fatty, unpleasant
107-92-6	Butanoic acid	60	71,54	Cheese, rancid
105-43-1	3-methyl valeric acid	60	55,46	Unpleasant, sour
7786-61-0	2-Methoxy-4-vinylphenol	150	54,97	Spicy clove
78-70-6	Linalol	71	101,46	Flowery
13679-85-1	Dihydro-2-methyl-3(2H)-Thiophenone	60	112,84	Balsamic

Concentrations of alcohols in both wines were the highest among aroma volatiles counting more than 60% and 40% in wines of NF and AF respectively. Concentration of Phenylethyl Alcohol in dessert wine obtained by NF of Marselan was higher than in another wine. Such tendency can explain that current alcohol rises with the degree of ripeness of grapes. According to information[15] Phenylethyl Alcohol has the high concentrations in dessert special wines that is agree with current findings and it is more abundant in white wines from Riesling, Chardonnay, Pinot blanc and Gewürztraminer [16].

Alcohol with mushroom odor 1-Octen-3-ol was found only in late-harvest wine which is in agreement with several studies [17], [18], [19]reporting occurrence of alcohol in wines made from overripe grapes and possible rotten by fungal infections. Aforementioned statements coincide with that Marselan grapes used for freezing in refrigerator were clean and health.

C_6 compounds are partly responsible for the green and herbaceous aroma of grapes and wines [20]. High water status in ground, especially during the later stages of ripening have negative effects on wine aroma. Too much water contributes to more vegetal in wine, bell pepper and grassy character [21]. The rainfall during experiment period from late October until December was high, above 200 mm in total, thus affecting the herbaceous character in Marselan wine made by natural freezing. It should be pointed out that the later harvest date (hanging time of berries on vine) also impacted on the highest concentrations in wines of 1-hexanol and Cis-3-Hexen-1-ol [22] [23]. Also the addition of antioxidation agents to the must affects the content of these compounds [24].

Isoamyl alcohol, 1-propanol and Isobutanol had highest concentrations in wine obtained by natural way due to spontaneous alcoholic fermentation of grape must conducted by action of different yeast genera and species [25] that probably were on Marselan grapes before harvest. Also the important factor of forming of higher alcohols as well as N-(3-Methylbutyl) acetamide is adding yeast nutrients including amino acids and ammonium used for must fermentation for both samples. Although, acetomide was not observed in wine produced from frozen grapes synthetically. The effect of the ammonium addition can be explained by the increased capacity of the yeast to transform the synthesized a-ketoacids, avoiding their accumulation and later expulsion to the medium after their reduction to higher alcohols [26], [27], [28]. Concentrations of 3-ethoxy-1-Propanol in natural sweet wine was denominated much. This fact accounts for actions of yeast during fermentation. Concentrations of 1-Butanol and 3-methyl-1-Pentanol had been noted distinction in both wine samples. The higher alcohols significantly influence on aromatic of wines possessing pungent and fusel odor, but the most significant aspect of them is their function in the formation of esters [29]. Such substances as 2-methyl-3-Pentanol, 4-methyl-1-Pentanol and alpha-Terpineol were identified only in icewine made by alternative method. An alpha-Terpineol is derived from linalool itself and therefore implying its sensorial character [30].

The ethyl 5-Oxotetrahydrofuran-2-carboxylate and ethyl 4-hydroxy-3-methoxybenzoate were detected only in wine produced by alternative way and concentrations of majority of other esters were higher compared to esters presented in natural-made icewine. With reference to data [19] decrease of acids in late-harvest grapes effect to forming of esters. As expected concentration of 3-methyl-1-Butanol, (Isoamile acetato) was the highest among all esters in wines that plays important role in aroma background in wines [31]. Ethyl hexanoate, ethyl lactate and ethyl butyrate are responsible for the full-bodied fruity and floral aroma of wine [32]. Tendency to a limited increase of isoamyl and 2-phenethyl acetate was found in dessert wine obtained naturally and previously had been observed in botrytized wines due to the esterase activity of B. cinerea, which probably persisted in the juice [33].

The fatty acids, formed enzymatically during fermentation, constitute an important group of aroma compounds that can contribute with fruity, cheese, fatty, and rancid notes to the wine's sensory properties [34]. Volatile acids such as hexanoic, octanoic and decanoic acids existed in our study were also found in sweet wines from Muskat and Malvasia grapes [35].

In wines made by NF and AF phenylethyl alcohol, 3-methyl- 1-Butanol, 3-methyl-1-Butanol, (Isoamile acetato) and octanoic acid had the highest concentrations among others volatiles. Also in wine produced by alternative method concentrations of n-decanoic acid, ethyl hexanoate, acetic acid, acetoin, hexyl acetate, 2-phenethyl acetate, ethyl decanoate, ethyl octanoate and 2,3-butanediol were found in biggest amount compared to natural-made icewine. The standard deviations of volatile substances of 2 dessert wines were not

significantly high with the exception of ethyl hexanoate and ethyl hydrogen succinate (monoethyl ester) in both samples. The standard deviation of 3-methyl-1-Butanol (Isoamile acetato) of classic icewine was identified as highest among alcohols.

Conclusions

Firstly, in Ukraine icewine was produced from dark-skinned variety Marselan according to agricultural climatic conditions of Northern Black Sea coast in Odesa region. The physicochemical and aromatic profiles were determined for comparative evaluation of dessert wines obtained by different methods of freezing:

1. Chemical attributes: both wine sample had the same correlations between variables – parameters including sugar content, titraTable acidity (TA), volatile acidity (VA), ethanol but pH was not associated with abovementioned properties.
2. Sensory analysis: nuances of pear, plum and apricots and longest of aftertaste were inherent for natural-made icewine from Marselan and in wine by AF tropical fruits such as figs, banana and citrus perception were identified.
3. Chromatographic analysis: both wine samples were similar to majority of volatile compounds but differ by its concentrations where alcohols and esters were determined as the main aroma indicators characterized by fruity and flowery odors.

Agricultural climatic conditions of Northern Black Sea coast allow to harvest Marselan grapes in winter without alternative freezing, which is energy-consuming in the production of elite wines.

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Influence of Seasonal Environmental Changes on The Biochemical Composition of Sea Cucumber (*Holothuria tubulosa* Gmelin, 1791) in The Dardanelles Strait

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Abstract

Introduction. There is a serious worldwide protein deficiency problem, so it is the obligation to know about edible species and their biochemical composition. Sea cucumbers have great value because of its high protein content. The study comprises monthly data on biochemical content of *H. tubulosa*.

Materials and methods. Monthly variations in biochemical composition of sea cucumbers and environmental interrelationship were investigated from April 2013 to March 2014, from three stations (Gelibolu, Umurbey and Dardanos) in Dardanelles Strait, Turkey.

Results and discussion. Temperature pattern was similar at the stations while salinity and organic matter values at Dardanos was different than others stations. Protein was maximum (52.48%) in March at Gelibolu; in May (52.81%) at Umurbey and (56.93%) at Dardanos; lipid was maximum (1.70%) in February at Gelibolu; in March (1.77%) at Umurbey and in September (1.42%) at Dardanos; ash was maximum (43.51%) in November at Gelibolu; in September (44.22%) at Umurbey and in December (44.98%) at Dardanos. Carbohydrate reserves were reduced due to being used as energy for lipid synthesis in September and also carbohydrate and lipid reserves could be used as an energy source during periods of lower available nutrition for basic metabolic function. Protein, lipid, carbohydrate, ash and moisture values varied depending on food supply and reproduction period and might have been indirectly affected by environmental conditions.

Conclusions. The study clearly showed that protein, lipid, carbohydrate and ash values varied depending on food supply and reproduction period and might have been indirectly affected by environmental conditions.

Introduction

The world's population is growing rapidly that means more people, more water and more food will be needed. Therefore, it is the obligation to know about edible species and their biochemical composition. Aegean Sea, Mediterranean Sea and Marmara Sea are home formany commercial sea cucumber species; *Holothuria tubulosa, H. sanctori, H. polii, H. mammata, Stichopus regalis* and *S. japonicus* species distributed along Turkish waters, are all exported as frozen, dried and salted, mainly Asian countries [1]. The overall trend in the export of sea cucumber is a continuous increase; total exportation amount carried out in 2014-2015 years was 154.203 kg, and it contributed 3.225.393 € to economy of the country [2, 3]. The demonstrated economic value of sea cucumber enterprises in Turkey reflects the potential value to coastal areas. However, harvests of natural stocks by commercial fisherman could lead to rapid over-exploitation of sea cucumber. The species could potentially be developed into a new viable crop for future aquaculture [4]. In the light of these information, the current trade opportunity in sea cucumber highlight need for developing aquaculture facility. Before starting an aquaculture production of any species, one of the primary factors that what is the relationship between biochemical content and environmental factors. Sea cucumber is susceptible to changes of several environmental factors, e.g., UV exposure and elevated temperature. Under the extreme stress, it will vomit intestine and easily be subjected to autolysis, consequently causing heavy economic losses [5]. Holothurians, from a nutritional point of view, is a healthy diet with high nutritional value, as it contains high protein and low lipid rate. The major edible part of sea cucumber is body wall, in which protein is the main nutrient component [5]. Proteins, lipids and minerals which are related to the physiological and nutritional value [6, 7, 8]. Proteins play an important role in most biological processes and lipids serve as energy reserves [9].

Increase of the commercial value of sea cucumber necessitated more detailed investigation and emphasized the need to develop aquaculture studies. Biochemical composition as one of the most important of all subjects varies in accordance with geographical region of the species [10]. Only a few studies on sea cucumber in Turkey [11, 12, 13, 14]. The significance of the present study is that it comprises monthly data on biochemical content of *H. tubulosa* and its relationship with environmental factor at three stations in Marmara Sea, Turkey.

Material and methods

The study was carried out between April 2013 – March 2014 at the three stations in Dardanelles Strait. The sampling stations were Gelibolu, 40.367778° N, 26.6325° E is close to the Marmara Sea (S1); Umurbey, 40.2525° N, 26.548056° E is in the central region of the Dardanelles Straits (S2); Dardanos 40.073333° N, 26.352778° E is near the Aegean Sea (S3), respectively. Sea cucumbers were monthly taken as 15–20 samples (total 240 specimens) from depths of 0-5m by divers. Sampling could not be performed in December 2013 since no individual was present at the Station 1 and 2.

Temperature and salinity of the sea water were measured from water surface with WTW Multi 3420 Model hand-held portative multiparameter device. The sediments sampled from the all stations and burned for determination of organic matter in sediment (OM) according to Buchanan [15]. Sea cucumber samples taken from the sea were placed in ice boxes and transferred to laboratory for analyses. After the removal of coelom fluid of the samples, intestinal organs and gonads were removed. Tissues were dried before

biochemical analyses, and the dry meat samples were kept in a deep-freezer for biochemical analyses. Biochemical composition analyses were performed solely in body wall tissue as dry weight.

The biochemical composition of the tissue was expressed as percentage of protein, lipid, ash, carbohydrate and moisture on the *H. tubulosa*. Moisture amount was measured with oven drying method [2] and ash determination AOAC method [16]. Protein was determined by using Kjeldahl method [17]. A conversion factor of 6.25 was used to convert nitrogen to crude protein for all varieties of sea cucumber. Total lipids of *H. tubulosa* species were extracted according to the Folch et al., [18]. The following formula was used for determining carbohydrate content:

Carbohydrate (%) = 100-[lipid (%) + protein (%) + ash (%)].

At the end of the study, all percentage of the data was transformed by arc-sin transformation [19] prior to the ANOVA and reversed afterwards. The variations were analysed using the one-way ANOVA followed by Tukey tests for mean comparison. Correlation matrix was used to determine the relationships between the environmental factors and biochemical parameters at the significance levels. Statistical analyses were carried out using Microsoft Excel and the software program MINITAB 13A (Minitab Inc., State College, PA, USA).

Results and discussion

Figure 1 displays monthly temperature, salinity and OM at three stations while the maximum, minimum and mean temperature, salinity and OM were shown Table 1.

Table 1

Maximum, minimum and mean temperature, salinity and OM values at S1, S2 and S3

		Temperature, °C	Salinity, ‰	OM, %
S1	Min.	8.70 (January)	22.4 (June and July)	1.84 (March)
	Max.	25.10 (June)	26.40 (February)	8.81 (April)
	Mean	17.63±1.85	24.10±0.43	3.62±0.74
S2	Min.	9.40 (January)	22.7 (June and July)	2.16 (February)
	Max.	25.10 (August)	27.20 (December)	6.96 (June)
	Mean	17.73±1.76	24.68±0.51	4.31±0.51
S3	Min.	10.40 (January)	26.10 (September)	2.88 (May)
	Max.	24.00 (September)	32.30 (November)	9.79 (August)
	Mean	17.92±1.38	30.33±0.49	6.24±0.67

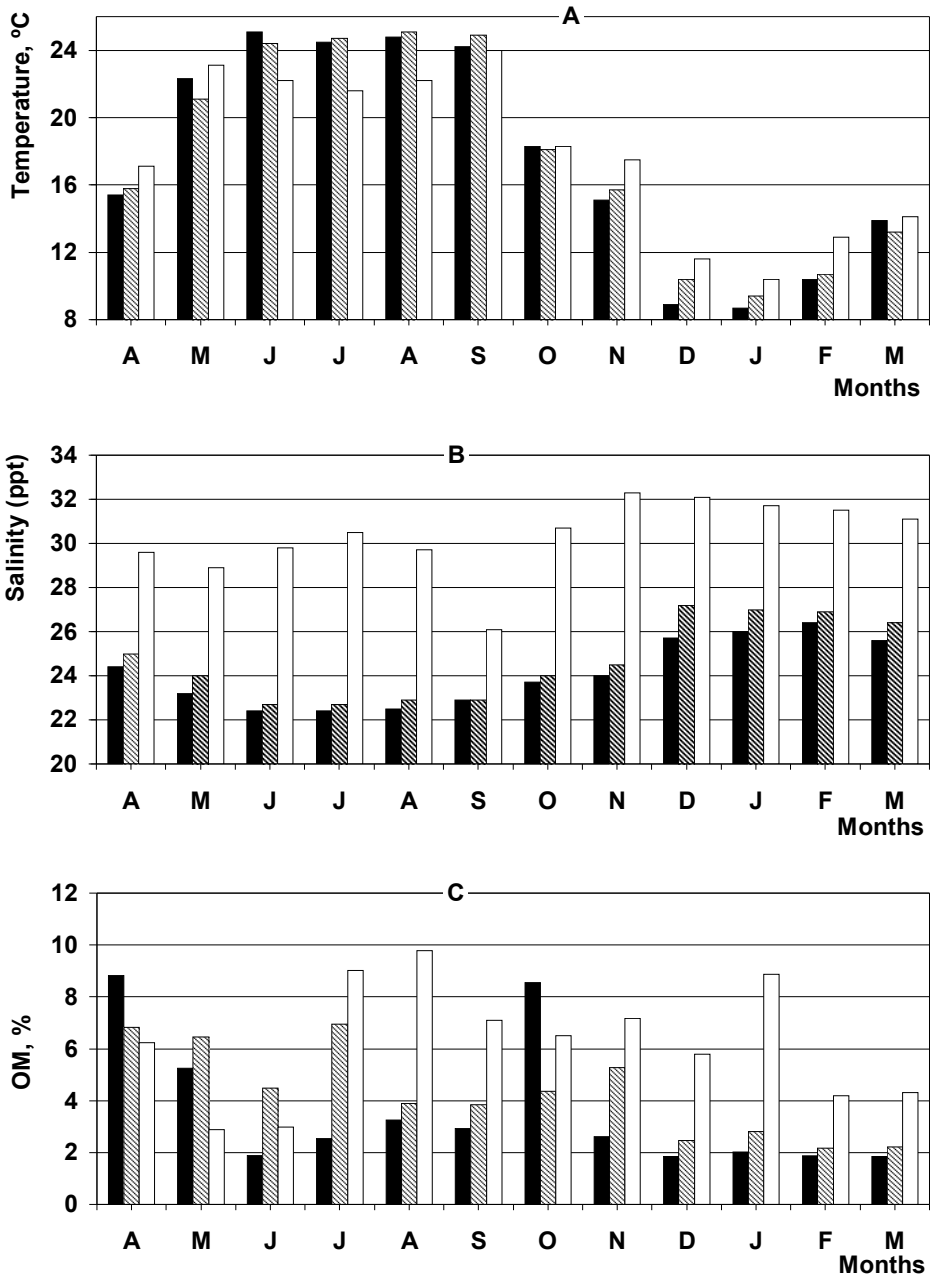

Figure 1. Monthly distribution of mean temperature (A), salinity (B), organic matter in sediment (OM) (C):
■ S1 ▨ S2 □ S3

Monthly percentages of protein, lipid, carbohydrate, moisture and ash content for all stations are presented in Figure 2 while the maximum, minimum and mean values are shown Table 2 at three stations.

Table 2

Maximum, minimum and mean protein, lipid, carbohydrate, moisture and ash values at S1, S2 and S3

		Protein (%)	Lipid (%)	Carbohydrate (%)	Moisture (%)	Ash (%)
S1	Min.	30.38±1.41 (November)	0.57±0.13 (May)	8.37 (July)	82.24±3.92 (March)	36.40±1.02 (February)
	Max.	52.48±1.60 (February)	1.70±0.45 (February)	27.19 (August)	88.93±0.19 (September)	43.51±0.42 (November)
	Mean	42.35±2.17	1.07±0.10	16.53±2.05	85.55±0.61	40.05±0.63
S2	Min.	30.26±0.23 (November)	0.50±0.04 (July)	6.79 (May)	84.04±0.58 (January)	31.75±0.77 (February)
	Max.	52.81±0.80 (May)	1.77±0.42 (March)	28.48 (November)	85.81±0.22 (November)	44.22±0.80 (September)
	Mean	44.86±2.38	0.97±0.09	15.42±2.17	85.04±0.17	38.75±1.26
S3	Min.	31.70±0.38 (November)	0.76±0.08 (April)	4.2 (May)	83.98±0.08 (January)	32.06±0.96 (October)
	Max.	56.93±2.89 (May)	1.42±0.12 (September)	31.65 (October)	88.09±0.29 (August)	44.98±0.73 (December)
	Mean	45.60±2.28	1.02±0.07	15.19±2.33	86.09±0.37	38.19±1.22

The correlation analyses were made for all station. The results showed that salinity was negatively correlated with ash ($r=-0.612$, $p\leq0.05$) for S1. In addition, salinity was negatively correlated ash ($r=-0.727$, $p\leq0.01$) and OM ($r=-0.621$, $p<0.05$) and also temperature was positively correlated with ash ($r=0.690$, $p\leq0.01$) for S2. Temperature was negatively correlated with moisture ($r=-0.654$, $p<0.021$) for S3. It was found that seasonal pattern in environmental factors and biochemical parameters. All parameters at three stations showed insignificant difference ($p>0.05$) except OM and salinity in Dardanos was significantly difference ($p<0.01$).

Environmental variables affect the feeding biology and reproduction and therefore biochemical variation of marine organisms. Several researchers determined the biochemical values of sea cucumber in different seas of Turkey and of the world (Table 3).

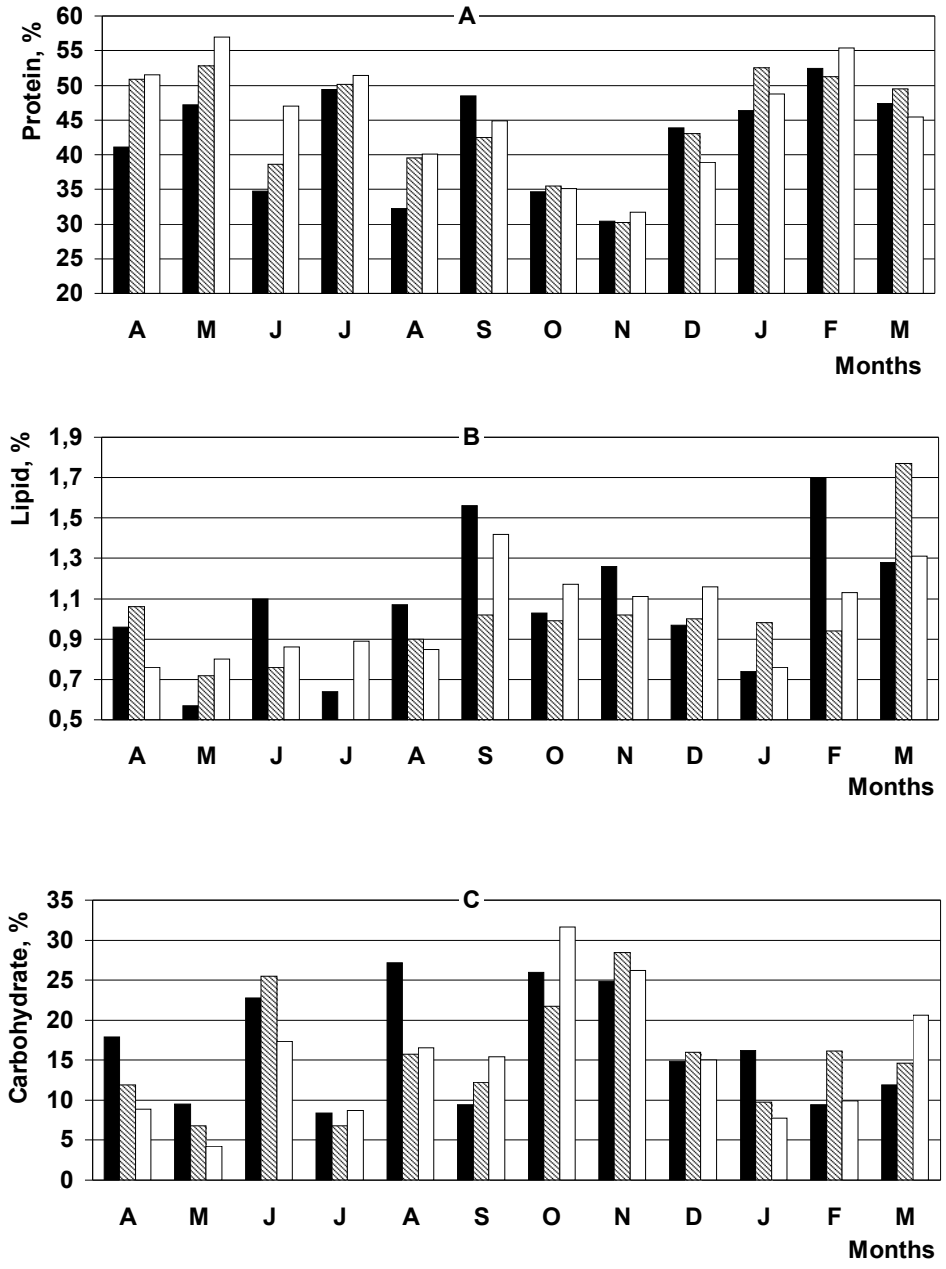

Figure 2. Monthly variation in mean moisture and protein (A), lipid (B), carbohydrate (C), moisture (D) and ash (E):

■ S1 ▨ S2 □ S3

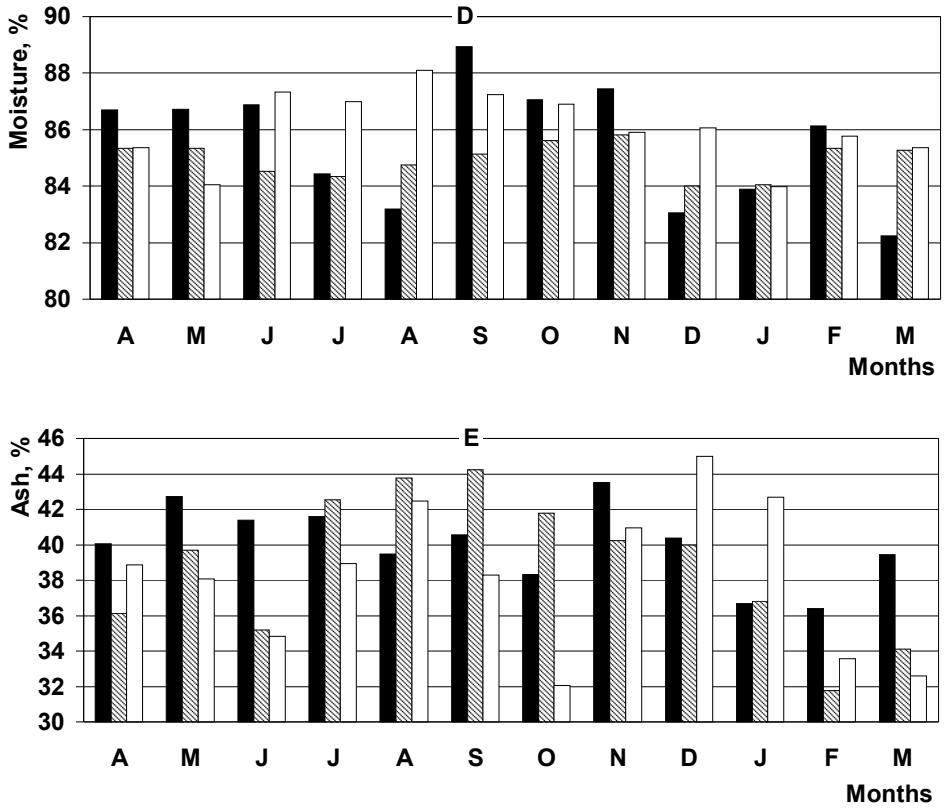

Figure 2 (the continue). Monthly variation in mean moisture and protein (A), lipid (B), carbohydrate (C), moisture (D) and ash (E) :

■ S1 ▨ S2 □ S3

Table 3

Biochemical composition of sea cucumbers sampled in Turkish waters and in other regions

Species	Moisture	Protein	Lipid	Ash
H. tubulosa [12]	86.74±0.74	8.18±0.04	0.16±0.07	--
H. tubulosa [11]	84.30±0.2	8.82±0.3	0.18±0.05	5.13±0.6
H. tubulosa [4]	--	44.58±1.01	0.71±0.12	46.43±0.51
H. polii [29]	--	36.99±0.62	0.55±0.12	48.22±1.09
H. parva [10]	67.92±3.81	17.61±0.95	2.43±0.53	32.74±1.17
H. arenicola [10]	69.49±3.09	24.37±1.93	2.88±0.47	10.86±0.40
H. sacbra [28]	87.03	9.94	0.54	1.86
C. frondosa [36]	87.4±0.30	8.34±0.50	0.50±0.06	2.97±0.09
H. fuscogilva [35]	11.6 ± 0.28	57.8 ± 0.41	0.3 ± 0.01	26.4 ± 0.31
H. fuscopunctata [35]	7.0 ± 0.14	50.1 ± 0.38	0.3 ± 0.01	39.6 ± 0.24
P. californicus [26]	4.03±0.19	47.03±0.53	8.19±0.27	25.73±0.25

In the present study, temperature pattern was similar between stations, salinity and OM values at Dardanos was different than other stations. The higher salinity values at S3 station were caused by the Mediterranean-derived salty water that enters the strait from Aegean Sea as an undercurrent and the influence of surface seawater of Marmara Sea [20, 21]. In addition, the highest mean OM value was observed at Dardanos ($p<0.05$) which was affected by accumulation of organic substance depending on excessive different pollution sources (such as industry and agriculture), human being activity, and heavy ship traffic [22, 23]. In the present study, biochemical pattern was not significantly different among stations ($p\geq0.05$) and generally affected by temperature, feeding rate and reproduction. Ash negatively correlated to salinity at S1 and S2. The reason of this result might be explained that salinity fluctuation was interrelated with seasonal temperature that temperature affects many biological functions of individuals (survival, feeding rate, hibernation, aestivation, gonadal development, ext.) and biological cycle of the sea (phytoplankton availability, organic matter in sediment, detritus ext.) [23, 24, 25]. Our study demonstrated the relationship among biochemical pattern and feeding rate of *H. tubulosa* and environmental factors. The chemical composition varied seasonally and was influenced by gonadal development. Many authors reported same results that nutritional value of sea cucumber can vary depending on the feeding behavior and seasonal variations [8, 11]. The present experiment described parallel results with various workers that ash value was high due to calcareous spicule structure embedded in muscle tissue of the living. Skeletal spicules used in species determination of *H. tubulosa* are present as distributed in muscle tissue of the living [26, 27, 28, 29]. In addition, ash content of organism is influenced by feeding and depends to the food components, strongly on the origin of the inorganic matter [30, 31]. The feeding rate might be reduced when temperature decreases below 12 °C in all station and have caused the drop of metabolic rate. The drop of metabolic rate can be attributed to a drop of the feeding at hibernation time in *H. tubulosa* which might be entered the prophase of hibernation. Many authors declared similar results for holothurians that metabolic rate is directly affected by feeding during hibernation [13, 32, 33]. However, the data showed that ash pattern of *H. tubulosa* at S3 was different from S1 and S2 because of high organic matter content. This may be reason that the predominant bottom structure consists of fine sand and mud that particle size fractions smaller than 63 μm (silt-clay) at S3 [20] (data is from same project but at different viewpoints).

Dereli et al. [34] found that gonadal development of *H. tubulosa* started in May, picked in July and spawn occurred in August in Dardanelles Strait. Carbohydrate started to increase with temperature increment that could be explained by starting feeding activity in March and continued to rise independently of gonad formation until September. This result displayed that glycogen reserves were not used during gametogenic processes. Carbohydrate was negatively correlated with protein in all stations ($p<0.01$). Celik et al. [9] found parallel results. Protein reserves started to decrease from May and varied until November when minimum value was obtained. This fluctuation might occur by variation of food availability and reproduction activity. In general, lipid value was minimum in July when was signed spawning time for *H. tubulosa* by Dereli et al. [34]. Carbohydrate reserves were reduced due to being used as energy for lipid synthesis in September. Carbohydrate and lipid value were generally low (inversely protein content in winter months) [9].

It could be reason that carbohydrate and lipid reserves could be used as an energy source during periods of lower available nutrition for basic metabolic function. This study generally demonstrated that protein, lipid, carbohydrate, ash and moisture values varied depending on food supply and reproduction period and might have been indirectly affected by environmental conditions.

Conclusion

The biochemical content of *H. tubulosa* was mainly affected by food and gonadal development. Protein is the major energy source used for gonad formation while their carbohydrate energy reserves could be affected by this metabolic energy requirement at all stations. These results indicate that protein and carbohydrate reserves were not used for the same purpose.

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Restoring and emulsifying properties of the dried meat semi-finished product

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Abstract

Introduction. The technological properties of the dried meat semi-finished product (SFP) made by the DMSF-drying (mixed heat supply) method are studied, on the basis of which the mathematical dependence of the complex characteristic of the SMC on the drying temperature and the degree of product dispersion is difficult.

Materials and methods. The materials of researches were: beef meat vivarene and dried by convective method, as control, and dried meat semi-finished product of high degree of readiness, obtained by the mixed heat-transfer method. Based on the results of analysis of the spectra obtained by the IR-spectroscopy method, changes in the chemical composition of the dried meat semi-finished product and after its reduction are characterized. The volume and average diameter of the pores of the dried meat semi-finished product were characterized with sorption-desorption isotherms obtained by the weight method.

Results and discussion. The researches complex of technological properties of the dried meat semi-finished product showed that using the drying method with mixed heat-water reducers promotes obtaining the product with a lower moisture content (twices) and improved its ability to restore while maintaining a high water-holding capacity (compared to the control, the water-holding capacity is more by 7,2%) and the coefficient of water absorption (more than 1,3 times). The production of dried meat semi-finished products by the method of mixed heat-reduced content of volatile aromatous substances in comparison with the control is 1.3 times higher.

The analysis of the IR absorption spectra of dried meat semi-finished product in the region of deformation vibrations of OH groups indicates that drying with mixed heat and water conductivities contributes to the formation of a capillary-porous structure that allows to increase the amount of adsorption-bound water by 1,5 times, and causes high rehydration and emulsification properties finished semi-finished product. The mathematical model of formation of the complex indicator of technological properties of the dried meat semi-finished product depending on the drying temperature and the degree of grinding of the semi-finished product is obtained.

Conclusions. The formation of high technological properties of the dried meat semi-finished product is established. The obtained data make it possible to recommend the semi-finished product as an independent product for a wide range of food products.

Introduction

We know that the drying process, due to the realization of which the original properties of the materials should be kept as much as possible. Therefore, to the formation of functional and technological properties of the dried raw materials, a drying method with mixed heat and water (DMSF-drying) was used. This method, as shown in the review of the literature, is characterized by small economic and raw materials costs, and the final product is characterized by increased consumer properties compared to products obtained by other methods close to native raw materials [1–2].

For this drying method, a functional container with mass exchange gaps is used, in which the raw material is located, is dewatered. At the same time, the main heat flux to the evaporation zone of moisture flows through the heat exchange wall of the FM under conditions of a certain flow velocity of the mass exchange gap by the drying agent (steam-air mixture). The driving force of heat transfer is the process temperature gradient. Heat is dissipated in the raw material zone, where the maximum intensity of evaporation of moisture is noted.

The conditions of the DMSF -drying for the preservation of vitamins are due to the low integral temperature effect on the raw material, the short duration of the process, the isolation of the raw material from the intensive action of the drying agent and light [1–4].

The above features of the implementation of the method of drying with mixed telopehydrates have made it necessary and expedient to use it to form the functional and technological properties of animal raw materials (beef meat) and vegetable (vegetable) origin.

Thus, dried dried meat is prepared in a high degree of preparedness.

DMSF is a concentrate of biologically active compounds, natural raw materials, has a long shelf life, has a pleasant smell, flavor, increases the nutritional and biological value of the diet, can act as an independent product and additive to some food products [5].

Formulations and technology of a dry mix, which is obtained from meat, vegetables and thickener, are known. It is reconstituted in water and used in the form of minced meat for floury culinary products. This mixture is stored for 18 months. In vacuum packing [6–7]. However, there are various ways to make it using the method of convection drying.

Therefore, the aim of this research was to study the recovery and emulsifying properties of DMSF for further justification of the valuation and the method of its introduction in multicomponent food system.

Materials and methods

Materials

Materials of the research in the article were: beef boiled meat and dried by convective method, as control, and dried meat semi-finished product of high degree of readiness, obtained by the mixed heat-transfer method, as a prototype. To compare the properties and composition of powders, the IR spectroscopy method is used where the IR spectra give a chemical composition by the number and position of peaks in the reflection (or absorption) spectra, indicating the nature of the substance, that is, a qualitative analysis is carried out, and the intensity of the bands is about Amount of substance, that is, quantitative analysis.

Methods

IR absorption spectra were recorded for the grinded powdered samples, the optical element is a diamond, the angle of the incident beam θ=45°. Range 4000–400 m^{-1}, number of scans – 128, a resolution of 0.04 m. The background was recorded relative to the optical element without the sample.

The penetration depth of the infrared radiation into the sample (d_e) as a function of the radiation wavelength (λ) was calculated from the formula:

$$d_e = \frac{\lambda}{2\pi n_O \sqrt{\left[\sin^2\theta - \left(\frac{n_S}{n_O}\right)^2\right]}}$$

where n_s – refractive index by sample; n_o – by optical element [8, 9].

The removal of the vapor adsorption isotherms of dried objects was carried out by the gravimetric method in a vacuum plant with spring quartz scales Mack-Ben [10–17]. The isotherms were represented graphically:

$$a = f(P / Ps),$$

where a – value of adsorption in mm/g,

P / Ps – relative vapor pressure of adsorbent.

On the basis of experimental isotherms of adsorption-desorption were calculated specific surface of the sample S, the maximum sorption pore volume Vs average pore diameter D.

The value of the specific surface of the samples was calculated from the isotherms of vapor adsorption by the method of multi-molecular theory of adsorption of vapors of Brunauer, Emmett and Teller (BET method).

The water absorption coefficient (CV) of the samples was determined using a Dogadkin device (Figure 1) [18], which consists of a funnel 1 connected by the principle of communicating vessels with a graduated tube 2. The connecting path is an extension 3, which is a receiver for replenishing the liquid. In the lower part, the connecting tube has a branch 4 with a rubber tube and a clip 5. The tap serves to start water from the system at the end of work.

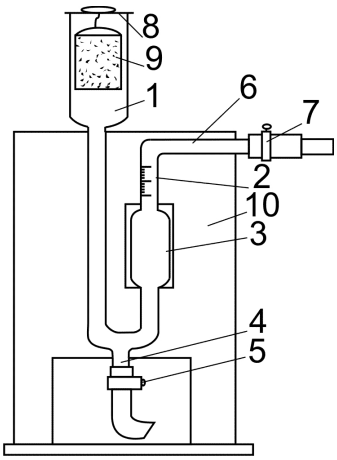

Figure 1. Installation of Dogadkin

The graduated tube has a right angled bend 6 from the rubber tube and the clamp 7. The funnel is covered with a lid 8 with a hook on which the wire mesh 9 is suspended, into which the sample of the research material is placed. If the phone is not calibrated and there is a scale on the instrument board with millimeter paper, the linear scale of the tube may not correspond to the volume amount of water in it.

In this case, the device must be pre-graduated and indicate the conversion factor on which the linear scale should be multiplied in order to obtain volumetric values.

Graduations of the device are carried out in the following way: in a device installed on a flat surface, water is poured to the bottom of the scale, burettes with water are placed

above the funnel of the instrument, from which 0,005 liters of water are added to the device and the level of water in the tubes is marked on the scale of the device in parallel.

The obtained values are recorded. Water from the burette is added until it rises to the upper division of the scale. Then, the water from the device is poured out through the tap 4 and the calibration is repeated. Of the three calibration measurements, an average value is output, which sets the scale division price and the conversion factor.

The water binding capacity (WBC) of the samples was determined by the pressing method. A crushed sample of 0,003 kg was weighed on a torsion balance on a polyethylene plate 0,015-0,020 m in diameter. The sample was transferred to a filter placed on a glass plate so that the sample was under a polyethylene mug. On top, the sample was covered with the same plate and a weight of 1 kg was placed and held for 10–60 s. After this, the filter with a sample was released from the load and the upper plate and a contour of the spot around the compressed sample was applied to the filter with a pencil. The outer contour is visible when the filter paper is drying in air.

With the aid of a planimeter, the spot area of 0,01 m^2, determined by the reconstituted sample and moisture, which was absorbed into the filter paper, was determined. The size of the wet spot was expressed as the difference between the area of the wet spot and the area of the spot formed by the sample.

It was experimentally established that 0,01 m^2 of the area contains 0.0084 kg of water. The composition of the bound moisture (in % to the sample) was determined by the formula [19].

$$X = \frac{(M - 8,4) \cdot S}{m} 100, \%$$

where X – bound moisture content, %;

M – moisture content in the sample, 10^{-3} kg;

S – wet spot area, 0,01 m^2;

m – batch weight, 10^{-3} kg.

In the study of the water-retaining capacity (WRC) of powders, a weight method was used. To do this, a sample of the powder was added to the centrifuge tube and water was added in a ratio of 1:20. The mixture was stirred and allowed to swell at 313 °K (40 °C) for $2 \cdot 60^2$ s. After that, centrifugation was performed for $15 \cdot 60$ s at a speed of 5000 s^{-1}. The formed liquid over the precipitate was drained, having previously determined the content of solids by means of a refractometer. The mass of the wet residue remaining determined by weighing the WRC was determined by the formula:

$$B = \frac{M_в}{M_н \times (100 - \alpha)} \times 100 , \%$$

where B – WRC of product, %;

$M_в$ – a wet cake after centrifugation, 10^{-3} kg;

$M_н$ – dry weight, 10^{-3} kg;

α – correction factor, taking into account the content of dry matter in the supernatant, %, determined by the formula:

$$\alpha = \frac{(в - M_в) \times p \times 100}{c \times M_н} ,$$

where $в$ – the amount of water that was taken to prepare the suspension, 10^{-3} kg;

c – mass fraction of solids in powder, %;

p – content of dry matter in the supernatant, % [20].

A 0,002 kg sample was placed in a porcelain mortar to determine the grease-resisting capacity (WRC) [21], to which 0,0025 kg (0,01 m^3) of fine calcined sand and 0,006 kg (0,043 m^3) α-monobromonaphthalene were added. The contents of the mortar were carefully triturated for 4·60 s and then filtered through a folded paper filter.

The test solution (3–4 drops) was uniformly applied with a glass rod on the lower prism of the refractometer. The prisms were closed and fastened with a screw. A ray of light was directed with a mirror on the prism of the refractometer, setting the telescope so that the intersecting threads (Aliados) were clearly visible. The aliados were moved until the boundary between the illuminated and dark parts coincided with the point of intersection of the filaments, after which the refractive index was deducted.

The WRC was determined by the formula:

$$WRC = \frac{g_1}{g_2} \cdot 100, \%$$

where g_1 – mass fraction of fat in the sample after heat treatment, %;

g_2 – mass fraction of fat in the sample for heat treatment, %.

The mass fraction of fat in the sample was determined from formula:

$$g = \frac{(10^4 \cdot \alpha \cdot (n_1 - n_2) \cdot m_1}{m}, \%$$

where α – the coefficient characterizing such a fat content in the solvent, which changes the refractive index by 0.0001%;

n_1 and n_2 – refractive indices of the respectively pure solvent and test solution;

m_1 – mass of 0,043 m^3 of α-monobromonaphthalene, 10^{-3} kg;

m – weight of the brave, 10^{-3} kg.

The emulsifying capacity (EC) of the samples was determined from the phase inversion point according to the method of Gurov O. [22]. For this, 0,01 liters of a suspension was placed in a 0,1 liter beaker, then oil was introduced with a divisible burette at a rate of (70–80)·60 drops/60 s before the moment of inversion of the phases, that is, the transition of the oil / water emulsion into the water / oil emulsion. The type of emulsion was determined by dilution method. The volume of oil that is used from the burette corresponds to the value of the phase inversion point.

Aggregative stability (AS) of the emulsion was determined by fixing the volume of oil separated after centrifugation at a rotation speed of $1500 \cdot 60^{-1}$ s^{-1} for 5·60 s. Then this tube was placed on a water bath for 3·60 s and again centrifuged for 5·60 s. The value of AS was determined as the ratio of the volume of oil remaining in the emulsion to the total volume of oil in the emulsion

$$\mathrm{AS} = \frac{V_1 - \mathrm{V}_2}{V_1} \cdot 100\%$$

where AS – aggregative stability of emulsion, %;

V_1 – volume of fat phase in emulsion, 10^{-3} l;

V_2 – volume of fat phase, separated, 10^{-3} l [20].

The content of soluble and water-soluble proteins in the DMSF was determined by conventional methods [23].

The two-factor experiment was used to construct the mathematical model for the formation of a complex indicator of the technological properties of a dried meat semi-finished product, depending on the drying temperature and the degree of refinement of the semi-finished product. At the same time, the variation of the indices was within the range of temperatures from 50 (-1) to 90 (+1) °C and particle sizes from $35 \cdot 10^{-6}$ (-1) to $55 \cdot 10^{-6}$ (+1) m [24].

Results and discussion

Drying is the optimal method of producing shelf stable products while preserving their original quality without using preservatives or additives, because today, in the foreground, is the degree of naturalness and nutritional value of food products.

For the formation of technological properties of raw meat was used drying, as shown in the literature review, it is characterized by a small economic and commodity costs, and the final product is characterized by improved consumer properties compared to products obtained in other ways, similar to the native raw materials [1-2]. For this purpose beef previously boiled steamed, crushed, minced and dried by a new method. As a control sample in the studies selected boiled meat convection drying.

While drying, the nutritional value of meat from the point of view of the content of vitamins, irreplaceable amino acids is virtually unchanged in that time, as the physicochemical properties of muscular tissue in varying degrees, can affect the quality of the dried product.

Results of the research confirm that the majority of meat proteins are water soluble (moialbumin, myoglobin, globulin – 8,5 % in meat of dried mixed method of draining drying and 5,8 % in the convective drying of meat) and salt- soluble (actin, myosin and actomyosin – 51,2 and 45,6 %, respectively) – Table 1.

Table 1

Indicators of meat quality convective and dried mixed method of draining

Exponent	Sample of the meat	
	Convective drying control	Dried mixed method of draining drying
Final moisture content, %	14,0±0,5	7,0±0,5
Fat content,%	3,3±1,0	3,3±1,2
CD, per unit value	2,7±0,2	3,4±0,1
WHC, %	46,1±0,4	53,3±0,5
Duration of the recovery in the water - 60	40±5	30±5
Content of water-soluble protein, % Br	6,8±0,3	7,5±0,5
Contents salt-soluble protein, % Br	47,6±0,5	51,2±1,5
Contents of extractives, %	1,10±0,05	1,30±0,05
Number of flavor, units	14,0±0,5	18,0±0,5

As shown from Table 1, the meat dried mixed method of draining drying and the convective drying values are 1,3 times higher than in controls, which correlates with the index of water-holding capacity samples (50,2 % and 45,1 % in the form of meat for the water temperature (48±2) °C. With and 46.1 and 53,3% in a divided state, respectively). The duration of the recovery control samples for 10 · 60 more and is 40·60 sec.

The number of flavor of meat dried mixed method of draining drying (18 units) is directly proportional with the content of extractives, which indicates the maximum preservation of aroma of boiled meat in comparison with the sample of convective drying, where the loss of volatile substances fragrant occurred to a greater extent.

The obtained data correlate with the results of studies on the use of IR spectra with the FTIR transformation using a spectrometer Nicolet Nexus 470.

In Figure 2 presents IR absorption spectra of boiled meat, meat dried mixed method of draining drying of native and restored to moisture boiled.

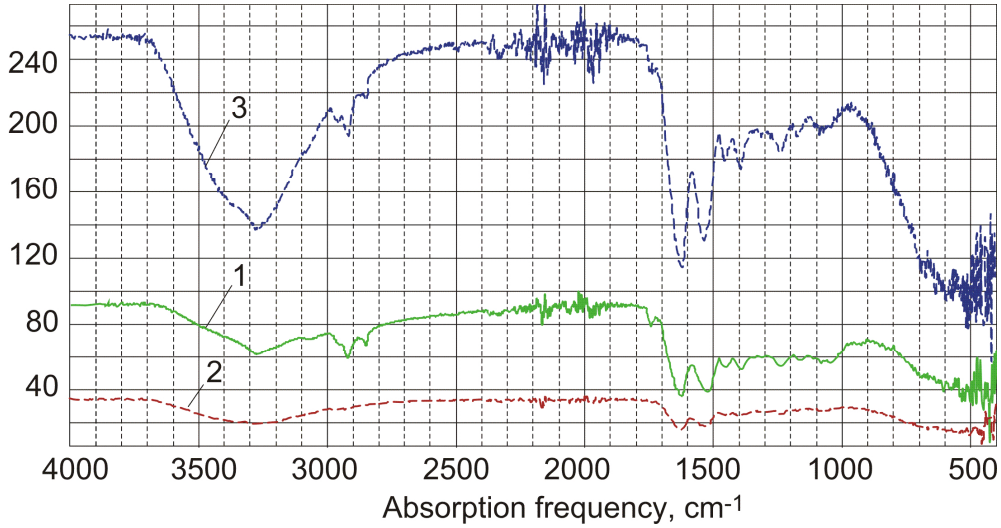

Figure 2. Infrared absorption spectra of meat:
1 – boiled the main method of control;
2 – dried mixed method of draining drying;
3 – dried mixed method of draining drying, restored to a moisture content of boiled.

IR spectra of the control (boiled meat) and test samples of meat, dried and restored in the frequency range from 3000–3600 cm^{-1}, characteristic for stretching vibrations of functional groups – OH is involved in the formation of intramolecular and intermolecular hydrogen bonding of free and bound moisture, sugars and biopolymers, etc., indicate the increasing intensity of the spectra, and, consequently, the formation of additional hydrogen bonds in the meat dried mixed method of draining drying the recovered in comparison with the control.

Shown that in the frequency range 2900–2000 cm^{-1}, characteristic for stretching vibrations of NH_2- and NH-group, boiled meat and the meat recovered is observed the same intensity of absorption spectra.

In the area of deformation vibrations -OH groups is the intensity of the absorption bands 1648,2 cm^{-1} in meat dried mixed method of draining drying the recovered 2.4 times more compared to the corresponding band in the control sample. The results indicate that dried mixed method of draining drying promotes to maximize the preservation of the original quality of the raw materials, the formation of capillary-porous structure, which allows to increase the number of bound water adsorption in 1,5 times more.

In the area of 1743 cm^{-1}, characteristic for stretching vibrations of C=O groups indicate the presence proxies , ketones and conjugated acyclic anhydrides in the product. There is an insignificant intensity of the absorption spectra of boiled beef and dried meat restored. This suggests that lipid peroxidation products do not formed during dried mixed method of draining drying.

Thus, dried mixed method of draining drying allows obtaining products with maximum preservation of nutritional and biological value in comparison with other drying methods that approximate products sublimation method.

For studies of porosity structure used a vacuum Mack-Ben – Figure 3 and Table 2.

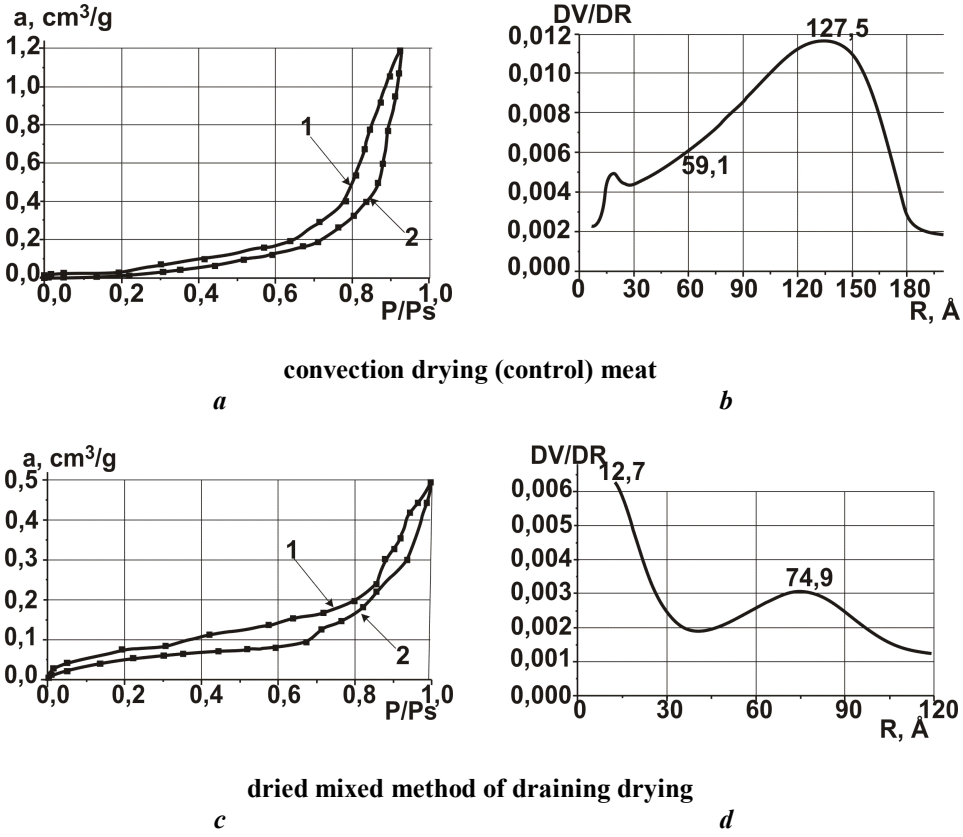

Figure 2. Adsorption isotherms of water vaporization (a, c) and the distribution of pores with radii (b, d), DMS
1 – sorption; 2 – desorption

Table 2

Structural characteristics of DMSF that were filmed in water vapor

Exponent	Value in the test samples	
	Convective drying control	Dried mixed method of draining drying
Activation energy of water, kJ/mol	0,10	0,46
Structural characteristics:		
Specific surface of the sample S, m^2/g	196	171
Standard error of calculation of the surface R^2	0,95	0,91
Sorption pore volume, Vs, cm^3/g	0,79	0,66
Pore diameter, D, 10^{-10}, m	189	154

As can be seen from Figure 3, the curve of sorption–desorption of DMSF below the curve of sorption–desorption control sample, indicating a smaller pore volume of the prototype. Moreover, the nature of the hysteresis loop in the control sample is first narrowed, and further observed its expansion, evidence of slow restoration of the structure of the sample in the liquid.

Loop is characterized by early expansion–contraction–expansion, allowing you to absorb and retain moisture to a greater degree than the control.

Structural characteristics of samples (tab. 2) show that the volume of pores in DMSF is Vs=0.66 cm^3/g, while sample convective drying indicator value equal to Vs=0.79 cm^3/g. This is also evidenced by the distribution curve of the pore radius where the curve distribution in a sample of DMSF below the curve of the sample of meat of convective drying, which indicates a greater number of pores (area under curve).

Thus, studies of capillary-porous structure of DMSF, obtained the dried mixed method of draining drying indicate a preference for the current porosity in comparison with meat convection drying.

For implementation concept of work on formation rehabilitation and emulsifying properties conducted complex researches: water absorption coefficient (WAC, units); water-holding capacity (WHC, %); emulsifying capacity (EC, %); aggregate stability (AS, %); the number of flavor (NF) depending on the drying temperature and the degree of grinding dried mixed method of draining drying raw meat.

The absolute values of the specified technological properties were converted using the scale of Harrington in relative units. With mathematical processing of the results obtained by a conceptual mathematical model of the complex index of technological properties of DMSF. The surface response of this index to the temperature Figure 4.

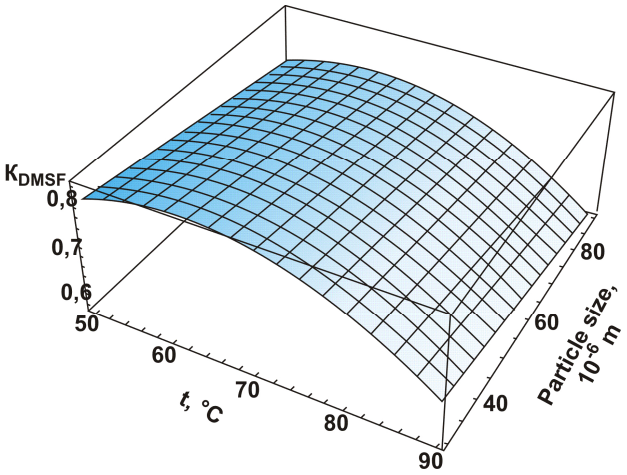

Figure 4. The surface response of a complex indicator of the technological properties of the temperature dried mixed method of draining drying and grinding degree of DMSF

A mathematical model of the formation of a complex indicator of technological properties of DMSF:

$$Y = 0{,}035626 + 0{,}0027608x_1 - 0{,}001494x_2 - 0{,}000223x_{12} - 0{,}000003x_{22} + 0{,}000002x_1x_2$$

The presented equation is adequate for DMSF at the temperature within the range of 50–90 °C and the particle dispersion is $35–85 \cdot 10^{-6}$.

Based on these data, formulated the potential of technological properties of the DMSF for use in technology of culinary products – Table 3.

Table 3

The potential of functional and technological properties DMSF for use in technology of culinary products

Technological properties	Functional properties	The range of culinary products
The minced particle size $(5–6) \cdot 10^{-3}$ m	Uniformity of mixing of dry bulk materials, water-holding ability fat-holding ability, aggregate stability	First and second courses
		Flour culinary products from meat and meat-vegetable stuffing
Powder with a particle size of $(90–200) \cdot 10^{-6}$ m		Chopped products, puddings
$(60–90) \cdot 10^{-6}$ m		Baked dishes (dumplings)
$(30–60) \cdot 10^{-6}$ m		Sauces, snacks, soufflé
Recovery	Water-binding ability	Toppings, stuffing for baked food products
The flavor of cooked meat	The number of flavor	Aromatic additive

Conclusions

1. It was shown minor changes in the chemical composition of the semi-finished product in comparison with the control sample by IR spectroscopy.
2. It was studied the porosity structure of DMSF. Proved that during the traditional convective drying there is a significant narrowing of the capillaries, due to shrinkage, while the dried product dried mixed method of draining drying has a porous structure, which causes to its high rehydration and emulsifying properties.
3. Complex research of technological properties of DMSF on which was found the mathematical dependence of the complex index depending on temperature dried mixed method of draining drying and degree of dispersion**.**

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Identification of equilibrium state of hydroxyl protons in vodkas by ^{1}H NMR spectroscopy

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Abstract

Introduction. The aim of this work is to identification of equilibrium state of hydroxyl proton of ethanol and water in vodkas, using *^{1}H NMR* spectroscopy.

Materials and methods. Aqueous-alcoholic mixtures (AAM, vodkas) was prepared by volumetric method. *NMR* spectra was obtained according to the manuals of *FT-NMR* Bruker Avance II (400 MHz) spectrometer and Bruker TopSpin. As an external standard for deuterium stabilisation and chemical shifts determination was used a deuteroacetone in special form glass capillare inserted in *NMR* tube.

Results and discussion. Experimentally determined elements thermodynamic equilibrium of hydroxyl proton of ethanol and water in vodkas, using *^{1}H NMR* spectroscopy. In this work, we identified three groups of samples with equilibrium of hydroxyl protons of water and ethanol: steady; transitional; unsteady equilibrium.

Steady equilibrium is characterized by a presence in hydroxyl group combined unitary signal of $EtOH+H_2O$. The component of protons of $EtOH+H_2O$ in each sample presented as singlet (*s*), located in a «weak field» with a chemical shift, which is in a range $\delta_{EtOH+H2O}$=4,75–4,80 ppm. Waveform of $EtOH+H_2O$ protons – is distorted Gaussian curve, with a broadened base and a slight asymmetry of apex, which is offset from the center line.

It was found that the transitional equilibrium characterized by a presence of hydroxyl groups two separate signals of *EtOH* (δ_{EtOH}=5,34 ppm) and H_2O (δ_{H2O}=4,75 ppm). The difference between the chemical shifts of hydroxyl protons of ethanol (*EtOH*) and proton of water (H_2O) in each sample is Δf_1=236 Hz. Transitional equilibrium is characterized by the presence of hydroxyl proton, which is barely noticeable, which characterizes the transition from steady equilibrium to unsteady equilibrium. This may indicate that certain prerequisites have not yet been created to establish equilibrium structure (unsteady/steady equilibrium).

Unsteady equilibrium characterized by a presence of hydroxyl groups two separate signals of ethanol (*EtOH*) (δ_{EtOH}=5,34 ppm), which is obvious and H_2O (δ_{H2O}=4,72–4,75 ppm). The difference between *EtOH* and H_2O – Δf_1=248 Hz.

Conclusion. The conducted researches set a fundamental difference of behavior of hydroxyl proton of ethanol and water in vodkas, using *^{1}H NMR* spectroscopy. Istablished criteriums of the systems equilibrium allow to improve the technological process of vodka on distillery enterprises, to stabilize quality of finished product.

Introduction

Nowadays *NMR* spectroscopy has worthily gained popularity among physical methods of research in different fields of science, i.e. medicine, biology, physics, chemistry, in agriculture and industry as well. It is difficult to overestimate the role of *NMR* in food industry, in the study of complex systems from the simplest organic molecules to the most complex molecular compounds (Oliveira I.S. et al, 2007, Minoja, Napoli, 2014; Singh, Blümich, 2016; Hore, 2017) [1–4]. The most wide-spread is *NMR* spectroscopy on nuclei of hydrogen isotope ^1H (^1H-protons). They account for 90% of all the studied *NMR* spectra (Jeffrey H. Simpson, 2008; Terence N. Mitchell, Burkhard Costisella, 2007; Siegfried Stapf, Song-I Han, 2006) [5–7].

NMR spectroscopy principle of operation is based on the usage of magnetic properties of some atomic nuclei, being able to resonate at characteristic frequencies of electromagnetic spectrum in external magnetic field and, that allows to identify nuclei in different chemical environment (Oliveira I.S. et al, 2007; Jeffrey H. Simpson, 2008; Siegfried Stapf, Song-I Han, 2006) [1, 5, 7].

Bloch F. obtained ^1H *NMR* spectra with "low-resolution" of H_2O for the first time in 1946 (Bloch et al. 1946) [8], and in 1951 Arnold J.T. for the first time obtained ^1H *NMR* spectra with "high-resolution" of ethanol C_2H_5OH (Arnold et al. 1951) [9]. Up to now, many scientists (Oliveira I.S. et al, 2007; Jeffrey H. Simpson, 2008; Bing Yan, 2004; Edwin D. Becker, 2002; Edwin D. Becker et al, 2002; Gerard J. Martin, Maryvonne L. Martin, 2002; S.A. Richards, J.C. Hollerton, 2011; Jacob Bart, 2009; Cherif Ibrahima Khalil Diop et al, 2012; Bao Qiong Li et al, 2017; N.R. Sucupira et al, 2017) [1, 5, 10, 11–18] bring ethanol *NMR* spectrums as the simplest and best understood from the analytical point of view of the substance.

At the same time *NMR* spectroscopy exhibits variations in characteristics of ethanol such as chemical shift, spin-spin interactions and the effect of chemical exchange (Oliveira I.S. et al, 2007; Edwin D. Becker, 2002; Gerard J. Martin, Maryvonne L. Martin, 2002; S.A. Richards, J.C. Hollerton, 2011) [1, 11, 13, 14] in solutions.

Vodka is a simple physico-chemical system: mixture of ethanol and water. But every brand has some observable differences on the molecular level and as to the taste perception. Studies conducted by Hu N. and others in the work (Hu et al, 2010) [19] prove that these differences are significant either on the stage of AAM making or in the final product – commercial vodka. The main differences are connected with hydrogen bonds (with their strength) that is proved by different research methods, for example by ^1H *NMR* spectroscopy, *FTIR* spectroscopy, Raman spectroscopy. The results of the ^1H *NMR* and *FTIR* spectroscopy researches show that in water there are hydrates with the structure of $EtOH*(5{,}3\pm0{,}1)H_2O$, that are observed either in AAM or in vodka. Authors (Hu et al, 2010) [19] connect hydrate proportion EtOH*(5,3±0,1)H2O and its influence on the following organoleptic indicators of vodka.

In the work by Nose A. and others (Nose et al, 2005) [20] the influence of admixtures such as salts, acids and phenols on the strengthening of hydrogen bonds in AAM and in finished products as well, in this case sake, is studied. In the work (Hu et al, 2010) [19] it is set that admixture bonds influence on molecular dynamics in the process of ethanol hydration.

In the work (Hu et al, 2010) [19] the notion "structurability" had introduced, that is "ability to structuring", a parameter that determines the ability of vodka (or in a wide sence the alcoholic products) to order molecules of water in its structure.

In the work (Hu et al, 2010) [19] great attention is given to ^1H *NMR* spectra of the *OH* proton of water and alcohol. Protons of water in all the samples was found as a narrow signal with the chemical shift on about 5 ppm. Spectra also showed that in some samples there appears the second widened peak of the *OH* signal that is on the 5,5 ppm. That low-field peak is the signal of *OH*-ethanol that separated from the conditionally high-field signals of *OH*-water.

Presence of the separate *OH*-ethanol signal in the samples (according to the opinion of the authors (Hu et al, 2010) [19]) points out weak hydrogen bonds of ethanol.

The preliminary conducted *^{1}H NMR* studies, which are described in a work (Kuzmin O. et al, 2013–2014) [21–24], relate to the study of hydroxyl protons of AAM modifications in the process of making vodkas. The obtained results give grounds to assert a fundamental difference in the behavior AAM prepared from the alcohol and water passing through various processes. During the study we have determined the systems of unsteady and steady balance depending on the transformation of hydroxyl proton's of ethanol and water. Systems with unsteady balance typical for AAM used with ethanol and drinking water, with a tasting score – 9,43 points. This also includes the AAM made from ethanol and demineralized by the reverse osmosis water, with a tasting score – 9,30 points. Systems with a steady balance that are typical for AAM made of ethanol and water softened by *Na*-cationization, with tasting score – 9,49 points were defined.

Thus, in the work (Kuzmin O. et al, 2013–2014) [21–24] was established experimental evidence of stationary nature / (non- stationary) of thermodynamic balance, taking into account the organoleptic characteristics of AAM in dependence on water treatment method and time of system's functioning. However, the questions related to internal mechanism's specification and the rate of establishment of thermodynamic balance depending on type of water used in the process of creating the AAM are remain unsolved.

The aim of this work is to identification of equilibrium state of hydroxyl proton of ethanol and water in vodkas, using *^{1}H NMR* spectroscopy.

Materials and methods

^{1}H NMR analysis of AAM was conducted with the usage of:

– *FT-NMR* Bruker Avance II spectrometer (400 MHz) equipped with 5–mm broadband inverse Z-gradient probe; thermostatic system (+25°C ... +100°C). The measurement error of the chemical shifts for *^{1}H* is ± 0,005 ppm;

– Specially shaped capillary with acetone-d_6 *$(CD_3)_2CO$* (atomic fraction of deuterium – 99,88 %; moisture content – 0,018%; *bp*=+56,3 ºC, *mp*=-94 ºC; chemical shift of the residual proton *^{1}H* δ=2,75 ppm);

– High accuracy ampoules №507–HP for high resolution *NMR*'s spectroscopy (400 MHz);

– Volumetric pipette;

– Dispenser;

– Sample of vodkas, flavored vodkas and moonshine, produced in Ukraine were used as experimental material for *^{1}H NMR* spectroscopy.

Experimental studies of *^{1}H NMR* were carried out in the following order:

– Preparation of samples to research;

– Recording of *^{1}H NMR* spectrum;

– Conclusion and interpretation of work results.

Work methodology (Kuzmin et al, 2013–2014) [21–24]:

– 0,3 ml of vodka prepared with a volumetric pipette with a predetermined strength (40,0 ± 0,2)% vol. External standard separated from the testing substance which is required for deuterium stabilization system of spectrometer (deuterium solvent acetone-d_6) is added into an ampoule in a special form capillary. The obvious advantage of using the external standard is the fact that standard substance's molecules and test's solution do not interact with each other;

– *^{1}H NMR* spectra records and data processing were performed according to the instruction of *FT-NMR* Bruker Avance II spectrometer (400 MHz).

Results and discussions

The 31 sample of vodkas, produced in Ukraine were used as experimental material for ^1H *NMR* spectroscopy. These samples were divided into 3 groups with steady equilibrium, transitional and unsteady equilibrium of protons hydroxyl group. Figure 1–31 shows proton spectra of vodkas for the following groups of protons: CH_3; CH_2; H_2O; *EtOH*. Where Δf_1 – is deviation between proton's hydroxyl group of ethanol (*EtOH*) and water (H_2O), Hz; Δf_2 – is deviation between proton's hydroxyl group of water (H_2O) and a methylene group of protons of ethanol (CH_2), Hz; Δf_3 – is deviation between ethanol's methylene group of protons (CH_2) and ethanol's methyl group of protons (CH_3), Hz.

The group of vodkas with steady equilibrium. This group has included 12 samples of vodkas (Figures 1–12). The selected samples of vodkas with a steady equilibrium characterized by a unitary signal of hydroxyl group ($EtOH+H_2O$). The component of protons of $EtOH+H_2O$ in each sample presented as singlet (*s*), located in a weak field with a chemical shift in a range $\delta_{EtOH+H2O}$=4,75–4,80 ppm. Waveform of $EtOH+H_2O$ protons – is distorted Gaussian curve, with a broadened base and a slight asymmetry of apex, which is offset from the center line.

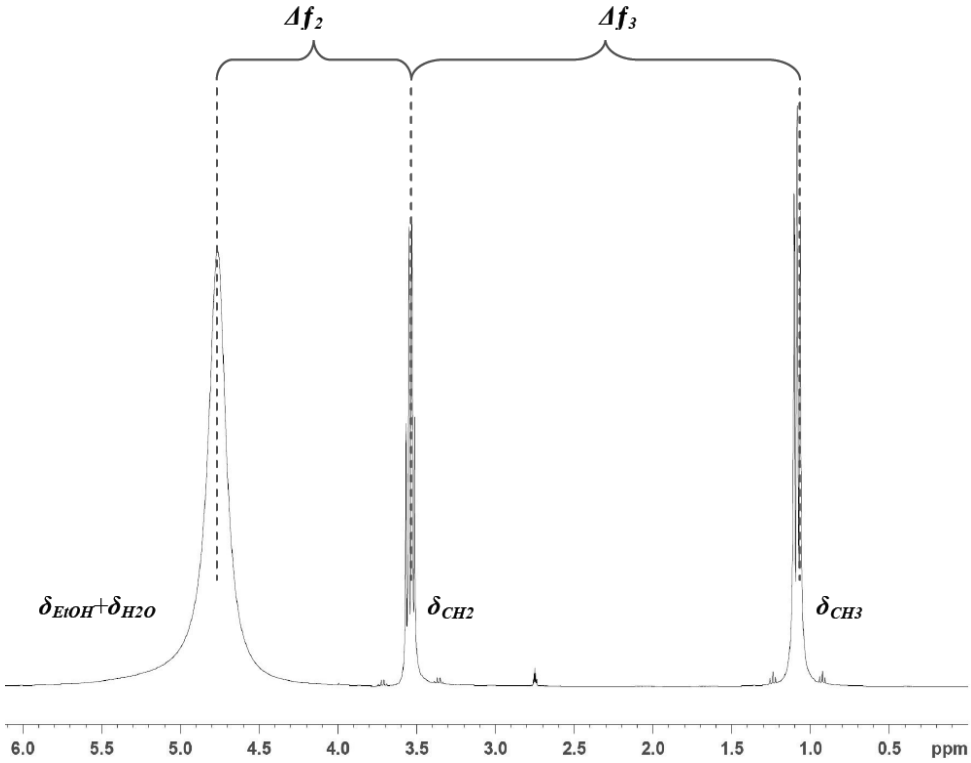

Figure 1. ^1H *NMR* spectra of proton groups of vodka (sample №1): CH_3; CH_2; $EtOH+H_2O$

Analysis of ^1H *NMR* spectra of methyl group's protons CH_3 in vodkas allows to state the following: methyl group of protons in each sample is located in a strong field and represented as a triplet (*t*) with a relative intensity (1:2:1). The average value of the chemical shift of the methyl group for the 12 samples is within δ_{CH3}=1,07–1,09 ppm. The distance between each components of the triplet (spin-spin coupling constant) is 8 Hz.

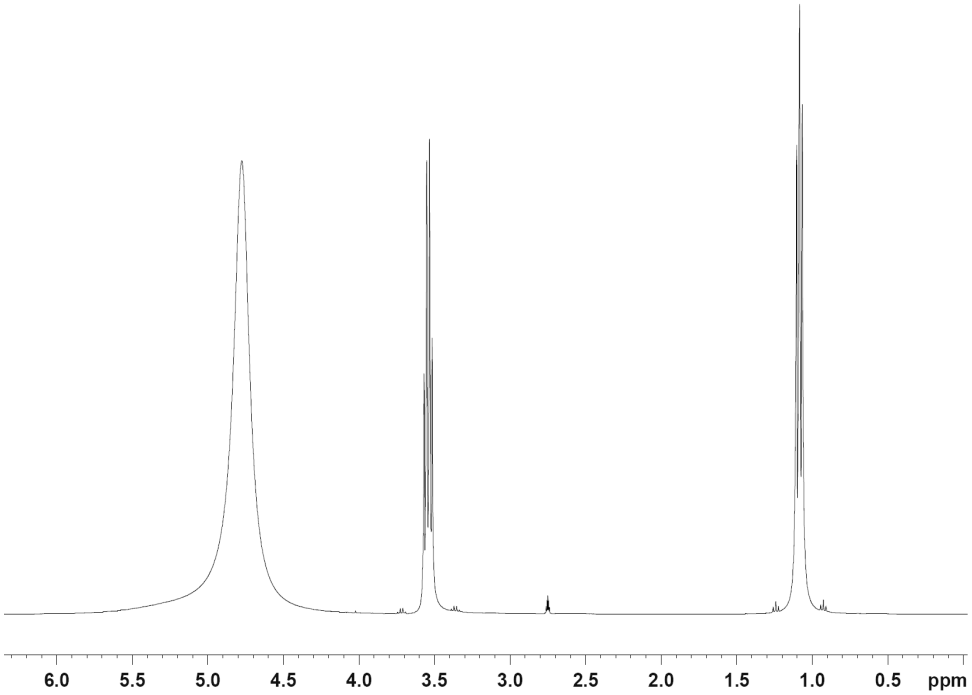

Figure 2. *^{1}H NMR* spectra of proton groups of vodka (sample №2)

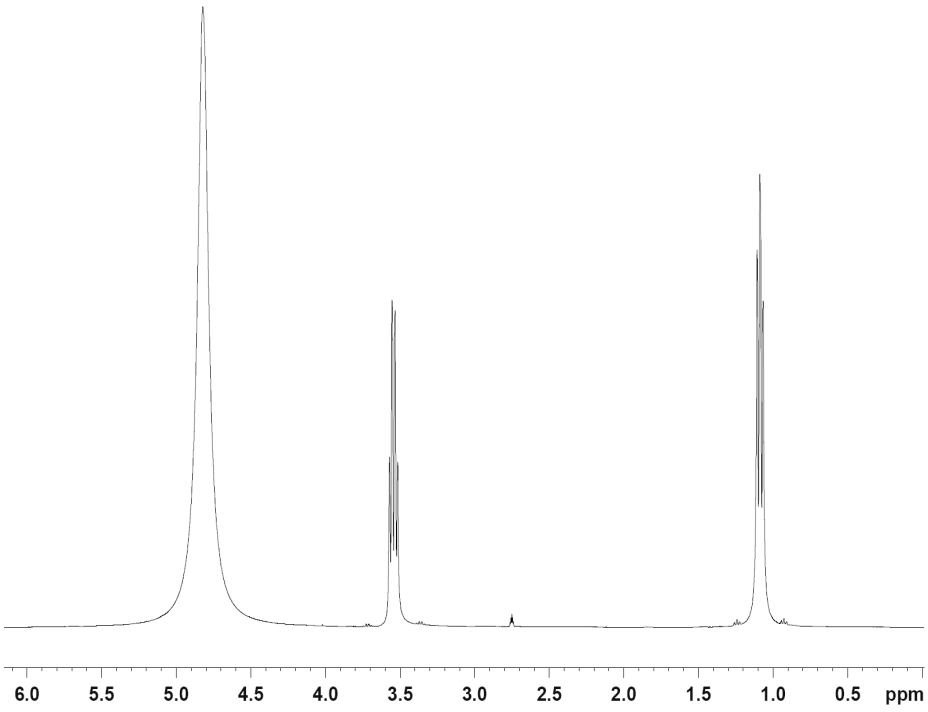

Figure 3. *^{1}H NMR* spectra of proton groups of vodka (sample №3)

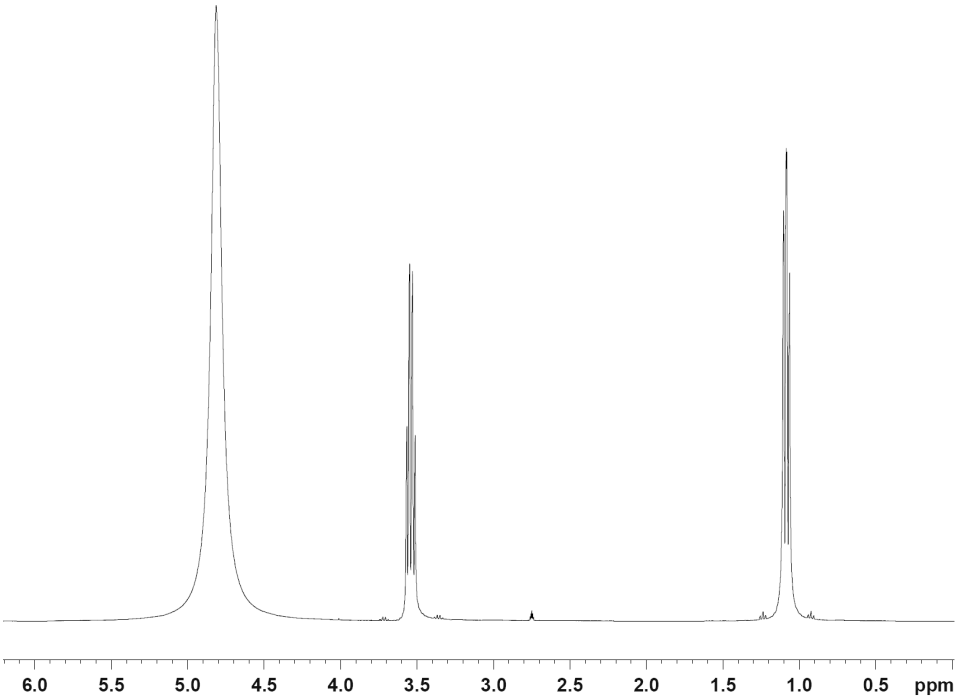

Figure 4. *^{1}H NMR* spectra of proton groups of vodka (sample №4)

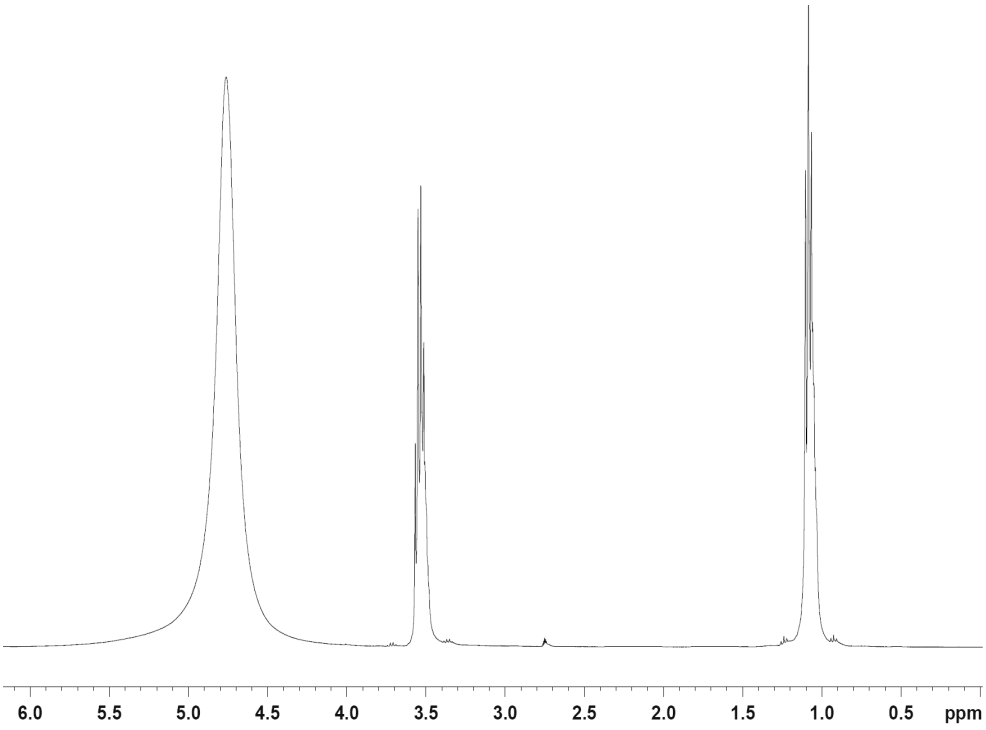

Figure 5. *^{1}H NMR* spectra of proton groups of vodka (sample №5)

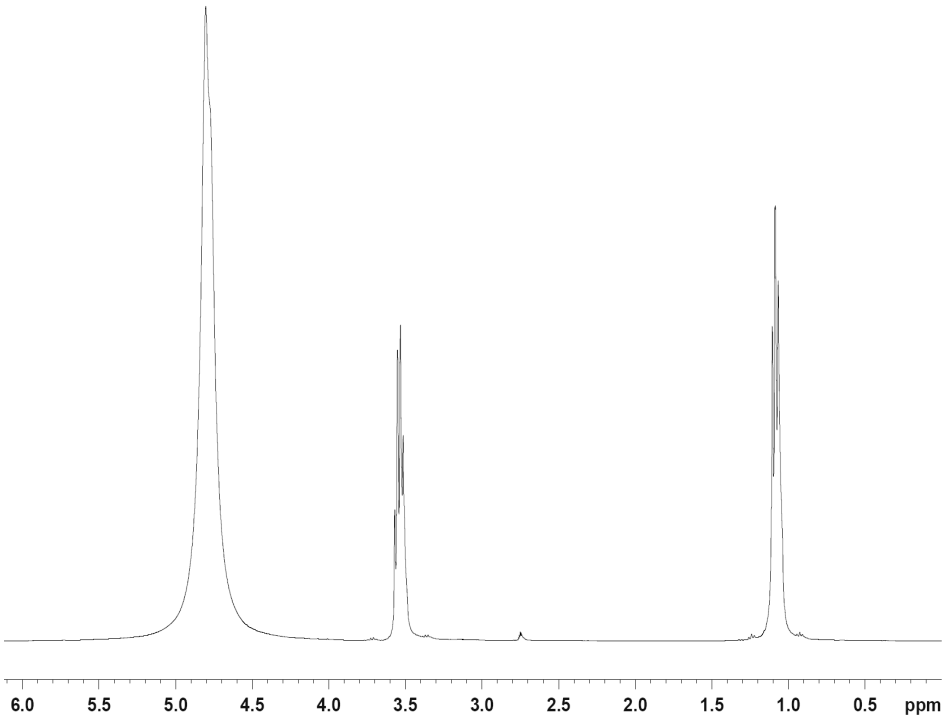

Figure 6. ^{1}H *NMR* spectra of proton groups of vodka (sample №6)

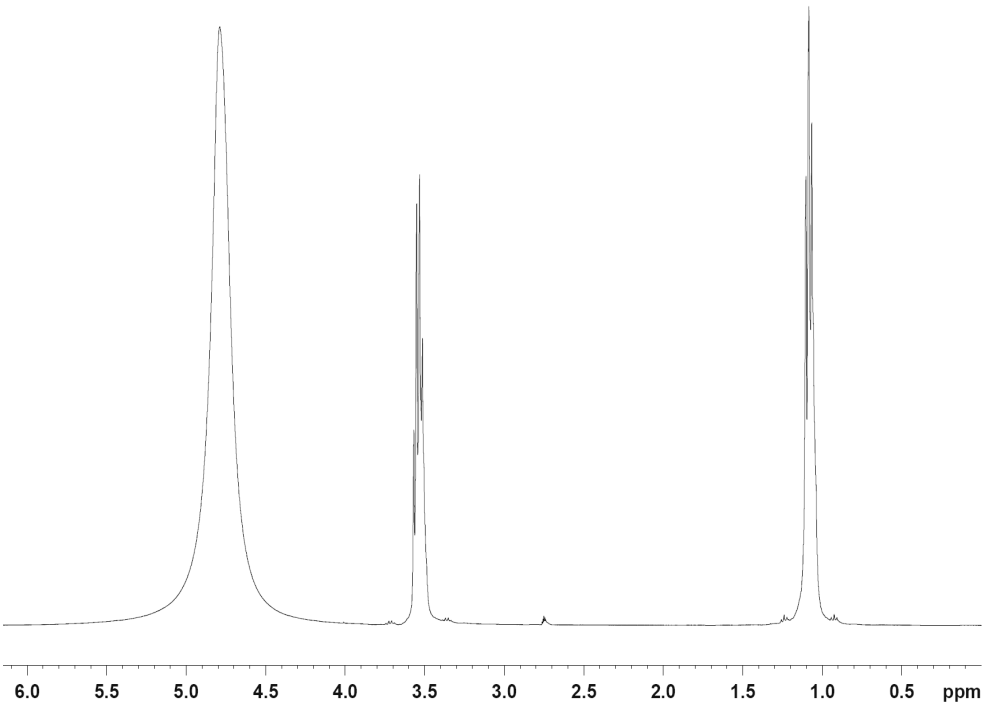

Figure 7. ^{1}H *NMR* spectra of proton groups of vodka (sample №7)

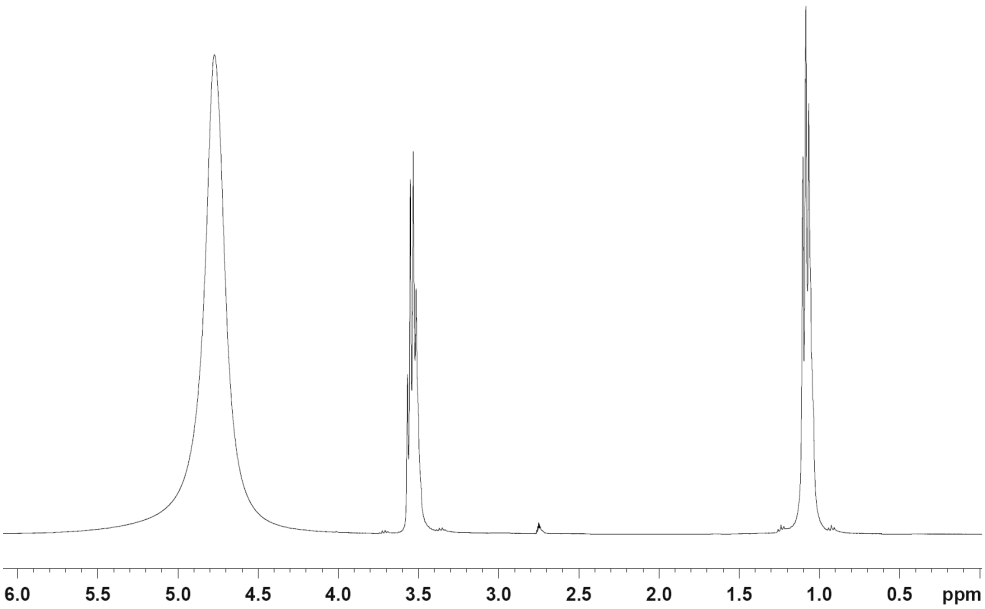

Figure 8. ^{1}H *NMR* spectra of proton groups of vodka (sample №8)

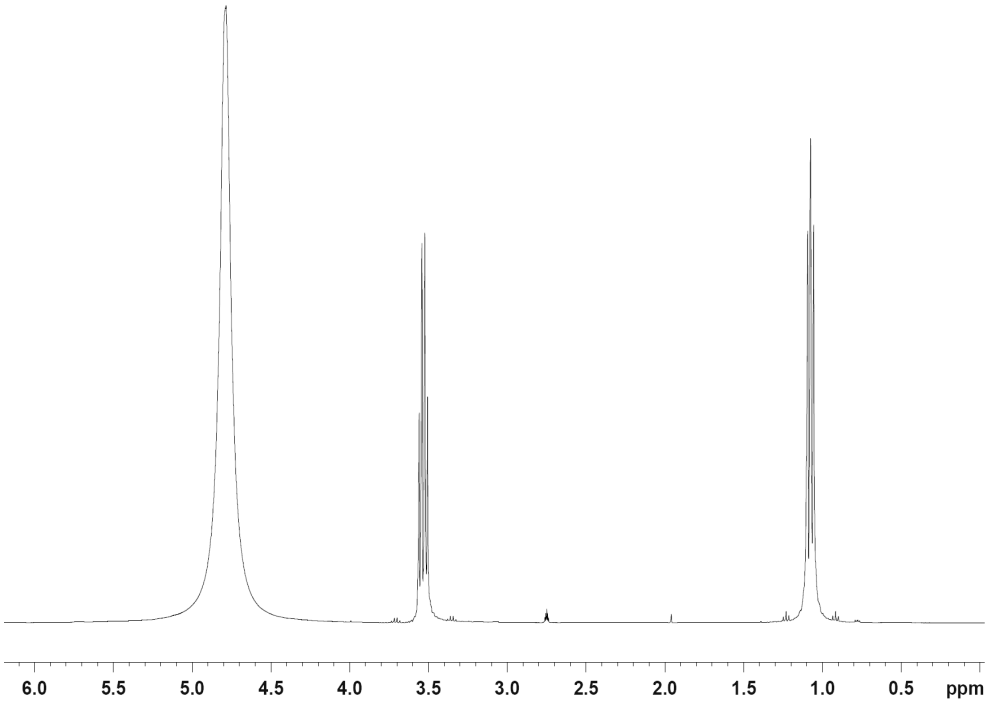

Figure 9. ^{1}H *NMR* spectra of proton groups of vodka (sample №9)

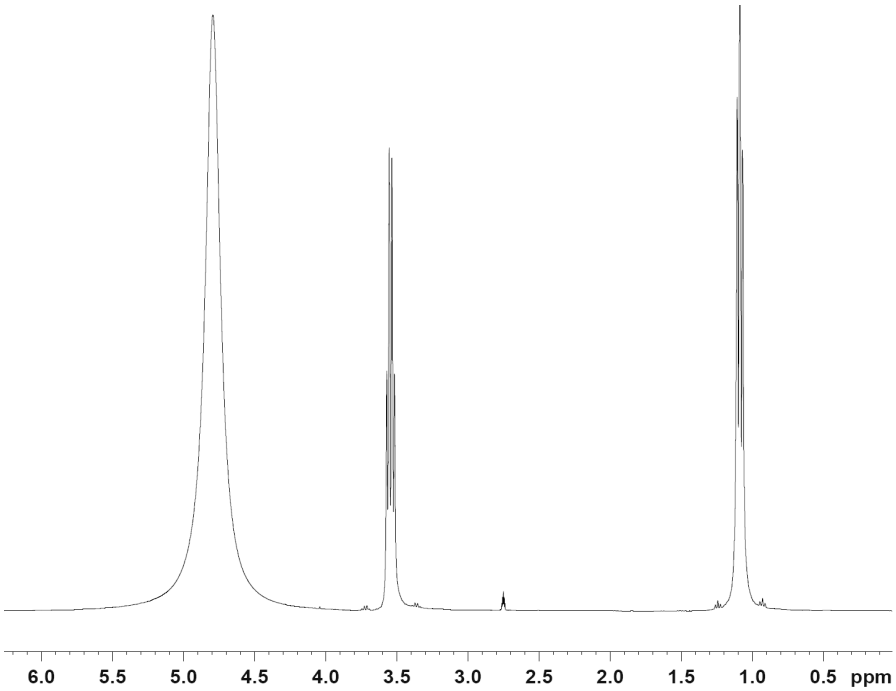

Figure 10. *^{1}H NMR* spectra of proton groups of vodka (sample №10)

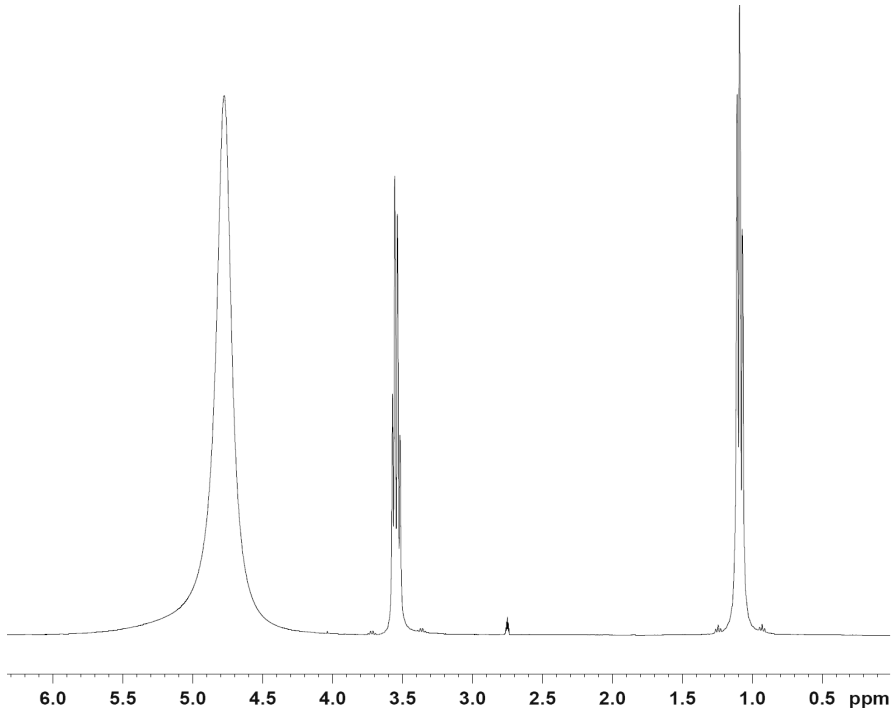

Figure 11. *^{1}H NMR* spectra of proton groups of vodka (sample №11)

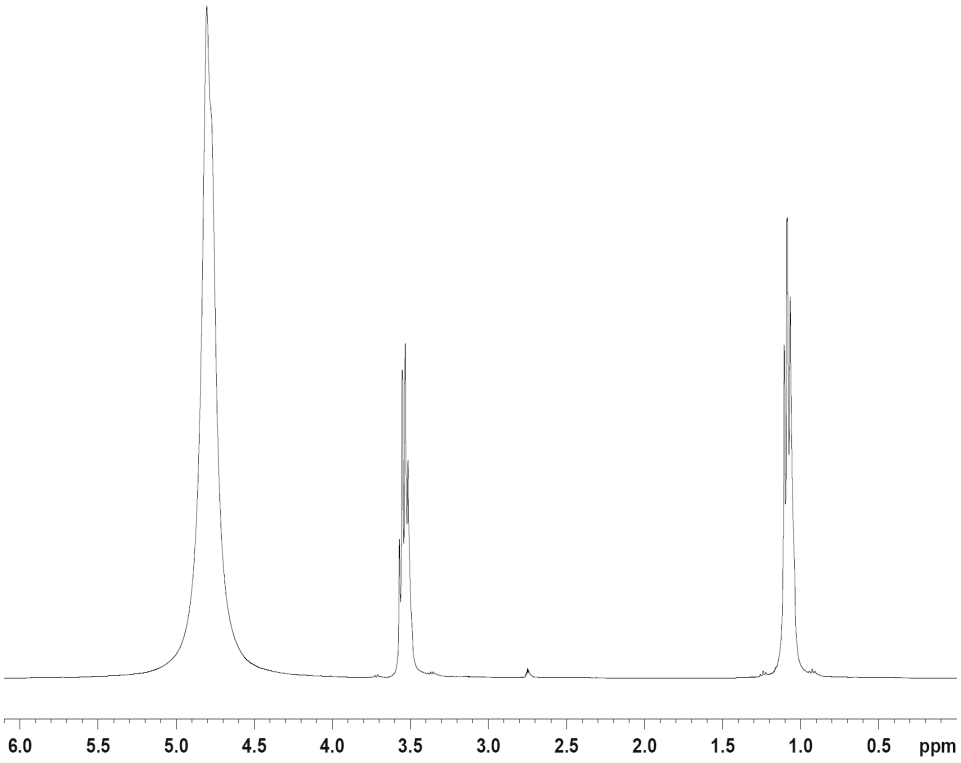

Figure 12. ^1H *NMR* spectra of proton groups of vodka (sample №12)

The analysis of ^1H *NMR* spectra of methylene group's protons CH_2 indicates that the group is represented as a quartet (q) with intensity (1:3:3:1), with an average value of the chemical shift δ_{CH2}=3,52–3,54 ppm. Most of the components of the methylene group have an average value of the chemical shift δ_{CH2}=3,53 ppm. The distance between each peak of quartet is also 8 Hz. The difference between chemical shifts of protons of methylene group of ethanol (CH_2) and hydroxyl group $EtOH+H_2O$ – $\Delta\delta_2$=1,23–1,27 ppm. The difference between chemical shifts of protons of methylene group of ethanol (CH_2) and methyl group of ethanol (CH_3) in each sample is $\Delta\delta_3$=2,45 ppm, which specifies on stability of chemical shifts between these groups, and strong links between methyl (CH_3) and methylene (CH_2) groups.

The group of vodkas with transitional equilibrium. This group has included 11 samples of vodkas (Fig. 13–23). The samples of vodkas with the transitional equilibrium as well as samples with unsteady equilibrium are characterized by the absence of unitary signal ($EtOH+H_2O$) therefor protons of hydroxyl group is presented by two separate picks of H_2O and $EtOH$. Signal of hydroxyl protons of ethanol ($EtOH$) in each sample is represented as a separate subtle signal of a rounded shape located in a weak field with a chemical shift δ_{EtOH}=5,34 ppm. Component of proton of water (H_2O) in each sample is represented as a singlet with a chemical shift δ_{H2O}=4,75 ppm. Waveform of H_2O signals is distorted Gaussian curve, with a broadened base and a slight asymmetry of apex, which is offset from the centerline. The difference between the chemical shifts of hydroxyl protons of ethanol ($EtOH$) and proton of water (H_2O) in each sample is about $\Delta\delta_1$=0,59 ppm (Δf_1=236 Hz). This may indicate that certain prerequisites are created to establish equilibrium structure (unsteady/steady equilibrium).

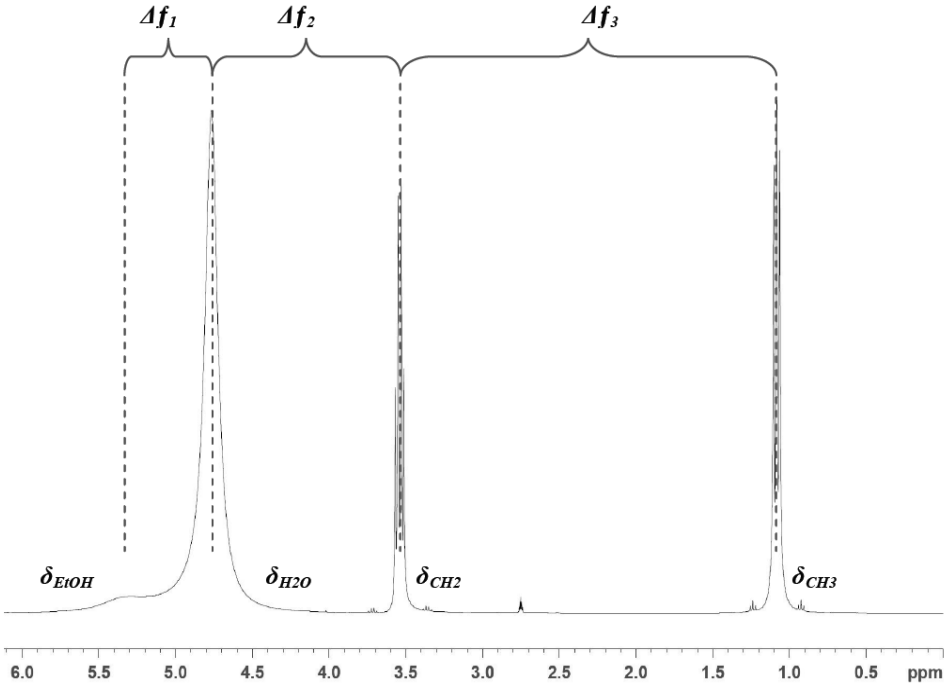

Figure 13. ^1H *NMR* spectra of proton groups of vodka (sample №13)

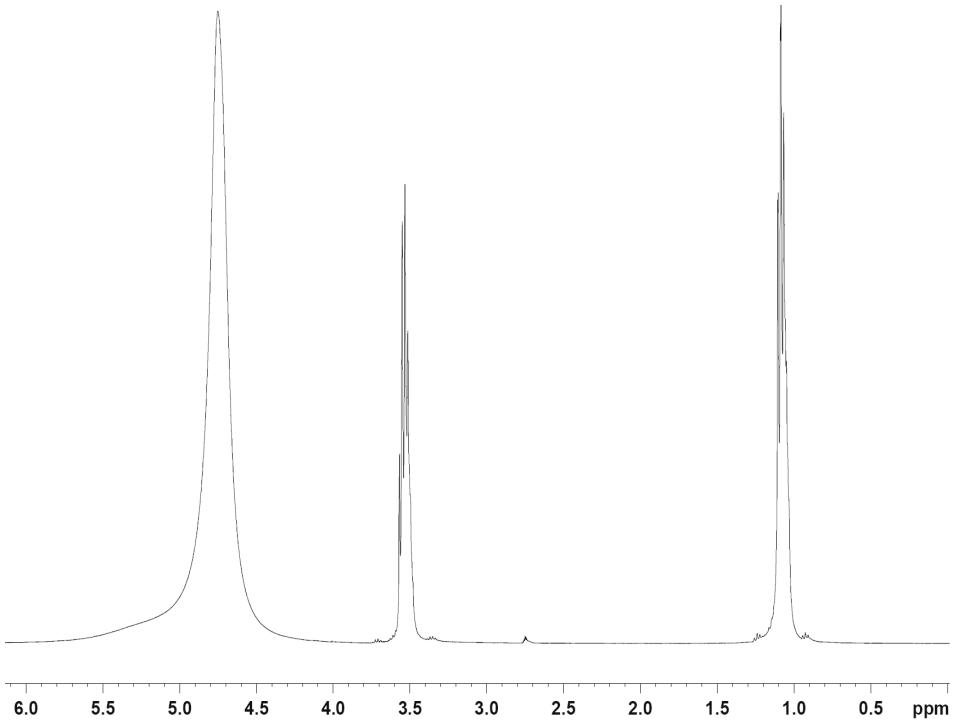

Figure 14. ^1H *NMR* spectra of proton groups of vodka (sample №14)

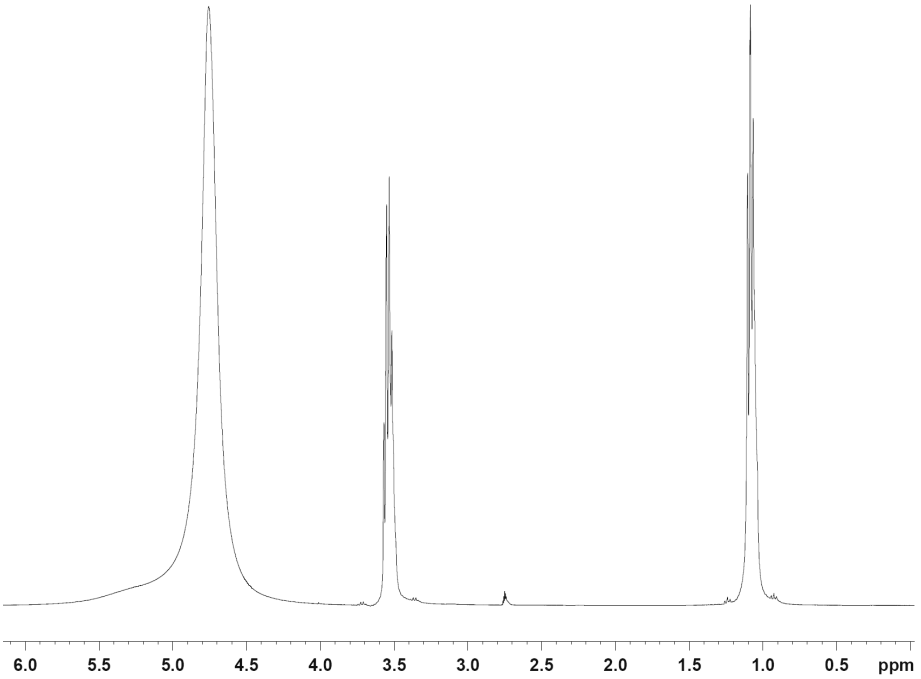

Figure 15. *^{1}H NMR* spectra of proton groups of vodka (sample №15)

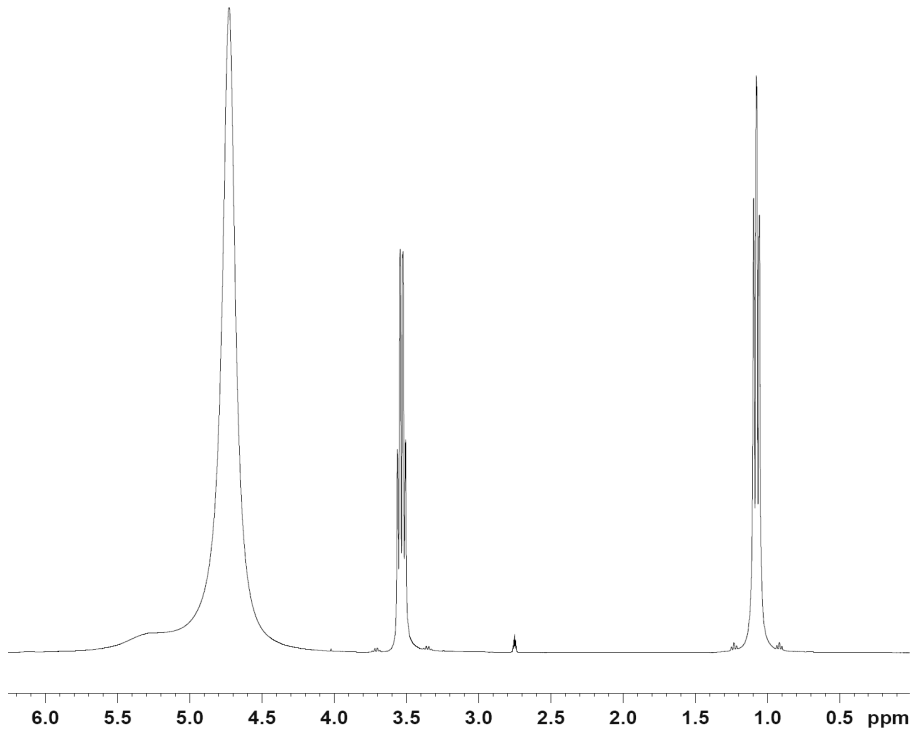

Figure 16. *^{1}H NMR* spectra of proton groups of vodka (sample №16)

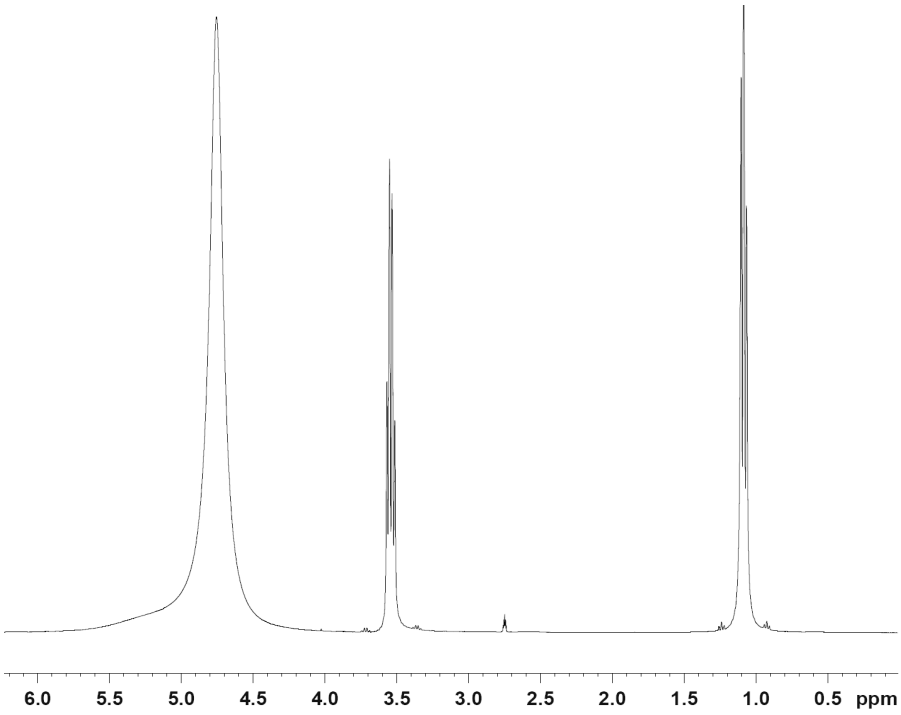

Figure 17. *^{1}H NMR* spectra of proton groups of vodka (sample №17)

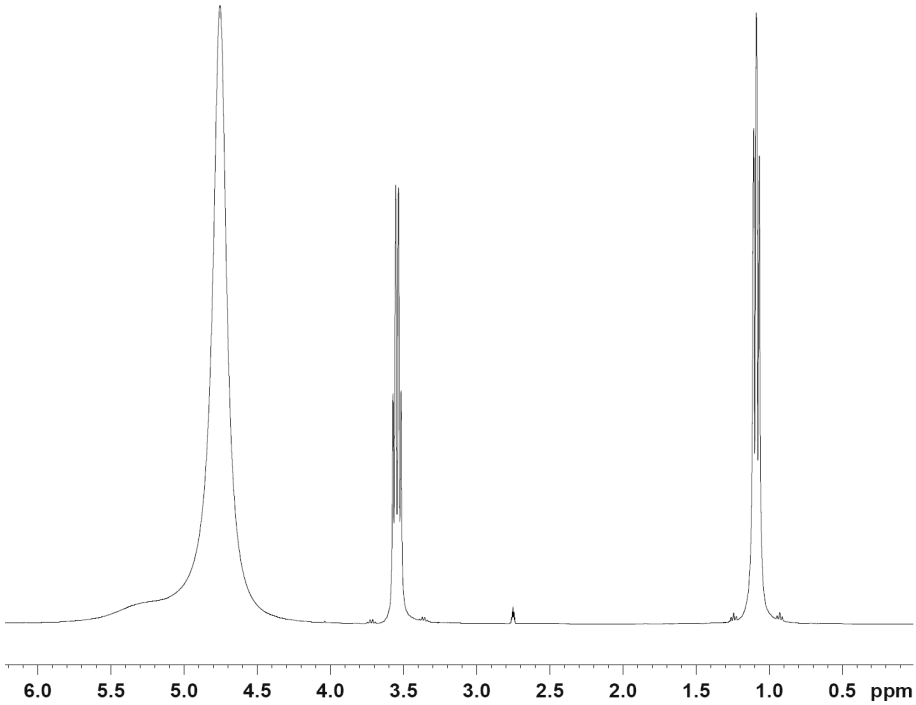

Figure 18. *^{1}H NMR* spectra of proton groups of vodka (sample №18)

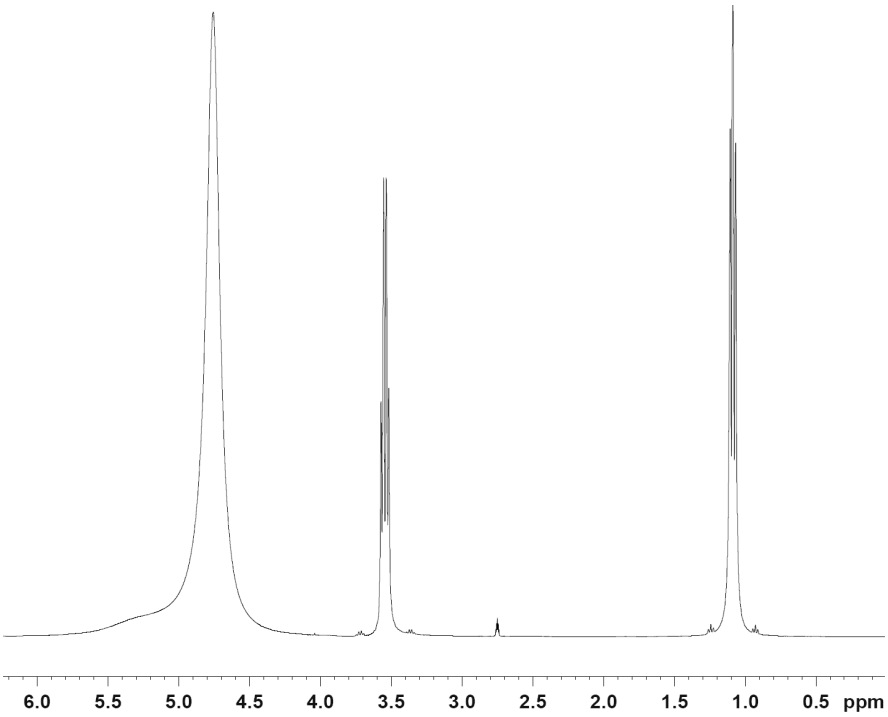

Figure 19. *^{1}H NMR* spectra of proton groups of vodka (sample №19)

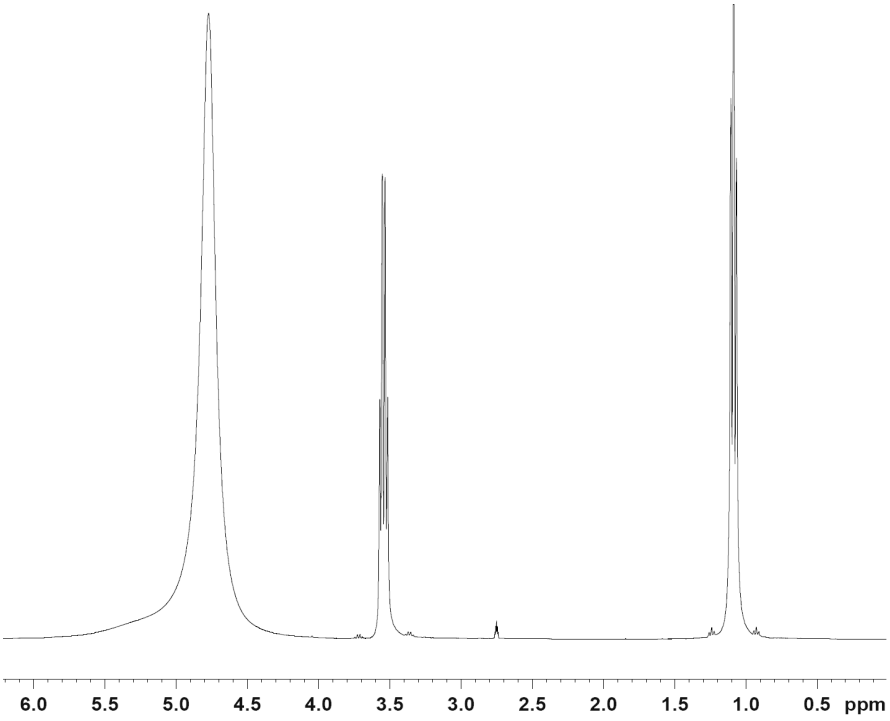

Figure 20. *^{1}H NMR* spectra of proton groups of vodka (sample №20)

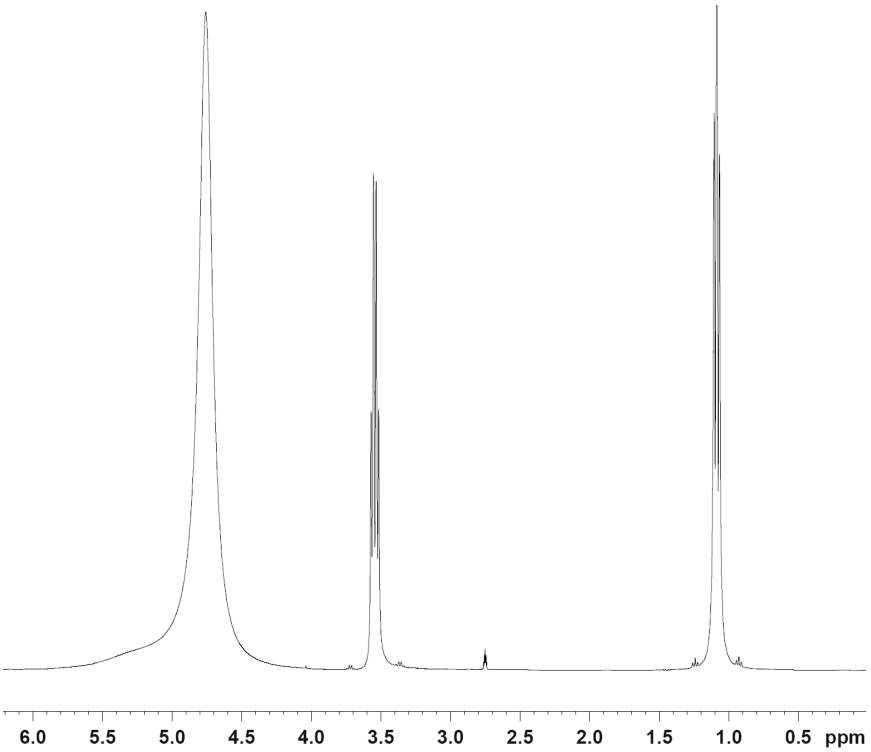

Figure 21. *^{1}H NMR* spectra of proton groups of vodka (sample №21)

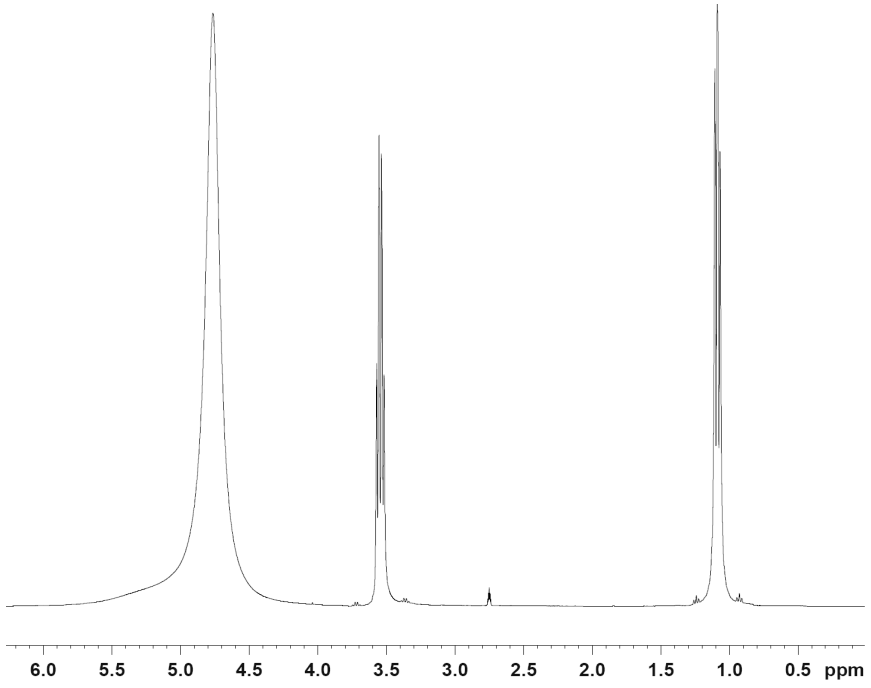

Figure 22. *^{1}H NMR* spectra of proton groups of vodka (sample №22)

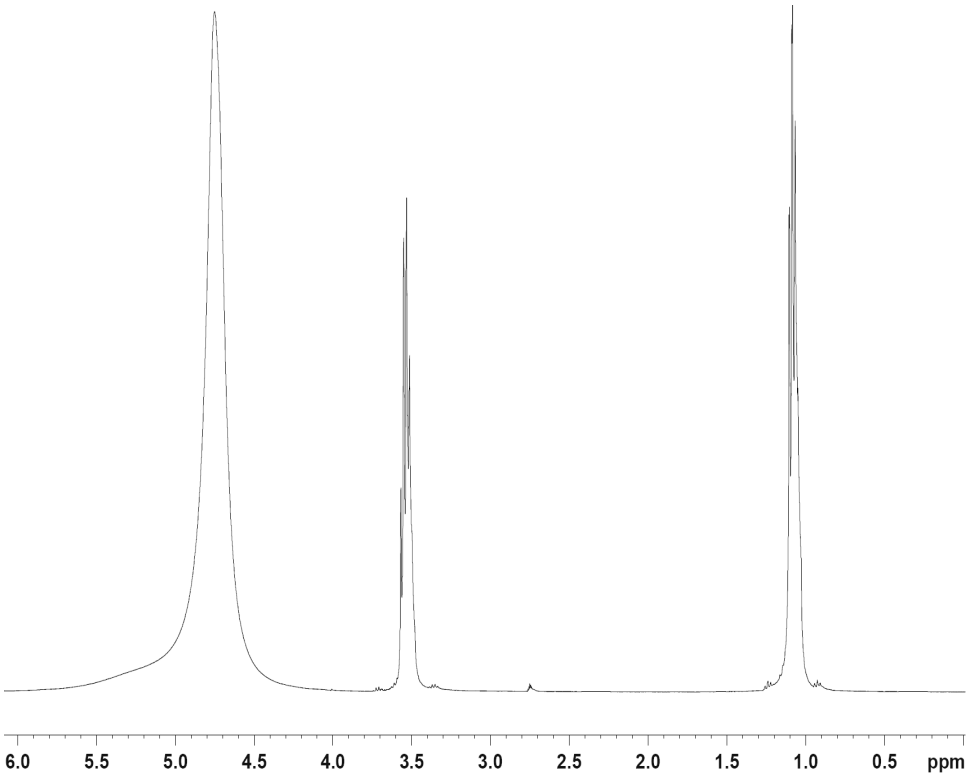

Figure 23. ^{1}H *NMR* spectra of proton groups of vodka (sample №23)

Methyl group of protons (CH_3) in each sample is located in a strong field and represented as a triplet (*t*) with a relative intensity of (1:2:1). The average value of chemical shift is δ_{CH3}=1,08 ppm. The distance between each peak of quartet is 8 Hz.

^{1}H *NMR* spectra of proton's methylene group (CH_2). The group is represented as a quartet (*q*) with intensity ratio of (1:3:3:1) and average value of chemical shift of δ_{CH2}=3,53 ppm. The distance between each peak of quartet is 8 Hz. The difference between the chemical shifts of ethanol's protons of methylene group (CH_2) and hydroxyl group of water (H_2O) in each sample is $\Delta\delta_2$=1,22 ppm (Δf_2=488 Hz). The difference between the chemical shifts of ethanol's protons of methylene group (CH_2) and methyl group of ethanol (CH_3) in each sample is $\Delta\delta_3$=2,45 ppm (Δf_3=980 Hz).

The group of vodkas with unsteady equilibrium. This group has included 8 samples. Figure 24–31 shows one-dimensional proton spectra of vodkas for the following groups of protons: CH_3; CH_2; H_2O; *EtOH*.

The selected samples of vodkas with unsteady equilibrium characterized by the absence of single signal ($EtOH+H_2O$), therefor hydroxyl group of protons is represented by two separate peaks of ethanol (*EtOH*) and water (H_2O). The signal of ethanols hydroxyl protons (*EtOH*) in each sample is represented as a single broad singlet (*s*) with a rounded shape, located in a weak field with a chemical shift δ_{EtOH}=5,34 ppm. The signal of water proton (H_2O) in each sample presented as singlet (*s*) with a chemical shift δ_{H2O}=4,72 ppm.

Waveform of H_2O protons – is distorted Gaussian curve, with a broadened base and a slight asymmetry of apex, which is offset from the centerline. The difference between hydroxyl protons of ethanol (*EtOH*) and water (H_2O) in each sample is $\Delta\delta_1$=0,62 ppm (Δf_1=248 Hz). This may indicate that conditions for the formation of water structure with hydroxyl proton of alcohol were not yet set, therefor we can state that thermodynamic equilibrium didn't appear in any of the samples.

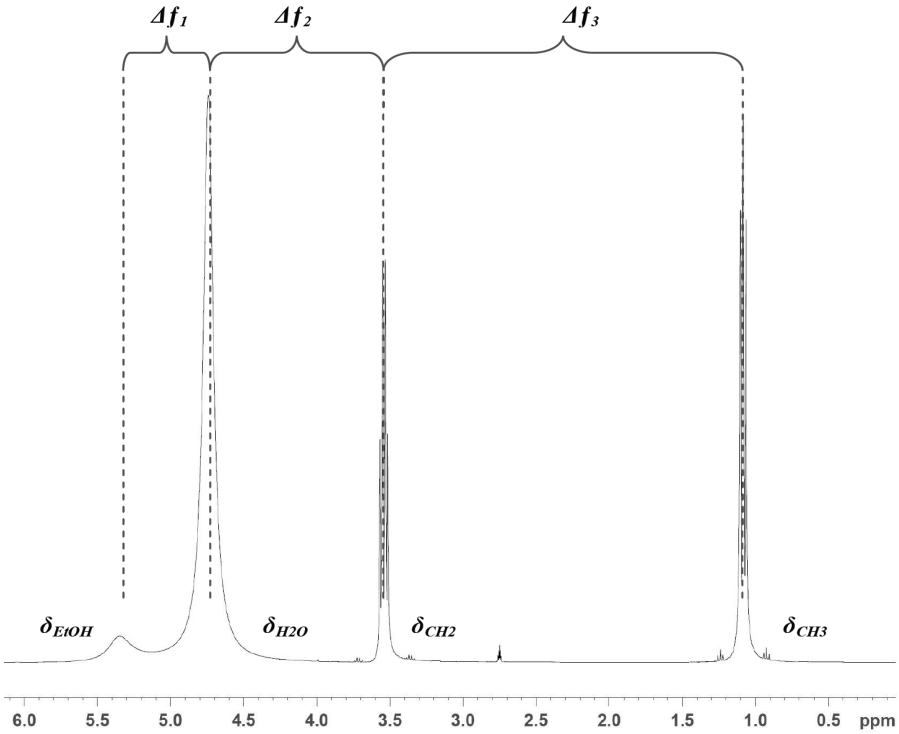

Figure 24. ^{1}H ***NMR*** **spectra of proton groups of vodka (sample №24):** CH_3; CH_2; H_2O; ***EtOH***

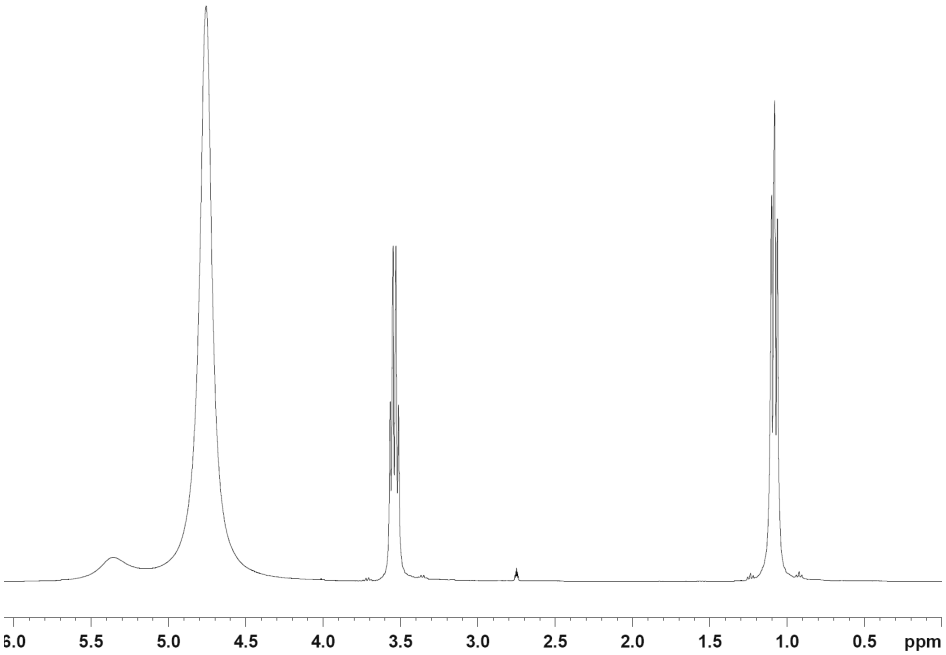

Figure 25. ^{1}H ***NMR*** **spectra of proton groups of vodka (sample №25)**

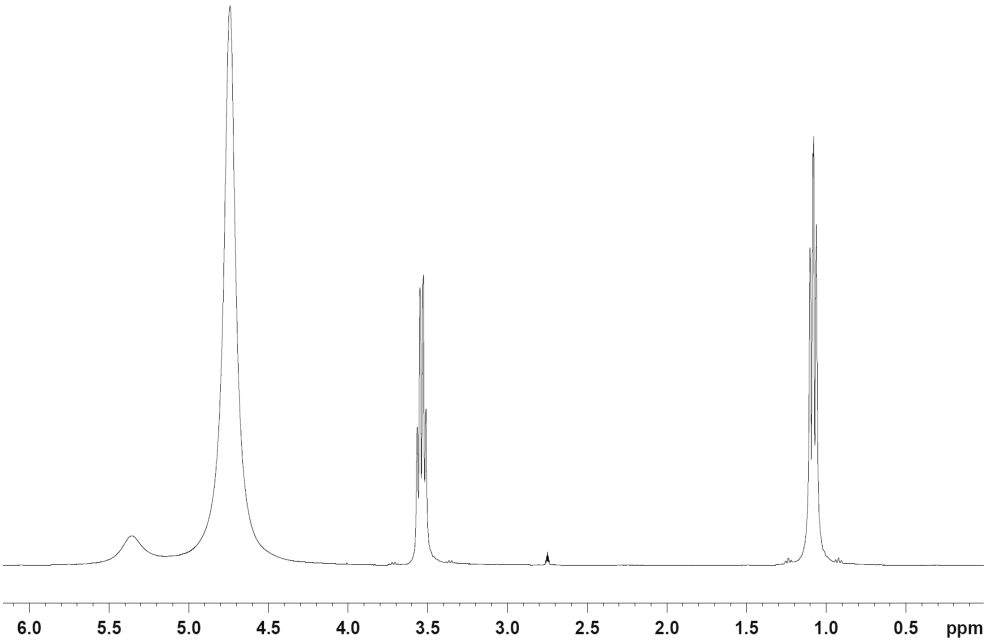

Figure 26. *^{1}H NMR* spectra of proton groups of vodka (sample №26)

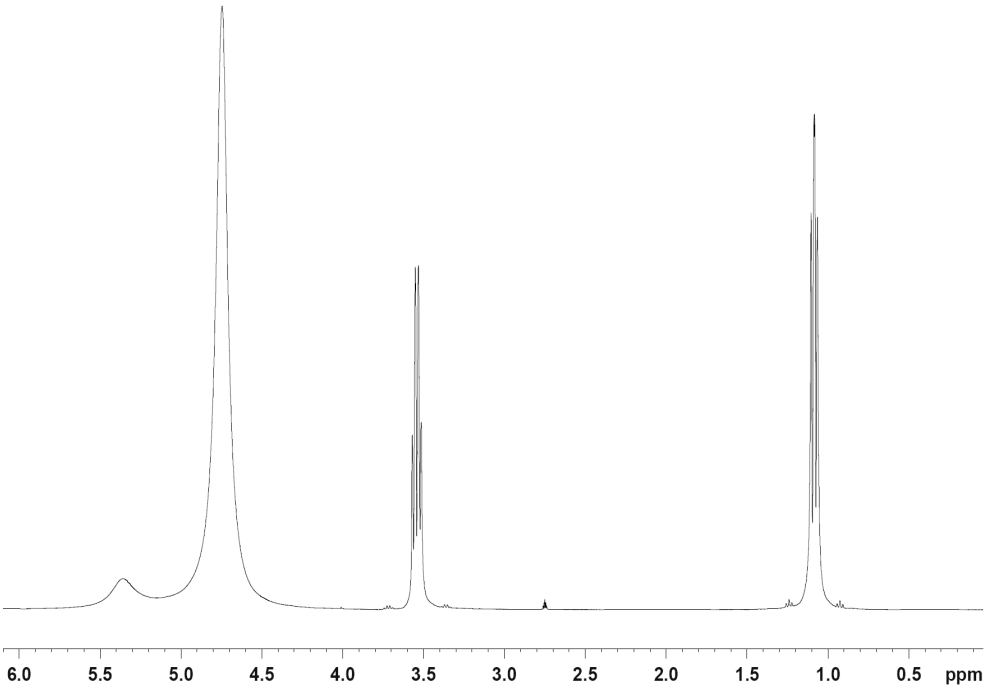

Figure 27. *^{1}H NMR* spectra of proton groups of vodka (sample №27)

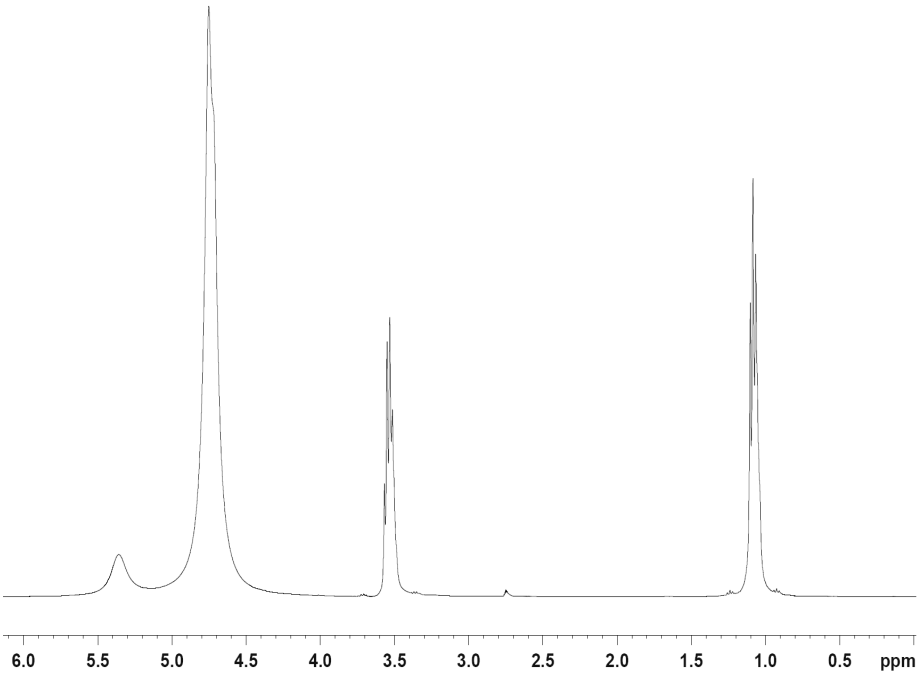

Figure 28. ^{1}H *NMR* spectra of proton groups of vodka (sample №28)

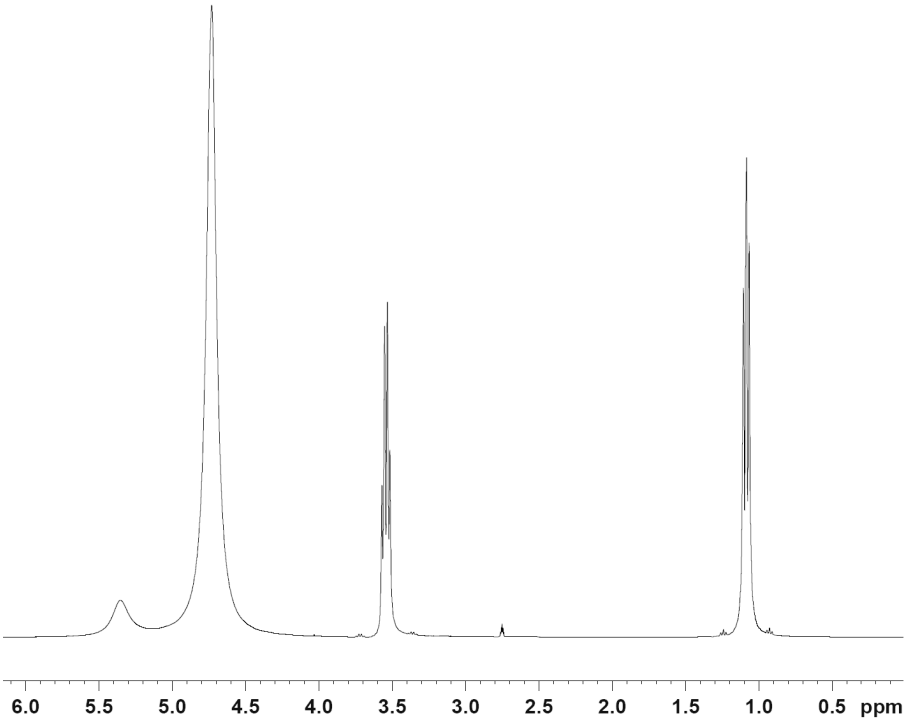

Figure 29. ^{1}H *NMR* spectra of proton groups of vodka (sample №29)

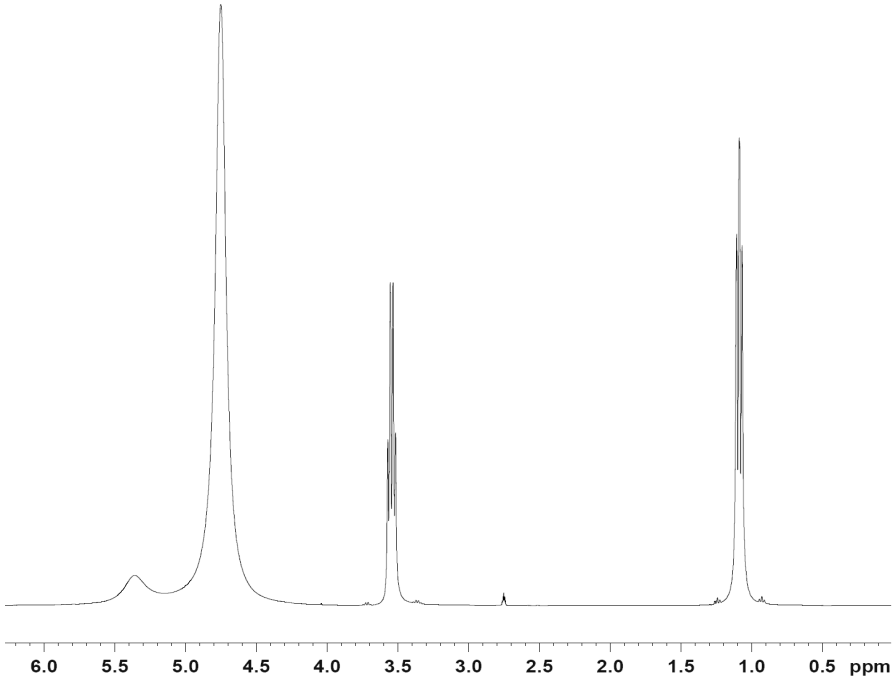

Figure 30. *^{1}H NMR* spectra of proton groups of vodka (sample №30)

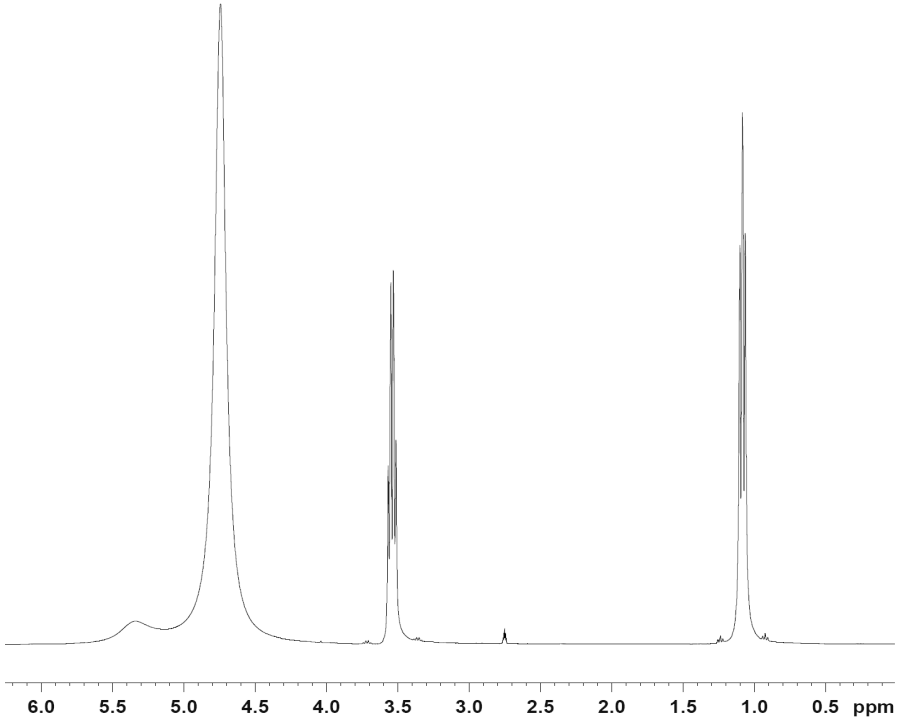

Figure 31. *^{1}H NMR* spectra of proton groups of vodka (sample №31)

Analysis of ^1H *NMR* spectra of methyl group's protons CH_3 in vodkas allows to state the following: methyl group of protons in each sample is located in a strong field and represented as a triplet (*t*) with a relative intensity (1:2:1). Based on spin-spin interaction of groups of protons, the methyl group's signals (CH_3) must be split by neighboring protons of the methylene group (CH_2) into a triplet (*t*), in accordance with Pascal's triangle with intensity ratio of (1:2:1). Thus, methyl group of protons (CH_3) is located in a strong field with an average value of chemical shift δ_{CH3}=1,08 ppm. The distance between each peak of quartet is 8 Hz.

The analysis of ^1H *NMR* spectra of methylene group's protons CH_2 indicates that the group is represented as a quartet (*q*) with intensity (1:3:3:1). This is confirmed by the spin-spin interaction of protons of methyl (CH_3) group. This group has to split signal of the methylene group (CH_2) into four components and form a quartet (*q*) with intensity ratio of 1:3:3:1. In turn, the protons of hydroxyl (*OH*) groups should split every component of methylene (CH_2) group's quartet into two components and form a double quartet. The absence of observable spin-spin interaction between hydroxyl (*OH*) and methylene (CH_2) groups should make signal of methylene (CH_2) group a quartet. At the same time methylene group of protons (CH_2) is located in a weak field, with an average value of chemical shift δ_{CH2}=3,53 ppm. The distance between each peak of quartet is 8 Hz. The difference between chemical shifts of protons of methylene group of ethanol (CH_2) and hydroxyl group of water (H_2O) in each sample is $\Delta\delta_2$=1,19 ppm (Δf_2=476 Hz). The difference between chemical shifts of protons of methylene group of ethanol (CH_2) and methyl group of ethanol (CH_3) in each sample is $\Delta\delta_3$=2,45 ppm (Δf_3=980 Hz).

Conclusions

We will draw conclusions on establishing of equilibrium hydroxyl proton of ethanol and water in vodka by ^1H *NMR* spectroscopy. We identified three groups of samples based on the equilibrium of the hydroxyl groups of protons of ethanol (*EtOH*) and water (H_2O): steady; transitional; unsteady.

Steady equilibrium is characterized by a presence in hydroxyl group combined unitary signal of $EtOH+H_2O$. The component of protons of $EtOH+H_2O$ in each sample presented as singlet (*s*), located in a «weak field» with a chemical shift, which is in a range $\delta_{EtOH+H2O}$=4,75–4,80 ppm. Waveform of $EtOH+H_2O$ protons – is distorted Gaussian curve, with a broadened base and a slight asymmetry of apex, which is offset from the centerline.

Transitional equilibrium characterized by a presence of hydroxyl groups two separate signals of *EtOH* (δ_{EtOH}=5,34 ppm) and H_2O (δ_{H2O}=4,75 ppm). The difference between the chemical shifts of hydroxyl protons of ethanol (*EtOH*) and proton of water (H_2O) in each sample is $\Delta\delta_1$=0,59 ppm (Δf_1=236 Hz). Transitional equilibrium is characterized by the presence of hydroxyl proton, which is barely noticeable, which characterizes the transition from steady equilibrium to unsteady equilibrium. This may indicate that certain prerequisites have not yet been created to establish equilibrium structure (unsteady/steady equilibrium).

Unsteady equilibrium characterized by a presence of hydroxyl groups two separate signals of ethanol (*EtOH*) (δ_{EtOH}=5,34 ppm), which is obvious and H_2O (δ_{H2O}=4,72–4,75 ppm). The difference between *EtOH* and H_2O – $\Delta\delta_1$=0,62 ppm (Δf_1=248 Hz).

The conducted researches set a fundamental difference of behavior of hydroxyl proton of ethanol and water in vodkas, using ^1H *NMR* spectroscopy. Istablished criteriums of the systems equilibrium allow to improve the technological process of vodka on distillery enterprises, to stabilize quality of finished product.

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Removal of Cd and Pb ions from model solutions using natural sorbent

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Abstract

Introduction. One of the limitations of chemical absorbents as a simple and effective method for removal the contamination due to surface absorption mechanism was their exorbitant costs. Therefore, the study of the potential of cheap and accessible natural adsorbents in the removal of heavy metals from industrial waste can be interesting.

Materials and Methods. For the study of absorbent quantity, pH and temperature effectiveness on absorption capacity of cherry core, first the artificial solution was supplied in 1000 mg/lit concentration and was mixed by certain amount of absorbent at certain temperature and pH for 60 minutes. The solutions filtered by filter paper and the contents of each ion in initial and filtered solution were determinate by atomic absorption spectrometry. Effect of absorbent quantity (0.2–2 g/100 ml), pH (3–7) and temperature (30–70 °C) on absorption rate of Lead and Cadmium investigated in Response Surface Methodology (RSM).

Results and Discussion. Increasing temperature improved the absorption rate of cadmium due to decrease of viscosity and accelerate mass transfer. Increasing of temperature limits the formation of boundary layer around the absorbent due to reduce of solution viscosity. So, ion absorption is intensified. Also, Increasing of absorbent quantity raises the surface contact and as results the chance of collision ions is improved with absorbent particles. In the other words, high quantity of absorbent increases the required cites to attach ions. Cadmium elimination at high value of pH was decreased due to conversion of ionic structure to molecular structure. Cadmium absorption rate was also increased by enlarging of absorbent; because of exist the more cites for absorption. Increasing the pH to 5 led to increase the Lead ions absorption, but rise of pH to 7 reduced absorption of Lead. The reason of this pneumonia is due to change of Lead ion structure to molecular state in alkaline pH. While in lower pH, competition hydrogen ions with cations decrease the absorption of metal ions.

Conclusion. The best experimental parameters for maximum absorption ions were determined at the following conditions: temperature 70 °C, pH 5 and concentration of absorbent 2 g/100ml. By applying these conditions, Lead and Cadmium ions were decreased 79.18 and 76.56% respectively from artificial solutions. Also, optimal conditions were tested on sugar industry wastewater, which results indicated the rate of absorption for Lead and Cadmium was obtained 98.98 and 76.1% respectively.

Introduction

Industrial contamination is one of the most important factors that pollute the water sources and spread infection to humans and animals. Household wastes, industrial wastes and agriculture drainage are a major contributor to pollutions. Limitation of water sources, lack of rain and water crisis on one hand and increase the contamination of surface and ground water by heavy metals on the other has caused that finding an effective method is necessary to removal the pollutants specially heavy metals as Cd, Pb, Ni [3].

Mechanism of heavy metal toxicity in biochemical is due to intense inclination of metals Cations to reaction with sulfur molecules. These binding were caused the inactivation of enzymes and lead to the bio failure and death [9–10].

Cadmium is a very toxic metal that its destructive effects have been proven on the lungs, kidneys and bones. Including serious damage of cadmium can be noted to a disease named Itai-Itai (Rheumatism bone pain). Cadmium through the contamination of sediment erosion left over the industries and agriculture slurry and manure is entered to aquatic ecosystems [4].

Also, Lead damages to nervous connections and leads blood and brain diseases. As far as, the 5 micrograms of Lead per deciliter of blood decrease the IQ and impair the focus and aggression in children [14].

Nowadays, various methods exist for reduction the contamination and heavy metals from water sources including membrane technology, exchanges ions resins, electrolysis and surface absorption. Among these methods, absorption processes has been applied widely due to existence of absorbent divers as carbon active, zeolite, silica and clay [10].

Absorption process as an economic and efficient method can be replacing to costly procedures like Revers osmose membrane process for removal heavy metals [2].

In recent years, waste of agriculture and industrial byproducts like threes leaf, peels of fruits, core of fruits even sawdust as natural absorbents have been used to removal the heavy metals in oil, chemical and textile industry, effectively. Application of solid agriculture wastes is growing as effectiveness absorbent because of abundance, low costs and their naturalness [1&8].

In 2007 Kamitz et al., reported that bagasse modified with succinic anhydride can be considered as useful natural absorbent for cu, Pb and Cd. This absorbent could remove the copper, lead and cadmium until 114, 196 and 189 mg/g, respectively.

Kelly-Vargas (2012) compared the adsorb capacity of lemon and banana peels to removal Copper, Lead and Cadmium ions. Results indicated that the lemon peels was more successful in absorbing Copper and Lead than other, but Cadmium absorption was better by banana peels (82%).

In similar study by Saka et al (2012) was shown that date fruit core in compare to onion peel was better in absorbing of Lead ions.

So, in this study, the potential of cherry core to removal the Lead and Cadmium ions from industrial wastewater was assessed and conditions of operation were optimized, too.

Materials and methods

Preparation of natural absorbent

First, cores of cherry were washed by distilled water several times to elimination their surface impurities and were dried in oven (Unitherm Model, Germany) at 103 °C for 2

hours. Then, due to increasing the capacity of contact surface, the cores were grinded and sifted (screen shaker, Retsch AS200, Germany) in sieve mesh > 35 and < 60. Dusty particles of cherry core maybe come in a hunch shape due to mixed in solutions, while shaper particles have a lower contact surface (area to volume ratio). Finally, cherry core powders were put to desiccator to prevent the absorption of moisture [7].

Preparation of artificial wastewater

By dissolving the Lead nitrate and Cadmium nitrate (Merck, Germany), the synthetic solutions was supplied in concentration of 1000 mg/lit. Also, sulfuric acid and NaOH solution (0.1 M) were used to adjusting the pH [7].

Experiment method

For the study of absorbent quantity, pH and temperature effectiveness as experimental variables on absorption capacity of cherry core, first the artificial solution was mixed by certain amount of absorbent at certain temperature and pH for 60 minutes that has been determined by statistical design (Table 1). pH and temperature adjusted by pH meter (Metrohm Model Germany) and magnetic stirrer equipped by heater (IKA Model, Germany) and finally, after 60 minutes, the solutions filtered by filter paper (Whatman, 42 micron). For calculation of absorption rate, the ion contents in initial and filtered solution were determinate by atomic absorption spectrometry (Analytik Jena Model, Germany). When the solution is exposed to high temperature, the electrons of atom can be excited due to absorbing energy which is different for each atom by atom [7].

Statistical design

Effect of absorbent quantity (0.2–2 g/100 ml), pH (3–7) and temperature (30–70 °C) on absorption rate investigated in Response Surface Methodology (RSM) statistical design and state of Box-Bhenken subject the full quadratic model (Equation 1) by Minitab Ver.17 software. Also, the best of parameter to elimination of cadmium and lead was optimized by this software.

$$f = b_0 + b_1T + b_2T^2 + b_3P + b_4P^2 + b_5C + b_6C^2 + b_7TP + b_8TC + b_9CP \qquad (1)$$

where: T – Temperature, P – pH and C – Concentration

Table 1

Experimental runs, independent variable levels and replicate runs in RSM (Box-Bhenken method)

Run Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Temp (^oC)	30	70	30	70	30	70	30	70	50	50	50	50	50	50	50
pH	3	3	7	7	5	5	5	5	3	7	3	7	5	5	5
C (g/100mL)	1	1	1	1	0.2	0.2	2	2	0.2	0.2	2	2	1	1	1

Result and discussion

Effect of independent parameter on Lead absorption

According to the Figure 1, increasing the pH to 5 led to increase the Lead ions absorption, but rise of pH to 7 reduced absorption of Lead. The reason of this pneumonia is due to change of Lead ion structure to molecular state in alkaline pH. While in lower pH, competition hydrogen ions with cations decrease the absorption of metal ions [17]. Also, at lower pH, the concentration of hydrogen ion is high and consequently the competition between metal ions and hydrogen ions is great for adsorbing on the absorbent surface. By adsorbing the hydrogen ions on absorbent surface, ionic repulsion is created. On the other hand, in higher value of pH due to increasing of hydroxide ions, the formations of metal hydroxides are increased and as a result the rate of absorption in decreased [11].

Increasing of absorbent quantity raises the surface contact and as results the chance of collision ions is improved with absorbent particles. In the other words, high quantity of absorbent increases the required cites to attach ions. Increasing of temperature limits the formation of boundary layer around the absorbent due to reduce of solution viscosity. So, ion absorption is intensified [16].

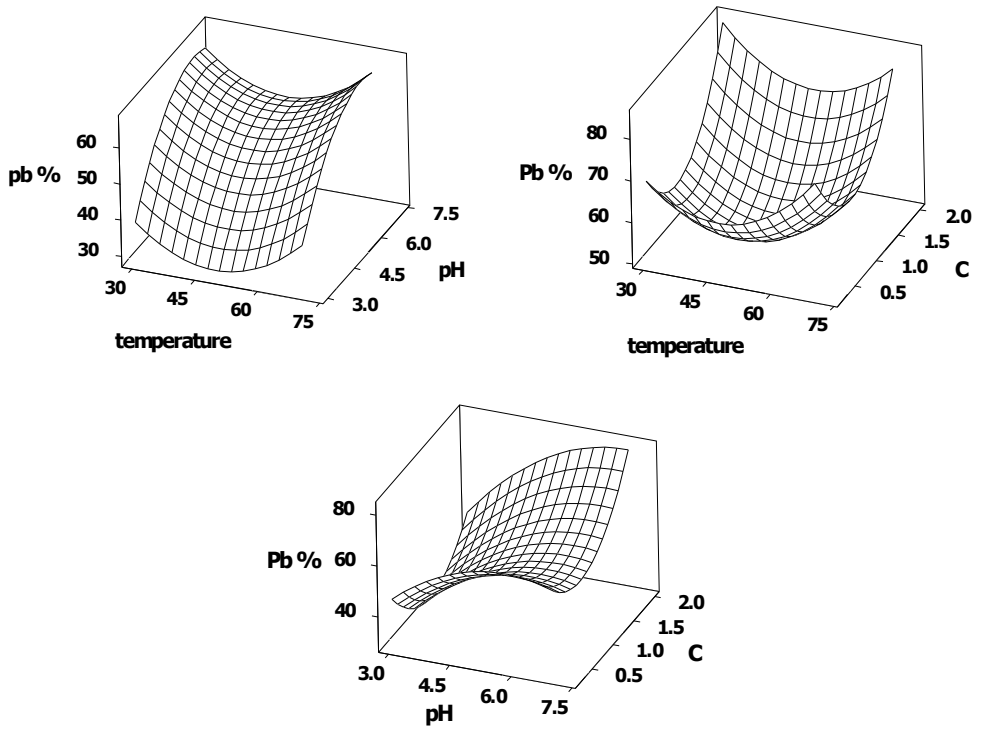

Figure 1. Effect of experimental variable on Lead absorption rate (Hold values are at temperature = 50 ^{o}C, pH 5 and C = 1.1)

Effect of independent parameter on Cadmium absorption

The effect of pH, temperature and absorbent concentration on the Cadmium absorption can be seen in the Figure 2. By increasing pH, Cadmium elimination was decreased due to conversion of ionic structure to molecular structure and formation of metal hydroxide due to exist of hydroxide ions. Cadmium absorption rate was also increased by enlarging of absorbent; because of exist the more cites for absorption [12]. Increasing temperature improved the absorption rate of cadmium due to decrease of viscosity and accelerate mass transfer.

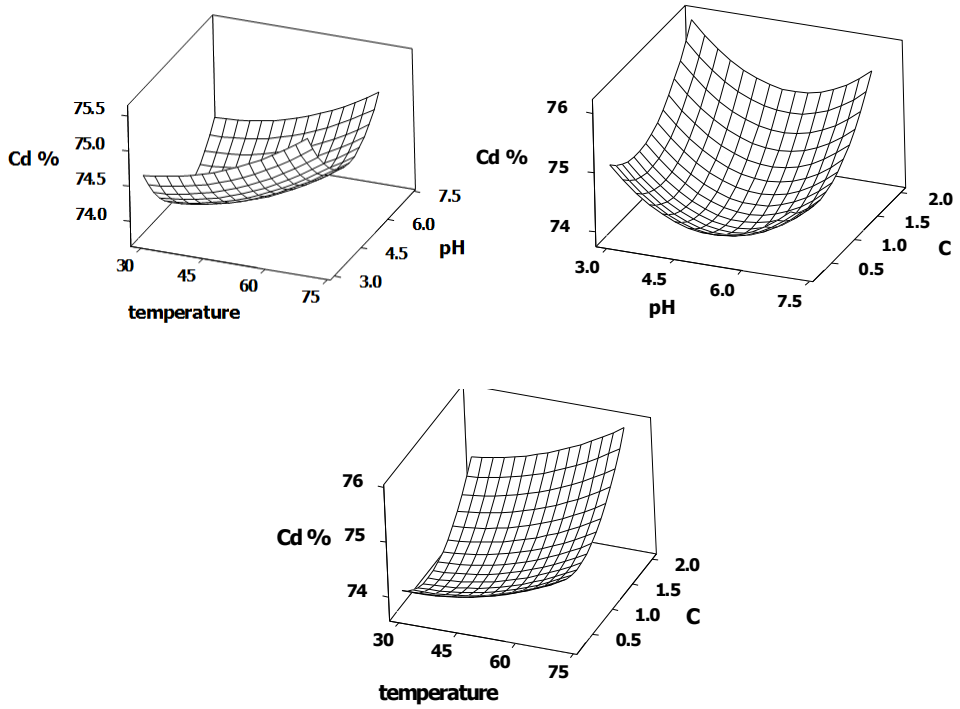

Figure 2. Effect of experimental variable on Cadmium absorption rate (Hold values are at temperature = 50 °C, pH 5 and C = 1.1)

Optimization

Minitab software was applied to optimization of experimental parameter. In setting section of software the goal of study was placed on maximum ions absorption. Also in this stage, must be graded the important of ions elimination. Since the risks of both ions from the point of toxicity and the health are same, the importance value of these indexes was considered equally.

Thus, the best conditions for maximum absorption ions were determined in the following conditions with satisfaction desirability (100%): temperature = 70 °C, pH 5 and concentration of absorbent= 2 g/100 ml (Figure 3). As shown in the Figure 4, in the best condition, Lead and Cadmium removal reached to 90.5 and 76.4%, respectively.

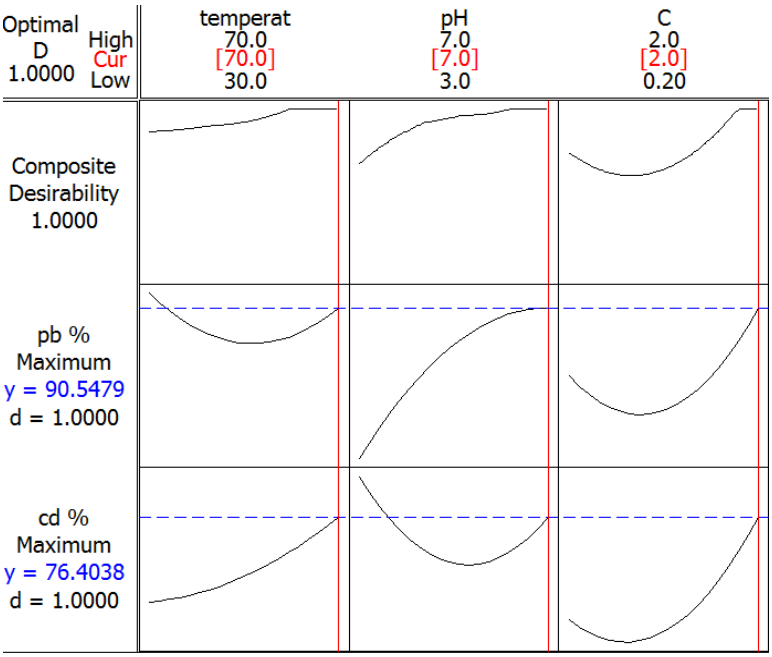

Figure 3. Determination of optimum experimental parameters by Minitab software

Table 2

Analysis of operational parameter and coefficient of full quadratic model

Source	DF	Lead			Cadmium		
		Coefficient	SS	P-Value	Coefficient	SS	P-Value
Model	9		3449.19	0.072		7.47662	0.026
Constant		51.4267		0	73.98		0.000
Linear							
T	1	0.8975	6.44	0.807	-0.4288	1.47061	0.019
P	1	12.7825	1307.14	0.014	-0.5162	2.13211	0.009
C	1	5.4	233.28	0.182	-0.21	0.35280	0.156
Quadratic							
T·T	1	10.2329	353.16	0.103	0.2825	0.25272	0.187
P·P	1	-9.2871	413.20	0.130	0.2525	0.22823	0.231
C·C	1	16.3829	991.02	0.024	0.06	0.01329	0.759
Interaction							
T·P	1	-0.0975	0.04	0.985	0.31	0.38440	0.142
T·C	1	-2.6125	27.30	0.619	-0.7675	2.35623	0.008
P·C	1	5.4225	117.61	0.321	0.2675	0.28623	0.193
Residual	5		485.46			0.63247	
Lack-of-fit	3		482.43	0.009		0.56587	0.154
Pure error	2		3.03			0.06660	
Total	14		3934.65			8.10909	
R^2 (%)		87.66			92.20		

After determination of optimum parameter, the study carried out at optimal conditions again. By applying these conditions, Lead and Cadmium ions were decreased 79.18 and 76.56% respectively from artificial solutions. Also, optimal conditions were tested on sugar industry wastewater, which results indicated the rate of absorption for Lead and Cadmium was obtained 98.98 and 76.1% respectively.

Conclusion

In this research the potential of Lead and Cadmium absorption was investigated by cherry core under the influence of different levels of temperature, pH and absorbent quantity variables with Response Surface Methodology statistical design. Results shown that, increasing temperature improved the absorption rate of cadmium due to decrease of viscosity and accelerate mass transfer. Increasing of temperature limits the formation of boundary layer around the absorbent due to reduce of solution viscosity. So, ion absorption is intensified. Also, Increasing of absorbent quantity raises the surface contact and as results the chance of collision ions is improved with absorbent particles. In the other words, high quantity of absorbent increases the required cites to attach ions. Cadmium elimination at high value of pH was decreased due to conversion of ionic structure to molecular structure. Cadmium absorption rate was also increased by enlarging of absorbent; because of exist the more cites for absorption. Increasing the pH to 5 led to increase the Lead ions absorption, but rise of pH to 7 reduced absorption of Lead. The reason of this pneumonia is due to change of Lead ion structure to molecular state in alkaline pH. While in lower pH, competition hydrogen ions with cations decrease the absorption of metal ions. The results showed, at optimal condition (T=70, pH 5 and C=2 g/100ml) the absorption rate for Lead and Cadmium reached to 79.18 and 76.56 % in artificial solution and 98.98 and 76.1% in sugar industrial wastewater respectively. The operational parameters in this research were effective on the variations of Temperature, pH and quantity of absorbent with appropriate R^2. Analysis of operational parameters effectiveness subject the full quadratic model summarized in the Table 2.

According to the Table 2, the full quadratic equations for adsorption rate of Lead and Cadmium were summarized as follows:

$$f_{Lead} = 51.4267 + 0.8975T + 10.2329T^2 + 12.7825P - 9.2871P^2 + 5.4C + 16.3829C^2 - 0.0975TP - 2.6125TC + 5.4225PC$$

$$f_{Cadmium} = 73.98 - 0.4288T + 0.2825T^2 - 0.5162P + 0.2525P^2 - 0.21C + 0.06C^2 + 0.31TP - 0.7675TC + 0.2675PC$$

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Drying rate and quality attributes of foam-mat dried tomato pulp

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Abstract

Introduction. Tomato is a short duration fruit that deteriorates easily after harvest, hence the need to process it using foam-mat drying as a technique, to produce tomato with good quality and investigate some process parameters (foaming agent and foam stabilizer concentration) that can influence drying rate and quality of the dried powder.

Materials and Methods. Randomized complete block design was used with about 27 samples of tomato pulp using egg white as foaming agent at 3 levels of concentration 5%, 10% and 15% and carboxyl methyl cellulose (CMC) at 0.2%, 0.4% and 0.8% the whipping time at 3 minutes and the samples were dried in a cabinet dryer at 70 °C.

Results and Discussion. The result show that the mean for samples treated with foaming agent concentration at 5%, 10% and 15% had drying rates of 19.21 g/hr, 21.53 g/hr and 20.46 g/hr, protein content of 24.66%, 24.72% and 24. 77% and vitamin C content of 1.70%, 1.44% and 1.34% respectively while those treated with CMC concentration at 0.2%, 0.4% and 0.8% had drying rates of 18.74 g/hr, 20.68 g/hr and 21.78 g/hr, protein content of 24.71%, 24.71% and 24.74% and vitamin C content of 1.43%, 1.56% and 1.49% respectively. Analysis of Variance shows that foaming agent and foam stabilizer concentration had no significant effect on drying rate at $P \leq 0.05$, but foaming agent had significant effect on protein and vitamin C contents of the sample. Analysis of Variance also shows that the interaction that exist between foaming agent and foam stabilizer had significant effect on the vitamin C and protein content of the sample but had no significant effect on the drying rate at $P \leq 0.05$. Furthermore the New Duncan Multiple Range Test (NDMRT) shows the means of protein content 24.66%, 24.72% and 24.77% at foaming agent concentration of 5%, 10% and 15% respectively.

Conclusions. Foaming agent concentration is an important parameter that influences the quality attributes of foam-mat dried tomato. In order to achieve maximum retention of the vitamin C content of foam-mat dried tomato pulp, 5% concentration of the foaming agent (egg albumin) is more ideal compared with higher concentrations as this will go a long way to minimize overall cost incurred during foam-mat drying process.

Introduction

Tomato (*Lycopersicon esculentum*) is a fruit of high economic value and importance. It is widely consumed in Sub-Saharan Africa, Nigeria inclusive [1] and other parts of the world [2, 3]. It is a fruit consumed on daily basis by people due to its enriching nutritional values, tomato has been known to be a supplier of important nutrients to the human body as one medium sized is capable of supplying the body with 57%, 35% and 8% of the Recommended Daily Allotment (RDA) of vitamin C, vitamin A and iron, respectively [4]. Tomato fruit has been known for its potency to help boost body immune system and as well prevent against some common and deadly diseases such as prostate, lung and stomach cancer [5, 6]. As good as tomato fruit is in Nigeria; it is relatively scarce during its off season and as result quite expensive following its season of abundance in large quantities and substantially wasted due to inadequate postharvest handling, processing and storage techniques. One major problem is that tomato is a short duration fruit which easily deteriorates after harvest leading to heavy postharvest losses [7]. As a result it is important to process the fruit, which will minimize wastages incurred and as well make the fruit readily available throughout the year for consumption. Drying has been known to be an economical food processing technique and is gaining popularity in Nigeria [7]. Drying has numerous methods which include Foam-mat drying, spray drying, vacuum drying, solar drying, hot-air drying, freeze drying, microwave drying, infra-red drying, drum drying, fluidized bed drying and osmotic drying etc.

Among these, foam–mat drying is considered to be advantageous in terms of drying of the foams at lower temperature compared with other methods of drying non-foamed materials in the same dryer type [8]. Also the residence time of the product in the dryer is shorter, since there is increased surface area by incorporation of air/gas which increases exposure to heat and aids mass transfer during drying. Drying by foam is a process in which liquid is beaten by various means to form stable foam that is then dried by evaporation of the water in form of thin layer [9]. According to [10], foams-mat process involves drying thin layers of foamed material in heated un-dehumidified air at atmospheric pressure and is reported to be considerably cheaper than vacuum, freeze and spray drying methods. The structure, expansion and stability of the foam provide an important function in the movement of the moisture during drying and, consequently, in the food quality [11, 12]. Foam drying allows for the processing of biomaterials that are difficult to dry, such as tomato paste and also allows for the production of materials that can easily rehydrate and retain several quality indicators, such as colour, aroma, texture and nutritional values. It is in view of this, this study was carried out purposely to investigate the effects of foaming agent and foam stabilizer on protein and vitamin C contents of powdered tomato.

Materials and Methods

Materials

The experiment was conducted in the department of food engineering, university of Ilorin, Ilorin, Nigeria at average room temperature of 31 °C and relative humidity of about 60%. Roma tomato fruits that were considered to be fresh, firm, and ripe were purchased from Oja-Oba market in Ilorin, Kwara State, Nigeria. The tomato fruits were sorted according to size and shape in order to ensure uniformity of the samples. Thereafter the samples were washed under running water and sanitized. The samples were blanched with

steam for 20 seconds to deactivate any enzyme activity and as well hinder the growth of microbes. The samples were deseeded sliced in quarters and were blended with an electric jug blender (Model no. SB-211, 350 W) to form tomato paste. The tomato paste was poured to fill the square containers made with stainless steel of 0.000144 m^3 volume.

Methods

All the containers were foamed with egg whites at different concentrations of 5%, 10% and 15% and carboxyl methyl cellulose (CMC) was used to stabilize the foam at different concentrations of 0.2%, 0.4%, and 0.8% according to the experimental treatment layout. The mixtures were agitated with the blender (which was opened at the top to admit in air) to produce foams at constant whipping time of 3 minutes. The experiment was conducted in a 3^2 factorial experiment in Randomized Complete Block Design (RCBD) with each of the treatments replicated thrice to ensure reliability of the experiments' result. Therefore the nine (9) treatments resulted in a total of 27 samples altogether. The containers with the samples labelled appropriately with tags based on their treatments and were loaded onto a mechanical dryer designed and constructed for this experiment (see the exploded view of the dryer in Figure 1). The dryer was run for 10 minutes at 70 °C and the temperature was monitored in the dryer with the aid of thermometers to ensure it has reached the desired temperature before the samples were loaded onto it. This temperature was chosen because it was considered to be the best for foam mat drying of tomatoes [13, 14]. During the process of drying the samples were being weighed with a weighing scale (CL 201) on hourly basis to determine their moisture loss and were recorded, drying process was terminated when the samples have reached a moisture content of 4.5% (db) and this took an average drying time of four (4) hours. Scrapers are used to scrape the dried tomato samples out of the containers and allowed to cool and then packaged in polythene with tags and were immediately taken to the laboratory for proximate analysis.

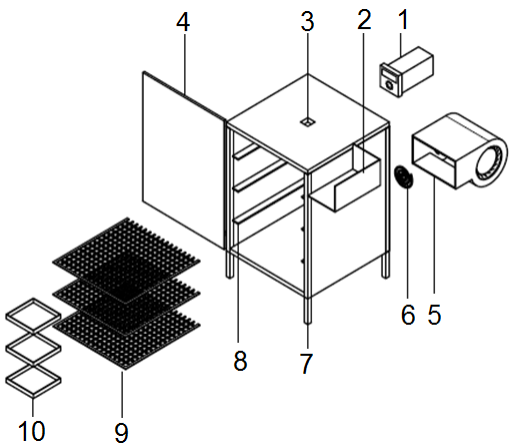

Figure 1. Exploded view of the mechanical dryer:
1 – Heat Regulator; 2 – Heat Regulator Frame ;3 – Chimney; 4 – Door;
5 – Blower; 6 – Heating Element; 7 – Frame/Stand; 8 – Tray Holder;
9 – Main Tray; 10 – Loading Tray; 11 – Dryer Tray/Net

The Drying rates of the samples were calculated based on the formula from [15]

$$R = \frac{dm}{dt} = \frac{m_i - m_f}{t} \quad (1)$$

where: R – Drying rate (g/hr)
dM – Change in mass (g)
dt – Change in time (hr)
t – Total time (hr)
m_i – Initial mass of the sample (g)
m_f – Final mass of the sample (g)

Proximate composition analysis was carried out at the Chemistry department laboratory to determine the vitamin C and protein contents of the dried samples using AOAC method [16].

Statistical analysis was carried out using a software SPSS version 16.0 to analyse the data at the level of significance of individual treatments and their interaction with one another at ($p \leq 0.05$) using analysis of variance (ANOVA).

Results and Discussion

Effects of foaming agents and foam stabilizers on the drying rate

Analysis of variance (ANOVA) table is presented in Table 1 to show the effect of foaming agent and foam stabilizer on the drying rate of foam-mat dried tomato powder as it can be seen in the table both foaming agent and foam stabilizer had no significant effects on the drying rate of the dried samples at $P \leq 0.05$ this result is similar to the findings of [17] that foaming agent concentration had no significant effect on the foam density of tomato pulp; and [18] and [12] had earlier stated that lower density of foamed materials are responsible for increased drying rate as a result of increased contact surface and interfacial area. That foam stabilizer had no significant effect on the drying rate of foam-mat dried tomato powder.

Table 2 was used to show the effects of various concentration of foaming agent (egg white) on the rate at which the samples dried using the new Duncan's multiple range test (NDMRT), from the table the use of foaming agent at 5%, 10% and 15% show mean drying rates of 19.21, 21.53 and 20.46 g/hr respectively which show that the fastest rate of drying was achieved with samples treated with 10% foaming agent and the slowest with those treated with 5% foaming agent but Table 2 also show that at significant level of $P \leq 0.05$ the use of foaming agent at various concentration had no significant differences from each other. This implies that varying foaming agent concentration may not be necessary when trying to get optimum drying rate.

Table 3 show the effect of foam stabilizer, carboxyl methyl cellulose (CMC) at different concentrations on the drying rate. Samples treated with 0.20%, 0.40% and 0.80% of CMC had mean drying rates of 18.74, 20.68 and 21.78 g/hr respectively. These show that the fastest drying rate was achieved at 0.80% CMC concentration, however the new Duncan's multiple range test (NDMRT) in Table 3 has been used to compare the mean of drying rate at different concentrations of CMC which reveals that they were not significantly different from each other statically at $P \leq 0.05$. Therefore energy, time and

resources should not be wasted varying foam stabilizer concentration when the aim of the drying experiment is to enhance drying rate. As it shown in Table 4 the interactive effect of foaming agent and foam stabilizer on drying rate is not significant at P≤0.05.

Table 1

Results of the analysis of variance (ANOVA) of effect of foaming agent and foam stabilizer on drying rate, vitamin C and protein content of foam-mat dried tomato pulp

SV	DF	SS	MS	F	Sig.
	Drying Rate (g/hr)				
Foaming Agent	2	8.09	4.05	1.10	0.39
Foam Stabilizer	2	14.25	7.12	2.68	0.15
	DF	**SS**	**MS**	**F**	**Sig.**
	Protein Content (%)				
Foaming Agent	2	0.020	0.01	26.31	0.001*
Foam Stabilizer	2	0.002	0.001	0.26	0.78
	DF	**SS**	**MS**	**F**	**Sig.**
	Vitamin C (%)				
Foaming Agent	2	0.204	0.10	7.87	0.02*
Foam Stabilizer	2	0.023	0.01	0.26	0.78

**Significant at P ≤0.05*

SV – Sources of Variation; DF – Degree of Freedom; SS – Sum of Squares; MS – Mean Squares; F – variance of group means per mean of within group variances; Sig. – Significant, P – estimated probabilities from experimental data.

Table 2

New Duncan multiple range test (NDMRT) of the effect of foaming agent on drying rate, vitamin C and protein content of foam-mat dried tomato pulp

Foaming Agent (%)	5	10	15
Drying Rate (g/hr)	19.21^{a}	21.53^{a}	20.46^{a}
Protein Content (%)	24.66^{a}	24.72^{b}	24.77^{c}
Vitamin C (%)	1.70^{a}	1.44^{b}	1.34^{b}

Means with the same letter are not significantly different from each other at P≤0.05

Table 3

New Duncan multiple range test (NDMRT) of the effect of foam stabilizer on drying rate, vitamin C and protein content of foam-mat dried tomato pulp

Foam Stabilizer (%)	0.20	0.40	0.80
Drying Rate (g/hr)	18.74^{a}	20.68^{a}	21.78^{a}
Protein content (%)	24.71^{b}	24.71^{b}	24.74^{b}
Vitamin C (%)	1.43^{c}	1.56^{c}	1.49^{c}

Means with the same letter are not significantly different from each other at P≤0.05

Table 4

Analysis of variance (ANOVA) showing the interactive effects of foam agent and foam stabilizer on the drying rate, protein and vitamin contents of foam-mat dried tomato pulp

SV		DF	SS	MS	F	Sig.
Foaming Agent (FA) x Foam Stabilizer (FS)	Drying Rate (g/hr)	2	14.947	7. 73	2.947	0.128
	Protein (%)	2	0.022	0.11	85.123	0.000*
	Vitamin C (%)	2	0.193	0.097	6.509	0.031*

**Significant at P ≤0.05*

SV – Sources of Variation; DF – Degree of Freedom; SS – Sum of Squares; MS – Mean Squares; F – variance of group means per mean of within group variances; Sig. – Significant, P – estimated probabilities from experimental data.

Effects of foam agent and foam stabilizer on the protein content of foam-mat dried tomato pulp

The ANOVA in Table 1 has shown that the effect of foaming agent concentration is highly significant on the protein content of treated samples at P≤0.05 significant level but foam stabilizer concentration had been found not to have any significant effect at this level. Table 2 has shown that foaming agent at various concentrations of 5%, 10% and 15% had mean protein content of 24.66, 24.72 and 24.77% respectively, which shows that there is increase in the value of protein retention of the samples as the foaming agent concentration increases and Table 2 has further shown through NDMRT that the mean of the samples were significantly different from one another at P≤0.05. Therefore it is important to vary foaming agent concentration and know the best one when the aim of the drying experiment is to have maximum retention of quality parameter such as the protein content. Table 3 has also shown the effect of foam stabilizer concentration on the protein content of the samples, which shows that at 0.20%, 0.40% and 0.80% CMC concentration, the mean protein content of the samples were 24.71, 24.71, 24.74% respectively and the NDRMT has shown that the means were not significantly different from one another at P≤0.05. Table 4 reveals that the interaction between foaming agent and foam stabilizer had significant effects at P≤0.05 on the protein content of the treated samples.

Effects of foam agent and foam stabilizer on the vitamin C content of foam-mat dried tomato pulp

Analysis of variance in Table 1 has shown that the effect of foaming agent concentration is significant on the vitamin C content of treated tomato at P≤0.05, but the effect of foam stabilizer concentration had no effect on the vitamin C concentration. These were further expressed in Table 2 and 3 using the NDRMT which in Table 2 show that foaming agent at 5%, 10% and 15% had mean values of vitamin C to be 1.70, 1.44 and 1.34% respectively, hence it can be infer that increase in foaming agent concentration led to decrease in the value of vitamin C retention this is similar to the findings of [19] on papaya pulp vitamin C content reduction with increased foam thickness also in agreement with the findings of [14] that beta carotene (an antioxidant like vitamin C) content of mango pulp decreases with increased foaming agent concentration. The mean of vitamin C at different foaming agent concentration were significantly different from one another at P≤0.05.

Therefore concentration of foaming agent is an important factor to be considered when putting vitamin C content retention in mind as a quality parameter. The effect of foam stabilizer is also shown in Table 2, which shows that CMC concentration at 0.2%, 0.4% and 0.8% had 1.43, 1.56 and 1.49% respectively as mean value of vitamin C content. Therefore the highest value of vitamin C was obtained at 0.4% CMC concentration but NDMRT show that the means of vitamin C content of samples at different concentration were not significantly different from one another at $P \leq 0.05$. Table 4 further express the interaction between foaming agent and foam stabilizer which is found not to be significant on the vitamin C content of the treated samples.

Conclusions

1. Drying rate of treated tomato pulp samples which were foam-mat dried is neither dependent on the foaming agent concentration level nor the foam stabilizer concentration level
2. Foaming agent concentration had significant effect on the protein content of treated tomato pulp samples, and increased foaming agent concentration resulted in increased protein content retention but foam stabilizer concentration had no significant effect at all on the protein content. Meanwhile the interaction between the two factors is considered to be highly significant on the value of protein derived.
3. Vitamin C content is an important quality parameter which is found that the foaming agent concentration had significant effect on its value, whereas foam stabilizer concentration had no significant effect on its value. But the interaction between the two factors is significant on the vitamin C level derived.
4. It is recommended that other factors should put into consideration for further research to ascertain which of them would have significant effect on drying rate of treated tomato pulp which will be subjected to foam-mat drying.
5. The foam stabilizer used (CMC) could be mixed with some other chemical solution at a certain proportion within safe limit for human consumption to be used for further research to determine how it would be able to influence the quality parameter, such as
6. Vitamin C and protein content of treated tomato pulp undergoing foam-mat drying process.

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Main problems of personal insurance and directions of their solution in the context of increasing the competitiveness of the insurance market

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Abstract

Introduction. Since there are no data on correlation and regression analysis of the main indicators of personal insurance. Also with the aim of identifying the main problems of personal insurance and directions of their solution in the context of increasing the competitiveness of the insurance market, we have carried out correlation and regression studies on the interdependence of insurance premium receipts, insurance premiums life, life insurance, pension contributions and retirement benefits.

Materials and methods. Scientific research of the main problems of personal insurance was based on the application of the following methods: abstract-logical, system analysis and grouping for studying the main problems of the insurance market and directions of problem solving. The method of correlation-regression analysis was used to study the statistical interdependence between such indicator, the amount of insurance premiums and the number of insurance contracts, the sum of insurance premiums in general and insurance premiums for health insurance, as well as medical insurance payments, etc.

Results and discussion. The main risks of the personal insurance market are global risks (the cyclical nature of the development of the world financial and economic system), macroeconomic and microeconomic risks (rates of changes in the national economy and individual branches), financial risks (unsatisfactory financial condition of insurance companies, low quality of assets of insurers) and commercial risks.

Correlation regression analysis of indicators of life insurance showed high reliance life insurance premiums of total premiums collected, as the correlation coefficient is 0,669, the relationship between the studied elements directly, with determination coefficient of 0,447, that factor variable (gross premiums) determines the 44,7% rate dependent life insurance premiums. Similar to the dynamics and nature of the situation characterizing the dependence of pension payments from pension contributions, higher values of correlation coefficients and determination.

Conclusions. Increasing the competitiveness of the insurance market will help to overcome such risks to the personal insurance market as global risks, macroeconomic and microeconomic risks, financial and commercial risks. The main problems of personal insurance are defined by the low level of public confidence in insurers, insurers' fraud, the slow pace of economic restructuring and low incomes. In addition, the high level of dependence of life insurance premiums from the total amount of insurance premiums shows positive trends in the country's insurance market development.

Introduction

The analysis of the personal insurance market, problems and prospects for its development in most cases is not comprehensive. The advantage of the methodology chosen by us is the use for research of the theoretical and methodical apparatus, statistical data of the insurance market and the results of correlation-regression analysis. This approach will increase the level of scientific feasibility of the proposed optimization measures.

Formation of an effective and efficient insurance market of the country, with the aim of increasing the competitiveness of its subjects, requires a continuous analysis of the current state of development of insurance relations, identification of the main problems existing, as well as finding directions and methods for their solution. In addition, it should be noted that personal insurance market today needs special attention, as it is evident from its low development and popularity among the population in comparison with European countries.

The European experience of the functioning of the insurance market as a whole, as well as, in particular, the personal insurance sector, shows the positive significance of its development. The European insurance market is characterized by a large increase in the collection of insurance premiums [9, 20], and also shows an increase in the amount of insurance payments, which, of course, is positive for all participants in the insurance market [4]: insurance companies, insurers, insured persons and intermediaries [12].

A characteristic feature of the development of the insurance market of foreign countries is the use in its activities of a wide range of non-standard [25] and newest insurance products [1]. Insurance companies are increasingly gaining clients by offering innovative insurance services [22]. This situation, together with other advantages of the insurance market of foreign countries, gives the sector a significant competitive advantage over the markets of other underdeveloped countries [18], including Ukraine.

Competitiveness is an important element and a sign of the activity of an insurance company [7, 11], which enables to increase the volume of collected insurance premiums and to improve other indicators of the activity of the insurance company.

During the study of the insurance market Baldwin B. [5] worked on scientific work «The new life insurance investment advisor». Brockmeier, Warren G. [6] studied the impact of consumer activism on the insurance industry; Cummins, J. D., Neil Doherty, Gerald Ray, and Terri Vaughan [8] worked about the insurance brokerage industry. Hamilton, Karen L., and Cheryl L. Ferguson [11] investigated the personal risk management and property-liability insurance and Huebner, S. S., Kenneth Black, Jr., and Bernard L.Webb [12] worked about property and liability insurance.

The analysis of studies and publications showed that a lot of researchers are engaged in research into the insurance market and, in particular, personal insurance in Ukraine, among which M. Andrus [3], S. Achkasova, Ye. Malyshko [2], H. Gryb [10], K. Ponomarenko, O. Marchenko [5], N. Prykazyuk, S. Shymkiv [6], T. Smirnova, I. Topii, Z. Talama [23] and many others. At the same time, it should be noted that the problem of the improvement of medical insurance, which such scientists-economists worked for M. Telishevska, O. Oleksyuk [24], K. Ponomarenko, O. Marchenko [17] and many others.

The purpose of the study is to analyse the main problems and shortcomings of personal insurance, as well as to find directions for increasing the competitiveness of the Ukrainian insurance market, which can also be used to improve the insurance market of foreign countries.

The main condition for increasing the competitiveness of an insurance company and improving all its performance indicators is to eliminate existing shortcomings [8, 13] and use of modern areas of optimization of activities [5], implementation of advanced foreign and domestic experience [25].

Materials and methods

Materials

The study of the main problems of personal insurance and directions of their solution in the context of increasing the competitiveness of the insurance market was conducted on the example of the data of the insurance market of Ukraine on the number of insurance companies, the amount of insurance premiums and the amount of insurance payments for 2010-2016. Initial data for scientific research are obtained from the National Commission, which carries out state regulation in the field of financial services markets in Ukraine.

Methods

Scientific research of the main problems of personal insurance was based on the application of the following methods: abstract-logical, system analysis and grouping for studying the main problems of the insurance market and directions of problem solving. The method of correlation-regression analysis was used to study the statistical interdependence between such indicator, the amount of insurance premiums and the number of insurance contracts, the sum of insurance premiums in general and insurance premiums for health insurance, as well as medical insurance payments, etc. Observation methods, generalizations and descriptions were used to analyze the dynamics of the insurance market subjects, to study the main problems of personal insurance, as well as to determine the directions of increasing the competitiveness of the insurance market.

In order to inform the submission of materials regarding the insurance market indicators presented in tables 2 and 3, the monetary amounts were converted into US dollars at the rate of NBU 26,9 UAH / USD at the end of 2016.

Results and discussion

Risks of the insurance market

The functioning of the Ukrainian insurance market in modern conditions requires effective external and internal regulation, as the current situation speaks about the risks of reducing the efficiency of activities in the whole insurance market, and in particular, personal insurance.

Today, the insurance market, according to O. Shulyak and O. Martsenyuk-Rozaryonova [21] is under the influence of such risks:

1. The global risks caused by the cyclical character of the development of the world's economic and financial systems, as well as the inability to predict the time [16] and scale of the next crisis [6];
2. Macroeconomic and microeconomic risks [14] associated with the preservation of the tendency to reduce the growth rates of the national economy or individual industries;
3. Financial risks [11], which include unsatisfactory financial condition of a large part of insurers, low asset quality level [5], etc.;
4. Commercial risks [21].

Analysis of the dynamics of participants in the insurance market

Analyzed on the example of the insurance market of Ukraine, certain financial and economic indicators that are important for the study of personal insurance.

The number of insurance companies, non-state pension funds and their administrators in Ukraine for 2010-2016 tends to decrease, which may mean reducing the level of competition between the subjects of the insurance market and, consequently, will negatively affect the level and quality of personal services. Insurance of the population of the country (Table 1).

Table 1

Dynamics of the number of insurance companies, non-state pension funds and their administrators in Ukraine for 2010-2016 [15]

Financial institutions	2010	2011	2012	2013	2014	2015	2016
Insurance companies, including:	456	442	414	407	382	361	310
«non-life» insurance companies	389	378	352	345	325	312	271
«life» insurance companies	67	64	62	62	57	49	39
Non-state pension funds	101	96	94	81	76	72	64
Administrators of non-state pension funds	43	40	37	28	24	23	22
Total	600	578	545	516	482	456	396

Data of table 1 show that in 2016 the total number of operating insurance companies was 310, including 39 «life» insurance companies and 271 «non-life» insurance companies. The number of companies in the Ukrainian insurance market has been showing a tendency to decrease for a long time.

It has been determined [15] that during 2010-2016 the number of insurance companies decreased from 456 to 310 units, a decrease of 32,0 %, including non-life insurance companies from 389 to 271 insurers (a decrease of 30,3 %), and «Life» insurance companies from 67 to 39 insurance companies, that is, the reduction is 40,6 %. With regard to non-state pension funds, their number for the period under investigation decreased from 101 to 64, that is, the reduction was 36,6 %, while the number of non-state pension fund administrators changed from 43 in 2010 to 22 in 2016, a decrease of 21 units or 48,8 %. In general, the dynamics of all the subjects analyzed shows a decrease from 600 units in 2010 to 396 in 2016, a decrease of 34,0 % [15].

Analysis of dynamics of indicators of the insurance market

The volume of gross insurance premiums received by insurers and reinsurers during the 9 months of 2016 amounted to UAH 24,84 billion, which is 14,4% more than the same indicator for the 9 months of 2015 [15] (Table 2).

Table 2

Indicators of the activity of insurance companies and non-state pension funds in Ukraine for 2010-2016, USD millions [15]

Financial institutions	2010	2011	2012	2013	2014	2015	01.10. 2016
Insurance companies							
Income insurance premiums	888,5	873,1	826,9	1103,8	1030,8	1142,3	1353,8
Gross insurance premiums, including:	888,5	873,1	826,9	1103,8	1030,8	1142,3	1353,8
Life insurance	34,6	50,0	69,2	96,2	84,6	84,6	84,6
Gross insurance payments, including:	234,6	188,5	200,0	180,8	196,2	311,5	338,5
Life insurance	1,9	2,7	30,8	3,8	7,7	19,2	15,4
Insurance premiums from reinsurers	411,5	226,9	100,0	211,5	188,5	265,4	334,6
Payments offset by reinsurers	19,2	26,9	19,2	19,2	23,1	50,0	46,2
Non-state pension funds							
Pension contributions to the non-state pension system	34,6	42,3	50,0	61,5	69,2	73,1	73,1
Retirement benefits of the non-state pension system	7,7	7,7	11,5	11,5	15,4	23,1	23,1

Based on the data of the table 2 it is possible to state the unstable dynamics of gross insurance premiums and insurance payments, including payments to compensated reinsurers, as well as pension contributions and payments of the system of non-state pension provision in Ukraine during 2010-2016 [15].

In order to analyse the causal relationships between the main indicators of personal insurance on the example of the Ukrainian insurance market for 2010-2016, a correlation-regression analysis of insurance premiums and insurance premiums for life insurance, insurance premiums, and life insurance payments was made. Regarding non-state pension insurance, a correlation-regression analysis of pension contributions and pension payments on the example of the Ukrainian financial market for 2010-2016 was carried out.

Correlation and regression analysis of insurance premiums

Correlation and regression analysis of insurance premiums and life insurance premiums showed the following results:

1. The correlation coefficient (r) is 0,669;
2. The connection between the investigated elements is direct, the binding density (force) under the chaddock scale is notable;
3. The number of degrees of freedom (f) makes up 5;
4. The student's t-test makes up 2,012;
5. The critical value of student's t-test at the given number of degrees of freedom makes up 2,571;
6. The values dependence is statistically not significant ($p>0,05$);
7. The equation of the pair linear regression is as follows:

$$y = -0,26030 + 0,07950 \cdot x$$

8. The determination coefficient r^2 makes up 0,447 (the factorial characteristic x defines 44,7% of the dispersion of the dependent indicator y);
9. The average approximation accuracy (characterizes the adequacy of the regressive model) makes up 23,9%.

Important for a high level of scientifically grounded work on personal insurance is the study of the receipt of insurance premiums for life insurance payments. Correlation-regression analysis of insurance premiums and life insurance payments showed the following results. The correlation coefficient (r) is 0,032. The connection between the investigated elements is direct; the binding density (force) under the Chaddock scale is weak. The number of degrees of freedom (f) makes up 5; the Student's t-test makes up 0,071. The critical value of Student's t-test at the given number of degrees of freedom makes up 2,571; the values dependence is statistically not significant ($p>0,05$)

The equation of the pair linear regression is as follows:

$$y = 0,25391 + 0,00183 \cdot x$$

The determination coefficient r^2 makes up 0,001 (the factorial characteristic X defines 0,1% of the dispersion of the dependent indicator Y). The average approximation accuracy (characterizes the adequacy of the regressive model) makes up 170,6%.

Non-state pension insurance today is developing at a rather high pace in European countries, but Ukraine still exists for problems that hinder its stable development. Correlation and regression analysis of pension contributions and pension payments of the Ukrainian market showed the following results:

1. The correlation coefficient (r) is 0,895;
2. The connection between the investigated elements is direct;
3. The binding density (force) under the chaddock scale is high;
4. The number of degrees of freedom (f) makes up 5;
5. The student's t-test makes up 4,494;
6. The critical value of student's t-test at the given number of degrees of freedom makes up 2,571;
7. The values dependence is statistically significant ($p<0,05$);
8. The equation of the pair linear regression is as follows:

$$y = -0,19490 + 0,37755 \cdot x$$

9. The determination coefficient r^2 makes up 0,802 (the factorial characteristic X defines 80,2% of the dispersion of the dependent indicator Y);
10. The average approximation accuracy (characterizes the adequacy of the regressive model) makes up 17,5%.

Problems of the personal insurance market

Thus, moving to the consideration of the personal insurance sector in Ukraine, it is possible to distinguish its main problems [2, 10, 21]:

– Unfinished health insurance reform: state-owned healthcare facilities are not currently interested in co-operating with insurance companies [2];
– Unfinished pension reform: the second level of the pension system has not been introduced and the third level, which provides for the provision of old age by means of

pension programs of insurance companies or other financial institutions, is not sufficiently popular [19];
- Ineffective activity of lawmakers in the field of insurance - the insurance market of ukraine once again enters a new phase without a long-term development program [3];
- Low level of trust in the market of personal insurance and insurance culture of the population as a whole [25];
- Fraudsters of insurers, fake reinsurance, insufficient regulation of insurance mediation [7];
- Slow pace of economic restructuring, low level of solvency of the population, protracted political crisis [3].

Investigating the problems of life insurance, T. Smirnova, I. Topii, Z. Talama [23] divide them into external and internal ones. To the first group the scientist considers the following problems:
- Imperfect legal and regulatory support [23];
- Insufficient demand of individuals and legal entities for insurance services in life insurance [17];
- Lack of safe investment programs for long-term placement of insurance reserves;
- Low efficiency [5] of strategic management of insurers;
- The information security of insurance companies is rather large;
- Imperfect financial reporting and information processing methods [23].

Among the main reasons, the main ones are:
–Narrow assortment [19] of insurance services;
–Insufficient level of diversification of insurance products;
–Low level of customer service;
–Technological performance of insurance operations remains low [2];
–Inefficiency of the risk management system and internal control;
–Low development of information and analytical support system [23].

In addition, the main problems of methodical insurance in Ukraine can be attributed to:
- Low level of financing of health care system;
- Unsatisfactory quality of medical services and medical care, as well as outdated equipment [3];
- Ineffective structure of medical care;
- Low quality and expensive medicines and pharmaceuticals [17, 19, 20].

As for non-state pension insurance, S. Achkasova and Ye. Malyshko [2] determine such a hierarchical model of problems, the solution of which will positively influence the development of non-state pension insurance:
- 1 level – the lack of a stable and secure source of pension funds and the structural basis of non-state pension insurance;
- 2 level involves two problems, firstly, the unequal competitive conditions between non-state pension funds, life insurance companies, as well as banks in the field of non-state pension insurance; And secondly, the lack of guaranteed returns and access to liquid markets [6];
- 3 level – low development of the stock market of the country to provide a sufficient choice of instruments for the formation of investment income;
- 4 level – distrust and low awareness of non-state pension insurance [2, 3, 16].

Analysis of dynamics of indicators of the market of personal insurance

The studies selected for the analysis of personal insurance indices in Ukraine reflect the positive dynamics of growth of practically all indicators for 2010-2016 in Ukraine (Table 3).

Table 3

Indicators of personal insurance in Ukraine for 2010-2016, USD millions [15]

Indicators	2010	2011	2012	2013	2014	2015	2016
Number of contracts on compulsory personal insurance against accidents in transport, thousand pcs.	22,8	22,6	5,5	3,8	3,8	3,6	4,5
Gross insurance premiums of voluntary personal insurance	64,6	89,6	107,4	139,5	124,2	124,0	162,0
Net insurance premiums of voluntary personal insurance	58,1	81,6	102,7	118,5	106,5	116,9	152,7
Gross insurance premiums medical insurance	33,1	44,8	50,9	57,2	62,5	74,2	90,6
Net insurance premiums of medical insurance	31,1	41,8	49,2	53,7	58,0	79,2	87,7
Gross insurance payments of voluntary personal insurance	30,7	35,7	42,8	48,2	52,2	57,3	66,1
Net insurance payments of voluntary personal insurance	30,5	35,7	42,8	48,2	52,1	57,2	66,0
Gross insurance payments of medical insurance	24,3	28,9	34,7	38,9	42,6	46,1	51,6
Net insurance payments of medical insurance	24,3	28,9	34,6	38,9	42,6	46,1	51,5

Data of table 3 show that the most unstable tendency is characteristic of compulsory personal insurance contracts for transport accidents: there is a decrease in the number of contracts from 2010 to 2013, and there is no clear trend until the end of the analysis period. Regarding gross and net premiums and expenses presented in table 3, then we can talk about positive changes in these types of personal insurance, since the rates of insurance premiums and wasted during 2010-2016 years constantly increased.

Correlation and regression analysis of insurance premiums and number of contracts on compulsory personal insurance

For a more detailed study, it is necessary to carry out a correlation-regression analysis of the interdependence between the main indicators of personal insurance in Ukraine. As a result, we obtained the following data on the dependence of gross insurance premiums on voluntary personal insurance on the number of contracts on compulsory personal insurance against accidents in transport:

- The correlation coefficient (r) is -0,833;
- The connection between the investigated elements is reverse;
- The binding density (force) under the chaddock scale is high;
- The number of degrees of freedom (f) makes up 5;
- The student's t-test makes up -3,361;
- The critical value of student's t-test at the given number of degrees of freedom makes up 2,571;
- The values dependence is statistically not significant (p>0,05);
- The equation of the pair linear regression is as follows:

$$y = 3747,33189 - 0,00297 \cdot x$$

- The determination coefficient r^2 makes up 0,693 (the factorial characteristic x defines 69,3% of the dispersion of the dependent indicator y);
- The average approximation accuracy (characterizes the adequacy of the regressive model) makes up 12,9%.

The correlative regression analysis of the number of contracts for compulsory personal insurance against transport accidents and gross insurance premiums on voluntary personal insurance showed the following results.

The correlation coefficient (r) is -0,811. The connection between the investigated elements is reverse; the binding density (force) under the Chaddock scale is high. The number of degrees of freedom (f) makes up 5; the Student's t-test makes up -3,097. The critical value of Student's t-test at the given number of degrees of freedom makes up 2,571; the values dependence is statistically не значима (p>0,05). The equation of the pair linear regression is as follows:

$$y = 1509,73710 - 0,00110 \cdot x$$

The determination coefficient r^2 makes up 0,657 (the factorial characteristic X defines 65,7% of the dispersion of the dependent indicator Y). The average approximation accuracy (characterizes the adequacy of the regressive model) makes up 10,9%.

The analysis of the dependence of gross insurance premiums of health insurance on gross insurance premiums of health insurance using correlation-regression analysis showed the following results:

- The correlation coefficient (r) is 0,981;
- The connection between the investigated elements is direct;
- The binding density (force) under the chaddock scale is very high;
- The number of degrees of freedom (f) makes up 5;
- The student's t-test makes up 11,207;
- The critical value of student's t-test at the given number of degrees of freedom makes up 2,571;
- The values dependence is statistically значима (p<0,05);
- The equation of the pair linear regression is as follows:

$$y = 235,44914 + 0,49299 \cdot x$$

- The determination coefficient r^2 makes up 0,962 (the factorial characteristic x defines 96,2% of the dispersion of the dependent indicator y);
- The average approximation accuracy (characterizes the adequacy of the regressive model) makes up 4,2%.

Regulation in the field of financial services markets

In order to solve the problems of the insurance market as a whole, as well as personal insurance in particular, the Ukrainian federation of insurance developed anti-crisis measures in the insurance market. The main of these is the decision by the National Bank of Ukraine and the National Commission that carries out state regulation in the field of financial services markets regarding [10]:

- Provision of an effective mechanism for the unimpeded return of deposit funds to insurers, such as those that are at the expense of insurers' insurance reserves and are directed towards the payment of insurance indemnities;
- Ensuring the availability of insurance coverage of property held in a pledge in a commercial bank for the entire period of the loan agreement [25];
- Establishment of transparent and equal conditions for cooperation between banks and insurers;
- The decision of the national security and defense council of ukraine to grant the powers of the national commission, which carries out the state regulation in the field of financial services markets in countering the dumping on the insurance market and artificially reducing insolvency of the insurers during the financial crisis;
- Enhancement of institutional capacity and status of the national commission that carries out state regulation in the field of financial services markets;
- Explanations provided by the tax authorities of ukraine on the basis of the insurance and taxation legislation regarding the taxation of exchange differences and investment income;
- Expansion of the sphere of compulsory insurance, first of all, property insurance of citizens;
- Providing the ministry of internal affairs of ukraine with effective permanent control over the availability of policies for compulsory insurance of civil liability of car owners [3].

Life insurance is a key element of personal insurance, whose optimization in Ukraine provides, above all, the following measures:

- Improvement of the methodology of formation of reserves for life insurance;
- The introduction of tax incentives for insurers offering pension insurance programs and they should be in the same conditions as the state pension fund;
- Introduce tax breaks for legal entities who enter into life insurance contracts for their employees [14];
- Establishing conditions that would allow insurers to offer attractive capital accumulation programs and would be accessible to the wider public [23];
- Increase of efficiency of work of state structures and their cooperation with insurance companies, and also creation of associations of insurers on the most important insurance problems;
- Improvement of their legal, resource and organizational support;
- Improving the activities of insurance companies themselves and improving the quality of services they provide based on a single system of criteria [4, 9, 22];
- Creation of an optimal structure of the relationship between compulsory and voluntary insurance;
- Optimization of processes of protection of consumer rights, encouragement to purchase insurance services and formation of an insurance culture of the population [3].

As for health insurance, the main directions of its improvement are [17]:

- To transfer separate services of state-owned medical institutions to paid institutions for raising funds for the renewal of medical equipment;
- To reconstruct health care institutions taking into account the need of each region of the country;
- To increase state control over the quality of methodical services, while accrediting medical institutions;
- To improve the system of state control over prices and quality of pharmaceutical products [10];
- To increase the salaries of doctors taking into account the level of their qualifications and professionalism, as a method of reducing the risk of bribery;
- To conduct an annual review of citizens for the prevention of serious diseases;
- To provide health insurance available to every citizen of the country [17].

Conclusion

The development of personal insurance is an important and objective indicator of the development of financial and economic relations and the quality of life of citizens of the country. The functioning of the financial services market in Ukraine today lags behind a number of significant steps from the average European level. Not an exception is the insurance service for personal insurance, the dynamics of insurance payments and premiums, which although they show a positive character, but the socio-economic mechanism for the implementation of personal insurance still has certain disadvantages, and therefore needs a scientifically substantiated refinement. In today's business environment, raising the level of competitiveness of an insurance company requires management of an entity to use the elimination of deficiencies identified during the financial and economic diagnosis of an insurance company; it is also necessary to scientifically substantiate the use of advanced foreign and domestic experience management of an insurance company. In addition, the experience of the European insurance market shows the effectiveness of the application and introduction of the latest and innovative insurance products, as a method of forming the competitive advantage of an insurance company and increasing the amount of insurance premiums.

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Purchasing pattern of bakery products among working and non-working women in Central India: Effect of socio-economic factors

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Abstract

Introduction. Bakery products are items of mass consumption in view of its low price and high nutrient value. With rapid growth and changing eating habits of people, bakery products have gained popularity among masses.

Materials and Methods. About 200 working and 200 non-working women were selected by simple random sampling method from Central India, Maharashtra, India and the data was collected using interview cum questionnaire method. Purchasing pattern of five bakery products viz., bread, buns, biscuit, cake and pizza bread were studied with respect to age group, qualification, family size, number of earning members and family monthly income of the working and nonworking women.

Results and Discussion. The results of the study showed that the average age of working women was 39.39± 6.15 years and non-working women was 38.36±5.7 years. The average monthly income of working and non-working women was Rs. 38,125±19,550 and Rs. 40,625±20,825 respectively. Bread was found to be the most consumed bakery products among both types of families (79.5% in working and 83.5% non-working) followed by biscuits (76.5% in working and 70.5% non-working). The purchasing of buns, cake and pizza bread among working women were 7.5%, 19 % and 14% whereas among nonworking families it was 13%, 23% and 18.5% respectively. The significant associations were observed between the purchasing pattern of bread (p=0.000), biscuits (p=0.000) and cake (p=0.010) with the educational status of working and non-working women. The age group, family size, number of earning members and monthly income of working and non-working women did not show any association with the purchasing pattern of bakery products.

Conclusion. Purchasing of bakery products was same in both working and nonworking women. Among demographic characteristics, education of women significantly affected the purchasing pattern of bakery products.

Introduction

Increasing urbanization, lifestyle changes, more number of working women and nuclear families are some of the major factors leading to the rise in demand for processed foods all over the world. Shift in economic power and demographics and empowered consumers are expected to change consumer food preference. This trend is resulting in greater consumer expectations with regards to safety, quality, integrity and traceability of food across all emerging economics [1]. Consumption of bakery products was not in the Indian culture; however with changing eating habits of the people and with rising western influence on food consumption patterns, bakery products today have got takers from all age groups in the country. Bakery products are items of mass consumption in view of its low price and high nutrient value. With rapid growth and changing eating habits of people, bakery products have gained popularity among masses. The sector typically constitutes bread, cake and biscuits [2].

Bakery market research is a necessity because the knowledge of specific correlations determines positive effects both for producers who can properly size the activities, and consumers who can purchase their desired products in the quantities required, the price appropriate for their purchasing power and in the preferred range [3]. Several scientists [4, 5, 6] have carried out studies on buying behavior and consumer preference of different bakery products and its association with socio economic status of families. The average expenditure on Biscuits has a positive relationship with innovative buying behavior, social factors, health factors, lifestyle and pester power [6]. The demographic variables such as age group, gender and occupation are having less impact on the factors of customer satisfaction [5]. Various important factors that affect the behavior of the customer consuming Biscuits are packaging, pricing, availability, quality, brand etc [7]. Taste was the most important factor which affects the customers buying decision and least important is nutritional value of the bakery products .The other important factors is the rate that changes the mind of customers [8]. However, there are negligible studies carried out in Central India on purchasing pattern of bakery products, particularly with reference to working and non working women. Hence the present study was proposed to be carried out on purchasing pattern of bakery products of working and non working women in Central India.

The objectives:

1. To study the socio-economic conditions of working and non-working women in Central India.
2. To assess the purchasing pattern of bakery products by working and non-working women of Central India.
3. To study the relationship between purchasing pattern of Bakery products and socio-economic conditions of working and non-working women of Central India.

Materials and methods

The present study was conducted in Nagpur City of Central India, Maharashtra, India. About 200 working and non-working women each were selected by judgmental sampling method. The working women were selected from schools, colleges, hospitals and different institutions. The non-working women were selected from kitty parties, temples, gardens etc. A structured questionnaire was developed to assess the socio- economic conditions and purchasing pattern of Bakery products. The questionnaire cum interview method was used to elicit information. Data was tabulated and was analyzed statistically using SPSS version 17. Mean, Standard Deviation and Chi square test were computed and the Confidence Interval was 95%.

Results and discussion

Demographic profile of women

Table 1 shows distribution of working and non-working women according to their demographic profile. The average age of working women was 39.39 ± 6.15 years and that of non-working women was 38.36 ± 5.7 years. The bakery products today have got takers from all age group in the country [4]. The majority of working women (33%) were post graduate with additional qualifications whereas majority non-working women were either only graduate (34%) or post-graduate (34.5%). The working women were significantly (χ^2 =53.45, p =0.000) more qualified than that of non-working women. About 50.5% working and 58% non-working women were from joint families. Also, majority of both working (65%) and non-working (52.5%) women had 1 to 4 members in their families and a significant association (χ^2 =7.48, p = 0.024) was also observed between the working status of women and family size. The number of earning members were significantly more (χ^2 =12.42, p=000) in working women's family (73%) as compared to non-working (58.5%) women. The average monthly income of working women was Rs. 38,125 ± 19,550 and non-working women was Rs. 40,625 $\pm$ 20,825. The average income spent on food by working women was Rs. 8465.5 ± 5181.08 and non-working women was Rs.8625 ± 4716.25. The average monthly income spent on processed food for working and non-working women was Rs 1093.5 ± 1126.94 and Rs 1029 ± 972.60 respectively.

Purchasing Pattern of Bakery products

In the present era growing demand for the bakery products has become one of the most important necessities in the life of the people. Bakery products have become popular among different cross sections of population in recent years due to increased demand for convenient foods. Among bakery products, bread and biscuits are the most popular processed ready-to-eat food items in the country [9]. The purchasing pattern of bakery products by the working and non working women of the present study has been presented in Table 2.

According to Table 2 bread was found to be the most consumed bakery products among both types of families (79.5% in working and 83.5% non-working) followed by biscuits (76.5% in working and 70.5% nonworking). The purchasing of buns, cake and pizza bread among working women were 7.5%, 19% and 14% whereas among nonworking families it was 13%, 23% and 18.5% respectively. Though an insignificant association was observed between the working status of women and purchasing pattern of bakery products (p=0.293).

Table 1

Demographic profile of working and nonworking women

SN	Demographic Parameters	Category	Number of Women		
			Working N=200	Non-working N =200	Total
1	**Age(Years)**				
		30–35	63(31.5)	71(35.5)	134
		36–40	59(29.5)	70(35.0)	129
		41–45	39(19.5)	30(15.0)	69
		46–50	39(19.5)	29(14.5)	68
	Mean Age M + SD	39.39±6.1		38.36±5.7	
2	**Qualification**	Undergraduate	14(7.0)	5(2.5)	19
		Graduate	28(14.0)	68(34.0)	96
		Graduate+	54(27.0)	33(16.5)	87
		Post Graduate	38(19.0)	69(34.5)	107
		Post Graduate+	66(33.0)	25(12.5)	91
3	**Family Type**	Nuclear	99(49.5)	84(42.0)	183
		Joint	101(50.5)	116(58.0)	217
4	**Family Size**	1–4 members	130(65.0)	105(52.5)	235
		5–0 members	69(34.5)	91(45.5)	160
		Above 10 members	1(0.5)	4(2.0)	5
5	**Earning Members**	1 member	17(8.5)	117(58.5)	134
		2 member	146(73.0)	47(23.5)	193
		above2 members	37(18.5)	36(18.0)	73
6	**Monthly Income(Rs)**	Up to 25,000	57(28.5)	43(21.5)	100
		25,000–50,000	77(38.5)	71(35.5)	148
		Above 50,000	66(33.0)	86(43.0)	152
	M + SD	38,125±19,550		40,625±20,825	
7	**Monthly Income Spent on food (Rs)**	Up to 10,000	162(81.0)	164(82.0)	326
		11000 to 20000	35(17.5)	34(17.0)	69
		Above 20000	3(1.5)	2(1.0)	5
	M + SD	8465.5±5181.08		8625±4716.25	
8	**Monthly Income Spent on Processed Foods (Rs)**	Up to 10000	149(74.5)	159(79.5)	308
		11000 to 20000	37(18.5)	28(14.0)	65
		Above 20000	14(7.0)	13(6.5)	27
	M + SD	1093.5±1126.94		1029±972.60	

(Numbers in parenthesis indicates percent cases.)

Table 2

Distribution of women consumers according to purchasing pattern of bakery products

Bakery Products	Women		Total	$\chi^2$and p value
	Working	Non-working		
Bread	159(79.5)	167(83.5)	326	χ^2 = 4.938 p=0.293
Buns	15(7.5)	26(13)	41	
Biscuits	153(76.5)	141(70.5)	294	
Cake	38(19)	46(23)	84	
Pizza Bread	28(14)	37(18.5)	65	

(Numbers in parenthesis indicates per cent cases.)

Bread

According to Indian Bakery Industry, bread is a hygienically manufactured and packed snack food product available at comparatively cheap prices. Major consumers of bread are people from the lower middle class. It is also the most commonly available bakery product [2]. Though bread is not a staple food in the country, its consumption has increased over the years. In India it is still a secondary staple food when compared to *chapatti*, *puri* or *rice* [10]. Distribution of women of the present study according to demographic profile and purchasing of pattern of bread has been presented in Table 3.

Table 3

Distribution of women according to demographic profile and purchasing pattern of Bread

SN	Demographic parameters	Women		$\chi^2$and p value
		Working N=159	Non-working N=167	
1	**Age in years**			
	30–35	53(26.5)	59(29.5)	χ^2 = 1.685 p=0.640
	36–40	46(23.0)	56(28.0)	
	40–45	33(16.5)	29(14.5)	
	46–50	27(13.5)	23(11.5)	
2	**Qualification**			
	Undergraduate	12(6.0)	4(2.0)	χ^2 = 48.526 p=0.000
	Graduate	17(8.5)	58(29.0)	
	Graduate+	50(25.0)	30(15.0)	
	Post graduate	32(16.0)	55(27.5)	
	Post graduate+	48(24.0)	20(10.0)	
3	**Family Size**			
	1 to 4 members	100(50.0)	91(45.5)	χ^2 = 2.947 p=0.229
	5 to 10 members	58(29.0)	73(36.5)	
	11 and above members	1(0.5)	3(1.5)	
	Earning Members			
4	**1 to 2 members**	130(65.0)	138(69.0)	χ^2 = 1.506 p=0.471
	3 to 4 members	24(12.0)	27(13.5)	
	5 or more members	5(2.5)	2(1.0)	
5	**Monthly Income(Rs.)**			
	<25000	43(21.5)	34(17.0)	χ^2 = 2.835 p=0.242
	25000 to 50000	59(29.5)	60(30.0)	
	>50000	57(28.5)	73(36.5)	

(Numbers in parenthesis indicates per cent cases.)

The result from Table 3 shows that the purchasing of bread in both working (26.5%) and non-working women (29.5%) in 30–35 years of age group was highest whereas it was found to be lowest in the 46–50 years of group (working women 13.5% and non-working women 11.5%). The general trend indicated that with an increase in age group of women, there is a decrease in the purchasing of bread in the family. However an insignificant association ($\chi 2$ =1.685, p=0.640) was observed between the age group of women and purchasing pattern of bread in the family. Families exercise some of the most important social and group influence on individual consumer decision. The fundamental demographic forces of age, marital status and presence of children in the family can together place a major role in shaping individual and point purchase behavior [11].

According to qualification, the usage of bread was found significantly more in non-working graduate (29%) and graduate with additional qualification (25%) in working women category. With the decrease in education level, the increase in purchasing of bread was observed. The purchasing was found to be lowest in undergraduate category for both non-working (2%) and working (6%) women. The purchasing of bread was significantly associated ($\chi 2$ =48.526, p=0.000) with educational status of women. A study reports that young generation mostly prefer the bakery product and they are mostly popular in urban areas, due to awareness and literacy [9].

It was further observed that the purchasing of bread was highest in families with 1 to 4 members in both categories (50% in working women and 45.5% non-working women). With the increase in number of family members, the decrease in purchasing of bread was observed. Table 3 clearly depicts that there was negligible purchasing of bread in families having more than 11 members in both working (0.5%) and non-working women (1.5%). However, no significant association ($\chi 2$ =2.947, p=0.229) was observed between the number of family members and purchasing pattern of bread.

While analyzing the data based on earning members in a family, it was found that most of the consumers were from the families having 1–2 earning members in both working (65%) and non-working (69%) women. It was also found that as the number of earning members in a family increased the purchasing of bread decreased. For families having more than five earning members, the purchasing was very minimal in both working (2.5%) and non-working women (1%). But no association ($\chi 2$ =1.506, p=0.471) was observed between the number of earning members and purchasing of bread.

The consumers of bread were least in both working (21.5%) and non-working women (17%) categories where the monthly income was less than Rs. 25000. The maximum purchasing of bread based on income groups was found to be in Rs. 25000–50000 category for working women (29.5%) and whereas in case of non-working women (36.5%) it was in the greater than Rs. 50000 category. An insignificant association ($\chi 2$ =2.835, p=0.242) was observed between the monthly income and consumers of bread. The major consumers of bread are people from the lower middle class and economically weaker segments consuming more than 90 per cent of the bread industry's total production. Bread is the cheapest and basic instant food available for consumption [12]. The most important amongst all is price of bread which decides whether to buy or not. Some people are very particular about the colour, taste, flavour and texture of bread [8].

Buns

Burger is a salty bakery product and is made of buns and various vegetables. Burger is a readymade product available immediately on demand and it needs no time to prepare. India also has its share of fast food with *Samosa, Vada pav, Parathas* and various types of

*chat*s [13]. Distribution of women of the present study according to demographic profile and purchasing of pattern of buns has been presented in Table 4.

Table 4

Distribution of Women according to Demographic profile and purchasing pattern of Buns

SN	Demographic Parameters	Women		χ^2 and p value
		Working N=15	Non-working N=26	
1	**Age (years)**			
	30 –35	2(1.0)	7(3.5)	$\chi^2 = 1.753$ p=0.625
	36 – 40	7(3.5)	13(6.5)	
	41 – 45	2(1.0)	2(1.0)	
	46 – 50	4(2.0)	4(2.0)	
2	**Qualification**			
	Undergraduate	0(0.0)	0(0.0)	$\chi^2 = 5.896$ p=.117
	Graduate	2(1.0)	9(4.5)	
	Graduate+	4(2.0)	5(2.5)	
	Post graduate	4(2.0)	10(5.0)	
	Post graduate+	5(2.5)	2(1.0)	
3	**Family Size**			
	1 to 4 members	10(5.0)	15(7.5)	$\chi^2 = 0.322$ p=.570
	5 to 10 members	3(1.5)	6(3.0)	
	11 and above members	2(1.0)	5(2.5)	
4	**Earning Members**			
	1 to 2 members	14(7%)	22(11%)	$\chi^2 = 0.891$ p=.641
	3 to 4 members	1(0.5)	3(1.5)	
	5 or more members	0(0.0)	1(0.5)	
5	**Monthly Income(Rs.)**			
	<25000	3(1.5)	2(1.0)	$\chi^2 = 1.561$ p=.458
	25000 to 50000	6(3.0)	10(5.0)	
	>50000	6(3.0)	14(7.0)	

(Numbers in parenthesis indicates per cent cases.)

The study from Table 4 clearly shows that the usage of buns was very limited in both working and non-working women categories. The purchasing of buns was found to be highest in 36–40 years age group in working (3.5%) and non-working women (6.5%). The purchasing was lowest in 41–45 years age group of working women (1.0%) non-working women (1.0%). An insignificant association ($\chi 2$ =1.753, p=0.625) was found between age groups and purchasing of buns.

The purchasing of buns was found to be more in non-working (5%) post graduate women and working post graduate with additional qualification of women (2.5%). It was observed that as the education level increases, the purchasing of buns also increases. Though, insignificant association ($\chi 2$ =5.896, p=0.117) was observed between the purchasing of buns and qualification.

The purchasing of bun was highest for families having 1– 4 family members in both working (5%) and non-working women (7.5%). As the number of family members increase, the purchasing of bun decreases. No purchasing was found in families with more

than 11 members, hence no significant association ($\chi 2$ =0.322, p=0.570) was found between purchasing of bun and family members. In Meerut Region, there is a healthy demand of Burgers among the children, youths and adults due to its good taste, high calorific value, easy accessibility and reasonable price. But like other bakery products its demand is confined to urban areas [9]. Burger is most preferred Fast Food items by younger generation which prove that they preferred Fast Food items because of its taste, variety and quality which tells about their consciousness towards food [14].

The higher purchasing of bun was noted in families of working (7%) and non-working women (11%) with less number of earning members (one to two members). As the numbers of earning members increases the (more than five) the purchasing of bun decreases in non working women (0.5%) and no purchasing was observed in more than five earning members group. Although no association ($\chi 2$ = 0.891, p=0.641) was established between purchasing of bun and the number of earning members.

The purchasing of bun was higher in the high income group Rs>50000 in both working (3%) and non-working women (7%) as compared to low income group Rs<25000 in both working (1.5%) and non-working women (1%). It was found that as the income increased the purchasing of bun also increased. However monthly income and purchasing of bun did not show significant association ($\chi 2$ =1.561, p=0.458) between them.

Biscuit

Confectionaries like cake and biscuits have vital importance among the public irrespective of the age, sex and the preference of the individual in all parts of the world. So, from childhood to retirement age every one of used to take biscuits as a delicious food during morning and evening tea breaks. Children up to age group of up to a particular age limit they consume more amount of confectionary items [4]. The Indian biscuit sector is dominated by players like *Britannia, Parle* and *Sunfeast* brand [15]. From the Britannia Good Day Biscuit research, it is inferred that majority of 54% respondents are consuming Britannia biscuits and majority of 66% respondents coming under age group 15–25 years are consuming Britannia biscuits and 70% of male are consuming Britannia biscuits. The demographic variables such as age group, gender and occupation are having less impact on the factors of customer satisfaction [5]. Distribution of women of the present study according to demographic profile and purchasing of pattern of biscuit has been presented in Table 5.

Above data from Table 5 clearly shows that the purchasing of biscuits was highest in 30–35 age group of working (24.5%) and 36–40 age group of non-working women (26.5%). The purchasing of biscuits was lowest in 41–45 age group of working (13.5%) and non-working women (10%). However, no significant association ($\chi 2$ =2.461, p=0.482) was observed between the age group and purchasing of biscuits.

The purchasing of biscuits was found to be more for post graduate working women with additional qualification (28%) and graduate non-working women (26%). Least purchasing was found for the undergraduate women in both working (6%) and non-working (2%) women category. It was observed that as the education level increases, the purchasing of biscuits also increases. A significant association ($\chi 2$ =43.394, p=0.000) was observed between the non-working women educational qualification and the purchasing of biscuits.

Table 5

Distribution of women according to demographic profile and purchasing pattern of Biscuits

SN	Demographic Parameters	Women		χ^2 and p value
		Working N=153	Non-working N=141	
1	**Age (years)**			
	30–35	49(24.5)	43(21.5)	$\chi^2 = 2.46$ p=0.482
	36–40	45(22.5)	53(26.5)	
	40–45	27(13.5)	20(10.0)	
	46–50	32(16.0)	25(12.5)	
2	**Qualification**			
	Undergraduate	12(6.0)	4(2.0)	$\chi^2 = 3.394$ p=0.000
	Graduate	20(10.0)	52(26.0)	
	Graduate+	39(19.5)	24(12.0)	
	Post graduate	26(13.0)	42(21.0)	
	Post graduate+	56(28.0)	19(9.5)	
3	**Family Members**			
	1 to 4 members	98(49)	75(37.5)	3.75 p=0.197
	5 to 10 members	54(27.0)	64(32.0)	
	11 and above members	1(0.5)	2(1.0)	
4	**Earning Members**			
	1 to 2 members	123(61.5)	115(57.5)	$\chi^2 = 3.37$ p=0.185
	3 to 4 members	24(22.0)	25(12.5)	
	5 or more members	6(3.0)	1(0.5)	
5	**Monthly Income(Rs.)**			
	<25000	42(21.0)	30(15.0)	$\chi^2 = 3.703$ p=0.157
	25000 to 50000	58(29.0)	47(23.5)	
	>50000	53(26.5)	64(32.0)	

(Numbers in parenthesis indicates per cent cases.)

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The lesser the number of family members, higher the purchasing of biscuit in the family and vice versa was observed. Likewise the purchasing of biscuit was more in the family with one to four members in both working (49%) and non- working women (37.5%). Purchasing goes down in family with 11 and more members in both working (0.5%) and non working women (1%). However no association ($\chi 2$ =3.755, p=0.153) was observed between the family size and purchasing of biscuit. A study on factors influencing consumer decision making process towards biscuits showed that parents and children were more or less equally involved in decision making [16].

The highest usage of biscuit was found in families with one to two earning members in both working (61.5%) and non-working women (57.5%). The lowest usage of biscuit was found in families with five or more earning members in both working (3%) and non-working women (0.5%). However insignificant association ($\chi 2$ =3.377, p=0.815) was observed between the earning members in the family and purchasing of biscuit.

The purchasing of biscuit showed different trends in working and non working women in monthly income categories. The purchasing of biscuit was found to be increasing as the income of the family increases. The purchasing of biscuit was highest in those families

whose monthly income was in between Rs 25000 to 50000 of working women (29.5%) and monthly income Rs. >50000 of non-working women (32%). No association ($\chi 2$ =3.703, p=0.157) was observed between the monthly income and purchasing of biscuit. The average expenditure on Biscuits has a positive relationship with Innovative buying behaviour, Social factors, Health factors, Lifestyle and Pester Power [6]. The reason for buying *Sunfeast* Biscuits is its quality and while few of them prefers it for its low prices. About 39 respondents are consuming for its quality, 28 respondents prefer for its price, 23 respondents are consuming for taste, and 12 respondents prefer for its packages [17]. Various important factors that affect the behaviour of the consumer consuming biscuits are packing, pricing, availability, quality, brand etc [7].

Cake

Cakes are used in all parties and on all happy occasions. Mostly the young generation has developed the taste of this item. But the use of cakes is mostly confined to urban areas. These are not very popular in rural areas due to its low accessibility. It is not available everywhere except big bakeries [9]. Distribution of women of the present study according to demographic profile and purchasing of pattern of cake has been presented in Table 6.

Table 6

Distribution of women according to demographic profile and purchasing pattern of Cake

SN	Demographic Parameters	Women		χ^2 and p value
		Working N=38	Non-working N=46	
1	**Age(years)**			
	30–35	17(8.5)	20(10.0)	χ^2 = 5.454 p=.141
	36–40	8(4.0)	18(9.0)	
	40–45	7(3.5)	6(3.0)	
	46–50	6(3.0)	2(1.0)	
2	**Qualification**			
	Undergraduate	3(1.5)	1(0.5)	χ^2 = 13.377 p=.010
	Graduate	6(3.0)	16(8.0)	
	Graduate+	11(5.5)	5(2.5)	
	Post graduate	4(2.0)	14(7.0)	
	Post graduate+	14(7.0)	10(5.0)	
3	**Family Size**			
	1 to 4 members	24(12.0)	26(13.0)	χ^2 = 1.086 p=.581
	5 to 10 members	14(7.0)	19(9.5)	
	11 and above members	0(0.0)	1(0.5)	
4	**Earning Members**			
	1 to 2 members	30(15.0)	37(18.5)	χ^2 = 0.036 p=.982
	3 to 4 members	7(3.5)	8(4.0)	
	5 or more members	1(0.5)	1(0.5)	
5	**Monthly Income(Rs.)**			
	<25000	13(6.5)	9(4.5)	χ^2 = 2.895 p=.235
	25000 to 50000	14(7.0)	17(8.5)	
	>50000	11(5.5)	20(10.0)	

(Numbers in parenthesis indicates per cent cases.)

The data presented in Table 6 shows the distribution of women and purchasing of pattern of cake. The highest purchasing of cake was found for age group 30–35 in both working (8.5%) and non-working women (10%). The lowest purchasing of cake was found for age group 46–50 in both working (3%) and non-working women (1%). The purchasing of cakes is more in the younger age group under consideration in this study and it goes down gradually as we move to the elder age groups. However no association ($\chi 2$ =5.454, p=0.141) was observed between the age group and purchasing of cake.

The purchasing of cake was found to be more in post graduate with additional qualification of working (7%) and graduate non-working women (8%). Least purchasing was found for the undergraduate women in both working (1.5%) and non-working(0.5%) category. It was observed that as the education level increases, the purchasing of cake also increases. A significant association ($\chi 2$ =13.377, p=0.010) was observed between the non-working women`s educational qualification and the purchasing of cake. The education level of the survey respondents predominantly shops customers who have a high school education (52.7%). Most of the customers bakery is dominated by a student or students as many as 89 people or 36.3 per cent, private sector employees 54 people, or 22 percent, self-employed, housewives, other work and rest, which owns the smallest percentage of employees the country as many as 10 people or 4.1 percent [18].

Purchasing of cake was found to be highest for families with one to four family members in both working (12%) and non-working women (13%). Purchasing of cake was found to be lowest for families with more than 10 family members in both working (0%) and non-working women (0.5%). It was observed that as the number of family members increased, the purchasing of cake decreased. However, no significant association ($\chi 2$ =1.086, p=0.581) was observed between the number of family members and purchasing of cake.

Purchasing of cake was found to be highest for families with one to two earning members in both working (15%) and non-working women (18.5%). Purchasing of cake was found to be lowest for families with more than four earning members in both working (0.5%) and non-working women (0.5%)category. It was observed that as the number of earning family members increased, the purchasing of cake decreased. However, insignificant association ($\chi 2$ =0.036, p=0.982) was observed between the number of earning family members and purchasing of cake.

Highest purchasing of cake was found to be for families with income between Rs. 25000–50000 for working (7%) women. For non-working (10%) women the same was found to be for families with income more than Rs.50000. Purchasing of cake was found to be lowest for families with monthly income Rs. <25000 in both working (6.5%) and non-working women (4.5%)category. It was observed that as the monthly income of family increased, the purchasing of cake also increased. However, no association ($\chi 2$ =2.895, p=0.235) was observed between the monthly income of family and purchasing of cake.

Pizza bread

Pizza is a round shaped bakery product. It is the most common fast food popular among the people especially the youths and the children. It is salty in taste. It is made in many flavours such as cheese pizza, onion capsicum pizza, mushroom, pizza etc. It needs various raw materials to prepare it. It is prepared on pizza base pasting cream on it and adding vegetables, cheese, mushroom, spices sauce etc [9]. Distribution of women of the present study according to demographic profile and purchasing of pattern of pizza bread has been presented in Table 7.

Table 7

Distribution of women according to demographic profile and purchasing pattern of Pizza Bread

SN	Demographic Parameters	Women		χ^2 and **P Value**
		Working N=28	**Non-working N=37**	
1	**Age (years)**			
	30 –35	11(5.5)	10(5.0)	χ^2 = 2.886 p=0.410
	36 – 40	8(4.0)	16(8.0)	
	40 – 45	7(3.5)	6(3.0)	
	46 – 50	2(1.0)	5(2.5)	
2	**Qualification**			
	Undergraduate	1(0.5)	0(0.0)	χ^2 = 7.133 p=0.129
	Graduate	6(3.0)	17(8.5)	
	Graduate+	6(3.0)	4(2.0)	
	Post graduate	7(3.5)	11(5.5)	
	Post graduate+	8(4.0)	5(2.5)	
3	**Family Size**			
	1 to 4 members	12(6.0)	20(10.0)	χ^2 = 2.841 p=0.242
	5 to 10 members	16(8.0)	15(7.5)	
	11 and above members	0(0.0)	2(1.0)	
4	**Earning Members**			
	1 to 2 members	18(9.0)	29(14.5)	χ^2 = 2.434 p=0.296
	3 to 4 members	9(4.5)	8(4.0)	
	5 or more members	1(0.5)	0(0.0)	
5	**Monthly Income(Rs.)**			
	<25000	8(4.0)	3(1.5)	χ^2 = 5.351 p=0.069
	25000 to 50000	8(4.0)	10(5.0)	
	>50000	12(6.0)	24(12.0)	

(Numbers in parenthesis indicates per cent cases.)

Table 7 shows the distribution of women according to demographic profile and purchasing pattern of pizza bread. The highest purchasing of pizza bread was found for age group 30–35 in working (5.5%) women whereas in non-working women (6%) for 36–49 years of age group. The lowest purchasing of pizza bread was found for age group 46–50 in both working (1%) and non-working (2.5%) women. However insignificant association ($\chi 2$ =2.886, p=0.410) was observed between the age group and purchasing of pizza bread.

It was found that the purchasing of pizza bread was more in non-working graduate women (8.5%) and working post graduate with additional qualification women (4%). Less purchasing was found for undergraduate working women (0.5%) and no purchasing was found in non-working undergraduate women category. It was observed that as the education level increases the purchasing of pizza bread also increases. Hence insignificant association ($\chi 2$ =7.133, p=0.129) was observed between the educational qualification and the purchasing of pizza bread.

Purchasing of pizza bread was found to be highest for families with 5–10 family members in working (8%) and one to four family members in non-working women (10%)

category. No significant association ($\chi 2$ =2.841, p=0.242) was observed between the number of family members and purchasing of pizza bread.

Purchasing of pizza bread was found to be highest for families with 1 to 2 earning members in both working (0%) and non-working women (14.5%). However, insignificant association ($\chi 2$ =2.434, p=0.296) was observed between the number of earning members in the family and purchasing of pizza bread.

The purchasing of pizza bread was found to be more for families with income more than Rs. 50,000 in both working (6%) and non-working (12%) women. As the income of the family increases, the purchasing of pizza bread also increases. Less purchasing of pizza bread was found to be for families with income less than Rs. 25,000 for both working (4%) and non-working (1.5%) women. The purchasing of pizza bread was insignificantly associated ($\chi 2$ =5.351, p=0.069) with monthly income for non-working women category.

Conclusion

The present study was undertaken to assess the purchasing pattern of bakery products viz., bread, buns, biscuits, cake and pizza bread among working and non-working women in Nagpur city. Bread was the most purchased bakery items followed by biscuits, cakes, pizza bread and buns and did not show significant association with the working status of women (p=0.293). The educational qualification of working and non-working women showed significant associations with the purchasing of bread (p=0.000), biscuits (p=0.000) and cake (p=0.010). Demographic characteristics viz., age, family size, earning members and monthly income did not show any significant associations with purchasing pattern any of the bakery products.

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InoBioProd: innovation challenges and scientific perspectives

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Abstract

Introduction. InoBioProd represents the project under the title „Innovative product from goat milk with high biological properties" listed as independent project for young researchers, domain „Biotechnology", grant agreement No 16.80012.51.23A.

Materials and methods. Agrofood industrial wests and by-products are used as a source of bioactive copounds. At the same time goat milk, indigenous lactic acid bacteria and fermented milk products with high biological properties are main objects of research. Project intends application of standard and innovative methods and processes.

Results and discussion. The scientific results, in particular the expected technologies are absolutely innovative for the Republic of Moldova and are in the framework of the UNICEF recommendations for food and nutrition policy. InoBioProd contribues to the development of investigations in the field of food biotechnology, engineering technology, food chemistry and microbiology, offering a high potential for application: innovative methods for manufacturing of bioactive compounds from local food sources; chemical composition and functional potential of the bioactive compounds; characteristics of goat milk; isolation and identification of lactic acid bacteria from dairy products of spontaneous fermentation; symbiotic indigenous cultures of lactic acid bacteria; justified scientific manufacturing processes and recipes for fermented dairy products from goat milk and scientific development of methods for evaluation of the self-life of designed fermented dairy products. Special attention of InoBioProd gives to the elaboration of BSc, MSc and PhD thesis, dissemination of scientific results at national and international levels.

Conclusions. The Project was developed under the main provision of the local market - the lack of industrial production of the goat milk and products. In addition, it aims to initiate, develop and strengthen new collaborations of young scientists from R&D and higher education institutions.

Introduction

In many regions of the world, food industry follows similar trends: increasing affluence, demographic changes and enhance consumer awareness of health. This trend has led to increased demand for ingredients and natural food products. For this reason, food industry experts are concerned on development of new, innovative products with ingredients that have additional benefits. One of the present trends of consumers is a greater consumption of foods with high content in biologically active compounds with positive effects on health.

Likewise, consumer interest has increased for „clean label" foods, with low content or without synthetic additives, but at the same time with high innocuity. InoBioProd proposes the use of indigenous agrofood sources known to have antioxidant and antimicrobial potential in order to improve food quality and durability and, therefore, food safety of fermented dairy products from goat milk. In addition, InoBioProd is aimed to strengthen scientific knowledge, promoting scientific cooperation and encouraging the interaction between the research institution and higher education and the creation of a common and shared scientific results, information and knowledge. Development of fundamental and applied studies with a high impact on the field of food technology, valorisation of local agrofood sources through innovative methods with the possibility of their use in diversification of fermented goat dairy products is an important issue of the InoBioProd.

In the Republic of Moldova is observed upward trend in the herd of goats, which currently lists about 120-130 thousand heads and produce about 70 thousand tons of milk annually. Goat milk has a promising source of protein, vitamins, minerals and fatty acids [2, 4, 7]. Goat milk has better digestibility, reduced allergenicity, due to the low content of lactose [11, 15]. From goat milk usually obtain butter, yogurt, sour milk, catic. Fermented dairy products has delicios sensory properties, fine consistency and pleasant specific taste. In the Republic of Moldova goat milk is not used at industrial level and in the markets those dairy products from goat milk is absent. Currently Moldova has no scientific results about goat milk processing.

Internationally the theme proposed for research is carried out on the preparation and optimization of manufacturing technology of yogurt from goat milk [3, 10, 20]. There are also conducted research on the analysis of physical-chemical, microbiological and sensorial properties of yogurt from goat, bovine and cow milk [9, 13, 23]. There are comparative study on influence of the incorporation of synthetic and natural preservatives on the yogurt characteristics [6]. Some researchers conducted studies regarding the improvement of the properties of goat milk yogurt by adding aromatic oils and plant [1]. The study conducted by scientists from Bulgaria showed the possibility of yougurt supplimentation with fruit juice [5]. Documented results are aimed to understand the correlation between fortification with shell pineapple and physico-chemical and rheological properties of yogurt with probiotics [21]. The results of researchers from Sri Lanka have shown that incorporation of beetroot juice can be an insight to improve the characteristic organoleptic properties of goat milk [8]. A group of scientists studied the effect of Cinnamomum verum yogurt fortification with Allium sativum and the bifidobacteria [24]. The level of applied knowledge about technology production of yogurt from goat milk and nutritional properties in our country is lower compared to other developed countries.

The research team has already achieved certain results in the field (scientific results have been disseminated in research journals and communicated at different scientific events) [16-19]. Scientific and research activities planned under the Project InoBioProd is strictly necessary to extend these achievements and obtain some of innovative elements of research.

Mission of the InoBioProd

Integration of the Republic of Moldova into the European Union imposes special requirements on the quality of food products in the country. Increased worldwide demand for goat milk production due to impressive health benefits [22, 25]. Ministry of Agriculture and Food Industry of the Rpublic of Moldova also notes the need of manufacturing of these products on industrial scale, and lack of advanced technologies, normative documents regarding the quality and safety of those products in accordance with international regulations.

InoBioProd Project provides the development and further research with impact in valorisation of goat milk through innovative methods [12, 16]. In particular, it is planned to develop and diversify fermented dairy products with indigenous lactic acid bacteria with characteristic symbiotic and bioactive compounds with functional potential (Table 1).

InoBioProd research Project solves scientifical and practical problems. Project research team includes young competent specialists in organizing and conducting investigation. A strong innovation potential resulting from large-scale approach to technology development of fermented dairy products with high biological properties, due to the direct colaboration of specialists in food technology, biotechnology and microbiology.

Potential Activities of InoBioProd

The Project facilitate the development of science in the field, ensure increasing of research capabilities, innovation and dissemination of obtained scientific results and strengthening scientific collaboration of young researchers from R&D and higher education institutions.

Reseachers use obtained bioactive compounds from local agrofood sources in the manufacture of fermented dairy products from goat milk with indigenous lactic acid bacteria. The InoBioProd potential activities are organized in 4 Work Packagies, each managed by a work package leader responsible for the outcome and timing of its work package (Figure 1).

The figure 1 shows the graphical presentation of the four WPs and their independencies. WPs include also the main outputs, which will be obtained thanks to the planned activitiess. Relationship with Scientific and Practical Institute of Horticulture and Food Technologies (SPIHFT) and Technical University (TUM) are also highlighted.

Methods and experimental protocols

The research is organized into special teams according to the activity directions. The Project is designed with technological, physico-chemical, biochemical and microbiological standard methods, in accordance with the ISO (Official Methods of Analysis of AOAC International). Statistical method, including the analysis of experimental data by means of control charts X-R, S^2, and other methods are applied. The Project applies new methods and processes (Figure 2).

Table 1

Strategies of the InoBioProd Project

Concept	– The Project is oriented for production (from laboratory to market). – Elaboration of methods, technologies and technical regulations for fermented dairy products from goat milk. – Project includes strategic direction of development of innovative and competitive food product with positive implications on consumer health.
Objects	– Bioactive compounds from local food sources. – Goat milk. – Indigenous lactic acid bacteria. – Fermented dairy products with high biological properties.
Objectives	– Fabrication and characterization of bioactive compounds from local vegetal sources using innovative techniques. – Isolation, selection and testing of new indigenous lactic acid bacteria for fermentation of goat milk. – Development of technology to produce yogurt from goat milk. Recipes and technological flux that keep native and curative nutritional properties of goat milk. – Testing functional potential of bioactive compounds on the quality and self-life of yogurt. – Evaluation of the quality characteristics of yogurt from goat milk. Safety and inoffensiveness properties. – Establishing the self-life of yogurt. Methodology for the evaluation of yogurt shelf-life. – Preparing young specialists/researchers in the field of biotechnology, engineering technology, quality and safety through the development of BSc, MSc and PhD theses.
Ideas and original features	– Advanced Processing of local food sources to obtain bioactive compounds with functional potential. – Use of lactic acid bacteria with symbiotic characteristics from indigenous sources. – Creation of fermented dairy products from goat milk with high biological properties for consumers benefits.
Interdisciplinary character	– Novelty and unique methodological approach of the Project consists in different fields of application (biotechnology, engineering technology, chemistry, microbiology) to obtain original data for the creation of innovative product. – Project team consists from young researchers of different profiles that will ensure a comprehensive approach in goals achievement. – The Project intends collaboration of young and experiensed researchers in the field of food industry.

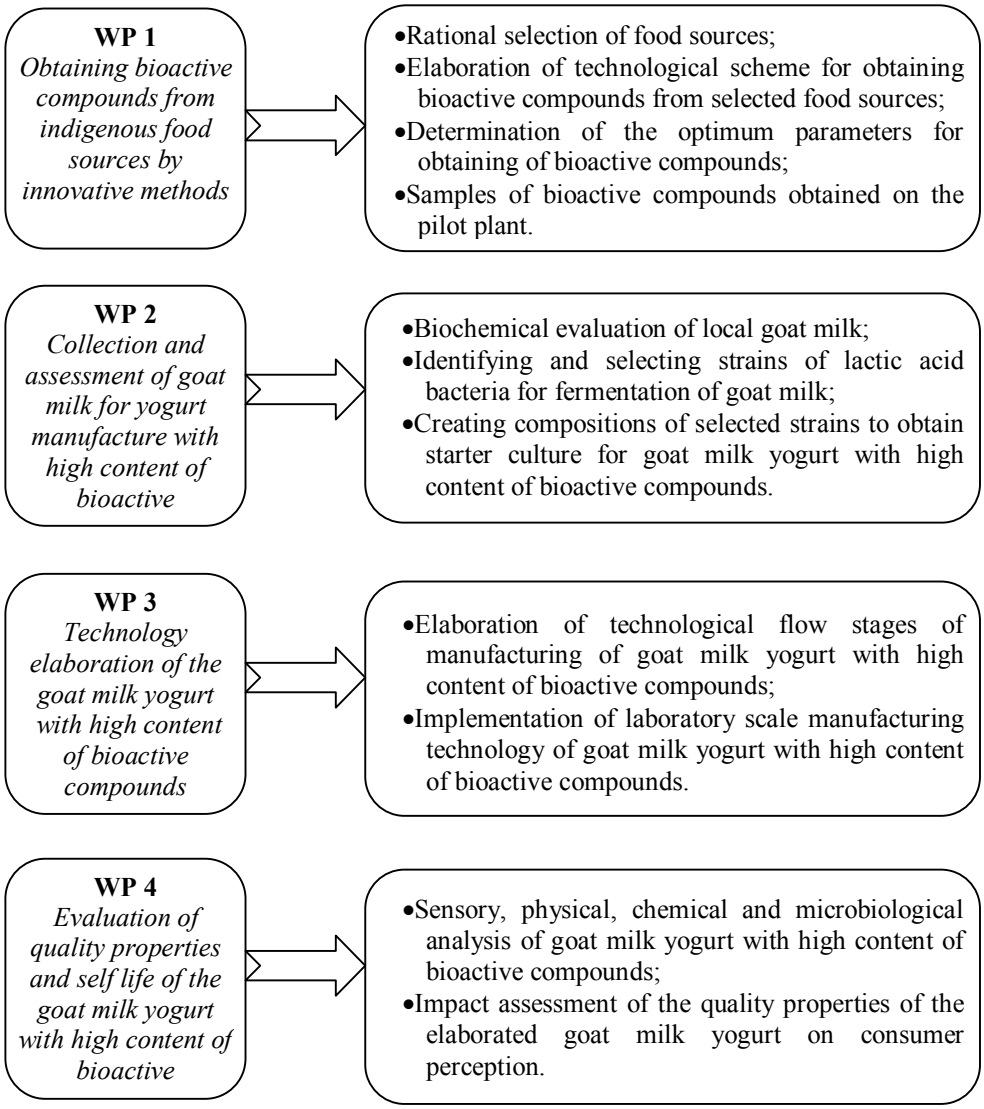

Figure 1. Main stages of realization of the InoBioProd

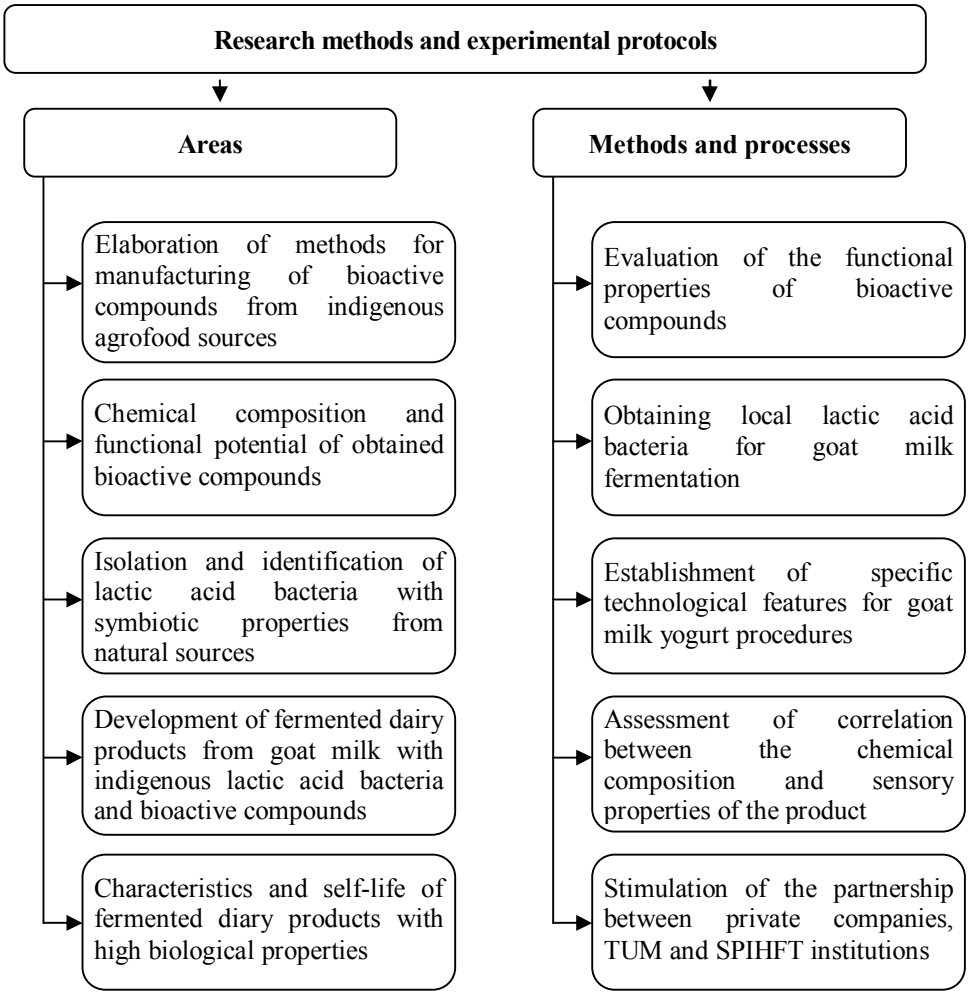

Figure 2. Research areas, methods and processes of InoBioProd

Expected scientific results

InoBioProd Project contribues to the development of investigations in the field of food biotechnology, engineering technology, food chemistry and microbiology, offering a high potential for application:

- Innovative technology for manufacturing of obtained bioactive compounds from local sources;
- General characteristic of functional potential of bioactive compounds;
- Scientifically justified process for producing of goat milk yogurt with high biological properties;

- Sensorial, physico-chemical, structural and microbiological properties of developed yogurt;
- Technical regulations for goat milk yogurt.

However, manufacturing technology of goat milk yogurt by using original physical and chemical methods is a perspective direction that has a real potential for patenting. Unordinary solutions for resolving actual problems are expected. Real objects for patent present know-how, intellectual property of authors. It is obvious that the degree of patent and intellectual capacities depend on the level of special knowledge and fundamentals of young researchers, the ability of creative thinking, problem solving skills in biotechnology, engineering and microbiological analysis. Predicting the level prior patent is planned based on the preliminary results of the team, the dynamics of obtaining these results, the number of patents remain in force, whose authors are members of the team, the number of patents can be estimated:

- Patents regarding to processing technologies of raw materials 1-2 patents;
- Patents regarding to elaboration of food products 1-2 patents.

We note that this "account" number of patents do not appreciate their quality parameter, which we consider basic to any business, especially the scientific research.

Benefits of InoBioProd

The Project contributes to the diversification of food technology through valorisation of emerging technologies to meet the demands of consumers. The Project induces increased use of existing infrastructure, improves documentation and scientific information on basic and applied research in the field of food quality and safety, helps to explore human, research and development resources. The most valuable results are planned to be implemented partially at specialized university courses. Benefits of the InoBioProd Project have several areas (Figure 3).

The InoBioProd Project contribute significantly in the training of young researchers through obtaining team building skills for planning and conducting scientific researches, accumulation of new knowledge, obtaining and dissemination of scientific results. To increase participation and capacity of team building of young researchers in the Project are intended to finish PhD thesis of team members.

Realization and defending of PhD thesis in the frame of InoBioProd Project will increase the number of young researchers with scientific grade and respectively national competitiveness of internationalization and participation in different international programs, including the Framework Programme H2020.

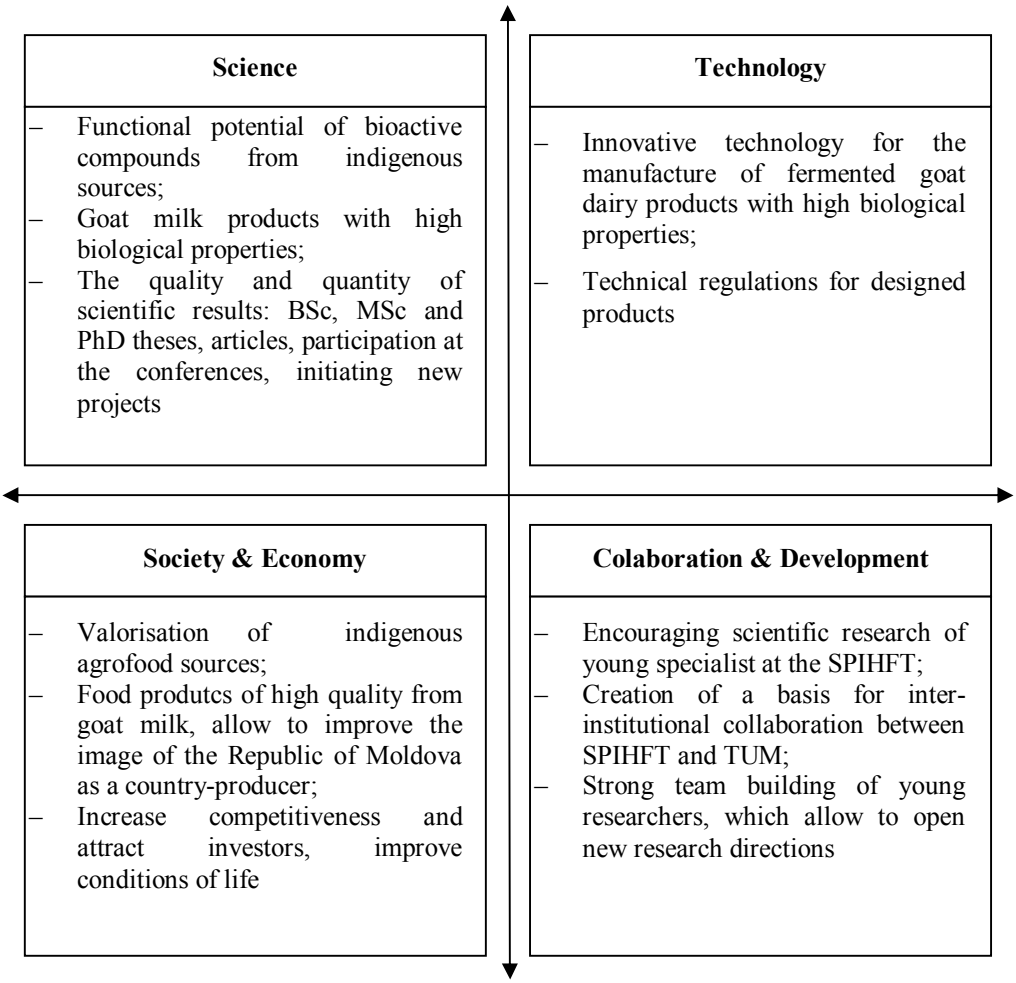

Figure 3. The Benefits of InoBioProd

Application of InoBioProd

Considering the importance of fermented dairy products from goat milk, which are in demand on internal and external markets, elaboration of the technological process for manufacturing of the products is necessary. Developed processes for the production of yogurt from goat milk with high biological properties will be approved in the *Laboratory of Food Biotechnology* of Scientific and Practical Institute of Horticulture and Food Technology and *Scientific Centre for Training and Technology Transfer in Food Industry of TUM* in the frame of "Etalon" enterprise. Application of the results on a large scale will be possible in case of producers motivation for investment in manufacturing new developed products, because all economic units, dealing with dairy production in the Republic of Moldova are private.

At the first stage of research results implementation, potential beneficiaries are small private enterprises (II and SRL) from the filed of dairy technology. Furthermore, the volume of internal production of goat milk allows loading of enterprises of SA "JLC" type with high volumes of work.

Application of InoBioProd Project results in research and education is a step of major importance. The results will be included in the cycle of lectures, seminars and laboratory works for training in higher education, first and second cycle disciplines: Dairy Technology, Food Biotechnology, Food Chemistry, Physical Chemistry (Figure 4).

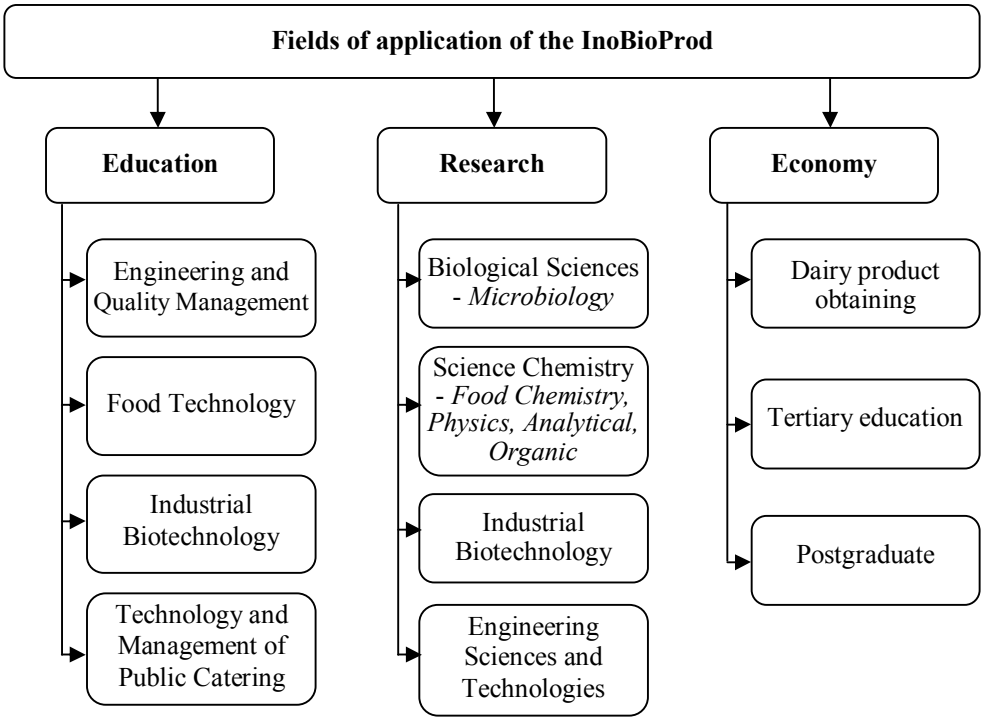

Figure 4. Application of InoBioProd

Perspectives and further research

Effective methods for bioactive compounds obtaining, identifying indigenous lactic acid bacteria, developement of yogurt with high biological properties and analysis of scientific results contribue to training and development of young researchers in the field.

During the Project work there is build a team of young researchers with high-potential, their results create perspectives for further research in the frame of the European Partnership for innovation and technology, increase competitiveness through creation of opportunities for new consortia (units, scientific researchers - businesses) to develop new

improved technologies to increase the added value of technology at enterprises. In addition, this create opportunities for international collaboration through achieving top results, with prospects for marketing of new products.

The Project contributes to the diversification of food technology through valorisation of emerging technologies to meet the demands of consumers. The Project induces increased use of existing infrastructure, improves documentation and scientific information on basic and applied research in the field of food quality and safety, helps to explore human, research and development resources. The most valuable results will be implemented at specialized university courses.

Conclusions

Consumer interest for potential health benefits of a proper alimentation has led to a growing importance of the relationship between diet, specific food ingredients and health. Through the InoBioProd, it facilitates the development of science to solve some problems in this field, ensures increased research capabilities, innovation and dissemination of obtained scientific results and strengthens scientific cooperation of young researchers of R&D and higher education institutions of the Republic of Moldova.

InoBioProd is planning to elaborate methods and recommendations on technological regimes for manufacturing of bioactive compounds from agrofood sources; technological scheme for obtaining of bioactive compounds; evaluate characteristics of nutritional, antioxidant and antimicrobial potential of samples of bioactive compounds and propose procedures and recipes justified scientifically regarding the manufacturing of yogurt with high biological properties according to the international regulations on food processing.

Acknowledgments

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Анотації

Харчові технології

Індукований вплив шляхом окиснення перманганатом калію на теплові, морфологічні, колориметричні та склеювальні властивості кукурудзяного крохмалю

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Вступ. Натуральні крохмалі є найбільш споживаними полісахаридами в раціоні людини. Вони використовуються в ряді галузей промисловості: харчовій, текстильній, фармацевтичній тощо. Однак через деякі обмеження крохмалі мають бути модифіковані хімічно.

Матеріали і методи. Кукурудзяний крохмаль, модифікований стандартними розчинами перманганату калію ($KMnO_4$), аналізували за допомогою одночасного термогравіметричного диференціального термічного аналізу, диференціальної скануючої калориметрії, швидкого віскоамілографічного аналізу, польової емісійної гарматно-скануючої електронної мікроскопії та енергетичної дисперсійної спектроскопії, дифракційної рентгенодифракції та колориметричного аналізу.

Результати і обговорення. Кукурудзяний крохмаль окислювався $KMnO_4$ в різних концентраціях (0,01, 0,02 і 0,05 моль mol L^{-1}) за pH 6,0 протягом 1 години. Після фільтрування, промивання і висушування за 40 °C протягом 24 годин, досліджувались властивості зразків. Термогравіметричні криві показали ендотермічний пік, пов'язаний з випаровуванням води та два екзотермічних піки, які відносяться до розкладання й окислення органічної речовини до утворення золи. Спостерігався період стабільності, який зменшувався після модифікації. Желатинізація окисленого крохмалю відбувалася за більш високих пікових температур. В'язкість зразків була значно зменшена, а відносна кристалічність збільшувалася пропорційно використаній концентрації окислювача. Вміст марганцю і калію під час модифікації збільшувався. Після окислення морфологічні зміни не спостерігалися, однак потемніння зразків відбувалося через наявність калію і марганцю, виявлених за допомогою енергетично дисперсійної спектроскопії (ЕДС).

Висновок. Отримана текуча паста з низькою тенденцією ретроградації свідчить про доцільність застосування окисленого крохмалю в різних галузях промисловості.

Ключові слова: *крохмаль, кукурудза, окислення, перманганат калію.*

Методологія прискореного контролювання і забезпечення санітарної якості та безпеки харчових продуктів

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Вступ. Охарактеризовано мікробіологічні критерії, які забезпечують санітарну якість і безпеку харчових продуктів, методи ідентифікації регламентованих мікроорганізмів, актуальність прискореного мікробіологічного контролю безпеки харчових продуктів.

Матеріали і методи. Досліджуються методологія оцінки безпечності продуктів та класичні й прискорені методи визначення регламентованих мікробіологічних показників, які ідентифікують наявність термостійких збудників харчових захворювань. Аналітичні дослідження виконані на основі сучасних літературних джерел і власних результатів.

Результати і обговорення. Охарактеризовані мікробіологічні критерії та вимоги до мікробіологічної безпеки харчових продуктів. Аналіз сучасних вимог до санітарної безпеки харчових продуктів показав необхідність проведення мікробіологічного контролю наявності термостійких мікроорганізмів – потенційних збудників харчових захворювань. Наведено види мікроорганізмів, що традиційно є основними в оцінці їх санітарного стану – *Clostridium botulinum, Bacillus cereus, Clostridium perfringens, Staphylococcus aureus*. Визначено фено- і генотипові властивості критеріальних мікроорганізмів – потенційних збудників харчових інфекцій і отруєнь. Дослідження методології і способів контролю регламентованих мікроорганізмів показало недостатність і неточність їх фенотипової діагностики у зв'язку зі схожістю морфо-тінкторіальних властивостей всередині окремих груп, непостійністю ряду біохімічних показників, слабкими антигенними властивостями деяких токсинів, появою нових метаболічних особливостей, пов'язаних зі здатністю синтезувати гени токсичності мікроорганізмами, які традиційно вважалися непатогенними, трудомісткістю і тривалістю аналізу. Генотипова діагностика мікроорганізмів з використанням сучасних молекулярно-генетичних методів і методологій, на відміну від фенотипової, забезпечує точність ідентифікації, можливість моніторингу і прогнозування поведінки збудників харчових інфекцій і токсикоінфекцій в продуктах при оцінці мікробіологічного ризику, дає змогу здійснити прискорений мікробіологічний контроль безпеки харчових продуктів з урахуванням особливостей їх складу і властивостей, є надійним методом санітарного контролю.

Висновки. Молекулярно-генетична діагностика збудників харчових захворювань є перспективним прискореним методом визначення безпеки харчових продуктів.

Ключові слова: *харчовий продукт, санітарія, безпека, контроль, ПЛР.*

Порівняння біологічної цінності і технологічних властивостей білків насіння олійних культур

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Вступ. Метою дослідження був порівняльний аналіз властивостей білків насіння основних олійних культур (соняшнику, сої та ріпаку), що вирощуються в Україні.

Матеріали і методи. Для визначення відносної біологічної цінності та токсичності білкових продуктів використовували тест-культуру інфузорію *Tetrachimena piriformis* (штам WH–14). Емульгувальну здатність білків визначали за максимальним об'ємом емульгованої олії стосовно до маси білка, піноутворювальну

− як відношення об'єму утвореної за стандартних умов піни до об'єму білкової суспензії.

Результати і обговорення. Згідно з одержанихми даними, біологічна цінність соєвих білків обмежена вмістом сірковмісних амінокислот метіоніну та цистину (2,1% від загального вмісту). Їх вміст складав лише 60% за шкалою ФАО/ВООЗ. Біологічна цінність білків насіння соняшнику була лімітована вмістом трьох амінокислот – сірковмісних амінокислот метіоніну і цистину (сумарний вміст − 1,6 %) та лізину (3,0% від загального вмісту). Вміст більшості незамінних амінокислот у білках насіння ріпаку приблизно на 8–57% вищий, ніж в ідеальному білку ФАО/ВООЗ. Винятком є лише валін і ізолейцин, скор яких становив 80–85%. Скор сірковмісних амінокислот у ріпаковому білку становив 157,1% щодо шкали ФАО/ВООЗ. Серед досліджених білків ізольовані білки насіння ріпаку мали найвищі технологічні властивості: їх розчинність становила від 16,4 до 38,6% за різних значень pH, вологозв'язувальна здатність – 211%, олієзв'язувальна – 130%, емульгувальна – 140 $см^3$/г, піноутворювальна – 122%.

Висновки. Досліджені білкові ізоляти насіння олійних культур (сої, соняшнику і ріпаку) не мали токсичності. Ріпакові білкові ізоляти мали найвищу відносну біологічну цінність і технологічні властивості.

Ключові слова: *соняшник, ріпак, соя, білок.*

Вплив знесолення води зворотним осмосом на процес утворення водно-спиртових сумішей. ^{1}H ЯМР дослідження

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Вступ. Метою публікації є дослідження впливу демінералізованої води зворотним осмосом на дрейф протонів етанолу і води, а також стабілізацію цих систем за допомогою ^{1}*H ЯМР* спектроскопії.

Матеріали і методи. ^{1}*H ЯМР* аналіз проводився з використанням: Фур'є-*ЯМР*-спектрометра Bruker Avance II (400 МГц); спеціального капіляра з ацетоном-d_6; ампул №507–НР високого розділення; дозатора; спирту етилового ректифікованого (СЕР); води, демінералізованої зворотним осмосом; водно-спиртових сумішей (ВСС) із СЕР і демінералізованої води.

Результати і обговорення. Встановлені нові ефекти в процесі створення ВСС, які пов'язані з демінералізацією води зворотним осмосом. Зміна хімічних зсувів протонів етанолу і води в процесі створення ВСС свідчить про складну динаміку процесів досягнення рівноваги в суміші. В інтервалі часу від 0 до 434 годин після змішування, при постійній концентрації спирту (міцність ВСС – 39,92% об.) і термостатуванні системи (t=+23,5ºС), не відбувається «відновлення» положення сигналу гідроксильного протона (*OH*) етанолу. Характерною рисою досліджених систем є те, що сигнали гідроксильного протона етанолу (*EtOH*) і води (H_2O) протягом інтервалу τ=12–432 h (δ_{EtOH}=4,93–5,01 ppm; δ_{H2O}=4,33–4,41 ppm) можна спостерігати окремо один від одного з різницею у хімічних зсувах $\Delta\delta$=0,59–0,61 ppm. Імовірно, розділ сигналів та їх характерний дрейф пов'язаноий з процесом

відновлення структури води, порушеної при демінералізації зворотним осмосом одночасно з встановленням сітки водневих зв'язків, характерної для розчину. Низькі швидкості обміну (роздільне спостереження сигналів гідроксилу і води) можна пов'язати з істотною мікрогетерогенністю системи і відповідним бар'єрним ефектом, що знижує ефективну швидкість обміну протонів.

Висновки. Експериментально, методом *^{1}H ЯМР* спектроскопії, встановлено вплив використання зворотного осмосу водопідготовки на спектральні характеристики рухливих протонів етанолу і води, а також стабілізацію системи у процесі створення водно-спиртових сумішей. Показано, що для таких систем процес стабілізації водно-спиртової суміші проходить одночасно з відновленням сітки водневих зв'язків у водній фазі.

Ключові слова: *зворотний осмос, етанол, вода, суміш, ^{1}H ЯМР.*

Оцінка харчового потенціалу какао Theobroma cacao L. і кави Coffee liberica W. Bull.

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Вступ. Споживання какао і кави збільшується через ряд корисних властивостей для здоров'я. Вивчення фітохімічних компонентів і харчового потенціалу цих цінних культур ще більше розкриває їх харчове та фітомедиційне значення в раціоні харчування людини.

Матеріали і методи. Какао та кавові зерна збирали на ферми в Адо-Екіті, штат Екіті, Нігерія, і вивчали їх основні, мінеральні й фітохімічні компоненти, використовуючи стандартні аналітичні методи. Зібрані какао і каву сушили протягом тижня, потім висушували повітрям, знімали оболонку, подрібнювали в порошок і аналізували їхній склад.

Результати і обговорення. Отримані результати показали, що обидва зразки рослин містять алкалоїди, дубильні речовини, сапоніни, флавоноїди, фенол і кардіоглікозиди. Проте стероїди, флобатанін і терпеноїди були наявні у C. liberica, але відсутні в T. cacao. Аналіз показав вміст вологи (12,16 і 10,84%), вуглеводів (57,19 і 62,51%), сирого протеїну (4,08 і 3,75%), сирого волокна (18,95 і 16,72%) та золи (6,82 та 5,58%) у C. liberica і T. cacao відповідно. Встановлено, що життєво важливі мінерали (мг/100г) у каві та какао включають Na (1050,14 і 1133,11), K (305,12 і 719,36), Ca (407,86 і 65,33), Mg (41,83 і 35,28), P (43,69 і 37,37), Mn (12,62 і 5,86), Fe (28,86 і 32,40) і Zn (2,41 і 3,61). Вміст нікелю знаходився в межах дозволеного рівня. У зразках рослин не було виявлено Pb та Cd.

Висновок. Какао та кавові зерна, що досліджувались, можна розглядати як багату біоактивними вторинними метаболітами сировину, що виправдовує їх широко відомі переваги для здоров'я.

Keywords: *какао, кава, склад, фітохімічний, Адо Екіті.*

Дослідження в'язкісних характеристик сумішей морозива з крохмальною патокою

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Вступ. Для виробництва морозива як підсолоджувач широко застосовують крохмальну патоку, але її структуруюча здатність недостатньо вивчена і потребує додаткових досліджень. Виявлення закономірностей структурування сумішей з патокою різного ступеня оцукрювання дасть змогу знизити потребу у стабілізаторах структури і досягти технологічного ефекту в процесі виробництва морозива за рахунок лише натуральних інгредієнтів.

Матеріали і методи. Реологічні характеристики сумішей морозива вершкового й ароматичного з глюкозно-фруктозним сиропом (HFCS-96), глюкозним сиропом (HFCS-42) і патокою карамельною (HFCS-30) досліджували за допомогою ротаційного віскозиметра.

Результати і обговорення. У разі повної заміни цукру на патоки крохмальні HFCS-30 та HFCS-42 початкова ефективна в'язкість сумішей вершкових підвищується на 22,1% та 2,5% відповідно, порівняно з контрольним зразком із цукром. У той же час повна заміна цукру на патоку HFCS-96 сприяє зниженню початкової ефективної в'язкості вершкової суміші на 15,3%. Початкова ефективна в'язкість сумішей для морозива ароматичного при повній заміні цукру на HFCS-30 та HFCS-42 збільшувалася на 27,1% та 14,8% відповідно і зменшувалася на 11,6% при повній заміні цукру на патоку HFCS-96.

Патоки марок HFCS-42 і HFCS-96 надають сумішам тиксотропних властивостей. Натомість системи з патокою HFCS-30 здатні не тільки повністю відновлювати структуру, але й виявляють слабкі реопексні властивості. Завдяки цьому в режимі зворотного зменшення швидкості зсуву ефективна в'язкість сумішей морозива вершкового й ароматичного, у разі повної заміни цукру, збільшується на 12,7% і на 18,8% відповідно, порівняно з початковими значеннями. У сумішах, що містять суміш паток HFCS-96 і HFCS-30 за співвідношення 30:70, ефективна в'язкість збільшується в режимі зворотного зменшення швидкості зсуву на 9,5% і на 12,5% для морозива вершкового й ароматичного відповідно, порівняно з початковими значеннями.

Висновки. Структуруюча здатність патоки крохмальної знижується з підвищенням ступеня її оцукрювання. Виявлена закономірність впливу патоки з різним декстрозним еквівалентом на в'язкісні характеристики сумішей різного хімічного складу дає можливість цілеспрямовано формувати показники якості морозива.

Ключові слова: *морозиво, цукор, патока, оцукрювання, в'язкість.*

Органолептичні та хімічні властивості десертних вин, виготовлених різним заморожуванням винограду сорту Марселан

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Вступ. Мета дослідження полягала в тому, щоб визначити вплив різних способів заморожування винограду сорту Марселан на сенсорний і фізико-хімічний склад отриманих крижаних вин.

Матеріали і методи. Солодке вино отримали двома способами заморожування винограду Марселан: природним шляхом і кріогенною екстракцією. При виробництві вина та визначенні фізико-хімічних атрибутів керувалися положеннями Міжнародної організації вина та винограду, що стосуються операцій переробки винограду на крижане вино. Кількісний та якісний склад ароматичних речовин у солодких винах визначали за допомогою газової хроматографії. Сенсорний аналіз, проведений відповідно до ISO 8586-2, встановив органолептичні властивості десертних вин.

Результати і обговорення. Відповідно до агрокліматичних ресурсів Північного Причорномор'я (Одеської області) із червоного сорту Марселан в 2016 р. отримано перше експериментальне десертне вино преміального сектору. Заморожування винограду кріогенною екстракцію відбувалося повільніше і при нижчій температурі (-10 °С), аніж традиційним способом (збір при -7 °С) отримання сусла із високим вмістом цукру.

За хімічним складом, вина із винограду сорту Марселан, замороженого різними способами, суттєво не відрізнялися. Позитивні кореляції поміж змінними, що відповідають за вміст цукру, етанолу, масових концентрацій титрованих і летких кислот були відзначені в обох зразках. Газовою хроматографією були знайдені 35 і 37 ароматичних з'єднань у винах, виконаних природним (ПЗ) та альтернативним заморожуванням (АЗ) відповідно. Концентрації спиртів в обох винах були найбільш високими серед летких речовин, що складають більше 60% і 40% у винах ПЗ та АЗ відповідно. Складні ефіри, вищі спирти, леткі кислоти відрізнялися лише за масовою концентрацією, а C_6 з'єднання були знайдені лише у вині, виробленому із замороженого винограду на лозі. Сенсорний аналіз показав відмінності між двома винами за інтенсивністю фруктових нот, горіховими відтінками і тривалістю післясмаку.

Висновки. Результати дослідження демонструють особливості формування унікальних ароматичних і хімічних профілів крижаних вин з Марселана, також спосіб заморожування впливає на визначальні характеристики вин.

Ключові слова: *крижане вино, Марселан, заморожування, Північне Причорномор'я.*

Відновлюючі та емульгуючі властивості сушеного м’ясного напівфабрикату

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Вступ. Досліджено технологічні властивості сушеного м’ясного напівфабрикату (СМН), виготовленого методом ЗТП-сушіння (змішаного підведення тепла), на підставі яких складно математичну залежність комплексної характеристики СМН від температури сушіння і ступеня дисперсності продукту.

Матеріали і методи. Матеріалами досліджень були: м’ясо яловичини, відварене і сушене конвективним способом, як контроль, і сушений м’ясний напівфабрикат

високого ступеня готовності, що отримано способом змішаного теплопідведення, як дослідний зразок. За результатами аналізу спектрів, отриманих методом ІЧ-спекторскопії, охарактеризовано зміни хімічного складу сушеного м'ясного напівфабрикату і після його відновлення. Характеристику об'єму та середнього діаметру пор сушеного м'ясного напівфабрикату здійснювали за ізотермами сорбції-десорбції, отриманих ваговим методом.

Результати і обговорення. Комплекс досліджень технологічних властивостей сушеного м'ясного напівфабрикату показав, що використання способу сушіння зі змішаним теплопідведенням сприяє отриманню продукту із меншим вмістом вологи (у 2 рази) та покращеною його здатністю до відновлення з одночасним збереженням високої вологоутримуючої здатності (порівняно з контролем вологоутримуюча здатність вища на 7,2 %) і коефіцієнтом водопоглинання (вище у 1,3 раза). Виявлено, що при виробництві сушеного м'ясного напівфабрикату методом змішаного теплопідведення вміст летких ароматутворюючих речовин порівняно з контролем вищий у 1,3 раза.

Аналіз ІЧ-спектрів поглинання сушеного м'ясного напівфабрикату в області деформаційних коливань груп –ОН вказують на те, що сушіння зі змішаним теплопідведенням сприяє формуванню капілярно-пористої структури, яка дає змогу збільшити кількість адсорбційно зв'язаної води у 1,5 раза, та обумовлює високі регідратаційні й емульгуючі властивості готового напівфабрикату. Отримано математичну модель формування комплексного показника технологічних властивостей сушеного м'ясного напівфабрикату залежно від температури сушіння та ступеня подрібнення напівфабрикату.

Висновки. Встановлено формування високих технологічних властивостей сушеного м'ясного напівфабрикату. Отримані дані дають змогу рекомендувати напівфабрикат як самостійний продукт і для широкого асортименту харчових продуктів.

Ключові слова: *м'ясо, напівфабрикат, сушіння, змішане теплопідведення, пористість, емульсія.*

Ідентифікація рівноважного стану гідроксильних протонів у горілках за допомогою ^{1}H ЯМР спектроскопії

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Вступ. Метою дослідження є ідентифікація рівноважного стану гідроксильних протонів етанолу і води у горілках з використанням ^{1}*H ЯМР* спектроскопії.

Матеріали і методи. Водно-спиртові суміші (ВСС, горілки) було підготовлено волюметричним методом. *ЯМР* спектри отримано згідно з керівництвом до Фур'є *ЯМР* спектрометра Bruker Avance II (400 МГц) і Bruker TopSpin. Для дейтерієвої стабілізації і визначення хімічних зсувів речовин використовували ацетон-d_6 – зовнішній стандарт, який відокремлений від досліджуваної речовини, вносили до ампули у капілярі спеціальної форми.

Результати і обговорення. Експериментально визначені елементи встановлення

термодинамічної рівноваги гідроксильних протонів етанолу та води у горілках за допомогою ^{1}H *ЯМР* спектроскопії. Ідентифіковано три групи зразків, виходячи з рівноваги гідроксильних груп протонів води та етанолу: сталої, перехідної, несталої рівноваги.

Стала рівновага характеризується наявністю в гідроксильній групі об'єднаного унітарного сигналу $EtOH+H_2O$. Компонента протонів $EtOH+H_2O$ для кожного зразка представлена у вигляді синглету (*s*), що знаходиться у «слабкому полі» з хімічним зсувом у діапазоні $\delta_{H2O+EtOH}$=4,75–4,80 ppm. Форма сигналу протонів $EtOH+H_2O$ – викривлена гаусова крива, з розширеною основою і незначною асиметрією вершини, пік якої має зміщення відносно осьової лінії.

Перехідна рівновага характеризується наявністю в гідроксильній групі двох роздільних сигналів *EtOH* (δ_{EtOH}=5,34 ppm) і H_2O (δ_{H2O}=4,75 ppm). Відхилення між хімічними зсувами гідроксильних протонів етанолу (*EtOH*) і протона води (H_2O) для кожного зразку складає Δf_1=236 Гц. Перехідна рівновага характеризується наявністю ледве помітного гідроксильного протона, що характеризує перехід від сталої до несталої рівноваги. Це вказує та те, що не було створено певних передумовдля того, щоб встановити рівноважну структуру (несталу/сталу рівновагу).

Нестала рівновага характеризуються наявністю в гідроксильній групі двох роздільних сигналів етанолу (δ_{EtOH}=5,34 ppm), який є явним, і H_2O (δ_{H2O}=4,72 ppm). Відхилення між *EtOH* і H_2O – Δf_1=248 Гц.

Висновки. На підставі проведеного дослідження встановлена принципова відмінність поведінки гідроксильних протонів етанолу та води у горілках за допомогою ^{1}H *ЯМР* спектроскопії. Отримані рівноважні системи дають змогу удосконалити технологічний процес виробництва горілок на лікеро-горілчаних підприємствах для стабілізації якості готової продукції.

Ключові слова: *горілка, етанол, вода, гідроксил, ^{1}H ЯМР спектроскопія.*

Видалення іонів кадмію і свинцю з модельних розчинів з використанням натуральних сорбентів

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Вступ. Одним із обмежень хімічних абсорбентів як простого й ефективного способу видалення забруднень за рахунок механізму поверхневого поглинання є їх надмірні витрати, тому вивчення потенціалу дешевих і доступних природних адсорбентів для видаленні важких металів з промислових відходів становить науковий інтерес.

Матеріали і методи. Для вивчення кількості абсорбенту, pH та впливу температури на абсорбційну здатність вишневого ядра штучний розчин у концентрації 1000 мг/л змішували з певною кількістю абсорбувального матеріалу за певної температури та pH протягом 60 хвилин. Розчини фільтрували фільтрувальним папером. Вміст кожного іона в початковому і відфільтрованому розчині визначали атомно-абсорбційною спектрометрією. Вплив вмісту абсорбованої речовини (0,2-2 г/100 мл), pH (3–7) й температури (30–70 °C) на швидкість абсорбування досліджуваного свинцю і кадмію досліджувався методом поверхні відгуку (RSM).

Результати і обговорення. Підвищення температури покращило швидкість абсорбування кадмію за рахунок зменшення в'язкості та прискорення масопереносу.

Підвищення температури обмежує утворення граничного шару навколо абсорбенту через зменшення в'язкості розчину. Отже, поглинання іонів посилюється. Також збільшення кількості абсорбенту підвищує поверхневий контакт, і в результаті ймовірність зіткнення іонів із частинками абсорбенту підвищується. Іншими словами, велика кількість абсорбенту збільшує шанси для приєднання іонів. Видалення кадмію за високих значень pH було знижено через перетворення іонної структури в молекулярну структуру. Швидкість поглинання кадмію також збільшувалась за рахунок збільшення кількості абсорбенту завдяки наявності цитів для поглинання. Підвищення pH до 5 призвело до збільшення абсорбції іонів свинцю, але підвищення pH до 7 зменшило поглинання свинцю. Причина цього явища обумовлена зміною іонної структури свинцю в молекулярному стані за лужного pH. Хоча зі зниженням pH конкуренція іонів водню з катіонами зменшує абсорбування іонів металів.

Висновок. Найкращі експериментальні параметри для максимальної абсорбції визначаються такими умовами: температура 70 °C, pH 5 та концентрація абсорбента 2 г/100 мл. Застосовуючи ці умови, вдалося зменшити кількість іонів свинцю і кадмію, відповідно, на 79,18 та 76,56% із штучних розчинів. Також були перевірені оптимальні умови на стічних водах цукрової промисловості, результати яких показали зменшення для свинцю і кадмію на 98,98 і 76,1%.

Ключові слова: *абсорбція, кадмій, свинець, вишня, ядро.*

Швидкість і якісні параметри пінного сушіння томатної м'якоті

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Вступ. Помідор – плід короткотривалого зберігання, який швидко псується після збирання врожаю. Його потрібно обробляти методом пінного сушіння для забезпечення належної якості продукту. Необхідно дослідити деякі параметри процесу, зокрема, піноутворення і концентрацію стабілізатора піни, які можуть впливати на швидкість сушіння і якість сухого порошку.

Матеріали та методи. Було використано рандомізовану схему досліджень з 27 зразків томатної м'якоті, використовуючи яєчний білок як піноутворювальний агент із трьома рівнями концентрації – 5%, 10% та 15%, карбоксилметилцелюлозу (КМЦ) із концентрацією 0,2%, 0,4% і 0,8%. Час збивання – 3 хвилини. Зразки сушили в сушильній шафі за температури 70 °C.

Результати і обговорення. Для зразків з концентрацією піноутворювальних речовин 5%, 10% та 15% швидкість висушування становила 19,21 г/год, 21,53 г/год і 20,46 г/год, вміст білка становив 24,66%, 24,72% і 24.77% ,і вміст вітаміну С - 1,70%, 1,44% та 1,34% відповідно. В той же час зразки із додаванням КМЦ з концентрацією 0,2%, 0,4% та 0,8% мали швидкість сушіння 18,74 г/год, 20,68 г/год і 21,78 г/год, вміст білка 24,71%, 24,71% і 24,74%, а вміст вітаміну С - 1,43%, 1,56% та 1,49% відповідно. Аналіз варіації показує, що концентрація піноутворювача і стабілізатора з піною не впливає на швидкість сушіння за $P \leq 0,05$, проте піноутворювач істотно впливає на вміст білка і вітаміну С у зразках. Аналіз варіації також показує, що взаємодія, яка існує між піноутворювачем і стабілізатором піни, має значний вплив

на вміст вітаміну С і білка у зразку, але не має суттєвого впливу на швидкість сушіння. Крім того, новий багатодіапазонний тест Дункана демонструє вміст білка 24,66%, 24,72% та 24,77% за концентрації піноутворювача відповідно 5%, 10% та 15%.

Висновок. Концентрація піноутворювачів є важливим параметром, який впливає на показника якості пінновисушених помідорів. Для досягнення максимального збереження вмісту вітаміну С у сухій речовині помідорів, п'ятивідсоткова концентрація піноутворювального агента (яєчного альбуміну) є більш доцільною у порівнянні з більш високими концентраціями, оскільки це дасть змогу мінімізувати загальні витрати, що виникають під час пінного сушіння.

Ключові слова*: помідор, м'якоть, сушіння, швидкість, піна.*

Економіка і управління

Основні проблеми особистого страхування та напрями їх вирішення в контексті підвищення конкурентоспроможності страхового ринку

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Вступ. Оскільки відсутні дані з питань кореляційно-регресійного аналізу основних показників особистого страхування, а також передбачаючи мету виявлення основних проблем особистого страхування та напрями їх вирішення в контексті підвищення конкурентоспроможності страхового ринку, нами було проведені кореляційно-регресійні дослідження взаємозалежності надходження страхових премій, премій зі страхування життя, виплат зі страхування життя, пенсійних внесків і пенсійних виплат.

Матеріали і методи. Наукове дослідження основних проблем особистого страхування ґрунтувалось на застосуванні таких методів: абстрактно-логічного, системного аналізу та групування для дослідження основних проблем страхового ринку та напрямів подолання проблем; метод кореляційного-регресійного аналізу використовувався для дослідження статистичної взаємозалежності між такими показниками, як обсяг страхових премій і кількість договорів страхування, сума страхових премій в цілому та страхові премії з медичного страхування, а також виплати зі медичного страхування тощо.

Результати і обговорення. Встановлено, що основними ризиками ринку особистого страхування є глобальні ризики (циклічний характер розвитку світової фінансово-економічної системи), макроекономічні та мікроекономічні ризики (темпи зміни національної економіки та окремих галузей), фінансові (незадовільний фінансовий стан страхових компаній, низький рівень якості активів страховиків) та комерційні ризики.

Кореляційно регресійних аналіз показників особистого страхування показав високий рівень залежності премій зі страхування життя від загальної суми зібраних страхових премій, адже коефіцієнт кореляції становить 0,669, зв'язок між досліджуваними елементами прямий, при цьому коефіцієнт детермінації становить 0,447, тобто факторна ознака (загальна сума премій) визначає 44,7 % залежного

показника премій зі страхування життя. Аналогічна за динамікою та характером ситуація, що характеризує залежність пенсійних виплат від пенсійних внесків: високі значення коефіцієнтів кореляції та детермінації.

Висновки. Підвищення конкурентоспроможності страхового ринку сприятиме подолання таких ризиків ринку особистого страхування, як глобальні ризики, макроекономічні та мікроекономічні ризики, фінансові та комерційні ризики. Основними ж проблемами особистого страхування визначено низький рівень довіри населення до страховиків, шахрайство страхувальників, повільні темпи реструктуризації економіки та невисокі доходи населення. Крім цього, високий рівень залежності премій зі страхування життя від загальної суми страхових премій показує позитивні тенденції розвитку страхового ринку країни.

Ключові слова: *страхування, особа, життя, медицина.*

Модель купівлі хлібних виробів серед працюючих і непрацюючих жінок в Центральній Індії: вплив соціально-економічних факторів

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Вступ. Хлібобулочні вироби є продуктом масового споживання з огляду на низьку вартість та високу якість поживних речовин. У зв'язку із зростанням і зміною харчових звичок людей хлібобулочні вироби набули популярності серед населення.

Матеріали і методи. Близько 200 працюючих і 200 непрацюючих жінок були відібрані за допомогою простого методу випадкової вибірки з Центральної Індії, Махараштри та Індії, при цьому дані були зібрані за методом опитування, використовуючи анкети та інтерв'ю. Досліджено купівлю п'яти хлібобулочних виробів, зокрема хліба, булочки, бісквіту, торта та піцерійного хліба, з урахуванням вікової групи, кваліфікації, складу сім'ї, заробітку та сімейного місячного доходу працюючих і непрацюючих жінок.

Результати та обговорення. Результати дослідження показали, що середній вік працюючих жінок 39,39±6,15 років, непрацюючих – 38,36±5,7 років. Середньомісячний дохід працюючих і непрацюючих жінок становив 38,125±19,550 індійських рупій та 40,625±20,825 індійських рупій відповідно. Хліб виявився найбільш споживаним хлібобулочним продуктом серед обох типів сімей (79,5% у працюючих і 83,5% у непрацюючих), при цьому бісквіт (76,5% у працюючих і 70,5% у непрацюючих). Купівля булочок, торта та піцерійного хліба серед працюючих жінок становила 7,5%, 19% та 14%, в той час як серед непрацюючих жінок – 13%, 23% та 18,5% відповідно. Значна подібність спостерігалась між схемою купівлі хліба ($p=0,000$), бісквіту ($p=0.000$) і торта ($p=0,010$) у працюючих і непрацюючих жінок. Вікова група, розмір та склад сім'ї, місячний дохід працюючих і непрацюючих жінок не свідчать про зв'язок із схемою купівлі хлібобулочних виробів.

Висновок. Купівля хлібобулочних виробів була однаковою у жінок, що працюють і не працюють. Серед демографічних характеристик освіта жінок суттєво вплинула на модель купівлі хлібобулочних виробів.

Ключові слова: *придбання, хліб, модель, бісквіт, торт, булочка, піца.*

Управління проектами

ІноБіоПрод: інноваційний виклик і наукові перспективи

Крістіна Попович[1], Вавіл Караджія[2], Анатолій Карташев[2], Ольга Мигалтієв[2], Геннадий Коєв[2], Роман Голубь[2], Ніна Богдан[2], Іріна Грумеза[2]

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Вступ. ІноБіоПрод (Інноваційна харчовий продукт з козиного молока з підвищеними біологічними властивостями) є незалежним проектом молодих вчених, галузь "Біотехнолії", грант № 16.80012.51.23A.

Матеріали і методи. Відходи та продукти переробки сільськогосподарської продукції використовуються як джерело біологічно активних сполук. У той же час основними об'єктами дослідження є козине молоко, місцеві штами молочнокислих бактерій і кисломолочних продуктів із підвищеними біологічними властивостями. Проект передбачає застосування стандартних та інноваційних методів і процесів.

Результати і обговорення. Наукові результати, зокрема очікувані технології, є абсолютно інноваційними для Республіки Молдова і знаходяться в рамках реконструкції політики ЮНІСЕФ для харчових продуктів і харчування. ІноБіоПрод робить свій внесок у розвиток досліджень у галузі біотехнологій, харчової хімії та мікробіології, пропонує високий потенціал застосування: інноваційні методи виробництва біологічно активних сполук із місцевих харчових джерел; хімічний склад і функціональні властивості біологічно активних сполук; характеристика козиного молока, виділення та ідентифікація молочнокислих бактерій із самоквасних кисломолочних продуктів; науково обгрунтовані рецептури та процеси виробництва кисломолочних продуктів з козиної молочної продукції та науково-технічна розробка методів оцінки термінів придатності кисломолочних продуктів. Особливу увагу ІноБіоПрод приділяє виконанню дипломних, магістерських і дисертаційних робіт, публікації наукових результатів на національному та міжнародному рівнях.

Висновок. Проект розроблено з огляду на основні потреби місцевого ринку – відсутність промислового виробництва козиного молока і продуктів. Крім того, проект направлений на ініціювання і зміцнення нового співробітництва молодих науковців з науково-дослідних установ і вищих навчальних закладів.

Ключові слова: *ІноБіоПрод, молоко, коза, інновація, дослідження, освіта.*

Instructions for authors

Dear colleagues!

The Editorial Board of scientific periodical
«**Ukrainian Food Journal**»
invites you to publication of your scientific research.

Requirements for article:
Language – English, Ukrainian, Russian
Size of the article – 10–15 pages in Microsoft Word 2003 and earlier versions with filename extension *.doc (!)
All article elements should be in Times New Roman, font size 14, 1 line intervals, margins on both sides 2 cm.

The structure of the article:
1. The title of the article
2. Authors (full name and surname)
3. Institution, where the work performed.
4. Abstract (2/3 of page). The structure of the abstract should correspond to the structure of the article (Introduction, Materials and methods, Results and discussion, Conclusion).
5. Key words.

Points from 1 to 5 should be in English, Ukrainian and Russian.

6. The main body of the article should contain the following obligatory parts:
   - Introduction
   - Materials and methods
   - Results and discussing
   - Conclusion
   - References

   If you need you can add another parts and divide them into subparts.

7. The information about the author (Name, surname, scientific degree, place of work, email and contact phone number).

All figures should be made in graphic editor, the font size 14.

The background of the graphs and charts should be only in white color. The color of the figure elements (lines, grid, text) – in black color.
Figures and EXCEL format files with graphs additionally should submit in separate files.
Photos are not appropriate to use.

Website of Ukrainian Food Journal: http://ufj.ho.ua

Extended articles should be sent by email to: ufj_nuft@meta.ua

Шановні колеги!

Редакційна колегія наукового періодичного видання «**Ukrainian Food Journal**» запрошує Вас до публікації результатів наукових досліджень.

Вимоги до оформлення статей

Мови статей – англійська, українська, російська

Рекомендований обсяг статті – **8–15 сторінок** формату А4 (без врахування анотацій і списку літератури)**.**

Стаття виконується в текстовому редакторі Microsoft Word 2003, в форматі *.doc.

Для всіх елементів статті шрифт – **Times New Roman**, кегль – **14**, інтервал – 1.

Всі поля сторінки – по 2 см.

Структура статті:

1**.** УДК**.**

2. **Назва статті.**

3. Автори статті (ім'я та прізвище повністю, приклад: Денис Озерянко).

4. *Установа, в якій виконана робота.*

5. Анотація. **Обов'язкова** структура анотації:

- Вступ (2–3 рядки).
- Матеріали та методи (до 5 рядків)
- Результати та обговорення (пів сторінки).
- Висновки (2–3 рядки).

6. Ключові слова (3–5 слів, але не словосполучень).

Пункти 2–6 виконати англійською і українською мовами.

7. Основний текст статті. Має включати такі обов'язкові розділи:

- Вступ
- Матеріали та методи
- Результати та обговорення
- Висновки
- Література.

За необхідності можна додавати інші розділи та розбивати їх на підрозділи.

8. Авторська довідка (Прізвище, ім'я та по батькові, вчений ступінь та звання, місце роботи, електронна адреса або телефон).

9. Контактні дані автора, до якого за необхідності буде звертатись редакція журналу.

Рисунки виконуються якісно. Скановані рисунки не приймаються. Розмір тексту на рисунках повинен бути **співрозмірним** (!) тексту статті. **Фотографії можна використовувати лише за їх значної наукової цінності.**

Фон графіків, діаграм – лише білий. Колір елементів рисунку (лінії, сітка, текст) – чорний (не сірий).

Рисунки та графіки EXCEL з графіками додатково подаються в окремих файлах.

Скорочені назви фізичних величин в тексті та на графіках позначаються латинськими літерами відповідно до системи СІ.

В списку літератури повинні переважати статті та монографії іноземних авторів, які опубліковані після 2000 року.

Правила оформлення списку літератури

В Ukrainian Food Journalвзято за основу загальноприйняте в світі спрощене оформлення списку літератури згідно стандарту Garvard. Всі елементи посилання розділяються **лише комами**.

1. Посилання на статтю:

Автори А.А. (рік видання), Назва статті, Назва журналу (курсивом), Том (номер), сторінки.

Ініціали пишуться після прізвища.

Всі елементи посилання розділяються комами.

1. Приклад:
   Popovici C., Gitin L., Alexe P. (2013), Characterization of walnut (Juglans regia L.) green husk extract obtained by supercritical carbon dioxide fluid extraction, *Journal of Food and Packaging Science, Technique and Technologies,* 2(2), pp. 104–108.

2. Посилання на книгу:

Автори (рік), Назва книги (курсивом), Видавництво, Місто.

Ініціали пишуться після прізвища.

Всі елементи посилання розділяються комами.

Приклад:

2. Wen-Ching Yang (2003), *Handbook of fluidization and fluid-particle systems*, Marcel Dekker, New York.

Посилання на електронний ресурс:

Виконується аналогічно посиланню на книгу або статтю. Після оформлення даних про публікацію пишуться слова ***Available at:*** та вказується електронна адреса.

Приклади:

1. (2013), *Svitovi naukovometrychni bazy*, available at: http://www1.nas.gov.ua/publications/q_a /Pages/scopus.aspx
2. Cheung T. (2011), *World's 50 most delicious drinks [Text]*, Available at: http://travel.cnn.com/explorations/drink/worlds–50-most-delicious-drinks–883542

Список літератури оформлюється лише латиницею. Елементи списку українською та російською мовою потрібно транслітерувати. Для транслітерації з української мови використовується паспортний стандарт, а з російської – стандарт МВД (в цих стандартах використовуються символи лише англійського алфавіту, без хвостиків, апострофів та ін).

Зручні сайти для транслітерації:

З української мови – http://translit.kh.ua/#lat/passport

З російської мови – http://ru.translit.net/?account=mvd

Додаткова інформація та приклад оформлення статті – на сайті

http://ufj.ho.ua

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УДК 663/664

Ukrainian Food Journal публікує оригінальні наукові статті, короткі повідомлення, оглядові статті, новини та огляди літератури.

Тематика публікацій в Ukrainian Food Journal:

Харчова інженерія
Харчова хімія
Мікробіологія
Фізичні властивості харчових продуктів
Якість та безпека харчових продуктів
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Нанотехнології
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Упаковка для харчових продуктів

Періодичність виходу журналу 4 номери на рік.

Результати досліджень, представлені в журналі, повинні бути новими, мати чіткий зв'язок з харчовою наукою і представляти інтерес для міжнародного наукового співтовариства.

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Авторське право. Автори статей гарантують, що робота не є порушенням будь-яких авторських прав, та відшкодовують видавцю порушення даної гарантії. Опубліковані матеріали є правовою власністю видавця «**Ukrainian Food Journal**», якщо не узгоджено інше.

Політика академічної етики. Редакція «Ukrainian Food Journal» користується правилами академічної етики, викладених в роботі Miguel Roig (2003, 2006) "Avoiding plagiarism, self-plagiarism, and other questionable writing practices. A guide to ethical writing". Редакція пропонує авторам статей і рецензентам прямо слідувати цьому керівництву, щоб уникнути помилок у науковій літературі.

Інструкції для авторів та інша корисна інформація розміщені на сайті
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