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PHYSICO-CHEMICAL STUDY OF MACRO - AND MICROELEMENT COMPOSITION OF THE ENRICHED MACARONI PRODUCTS

Abstract. The results of organoleptic and physico-chemical studies of enriched macaroni products are presented. As dietary supplements powder of carrot and holy thistle (*Silybum*) is offered that are sources of antioxidants, flavonoids and various vitamins. By using the Raster Electronic Microscope (REM) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) devices, the macro- and microelement composition of the obtained samples were investigated. The significantly increasing in the mass fraction of the main micronutrients, such as macroelements: Na, Mg, P, K; and microelements: Fe, Al, Si, Cl were found. Additional enrichment is carried out by phenolic compounds of holy thistle (*Silybum*) of flavonoid class in the form of flavolignans (silybin, isosilibine, silidianin, silicristin, isosilicristin et al) that have hepatoprotective and antioxidant properties. Also improvement by carotenoid-carotenes, flavonoids and various vitamins in carrots are provided. The obtained study results testify that the enriched macaroni products with carrots and holy thistle (*Silybum*) powder additives can quite correspond to the functional food stuffs with biologically active properties.

Key words: antioxidants, carrot, dietary supplements, flavonoids, holy thistle (*Silybum*), micronutrients, pasta.

Introduction

Macaroni products have several advantages over the most common food products. At the storing pasta without stale food, like bread, and less hygroscopic in comparison with breadcrumbs, it is well transported and stored (up to a year and more) without deterioration of taste and food properties. Macaroni products in terms of nutritional value are superior to a wheat bread, as they are made from wheat flour with the maximum content of protein substances. They contain 9-13% of proteins, 75-79 assimilable carbohydrates, 0.9 fats, 0.6% of minerals and vitamins B1, B2, PP, etc. The calorie content of pasta is 360 kcal per 100 g. The digestibility of their by human body is a higher then digestibility of cereals. Proteins of macaroni products are digested by 85%, carbohydrates by 98% and fats by 95%. Of these, it can be quickly prepared a dish, since the duration of their cooking is 5 - 15 minutes [3, 14].

Considering that macaroni products are popular and consumes in large quantities, an effective way in the improving of a quality and the increasing of a nutritional value provide prevention of various illness by dietary vitamin supplements. Depending on the type of added raw material, possibilities in the prevention of specific diseases perform [16].

Greater consumer demand for nutritious extruded food products with enhanced bioactive compounds has shifted research focus towards incorporation of bioactive rich ingredients with traditionally extruded starch materials [2].

As known that among the genotoxic and carcinogenic substances, the most part is made up of aromatic amines that are widely used in the aniline, rubber and rubber industries, as well as in the production of plastics. For the aromatic amines are applied aminobiphenyls that after metabolic activation in the body cause the formation of tumors and are called carcinogens of indirect action. Most procancers are hydrophobic, and their excretion from the human body reduces to the formation of hydrophilic metabolites. The main reactions of biotransformation of aminobiphenyls are their oxidation processes involving peroxidases and monooxygenases [4].

Antioxidants are compounds that can delay or inhibit the oxidation of lipids or other molecules by inhibiting the initiation or propagation of oxidizing chain reactions [20].

In general, there are two basic categories of antioxidants, natural and synthetic. Recently, interest has increased considerably in finding naturally occurring antioxidants for use in foods or medicinal materials to replace synthetic antioxidants, which are being restricted due to their carcinogenicity [5].

Substances capable for the binding of free radicals of oxidized aminobiphenyls act as genoprotectors. This antimutagenic effect is specific for many phenolic compounds of plant origin. It seems expedient to investigate the possibility of the manifestation of the genoprotective properties of silymarin and individual flavolignans consisted in this substance [13].

Unique hepatoprotective and antioxidant properties have preparations based on holy thistle (*Silybum*) are associated with a high content of a rare class of phenolic compounds - flavolignanes (silybin, isosilibin, lihydrosilibin, silidainin, silicristin, isosilicristin, silimonin, siland, etc.) [7].

Silymarin, a mixture of flavanoid complexes, is the active component that protects liver and kidney cells from toxic effects of drugs, including chemotherapy [10].

Silymarin and silybin used so far mostly as hepatoprotectants were shown to have other interesting activities as e.g., anticancer and canceroprotective. These activities were demonstrated in a large variety of illnesses of different organs as e.g., prostate, lungs, CNS, kidneys, pancreas and others [7]. Moreover, various herbs along with vegetables and fruits contain numerous phytochemicals in addition to phenolic compounds, such as nitrogen compounds, carotenoids, and ascorbic acid [19].

The composition of carrots contains carotenoids-carotene, phytoene, phytofluene and lycopene; Vitamins B, B2, pantothenic acid, ascorbic acid; flavonoids, anthocyanidins, sugars (3-15%), fatty and in a small amount essential oil, umbelliferone; in the seeds - essential oil, flavone compounds and fatty oil in the colors of the content of anthocyanins and flavonoids (quercetin, kempepherol) [15].

The antioxidant activity of different vegetables was evaluated by using a widely accepted model system containing b-carotene and linoleic acid [6]. Carotenoids are not particularly good quenchers of peroxyl radicals relative to phenolics and other antioxidants but are exceptional in quenching singlet oxygen, at which most other phenolics and antioxidants are relatively ineffective [11].

Carrot is one of the important root vegetables rich in bioactive compounds like carotenoids and dietary fibers with appreciable levels of several other functional components having significant health-promoting properties. The consumption of carrot and its products is increasing steadily due to its recognition as an important source of natural antioxidants having anticancer activity [12].

Mineral substances play an important role in the human body. They are contained in protoplasm and biological processes; provide constant osmotic pressure that is a necessary condition for the normal vital activity of cells and tissues. Microelements are considered vital if they are deficient or disturbed by the external normal vital activity of the organism [1].

It should be noted that the development of scientific principles for the designing of the composition and improving the technology of multicomponent products by using of non-traditional types of raw materials is one of the actual problems with scientific and practical values.

Due to the above mentioned data, the purpose of the present work was the organoleptic and physicochemical studies of the enriched macaroni products by dietary supplements, such as carrot powder and holy thistle (*Silybum*) [18].

Materials and methods

As objects of study there were selected - wheat flour of the highest grade GOST 52189-2003 *Wheat flour. General specifications* [21]. Also functional vegetable additives: red carrot and holy thistle (*Silybum*).

Quality indicators were determined in accordance with GOST 51865-2002. *Macaroni products. General specifications* [22]. Important indicators of the quality of macaroni products were: organoleptic (color, shape, taste and smell) and physicochemical parameters (moisture, acidity, ash, mass fraction of ash, dry matter and safety of the welded products shape).

The content of minerals in the pasta was determined by using the Raster Electronic Microscope (REM) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) devices. The inductively coupled plasma mass spectrometry (ISP-MS) method makes it possible to determine a number of metals and several non-metals in concentrations up to 10^{-10}%, i.e. one particle of 10^{12}, with an atomic mass of 7 to

250, that is, from Li to U. It is able to determine the content of nanograms per liter to 10-100 mg per liter. The method is based on the use of inductively-connected plasma as a source of ions and a mass spectrometer for their separation and detection in an argon gas medium. Unlike atomic absorption spectroscopy that determines only one element at a time, the ISP-MS device can to determine all the elements simultaneously that makes it possible to significantly accelerate the measurement process [9].

The Raster Electronic Microscope (REM) makes it possible to observe fine features using a micro-analyzer of the chemical composition, and details of the structure of microobjects at the atomic-molecular level. It also allows to obtain images of the surface of an object with a high spatial resolution (up to 0.4 nanometers), as well as information on the composition, structure and some other properties of the near-surface layers. The SEM has a large depth of focus, which allows one to observe a three-dimensional image of the structure with the possibility of its quantitative evaluation [17].

Preparation of ash samples for the analysis of the chemical composition was carried out in accordance with GOST 26929-94 [23]. The method of dry mineralization is based on the complete decomposition of organic substances by burning the sample in an electric furnace at a controlled temperature regime of 450-500 °C.

Results and discussion

Table 1 and Figures 1-4 show the ash chemical composition of macaroni product with additives obtained by the REM.

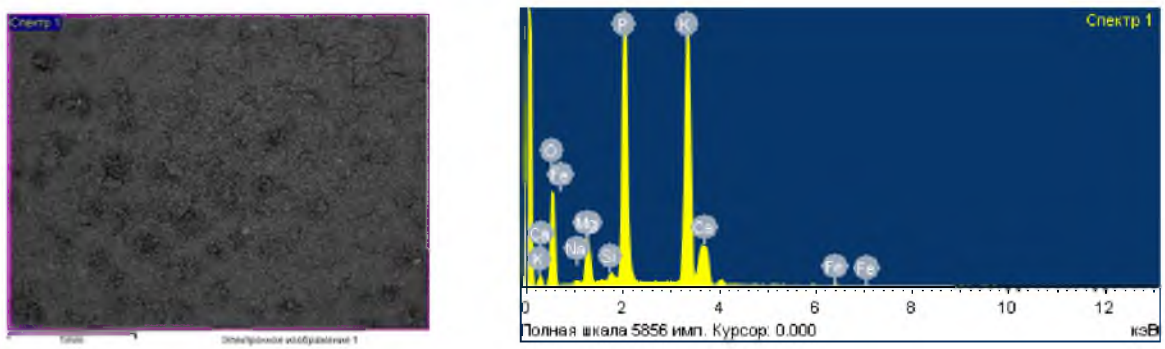

Figure 1 - Sample 1; Macaroni product without any additives

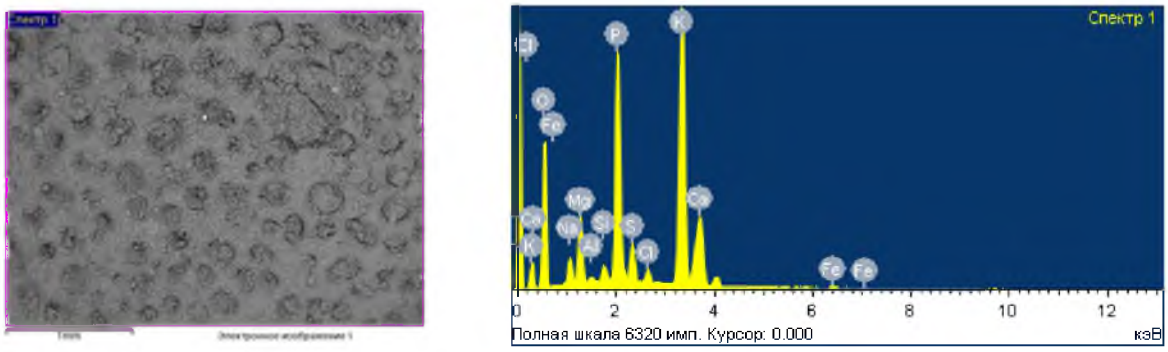

Figure 2. Sample 2; Macaroni products with carrot additives (5%) and holy thistle (*Silybum*) (5%)

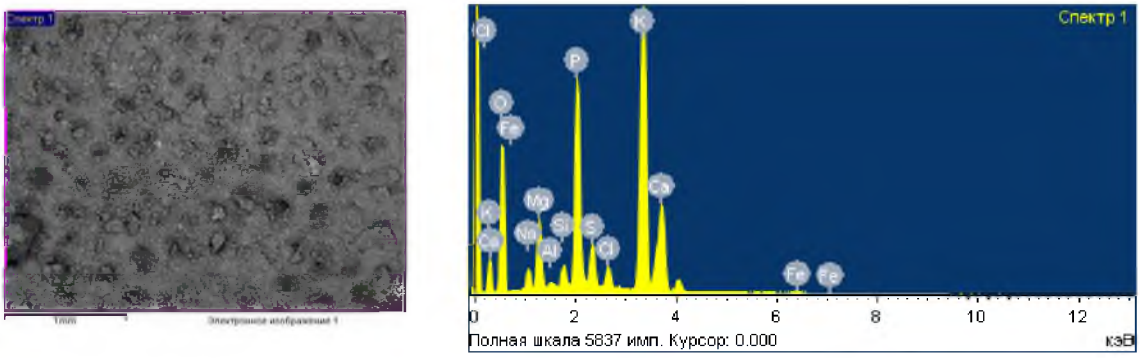

Figure 3. Sample number 3; Macaroni product with carrot additives (7%) and holy thistle (*Silybum*) (5%)

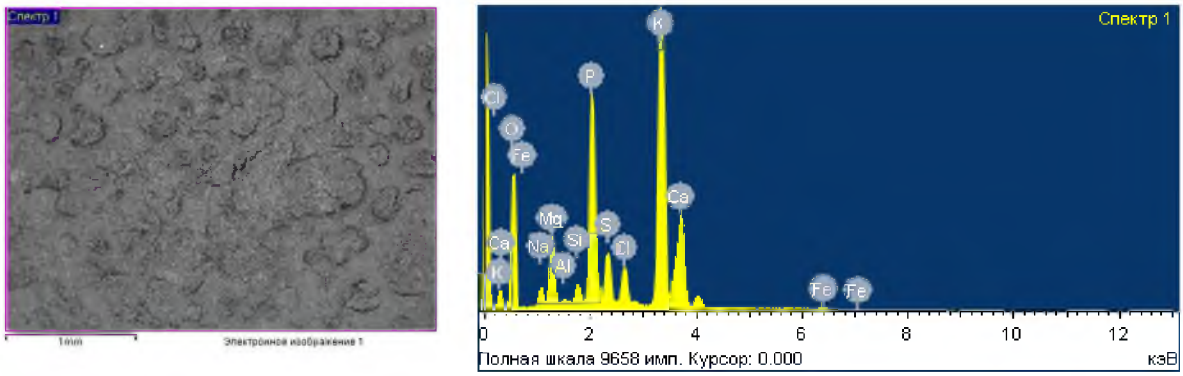

Figure 4. Sample № 4; Macaroni product with carrot additives (7%) and holy thistle (*Silybum*) (7%)

Table 1 - The chemical composition of macaroni product ashes with various additives studied by REM

Elements	№1 (initial), %	№2 (5+5), %	№3 (7+5), %	№4 (7+7), %
O	40,24	42,42	42,50	41,58
Na	0,29	2,69	2,02	1,93
Mg	3,93	4,41	4,66	4,43
Al	-	0,21	0,26	0,23
Si	0,45	0,70	1,11	0,84
P	21,31	13,96	12,06	11,86
S	-	2,51	2,81	3,16
Cl	-	0,97	1,44	2,77
K	28,58	24,54	23,79	24,00
Ca	4,94	7,25	9,07	8,83
Fe	0,26	0,31	0,26	0,32

For the comparative analysis, the sample 3 was chosen: macaroni product with carrot (7%) and holy thistle (*Silybum*) (5%) additives that by the organoleptic and physico-chemical properties, better meets the requirements of GOST.

Table 2 - Comparative analysis of macaroni product with various additives

	Elements	Macaroni product , %	Macaroni product with carrot additives (7%) and holy thistle (*Silybum*) (5%)	Increase in content,%
Macroelements	Na	0,29	2,02	697 %
	Mg	3,93	4,66	119 %
	P	21,31	12,06	- 43 %
	K	28,58	23,79	-17 %
	Ca	4,94	9,07	183 %
Microelements				
	Fe	0,26	0,26	0 %
	Al	-	0,26	26 %
	Si	0,45	1,11	247 %
	Cl	-	1,44	144 %

Investigation of microstructure in the form of macaroni product with various contents of carrot and holy thistle (*Silybum*) powder additives was carried out at a total moisture content of 13% for all samples (Figures 5-8).

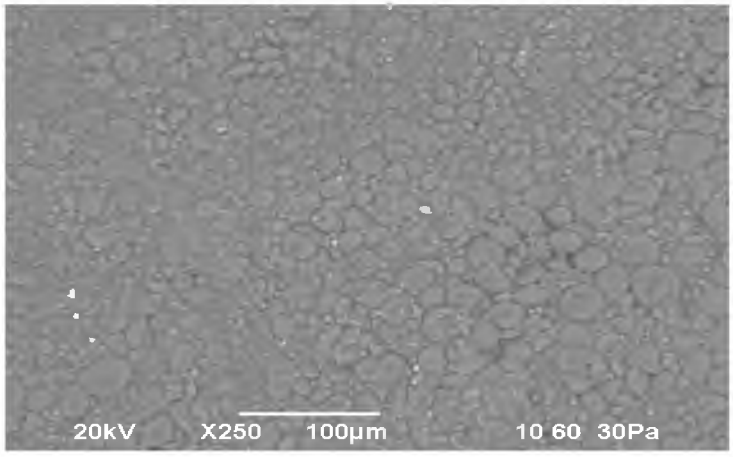

Figure 5 - Initial macaroni without additive

Figure 5 shows the microstructure of the dried initial macaroni product that has a loose structure with scattered flour grains and starch grains.

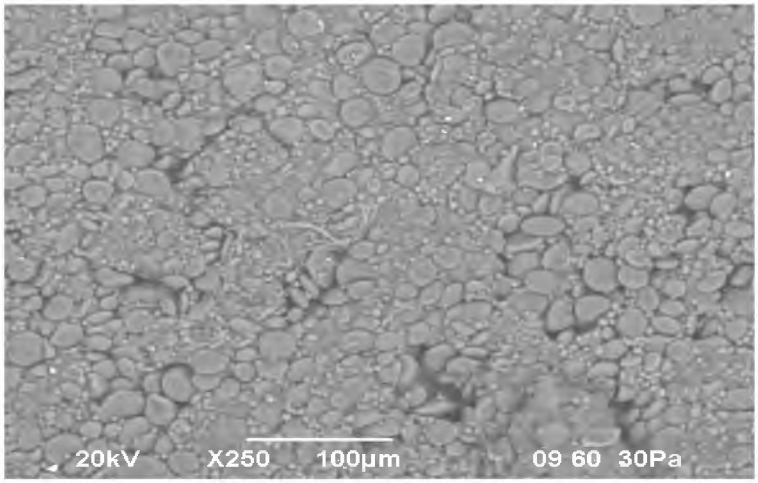

Figure 6 - Macaroni product with carrot (5%) and holy thistle (*Silybum*) (5%) additives

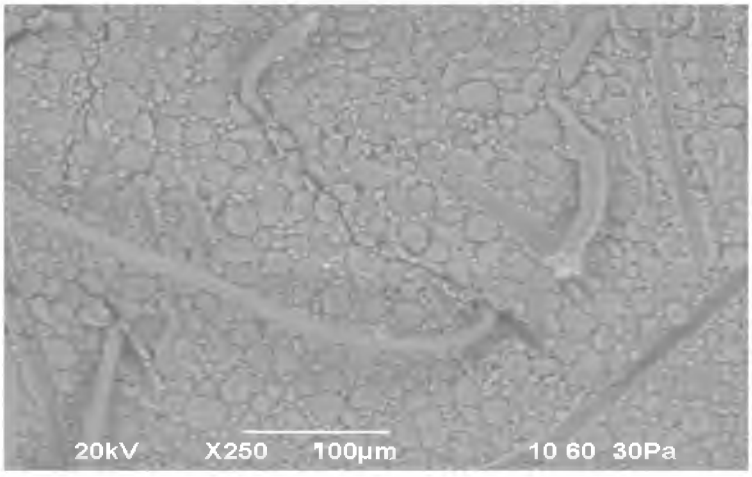

Figure 7 - Macaroni product with carrot additives (7%) and holy thistle (*Silybum*) (5%)

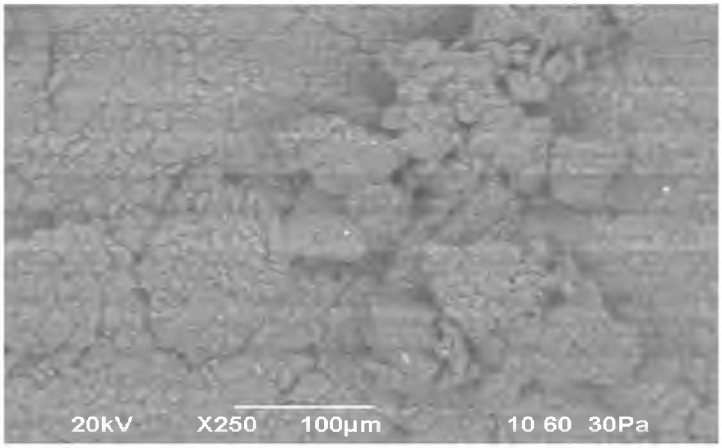

Figure 8 - Macaroni product with carrot (7%) and holy thistle (*Silybum*) (7%) additives

As well as the sample 3: Macaroni product with carrot (7%) and holy thistle (*Silybum*) (5%) additives was investigated for the organoleptic and physicochemical properties according to GOST 51865-2010.

Table 3 - Organoleptic characteristics of a new macaroni product

№	Name of the indicator	According to the requirements of GOST 51865-2010	Macaroni product with carrot (7%) and holy thistle (*Silybum*) (5%) additives
1	Color	Suitable for flour. The color of the product using additional raw materials varies depending on the type of this raw material.	Light orange, carrot
2	Forms	Corresponding to the type of products	Corrugated, long
3	Taste	Proper to this product, without foreign taste	Weak flavor of the vegetable additive
4	Smell	Characteristic of this product, without foreign smell	The faint smell of the vegetable additive

Table 4 - Physico-chemical indicators of new macaroni product

Indicators	According to the requirements of GOST 51865-2010	Macaroni product with carrot (7%) and holy thistle (*Silybum*) (5%) additives
Humidity,%, not more than	13	12
Acidity, ^{0}T, not more than	4	3,9
Ash insoluble in 10% HCl solution,%, not more than	0,2	0,2
Mass fraction of ash in terms of dry matter,%, not more than	1,4	1,5
Dry substance converted to cooking water,%, not more than	6,0	6,0
Preservation of the form of boiled products,%, not less than	100	100

Analysis of the obtained data shows that the addition of carrot (5%) and holy thistle (*Silybum*) (5%) powders gives for the macaroni product a fibrous-straw and loose structure (Fig. 6).

With the addition of carrots (7%) and holy thistle (*Silybum*) (7%), the structure of the dried pasta became uneven, due to the high content of additive powders that affects the quality of the dried pasta (Fig. 8). Therefore, the properties of macaroni product deteriorate, it becomes more elastic and firm that does not meet the requirements of macaroni semi-finished products.

However, a decrease in the amount of milk powder added from 7% to 5% (Fig. 7) gives the pasta a more homogeneous structure, but with individual sections of small discontinuities, apparently from the

influence of carrot dietary fibers. The structure of the dried pasta dough became dense, the carrot fiber binding fibers are visible [18].

The resulting stitched structure positively affects the quality of macaroni product and the process of heat treatment. The time of cooking is reduced from 8 minutes to 5 minutes. The process of cooking increases in 2 times for the total volume, but it does not boil and keep the form that is an important indicator of good quality for ready-made macaroni product.

Conclusion

The organoleptic and physicochemical studies show that the developed composition of a new macaroni product with dried carrot and holy thistle (*Silybum*) powder additives meet to the GOST requirements. Also by using the Raster Electronic Microscope (REM) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) devices, the macro- and microelement composition of the obtained samples were investigated. As a result of the addition of carrots and holy thistle (*Silybum*) the significantly increasing in the mass fraction of the main micronutrients, such as macroelements: Na, Mg, P, K; and microelements: Fe, Al, Si, Cl were found. Additional enrichment is carried out by phenolic compounds of holy thistle (*Silybum*) of flavonoid class in the form of flavolignans (silybin, isosilibine, silidianin, silicristin, isosilicristin et al) that have hepatoprotective and antioxidant properties. Also improvement by carotenoid-carotenes, flavonoids and various vitamins in carrots are provided. The obtained study results testify that the enriched macaroni products with carrots and holy thistle (*Silybum*) powder additives can quite correspond to the functional food stuffs with biologically active properties.

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БАЙЫТЫЛАТЫН МАКАРОН ӨНІМДЕРІНІҢ МАКРО ЖӘНЕ МИКРОЭЛЕМЕНТТІК ҚҰРАМЫН ФИЗИКА-ХИМИЯЛЫҚ ЗЕРТТЕУ

Аннотация. Байытылған макарон өнімдерінің органолептикалық және физикалық-химиялық зерттеу нәтижелері келтірілген. Тағам қоспалары ретінде антиоксиданттар, флавоноидтер және әртүрлі витаминдер көзі болып табылатын сәбіз ұнтағы және алатікен (Silybum) ұсынылады. Алынған үлгілердің макро және микроэлементтер құрамын растрлық электрондық микроскоп (РЭМ) және индуктивті плазмалық масс-спектрометрияны (ICP-MS) пайдалану арқылы зерттелді. Нәтижесінде негізгі микронутриенттер болып табылатын, макроэлементтер: Na, Mg, P, K; және микроэлементтер: Fe, Al, Si, Cl массалық үлесі едәуір ұлғаяды. Қосымша байыту гепатопротекторлық және антиоксиданттық қасиеттерге ие алатікеннің (Silybum) фенольды байланысымен жүзеге асырылады, флавоноид классының флаволигнан түрінде (силибин, изозилибин, силидианин, силикристин, изосиликристин және т. б.). Сондай-ақ, сәбіздің құрамындағы каротиноидтармен, каротинмен, флавоноидтармен және түрлі дәрумендермен жақсарту көзделген. Алынған зерттеу нәтижелері, алатікен (Silybum) және сәбіз қоспасымен байытылған макарон өнімдері, биологиялық белсенді қасиеттерге ие функционалдық азық-түлікке сәйкес келуі мүмкіндігін дәлелдейді.

Түйін сөздер: антиоксиданттар, сәбіз, тағамдық қоспалар, флавоноидтар, алатікен (*Silybum*), микроэлементтер, макарон өнімдері.

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ФИЗИКО-ХИМИЧЕСКОЕ ИССЛЕДОВАНИЕ МАКРО- И МИКРОЭЛЕМЕНТНОГО СОСТАВА ОБОГАЩЕННЫХ МАКАРОННЫХ ПРОДУКТОВ

Аннотация. Приведены результаты органолептических и физико-химических исследований обогащенных макаронных изделий. В качестве пищевых добавок предлагается порошок моркови и расторопши (Silybum), которые являются источниками антиоксидантов, флавоноидов и различных витаминов. С использованием растрового электронного микроскопа (REM) и масс-спектрометрии с индуктивно-связанной плазмой (ICP-MS) был исследован состав макро- и микроэлементов полученных образцов. В результате значительно увеличивается массовая доля основных микронутриентов, таких как макроэлементы: Na, Mg, P, K; и микроэлементы: Fe, Al, Si, Cl. Дополнительное обогащение осуществляется фенольными соединениями расторопши (Silybum) класса флавоноидов в форме флаволигнанов (силибин, изозилибин, силидианин, силикристин, изосиликристин и др.), которые обладают гепатопротекторными и антиоксидантными свойствами. Также предусмотрено улучшение каротиноидами-каротинами, флавоноидами и различными витаминами моркови. Полученные результаты исследования свидетельствуют о том, что обогащенные макаронные изделия с добавками моркови и расторопши (Silybum) вполне могут соответствовать функциональным продуктам питания с биологически активными свойствами.

Ключевые слова: антиоксиданты, морковь, пищевые добавки, флавоноиды, расторопша (*Silybum*), микроэлементы, макаронные изделия.