

Reduction of acrylamide formation in molded potato chips of increased nutrition value

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Abstract

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Introduction. The aim of the study is to determine the optimal temperature regimes for baking and drying potato dough to reduce formation of acrylamide in molded potato chips of increased nutritional value.

Materials and methods. The following raw materials were selected: potato grits, rye and barley bran, pumpkin seed meal, broccoli and red beet cryopowders. The amounts of aspartic acid and reducing sugars in raw materials, as well as acrylamide formed during the temperature treatment of the dough potato mass were determined.

Results and discussion. In order to increase the nutritional value of molded potato chips, the traditional raw material base has been expanded using various cereal bran, meal, dietary fibers, and vegetable powders. The recommended parameters for processing potato dough are: temperature of 125°C and a duration of 4.5 minutes without vegetable oil addition, in contrast to the traditional methods of molded potato chips production. The amount of aspartic acid in potato grain is 190.5 mg/g of protein and reducing sugars – 0.6%. The amount of aspartic acid in rye and barley bran is 77.5 and 72.6 mg/g of protein, respectively, in pumpkin seed meal – 80.5 mg/g of protein, in cryopowders of broccoli and red beet – 72.5 and 72.9 mg/g of protein. The content of reducing sugars in rye and barley bran is 0.74% and 0.8%, respectively, in pumpkin seed meal – 0.5%, in cryopowders of broccoli and red beet – 0.3% and 0.5%, respectively. After addition of non-traditional materials to the recipe, products were obtained in which no acrylamide was detected due to changes in the classical technology and parameters of molded potato chips production. It was investigated that when applying the classical technology of molded potato chips, the amount of acrylamide in the finished products is 61 µg in 100 g of the product. In molded potato chips without the addition of bran, meal and cryopowders, which were baked and dried, the amount of acrylamide is 9.35 µg in 100 g of the product.

Conclusions. The formation of acrylamide depends on the chemical composition of raw materials, the duration and temperature of baking-drying, and the technology of molded potato chips production.

Introduction

The the modern rhythm of life and the lack of time for a full meal lead to the habit of "quick snacking". Therefore, snack products are becoming popular in the diet of many peoples in the world. Nowadays one of the most popular food products are chips, which can quickly saturate the human body with energy and satisfy hunger (Ivanov et al., 2021). Along with this, scientists investigated that excessive consumption of chips can provoke various diseases due to the accumulation of toxic substances (methylpropanesulfonic acid and acryloyloxyethyltrimethylammonium chloride) in the human body (Howard et al., 2010; Majzooobi et. al., 2013).

In recent years, the use of non-traditional raw material based on pumpkin seeds, which after extracting the oil, are crushed to form a food meal, has become popular. Pumpkin seed meal fiber contains a balanced composition of amino acids and carotenoids, as well as a large amount of organic salts and good functional properties (Shevchenko, 2022a). Some vegetables (carrots, zucchini, cabbage, beets, peppers, and broccoli) are rich in insoluble dietary fibers, pectin, vitamins, and minerals. Modern equipment allows the production of vegetable powders due to various methods of drying without loss of useful nutrients (WHO, 2002). It was shown that bran, meal and cryopowders contain 4 times less starch than potato grits and 7 times more fiber. Cryopowders contain 2.5 times more mono- and disaccharides compared to potato grits, which affects further chemical processes in molded potato chips. In addition, the amount of fat in the cryopowders of broccoli and red beet is 0.2-0.3% of dry matter (DM). Therefore, these raw materials meet the requirements for initial parameters in the production of molded potato chips (Kovtun et al., 2018).

Scientists are concerned with the issue of reducing the amount of acrylamide formation in snack products. The toxicity of acrylamide is due to easy penetration into the human body through the gastrointestinal tract (Hunko et al., 2010).

Acrylamide is formed spontaneously in the process of cooking the product at a temperature above 120°C, especially during frying (WHO, 2005). According to the conclusions of experts of the FAO/WHO committee, the largest amount of acrylamide is found in such products: French fries (16-30%), chips (6-46%), coffee (13- 39%), confectionery and biscuits (10-20%), bakery products and bread fried in toasters (10-30%). Therefore, these products require a detailed study and justification of their production technology. Vacuum drying and infrared treatment are applied, addition of enzyme asparaginase, which is able to inhibit the reaction of melanoid formation and the formation of acrylamide are implemented in the technology of preparing foods for decrease acrylamide in them (Wenzl et al., 2003).

Research on the addition of asparaginase enzyme was carried out in the production of ginger cookies and crispbreads. It was established that when asparaginase was added to the dough for bread production, the acrylamide content decreased from 910 µg/kg to 740 µg/kg. As a result, the amount of acrylamide in ready-made loaves was reduced by 50%. For ginger cookies, the amount of acrylamide was 530 µg/kg, when asparaginase was added, the amount of acrylamide decreased to 60 µg/kg. As a result, it was possible to reduce the amount of acrylamide up to 90% (Sharma et al., 2017).

The use of antioxidants in combination with a mixture of vegetable oils is proposed to reduce acrylamide in chips from potato slices due to balance of the ratio of ω-3 and ω-6 fatty acids in them. It was established that when frying chips from potato slices of the 'Kimmeria' variety at a temperature of 140-180°C, the content of acrylamide in chips fried in palm oil was 194-252 µg/kg, meanwhile in a mixture of deep-fried (corn + rapeseed oil)

198-320 µg/kg. To reduce the amount of acrylamide, the optimal ratio (1:1) of blends of corn oil + rapeseed oil, which was used for frying, was selected due to experimental studies. These types of oil are balanced by polyunsaturated w-3 and w-6 fatty acids. In addition, the optimal thickness of potato chips was selected for frying (with a specific surface of 10.7 - 14.0 cm⁻¹), which allows to reduce the passage of the Maillard reaction. When eating 75 g of such chips, 184-188 µg of acrylamide is consumed by person, which does not exceed the permissible value according to WHO data (Kovalenko et. al., 2016a; Kovalenko et. al., 2016b). According to the FAO/WHO committee, the average intake of acrylamide with food is 1-4 µg/kg of body weight per day.

However, there is no research on the amount of acrylamide in molded potato chips that are made from dry mashed potatoes.

Therefore, the aim of the present research was to study the influence of the parameters of molded potato chips production on the amount of acrylamide formation.

Materials and methods

Materials

Potato grits ('Bikrampur', Germany), traditional raw materials – rye and barley bran, pumpkin seed meal ('Agrosilprom', Ukraine), as well as non-traditional raw materials (cryopowders of broccoli and red beet) ('Gammy', Ukraine) were chosen for the research. This choice of raw materials is due to their high nutraceutical composition, namely the increased amount of dietary fibers, cellulose, hemicellulose, pectin, minerals, fat-soluble vitamins in these raw materials (Kobets et al., 2016).

Amino acid composition

The determination of amino acid composition of studied materials was carried out on an automatic amino acid analyzer T 339 (Mikrotechna Praha a.s., Praha, Czech Republic). The eluent from the container is driven through the chromatographic column using a dosing pump. The area of the peaks on the chromatogram is calculated and compared with the area of the peaks of amino acids with a known concentration. From the comparison of these areas, the absolute amount of amino acid in the analyzed sample is calculated.

On the chromatogram, the peak area of each amino acid (peak height) is calculated. Hydrolysis is carried out as follows: a weighted sample with a dry protein content of about 2 mg is placed at the bottom of the test tube. 0.5 ml of distilled water and 0.5 ml of concentrated hydrochloric acid are added to a dry weight of protein in a test tube. An equal amount of concentrated hydrochloric acid is added to the aqueous protein solution. The tube is cooled in a mixture of dry ice with acetone or liquid nitrogen. After the content of the tube freeze, air is pumped out of it using a vacuum pump to prevent oxidation of amino acids. Then the test tube is sealed and placed for 24 hours in a thermostat with a constant temperature of +106°C. At the end of hydrolysis, the test tube is opened, previously cooled to room temperature. The contents are quantitatively transferred into a glass beaker and placed in a vacuum-desiccator over granulated caustic soda. Then air is removed from the desiccator using a water jet pump. After drying the sample, 3-4 ml of deionized water is added to the buxets and the drying procedure is repeated. The sample prepared in this way is dissolved in 0.3-normal lithium citrate buffer (pH=2.2) and applied to the ion exchange column of the amino acid analyzer (Litvynchuk et. al., 2022).

Mass fraction of sugars

Determined was provided by the accelerated iodometric method. The procedure for conducting the analysis consists of the following main stages: preparation of a water extract; hydrolysis of sucrose in the obtained extract and quantitative determination of sugar by its reducing properties.

30 cm³ of the obtained filtrate, 10 cm³ of a 6.9% solution of copper sulfate and 10 cm³ of an alkaline solution of potassium-sodium tartaric acid are added to a 50 cm³ conical flask and the content is brought up to the mark with distilled water. The flask is heated on a gas burner for up to 3 minutes and boiled for 2 minutes from the moment of boiling start and cooled. Then 10 cm³ of a 30% potassium iodide, 25% sulfuric acid solution are added to the flask and the released iodine is titrated with a 0.1 mol/dm³ solution of sodium thiosulfate to a light yellow color. Under these conditions, a control experiment is also conducted (Shevchenko et al., 2022b).

Determination of the amount of acrylamide

Determination was performed on an Agilent 7890A gas chromatograph (USA) with a Supelcowax chromatographic column (60 m, 0.53 mm, 1 μm). The gas chromatograph was equipped with electron capture (Agilent) and mass-selective (Finnigan Trace DSQ II) (USA) detectors, which worked alternately. Centrifugation of samples was carried out on centrifuges: 'Rotina 38' (Germany) and 'Eppendorf 5418' (Germany), shaking – in a shaker 'Biosan OS-10' (USA).

About 50 mg of acrylamide was weighed into a 50 ml volumetric flask. 20 ml of distilled water was added and stirred until complete dissolution. After that, the volume was brought up to the mark with distilled water and mixed (basic solution, concentration 1 μg/ml), 1 ml of the basic solution was transferred to a 100 ml volumetric flask, brought up to the mark with distilled water and mixed (working solution, concentration 10 μg/ml) then this solution was transferred to a gas chromatograph. For the control sample, dry milk was selected (preliminarily tested for the absence of acrylamide) and acrylamide was added in the amount of 0.005 to 5.0 mg/kg. The next step was extraction to remove proteins and fats, followed by bromination of the solutions and purification of the ethyl acetate extract. Chromatographic separation and detection conditions are: 140°C – 1 min, then 220°C – 5 min, isotherm – 33 min, nitrogen carrier gas 4 ml/min. Operating parameters of the electron capture detector are: temperature 300°C, blowing flow – 30 ml/min (Ghiasvand et. al., 2016).

Results and discussion

Considering the fact that in cereal products, unlike potato, the content of asparagine plays a decisive role in the formation of acrylamide, it was established that the highest content of it is in bran with a grain size of more than 560 μm (Table 1). Therefore, additional grinding of this raw material to sizes commensurate with potato grits and cryopowders of 30-40 microns was carried out. Cryopowders have asymmetric proportions in their chemical composition relative to bran and meal. Obviously, this is explained by the fact that all these types of raw materials contain dietary fibers that are able to retain asparagine even under the conditions of its extraction.

Table 1

Content of aspartic acid in raw materials

| Raw material | Amount of amino acid mg/g of protein | Amount of amino acid mg/100 g of product |
|-------------------------|--------------------------------------|--|
| Potato grits | 190.5 ±2.0 | 769.0±3.6 |
| Rye bran | 77.5±1.0 | 340.5±3.2 |
| Barley bran | 72.6 ±1.0 | 298.3±3.2 |
| Pumpkin seed meal | 80.5 ±1.5 | 354.7±3.2 |
| Broccoli cryopowder | 72.9 ±1.5 | 292.6±3.0 |
| Red beetroot cryopowder | 72.5 ±1.5 | 287.6±3.0 |

* Results given as: M ± SD (mean ± standard deviation) of triplicate trials.

Potato grits contain 2.5 times more aspartic acid than bran, meal and cryopowders. According to the proposed technology, a part of potato grits was mixed in a ratio of 4:1 with raw materials – bran, meal or cryopowder. Potato grits contain 2.5 times more aspartic acid than bran, meal and cryopowders, which contributes to the formation of acrylamide. According to the proposed technology, part of the potato grits was replaced by rye and barley bran, pumpkin seed meal, broccoli and red beetroot cryopowders in a prescription ratio of 4:1. At other ratios (1:1, 2:1, 3:1), which were chosen for the experiment, significant deviations of the organoleptic parameters of the finished chips (appearance, taste, smell, consistency) were observed, and the chips production technology did not meet regulatory requirements. The process of frying molded potato chips in frying oil was replaced by baking-drying, which will allow further prediction of changes in the amino acid composition of the finished molded potato chips and reduce the formation of acrylamide.

One of the main indicators affecting the quality of molded potato chips is the amount of reducing sugars in raw materials, which, in addition to color, affect the process of formation of complex substances (melanoidins) and the accumulation of acrylamide in finished products (Sharma et al., 2017). Therefore, it is advisable to determine the mass fraction of reducing sugars in the studied raw materials (Table 2)

Table 2

Mass fraction of reducing sugars in potato grits, bran, meal and cryopowders

| Raw material | Mass fraction of reducing sugars, % ofDM |
|-------------------------|--|
| Potato grits | 0.60±0.01 |
| Rye bran | 0.80±0.03 |
| Barley bran | 0.74±0.03 |
| Pumpkin seed meal | 0.50±0.02 |
| Broccoli cryopowder | 0.35±0.01 |
| Red beetroot cryopowder | 0.30±0.01 |

* Results given as: M ± SD (mean ± standard deviation) of triplicate trials.

The content of reducing sugars in potato grits is lower compared to rye bran by 33.3%, barley bran – by 23.3%. Scientists have researched that the content of reducing sugars in fresh potato tubers from which chips are made is more than 1%, therefore, such potatoes are washed well after cutting, and also blanched in order to decrease the content of reducing sugars and inactivate some enzymes, then frozen and dried (Burtron, 2013). On the other hand, the content of reducing sugars in the pumpkin seed meal is lower than in potato grits

by 23.3%, this is due to the fact that the pumpkin seeds from which meal is obtained belong to oil crops and chemical composition of this raw material differs from potato grits (Drobot et al. , 2021). Pumpkin seed meal is produced mechanically (by crushing the husk), which does not affect the quantitative content of reducing sugars. The amount of reducing sugars in cryopowders is 42-50% less than in potato grits. During the hydrothermal processing of vegetables and their drying in a hot stream of air, part of the reducing sugars may partially evaporate, thereby reducing the content of reducing sugars, which is a positive factor in the production of molded potato chips. Such values are related to the features of technological processing of raw materials and their chemical composition. Based on the obtained experimental data all the presented samples of raw materials are suitable for the further production of molded potato chips from the point of view of safety.

To reduce the amount of acrylamide in molded potato chips, part of the potato grits was replaced in a ratio of 4:1 with one of the studied raw materials: rye or barley bran, pumpkin seed meal, broccoli and red beet cryopowders. Pre-prepared raw materials with a size range (raw material coarseness up to 40 μm) were mixed in a dry form, gradually (in equal parts) a salt solution of water with a temperature of 20°C was added, until the moisture content of the potato dough was 42%. The obtained mass was mixed until a homogeneous consistency, formed and left for 20 minutes for the passage of physico-chemical processes. One sample of molded potato chips without the addition of secondary raw materials was fried in oil according to a standard technology, other samples of molded potato chips were baked and dried. The results of studies on the amount of acrylamide formation are shown in Figures 1–7.

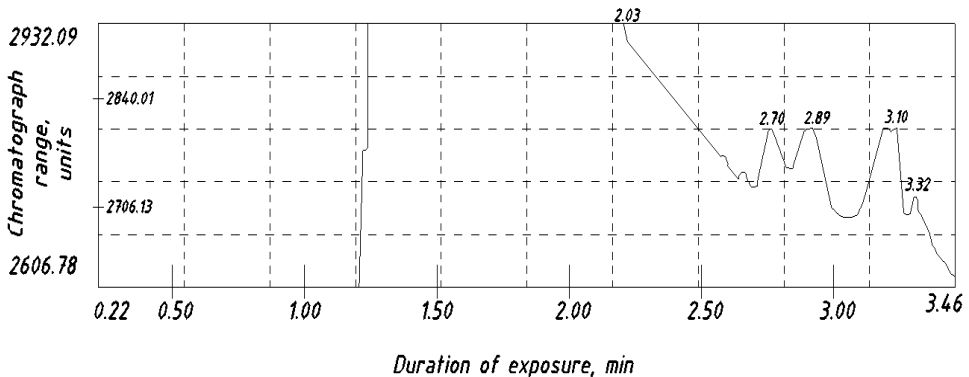


Figure 1. Amount of acrylamide in molded potato chips without oil (control sample)

A small amount of acrylamide – 9.35 μg per 100 g of product, was found in molded potato chips (control) on the 2.8 min of heating. Chips were baked and dried without oil at a temperature of 125°C for 4.5 min. With further heating up to 3.3 min, the amount of pre-fixed acrylamide did not increase. A small amount of acrylamide is formed due to free asparagine, which is contained in potato grain. In addition, potato grits contain amylose and amylopectin. Intact starch grains, which are insoluble in water, can absorb water initially in a limited amount, and when the temperature rises above 100°C, they actively absorb moisture in an unlimited amount. Baking-drying was carried out at a temperature of 125°C without the use of additional raw materials, which accelerates the release of moisture, therefore reducing sugars react with amino acids and the Maillard reaction occurs, which leads to the formation of acrylamide.

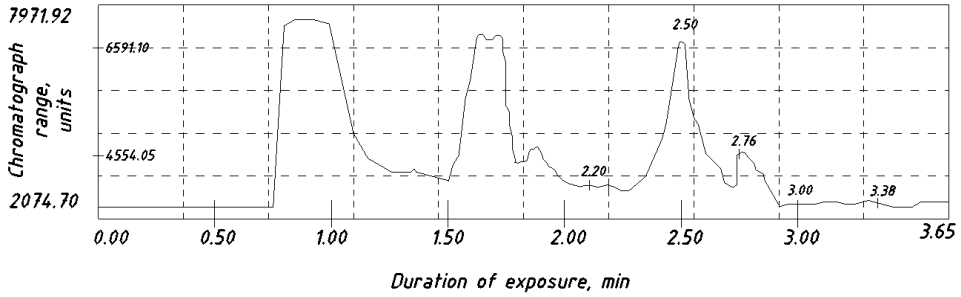


Figure 2. Amount of acrylamide in molded potato chips fried in oil

In a sample of molded potato chips, which were fried under standard conditions (temperature – 160°C, duration – 1.5-2 minutes) using oil, an increased concentration of acrylamide begins to be recorded on the chromatogram starting from 2.2 minutes, the point at which the maximum value of acrylamide accumulation was after 2.5 min of heating – 61 µg in 100 g of product. Starting from 2.76 min, the peak of acrylamide formation falls and the amount of acrylamide does not increase within 1 min.

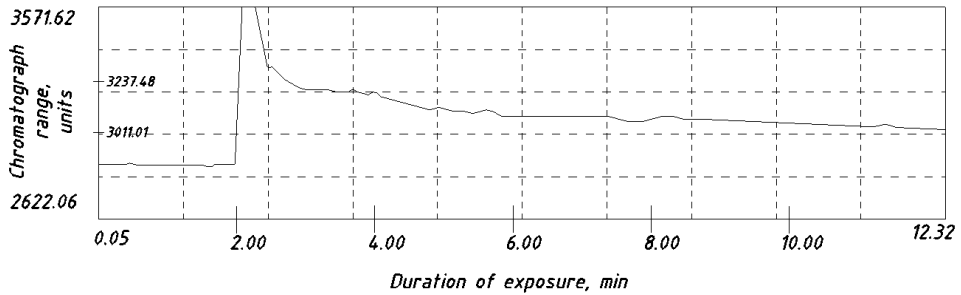


Figure 3. Amount of acrylamide in molded potato chips with rye bran

The heating time of the studied sample of molded potato chips with rye bran is 12.32 minutes. The oscillation range of the chromatograph starts from 0.05 min, while there is a sharp jump in the bromination of the extract of the studied mixture, but the peak of acrylamide formation in this sample was not recorded. It is due to the presence of fiber in the secondary raw material (47.6% by weight of the DM) because cellulose, hemicellulose, lignin, which speeds up the removal of moisture, are included in its composition.

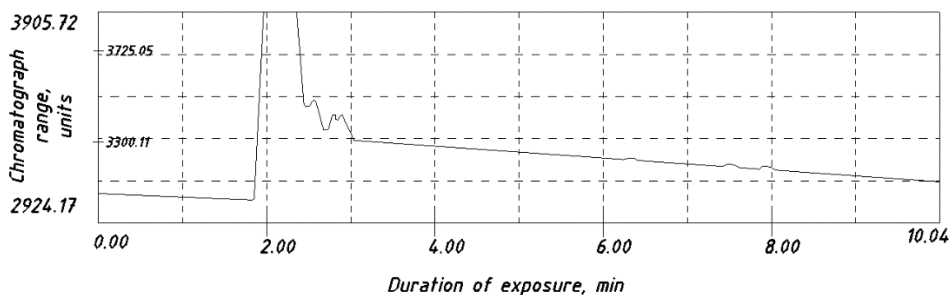


Figure4. Amount of acrylamide in molded potato chips with barley bran

The heating of the sample of molded potato chips with barley bran occurs immediately. At 2 min, a jump on chromatogram is observed, which does not record the formation of acrylamide. The final stage of completion of the reaction takes place during 10 minutes of heating the test sample. The process of completing the research is 1.2 times faster than for the sample with rye bran. This is due to the fact that the dietary fibers of barley bran are more easily brominated and therefore the process of completing the experiment is shortened.

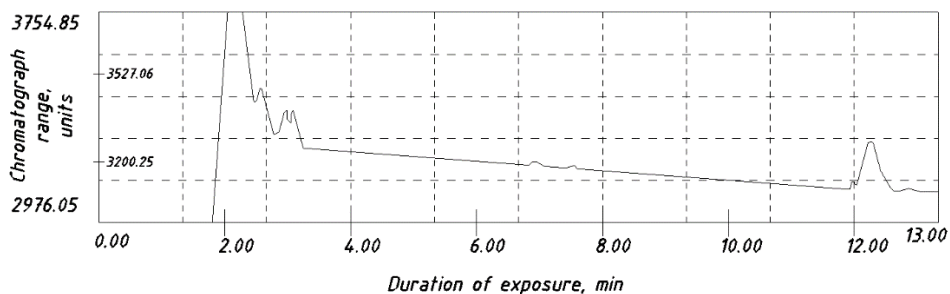


Figure 5. Amount of acrylamide in molded potato chips with pumpkin seed meal

For sample with pumpkin seed meal closer to 2 min, the peak of the reaction occurs with a gradual decline starting from 2.7 min to 3.3 min. Then the system stabilizes and the bromination process stops. A slight peak is observed at 12 min, which leads to the completion of the reaction. These data are explained by the fact that the pumpkin seed meal contains a small amount of oil, which can provoke sudden fluctuations in the system.

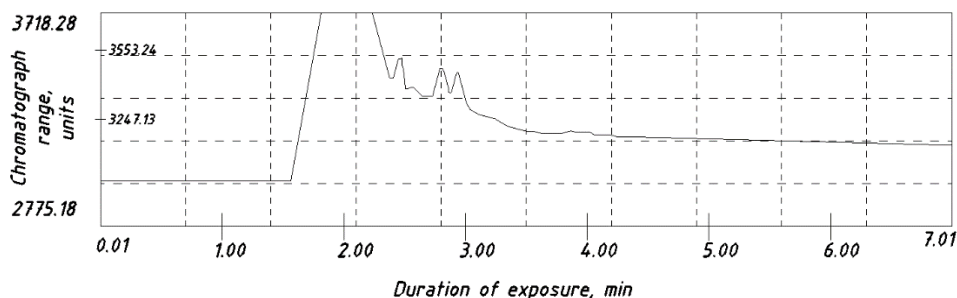


Figure 6. Amount of acrylamide in molded potato chips with broccoli cryopowder

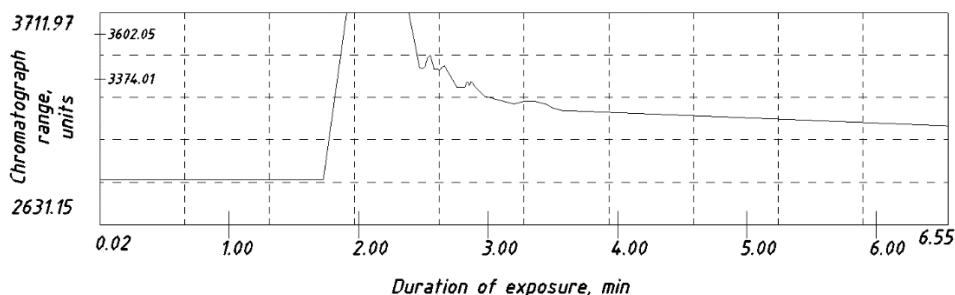


Figure 7. Amount of acrylamide in molded potato chips with red beet cryopowder

The process of heating the samples with cryopowders begins at 0.01-0.02 min. When approaching 2 min, a reaction peak is observed, which gradually stabilizes to 6.55 min and 7.01 min in samples with broccoli cryopowder and red beet cryopowder, respectively. Compared to the samples of molded potato chips with bran and pumpkin seed meal, the reaction time for molded potato chips with cryopowders is 2 times shorter. This is obviously due to a decrease in the pH level due to the content of organic acids and a reduced amount of aspartic acid.

Analyzing the obtained data of chromatograms of samples of molded potato chips minor peaks were found on all chromatograms that did not reach the critical point at which acrylamide formation occurs. This is due to the fact that the potato dough has a high moisture content – more than 42%, and the baking-drying process itself takes place at a relatively low temperature of 125 °C for up to 4.5 minutes. Therefore, part of the acrylamide can evaporate from the product. It is important that acrylamide begins to form only when the temperature in the middle of the product reaches above 120°C due to the chemical composition of the studied raw materials, namely the content of dietary fibers. During the keeping of the potato dough, there is a uniform redistribution of moisture due to which, at a baking-drying temperature of 125°C, the temperature in the middle of the formed potato chips fluctuates is about 115°C (Sharma et al., 2017).

Therefore, it is proposed to produce molded potato chips according to improved technology and to changed the temperature treatment parameters. It's advisable to remove the vegetable oil used in frying, and to carry out baking-drying of molded potato chips without the use of oil under the following parameters: the potato mass of the semi-finished product of one sample of molded potato chips is no more than 20 g, processing time – up to 4.5 min, baking-drying temperature – no more than 125°C.

Since the rye and barley bran, and pumpkin seed meal are secondary raw materials and are made from rough fruit shells of plants, they contain a small amount of aspartic acid and sugars. Potato grits, broccoli and red beet cryopowders are produced by cryogenic drying at high pressure and multi-stage cryo-shredding. At the same time, it is possible to significantly reduce the amount of aspartic acid and reducing sugars in chips when these additives are added to the recipe.

Conclusions

1. Traditional and non-traditional raw materials were selected for the production of molded potato chips, and the frying process was replaced by baking-drying at a temperature of 125 °C to reduce formation of acrylamide.
2. It was established that the bran, meal and cryopowders included in the formulation of molded potato chips have a small amount of reducing sugars (content does not exceed 1%), as well as 2.5 times less aspartic acid compared to the potato grits.
3. The presence of acrylamide in chips with rye and barley bran, pumpkin seed meal, broccoli and red beet cryopowders was not detected during chromatographic studies. It is due to the use of raw materials with a reduced amount of aspartic acid and reducing sugars, as well as a temperature processing method without frying in oil and a reduced baking-drying time of up to 4.5 minutes.

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Зменшення вмісту акриламід у формованих картопляних чіпсах підвищеної харчової цінності

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Вступ. Метою дослідження є визначення оптимальних температурних режимів випікання-висушування картопляного тіста для зменшення акриламід у формованих картопляних чіпсах з підвищеною харчовою цінністю.

Матеріали і методи. В якості досліджуваної сировини обрано: картопляну крупку, висівки жита, ячменю, жмих гарбузового насіння, кріопорошки броколі та червоного буряка. Визначали кількість аспарагінової кислоти, редукувальних цукрів в основній та додатковій сировині, а також кількість утвореного акриламід у процесі температурного оброблення тістової картопляної маси.

Результати і обговорення. Для підвищення харчової цінності формованих картопляних чіпсів розширено традиційну сировинну базу за рахунок застосування різних висівок зернових, жмиху, харчових волокон, порошоків овочів, тощо. Рекомендовані оптимальні параметри оброблення картопляного тіста при температурі 125°C та тривалості 4,5 хв без застосування рослинних олій на відміну від традиційних способів виробництва формованих картопляних чіпсів. Визначено кількість аспарагінової кислоти – 190,5 мг/г білка і редукувальних цукрів – 0,6 % в картопляній крупці. У висівках жита та ячменю кількість аспарагінової кислоти 77,5 та 72,6 мг/г білка відповідно, у жмиху гарбузового насіння – 80,5 мг/г білка, у кріопорошках броколі та червоного буряка – 72,5 та 72,9 мг/г білка відповідно. Масова частка редукувальних цукрів у висівках жита та ячменю складає 0,74 та 0,8 %, у жмиху гарбузового насіння – 0,5 %, у кріопорошках броколі та червоного буряка

– 0,3 та 0,5 % відповідно. Отримані кінцеві продукти, в яких не виявлено акриламід у завдяки зміни класичної технології і параметрів виробництва формованих картопляних чіпсів. Досліджено, що при застосуванні класичної технології формованих картопляних чіпсів кількість акриламід у готових виробах становила 61 мкг в 100 г продукту. В формованих картопляних чіпсах без додавання висівок, жмиху та кріопорошків, які випікалися-висушувалися, кількість акриламід була 9,35 мкг в 100 г продукту.

Висновки. Утворення акриламід у залежить від хімічного складу сировини, тривалості та температури випікання-висушування та технології виробництва формованих картопляних чіпсів.

Ключові слова: картопляна крупка, чіпси, висівки, кріопорошок, акриламід.