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THE RESEARCH OF THE AMOUNT OF HEAVY METALS AND NITROSO COMPOUNDS IN CONCENTRATED TOMATO PRODUCTS

V.V. Shutyuk, Ph.D., associate professor
S.M. Vasilenko, PhD, professor
A.S. Bessarab, Ph.D., professor, *E-mail:* a_bessarab@i.ua
O.V. Benderska, postgraduate, *E-mail:* olga_benderska@ukr.net
National University of Food Technologies, Kyiv-33, Volodymyrska str.68, Ukraine, 01601,

Abstract. The constant selling race results in need for improving the quality of nutrition products among in-house food and pharmaceutical processing industries, which is an all-important key to success on the consumer market. This requires constant improvement of the product producing technologies. The topical problem of quality is the presence of heavy metals and nitroso compounds in the products. The research aimed at studying the changes in the heavy metal concentration levels (including Zn, Cu, Pb) in tomato products at their thickening has been conducted at the national University of Food Technologies. On the basis of the received results the relationship between the lead, copper, zinc, nitrosocompounds and the solid substances' amount has been established. The conducted research allowed us to ascertain the fact that the amount of heavy metals and nitroso compounds in raw materials for the concentrated tomato products to be ofhigh quality must not exceed the values of 18 – 35 % of the limiting concentration.

Key words: nitrates, contaminants, food safety, quality, fruits and vegetables.

ДОСЛІДЖЕННЯ ВМІСТУ ВАЖКИХ МЕТАЛІВ І НІТРОЗОСПОЛУК В КОНЦЕНТРОВАНИХ ТОМАТОПРОДУКТАХ

В.В. Шутюк, доктор технічних наук, доцент
С.М. Василенко, доктор технічних наук, професор
О.С. Бессараб, кандидат технічних наук, професор, *E-mail:* a_bessarab@i.ua
О.В. Бендерська, аспірант, *E-mail:* olga_benderska@ukr.net
Національний університет харчових технологій, м. Київ-33, вул. Володимирська, 68, Україна, 01601

Анотація. Постійна боротьба за ринки збуту продукції вимагає від вітчизняних підприємств харчової та переробної промисловості підвищувати якість харчових продуктів – невід'ємну складову їхнього успіху на споживчому ринку. Для цього необхідно постійно вдосконалювати технологію виробництва продуктів. Надзвичайно актуальною проблемою якості є наявність в продуктах харчування важких металів і нітрозосполук. У Національному університеті харчових технологій проведені дослідження по вивченню зміни концентрації важких металів (Zn, Cu, Pb) і нітрозосполук в томатопродуктах при їх концентруванні. На основі отриманих результатів встановлено залежності зміни концентрації свинцю, міді, цинку і нітрозосполук від вмісту сухих речовин. Проведені дослідження дозволили встановити, що для отримання якісних концентрованих томатопродуктів вміст важких металів і нітратів у сировині не повинен перевищувати 18 – 35 % гранично допустимої концентрації.

Ключові слова: нітрати, контаміанти, продовольча безпека, якість, плоди та овочі.

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Introduction. The problem formulation

The chemical pollution, which drastically increases every year, affects all the media – water, air, ground – creating completely new conditions for living, differing from those plants, animals and humans were adapted to throughout millenia [1]. This fact gives rise to concerns. A variety of data indicates that the ecological factor substantially influences the element chemical content of plants and the products of their processing. The greatest danger is presented by the absorption of a range of toxic elements, including heavy metals, by plants [2,3].

During the production process of the concentrated tomato products the amount of heavy metals in them considerably increases at the increase of dry substances. In addition, the structural changes in products take place under the influence of high temperature – new compounds are being formed, including nitrosamines (NA). one of the most dangerous cancerogenes is N-nitrosodimethylamine (NDMA), which is formed at the nitrosation of the amino gen groups under the temperature influence [4-6]. This is a potent cancer-causing chemical, included by the International Agency for Research on Cancer along with another nitroso compounds to a group of compounds described as definitely cancerogenic to humans. The lack of profound research of the concentration level changes of heavy metals, nitrates, NA and NDMA at tomato compounds'

thickening resulted in the need for careful studying of these processes.

Literature review

The extraordinary problem of production of quality foodstuffs is that they have various harmful substances, heavy metals and radionuclides. As a rule, the harmful impurities in small concentrations remain out of attention. The most dangerous things for human health are cancerogenic substances which contained in negligible concentrations in foodstuffs and cause malignant formations in organism [5]. Their content in products can be identified by only a few laboratories in Ukraine. One of the most dangerous carcinogen is N - nitrozodymetylamin wich is formed during formation amine groups under the influence of temperature. Nitrates are normal products of metabolism of nitrogenous substances for any plant and animal organism, so there are not any products «without nitrates» in nature. The acceptable daily dose of nitrates for an adult is 325 mg per day. Maximum allowable concentrations of nitrates are defined for vegetables and fruits [2]. Nitrosamines are formed during production of many foodstuffs. Thus, they are contained in a large number in different beverages (juice, beer and Scottish whiskey), foodstuffs (dairy products, smoked products, pates, fruit and fruit and vegetable puree), cosmetics, cigarettes. They are mainly formed during thermal processing of foodstuffs – extraction, concentration, drying, etc. Nitrate content in canned products of plant origin is, mg/kg: vegetable juice – no more than 70 – 340, vegetable puree – to 160, canned vegetables – 50, fruit and vegetables canned 200. Maximum allowable concentrations of nitrates in dry dairy mixtures is 30 mg/kg in most European countries. The concentration of N-nitrozodymetylaminu in most sorts of beer is 40 – 70 μg/kg, the main part is accumulated during production of malt (N content – nitrozodymetylaminu in brewery malt is 300 μg/kg). The average N content – nitrozodymetylaminu in most varieties of cheese is 0,9 μg/kg, but in some areas it reaches to 9,1 μg/kg [7-8,10].

The purpose of research is identifying the amount of heavy metals and nitrates in the concentrated tomato products. Attracting attention to the problem of increasing pollution of plant products and the products of their processing. Giving practical recommendation as for the ways of decreasing the heavy metals' and nitrates' concentration levels at the stage of producing the concentrated tomato products.

The main part

Materials and methods. The tomatoes of the Lampo F1 sort served as the material of the research, which are used for processing totomato paste, juice and other tomato products with the high dry substance content (5,6 – 6,3 %), and are well adapted to all the areas of industrial tomato cultivation.

For tomato product concentration the laboratory vacuum rotary evaporator IKA RV 10 digital V was used. The heavy metal concentration (Zn, Cu, Pb) was measured using the atomic absorption spectroscopy method based on the procedure of the All Union State Standard 26929-94 «Raw materials and nutritive products. Sample preparation. Mineralization for identification of the amount of toxic elements». The amount of nitrates in tomato products was define don't he basis of the National Standards of Ukraine 4948:2008 «Fruits, vegetables and the products of their processing. Methods of measuring the nitrate content». The identification of the amount of N-nitrosamines was conducted according to the methodological guide linesan dinspection methods of MG4.4.1.011-93 «Measuring the volatile N-nitrosamines in the food raw materials and nutritive products ». (Approved by the State Committee on Sanitary and Epidemiology Surveillance (SCSES) of the Russian Federation on 22.12.1993).

Results. The research conducted in the National University of Food Technologies has shown that the amount of heavy metals in the concentrated tomato products linearly depends on the amount of dry substance (Table 1) and is described through the relation of $y = a + b^x$. The received experimental data have been processed with the help of the regression empirical series based on the least squares principle [5,7-8].

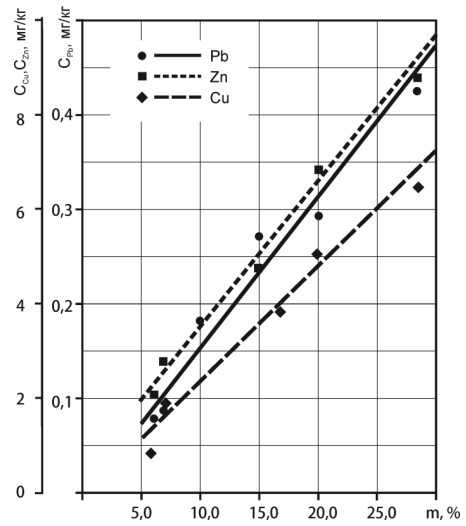
Table 1 – The amount of heavy metals in tomato products, mg/kg

Metal	The concentration level of tomato dry substances, %				
	5,6	6,3	15,0	20,0	28,5
Lead (Pb)	0,086	0,928	0,266	0,293	0,432
Copper (Cu)	0,908	1,869	3,870	5,020	6,575
Zinc (Zn)	2,107	2,415	4,826	6,901	8,985

As a result of the mathematical calculations coefficients and bof the relations concerning the amount of heavy metals in the concentrated tomato products (Graph 1) were defined. We have come to a conclusion that there lation ship between the lead concentration in tomato products and the dry substance amount is realized through the formula:

$$C_{Pb} = 0,006 + 0,016\ m,\ mg/kg, \quad (1)$$

in which m is the dry substance concentration, %.



Graph. 1.There lation between the values of the heavy metal concentration (Pb, Zn, Cu,) and the tomato product concentration

The copper amount depending on the dry substance concentration is expressed through the expression:

$$C_{Cu} = 0,42 + 0,23\ m,\ mg/kg \quad (2)$$

In order to define the relation between the zinc concentration and the dry substance content the following equation is used:

$$C_{Zn} = 0,01 + 0,35\ m,\ mg/kg \quad (3)$$

The careful consideration of the results of the conducted experiments indicates that at the in crease in dry substance on concentration as well as regular concentration by 6,33 times (the dry substance percentage in the un processed producte quals 5,6 – 6,3, in the concentrate it amounts to 28,5), the lead, copper and zinc concentration rises by 6,5 – 7,5 times.

The Sanitary Rules and Regulations 43-123-4089-86 have similar requirements concerning the maximum allowable concentration of heavy metals an darsenic in vegetables and vegetable canned goods including concentrated tomato products. Thus, we cannot eliminate the possibility that at the evaporation of tomato juice, the amount of heavy metals and arsenic in which equals 0,18 – 0,25 of their maximum allowable concentration or higher, the received tomato paste may have the amount of heavy metals and arsenic which exceeds the maximum allowable concentration, not satisfying the requirements of the Sanitary Rules and Regulations 43-123-4089-86. The given conclusion is proven by the results of the conducted experiments, when at the maximum allowable concentration of copper amounting to 5 mg/kg and its amount in the original material qualing 0,9 mg/kg, its concentration in creased up to 6,6 mg/kg, i.e.it exceeded the maximum allowable concentration value.

So, in order to receive the concentrated tomato products the amount of heavy metals and arsenic in which definitely won't exceed the maximum allowable concentration value, the requirements to the amount of these elements in the unprocessed materials have to be toughened. This value should not exceed (0,15 – 0,18) of the maximum allowable concentration established by the Sanitary Rules and Regulations 43-123-4089-86.

In the process of conserving and concentrating the juice under the temperature influence undergo the structural changes – new compounds, including nitrosamines, are formed. Particularly, fresh tomato juice contains 45 mg/kg of amino acids, whereas the conserved juice includes only 337 mg/kg of these chemical compounds (Table 2). That is why while designing the new equipment for production of the concentrated vegetable juice we have studied the mechanisms of NDMA formation.

Table 2 The amount of amino acids, mg/100 g of fresh and processed juice

Amino acid	Fresh juice	Canned juice
Asparaginic acid	5,5	51,6
Threonine	1,0	9,0
Serine	2,3	12,7
Glutamic acid	21,9	212,5
Phenylalanine	1,4	10,8
Lysine	0,9	5,1
Histidine	0,9	7,5
Other	11,2	28,4
Total amount	45,1	337,6

The graphical relations between the amount of nitrates, NDMA and the amount of dry substance in tomato products received as the result of the research is displayed on the graph 2. The mathematical model of nitrate concentration in the concentrated tomato products has been defined in the form of the expression $y = ax^b$. Such a kind of relations has been chosen, since at lengthy heating during the concentration process one part of the nitrates dissolves, while the other is extracted from the concentrated product in the form of volatile compounds [7,9].

After the regression coefficient calculation the following equation was received:

$$C_N = 23,78\ m0,3523,\ mg/kg \quad (4)$$

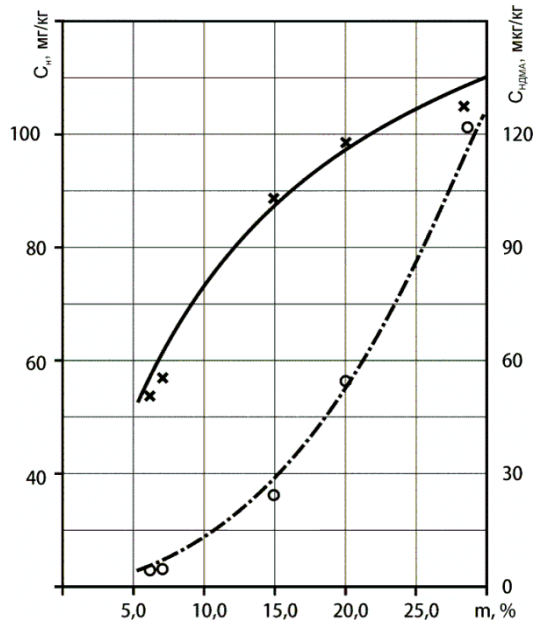
The increase in the nitrate concentration during the concentration process is not as drastic as the increase in metal concentration and in our case amounts to 2,66 times. The received results indicate that it is advisable to use tomato juice containing the amount of nitrates not exceeding 0,3 – 0,35 of their maximum allowable concentration for tomato paste production.

The amount of NDMA depending on the dry substance concentration is described through this expression:

$$C_N = 6,25 \cdot 10{-}3\ m2,2667,\ mg/kg, \quad (5)$$

It was established that the intensity of the NDMA accumulation during the tomato juice concentration rises at the increase of the amount of dry sub-

stance in the concentrate, which indicates nitrosation of amines and amides.Nitrates and the products of their processing also undergo nitrosation. The sharp increase in the NDMA formation at the end of the concentration process is explained by the fact that only secondary amines arestable. Thus, the amount of NDMA in the concentrated tomato products exceeds 120 mcg/kg.



Graph 2.The relation between the nitrate and N-nitrosodimethylamine concentration and the tomatoproducts' concentration degree.

Conclusion

The research of the heavy metal content during tomato product concentration in the vacuum laboratory evaporator allowed us to conclude that at the dry substance concentration in the product amounting up to 28 % the heavy metal concentration rises by 6,5 – 7,5 times and exceeds the maximum allowable concentration.

On the basis of the received results linear relations between the changes of concentration values in lead, copper, zinc and the dry substance content have been established.

We have also found that the nitrate concentration depends on the dry substance concentration [10]. The relation indicates that the increase in the nitrate amount is not as drastic as the rise of dry substance concentration. The received relation proves the findings of a number of researchers who claimed that the nitrate concentration plummets during the heat treatment of the product due to their dissolving as well as that these substances are extracted with the volatile compounds.

The conducted research allowed us to come to a conclusion that in order to receive concentrated tomato products, the amount of heavy metals and nitrates in which does not exceed the maximum allowable concentration, it is obligatory for the heavy metal content in the unprocessed material (tomato juice) not to exceed (0,18 – 0,25) of the maximum allowable concentration, whereas the amount of nitrates should be lower than (0,3 – 0,35) of their maximum allowable concentration.

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ИССЛЕДОВАНИЕ СОДЕРЖАНИЕ ТЯЖЕЛЫХ МЕТАЛЛОВ И НИТРОЗОСОЕДИНЕНИЙ В КОНЦЕНТРИРОВАННЫХ ТОМАТОПРОДУКТАХ

В.В. Шутюк, доктор технических наук, доцент
С.М. Василенко, доктор технических наук, профессор
А.С. Бессараб, кандидат технических наук, профессор, *E-mail*: a_bessarab@i.ua

О.В. Бендерская, аспирант, *E-mail*: olga_benderska@ukr.net
Национальный университет пищевых технологий, г. Киев-33, ул. Владимирская, 68, Украина, 01601

Аннотация. Постоянная борьба за рынки сбыта продукции требует от отечественных предприятий пищевой и перерабатывающей промышленности повышать качество пищевых продуктов – неотъемлемую составную их успеха на потребительском рынке. Для этого необходимо постоянно усовершенствовать технологию производства продуктов. Чрезвычайно актуальной проблемой качества является наличие в продуктах питания тяжелых металлов и нитрозосоединений. В Национальном университете пищевых технологий проведены исследования по изучению изменения концентрации тяжелых металлов (Zn, Cu, Pb) и нитрозосоединений в томатопродуктах при их сгущении. На основе полученных результатов установлены зависимости изменения концентрации свинца, меди, цинка и нитрозосоединений от содержания сухих веществ. Проведенные исследования позволили установить, что для получения качественных концентрированных томатопродуктов содержание тяжелых металлов и нитратов в сырье не должно превышать 18 – 35 % предельно допустимой концентрации.

Ключевые слова: нитраты, контаминанты, продовольственная безопасность, качество, плоды и овощи.

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