UDC 664

OPTIMIZATION OF THE PROCESS OF PROCESSING FRUITS AND BERRIES BEFORE FREEZING WITH SOLUTIONS OF CRYOPROTECTANTS

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Abstract. The interpretation of the mathematical model allows to connect practical tasks: to find the optimal parameters of the technological process in order to achieve the production of the highest quality product. In our case, we need to choose the optimal duration of processing, create a combined cryoprotectant that will ensure maximum preservation of vitamin C during freezing, as well as a forecast of changes in the content of vitamin C from external factors - changes in the concentration of cryoprotectant and the duration of processing of berries.

Keywords: freezing fruit and berry, cryoprotectants, statistical model, vitamin C, full factorial experiment.

Therefore, the use of mathematical modeling gives us new information about the object [1, p. 127], in a specific direction will contribute to the development and application of new effective methods of freezing, the main purpose of which is to preserve the maximum concentration of ascorbic acid in the target product as the most labile component of all berry and fruits.

The technology of freezing raw materials with cryoprotectants, developed by us, allows a purposeful change of all the most significant input factors (duration of processing raw materials with cryoprotectants and selection of a combined cryoprotectant) [2, p. 202]. Therefore, to build a mathematical model of our object, we used a full factorial experiment, that is, we carried out a procedure for choosing the number and conditions of research necessary and sufficient to obtain a mathematical model of the process of freezing bioobjects. At the same time, we sought to minimize the number of experiments, while simultaneously varying all the variables that determine the process; chose a clear strategy that allows making informed decisions after each series of experiments [3, p. 67].

It has already been mentioned that the goal of freezing fruit and berry raw materials is the maximum preservation of its valuable biocomponents, primarily vitamin C. Therefore, as an optimization parameter, we choose the indicator of the ascorbic acid content in fresh and frozen raw materials, since it is this that testifies to the perfection of the developed technology. Pretreatment of fruits and berries with solutions of cryoprotectants, their composition, and the duration of treatment have the most significant positive effect on the preservation of the content of ascorbic acid in frozen semi-finished products.

Consider the effectiveness of preliminary processing of fruit and berry raw materials (on the example of black currant berries). To check the reliability of the obtained results, we make mathematical models and build a plan of the actual experiment.

We carried out a three-factor experiment to determine the conditions of pre-treatment of blackcurrant berries with a combined cryoprotectant - a mixture of glucose and citric acid, which ensures minimal loss of ascorbic acid during freezing. Based on the results of previous studies, the content of citric acid was taken from 0,5 to 1,5%, since the increase in concentration had a negative effect on the organoleptic indicators of frozen berries. In a three-factor experiment, the following indicators act as variables:

x_1 (C_1) – glucose content, %;

x_2 (C_2) – citric acid content, %;

x_3 (t) – processing time, min.

y $(VitC)$ – the content of vitamin C in blackcurrant berries.

In general, the function can be represented as follows:

$$y = f(x_1, x_2, x_3)$$

The general scheme of the mathematical model looks like this (fig. 1.):

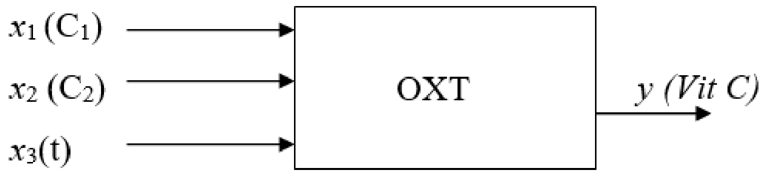

Fig. 1. General scheme of the mathematical and statistical model

The dependence of the input parameters on the output function is linear, based on this, we compile the regression equation:

$$y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3 + b_{123}x_1x_2x_3,$$

where b_0, b_1, b_2, b_3, b_{12}, b_{13}, b_{23}, b_{123} — regression coefficients.

To conduct the experiment, we compile special matrices for the planning of the experiment with the specified number of experiments and the limits of changing factors. In a dimensionless expression, the upper level will be marked (+1), and the lower one will be marked (-1).

The construction of the plan of the full factorial experiment will be carried out in the following order: we determine the number of experiments using the formula: $N=2^n$. Where n is the number of factors, in our case n=2. $N=2^3=8$. We will take the number of duplicate experiments m=2.

Taking into account the previous information, for this experiment it is possible to choose the levels of the factors and the intervals of their variation, given in the table 1, 2, 3.

Table 1

The matrix of the three-factor experiment

№	Factors			Optimization parameter (vitamin C content)			
	C_1,%	C_2,%	t, min	y_1	y_2	y_3	$y_{norm.}$
1	10	0,5	10	145,4	150,6	132,2	142,7
2	20	1,5	10	162,2	146,8	164,6	157,9
3	10	1,5	60	158,8	166,4	149,5	158,2
4	20	0,5	60	196,6	182,1	190,4	189,7
5	10	0,5	60	146,6	150,8	154,4	150,6
6	20	1,5	60	237,4	240,1	246,8	241,4
7	10	1,5	10	158,8	150,2	160,4	156,5
8	20	0,5	10	155,5	158,8	142,6	152,3

Table 2

Conditions of the experiment

Conditions of the experiment	**Marking**	Factors		
		Glucose content, C_1, %; *(x_1)*	Citric acid content, C_2, %; *(x_2)*	Duration of processing, t, min, *(x_3)*
Zero level	x_0	15	1,0	35
Variation step	Δx	5	0,5	25
Upper level	x_i^+	20	1,5	60
Lower level	x_i^-	10	0,5	10

Table 3

Active experiment plan matrix

№	x_1	x_2	x_3	y_1	y_2	y_3	y_{cep}
1	-	-	-	145,4	150,6	132,2	142,7
2	+	+	-	162,2	146,8	164,6	157,9
3	-	+	+	158,8	166,4	149,5	158,2
4	+	-	+	196,6	182,1	190,4	189,7
5	-	-	+	146,6	150,8	154,4	150,6
6	+	+	+	237,4	240,1	246,8	241,4
7	-	+	-	158,8	150,2	160,4	156,5
8	+	-	-	155,5	158,8	142,6	152,3

Statistical data processing

Verification of homogeneity of variances

a) we calculate the variance of parallel experiments of each row of the plan matrix according to the equation:

$$S_n^2 = \frac{1}{m-1}\sum_{k=1}^{m}(y_{nk} - \bar{y}_n)^2,$$

where m = 3 is the number of parallel experiments.

$S_1^2 = 90; S_2^2 = 93{,}3; S_3^2 = 71{,}6; S_4^2 = 52{,}9; S_5^2 = 15{,}2; S_6^2 = 23{,}4; S_7^2 = 30{,}1; S_8^2 = 73{,}3$

b) we determine the largest value $S_{n\ max}^2$ of all calculated:

$$S_{n\ max}^2 = S_8^2 = 93{,}3$$

c) calculate the sum of variances:

$$\sum_{n=1}^{N} S_n^2 = S_1^2 + S_2^2 + S_3^2 + S_4^2 + S_5^2 + S_6^2 + S_7^2 + S_8^2 =$$
$$= 90 + 93{,}3 + 71{,}6 + 52{,}3 + 15{,}2 + 23{,}4 + 30{,}1 + 73{,}3 = 449{,}9$$

d) we calculate the Cochran criterion:

$$G_{max} = \frac{S_{n\,max}^2}{\sum_{n=1}^{N} S_n^2} = \frac{93{,}3}{449{,}9} = 0{,}2073$$

e) we choose the tabular value of the Cochran criterion $G_{кр}$, for the values of the degree of freedom $f_1 = m$-1=3-1=2 and $f_2 = N$=8 and for the significance level α=5% and check the fulfillment of the condition:

$$G_{max} = 0{,}2073 < G_{кр} = 0{,}5157$$

We conclude that the variances of the initial parameter in parallel experiments are homogeneous, that is, the obtained regression equation is reproducible.

We calculate the total error of experiments:

$$S_0^2 = \frac{1}{N}\sum_{n=1}^{N} S_n^2 = \frac{449{,}9}{8} = 56{,}25$$

Calculation of coefficients of the regression equation:

$$b_0 = \frac{1}{N}\sum_{n=1}^{N} x_{0n}\bar{y}_n = \frac{1}{8}(142{,}7 + 157{,}9 + 158{,}2 + 189{,}7 + 150{,}6 + 241{,}4 + 156{,}5 + 152{,}3) = 168{,}66$$

$$b_1 = \frac{1}{N}\sum_{n=1}^{N} x_{1n}\bar{y}_n = \frac{1}{8}(-142{,}7 + 157{,}9 - 158{,}2 + 189{,}7 - 150{,}6 + 241{,}4 - 156{,}5 + 152{,}3) = 16{,}658$$

$$b_2 = \frac{1}{N}\sum_{n=1}^{N} x_{2n}\bar{y}_n = \frac{1}{8}(-142{,}7 + 157{,}9 + 158{,}2 - 189{,}7 - 150{,}6 + 241{,}4 + 156{,}5 - 152{,}3) = 9{,}833$$

$$b_3 = \frac{1}{N}\sum_{n=1}^{N} x_{3n}\bar{y}_n = \frac{1}{8}(-142{,}7 - 157{,}9 + 158{,}2 + 189{,}7 + 150{,}6 + 241{,}4 - 156{,}5 - 152{,}3) = 16{,}325$$

$$b_{12} = \frac{1}{N}\sum_{n=1}^{N} x_{12n}\bar{y}_n = \frac{1}{8}(142{,}7 + 157{,}9 - 158{,}2 - 189{,}7 + 150{,}6 + 241{,}4 - 156{,}5 - 152{,}3) = 4{,}492$$

$$b_{23} = \frac{1}{N}\sum_{n=1}^{N} x_{23n}\bar{y}_n = \frac{1}{8}(142{,}7 - 157{,}9 + 158{,}2 - 189{,}7 - 150{,}6 + 241{,}4 - 156{,}5 + 152{,}3) = 5{,}008$$

$$b_{123} = \frac{1}{N}\sum_{n=1}^{N} x_{123n}\bar{y}_n = \frac{1}{8}(-142{,}7 - 157{,}9 - 158{,}2 - 189{,}7 + 150{,}6 + 241{,}4 + 156{,}5 + 152{,}3) = 6{,}533$$

Checking the significance of regression coefficients

We check the significance of regression coefficients characterizing linear effects and pairwise interaction effects.

a) determine the variance of the regression coefficients:

$$S_{bi}^2 = \frac{S_0^2}{N} = \frac{56{,}25}{8} = 7$$

b) determine the deviation of any coefficient:

$$\Delta b_i = \pm t_T \sqrt{S_{bi}^2} = 2{,}12\sqrt{7} = 2{,}12 * 2{,}65 = 5{,}6$$

where t_T=2,12 is the tabular value of the Student's criterion for the degree of freedom $f_1= N(m-1) = 8(3-1) = 16$ and the level of significance α=0,05;

c) calculate the value of the Student's criterion for each regression coefficient:

$$t_{b0} = \frac{|b_0|}{S_{bi}} = \frac{|168{,}66|}{2{,}65} = 63{,}616$$

$$t_{b1} = \frac{|b_1|}{S_{bi}} = \frac{|16{,}658|}{2{,}65} = 6{,}283$$

$$t_{b2} = \frac{|b_2|}{S_{bi}} = \frac{|9{,}833|}{2{,}65} = 3{,}709$$

$$t_{b3} = \frac{|b_3|}{S_{bi}} = \frac{|16{,}325|}{2{,}65} = 6{,}157$$

$$t_{b12} = \frac{|b_{12}|}{S_{bi}} = \frac{|4{,}492|}{2{,}65} = 1{,}694$$

$$t_{b13} = \frac{|b_{13}|}{S_{bi}} = \frac{|13{,}917|}{2{,}65} = 5{,}249$$

$$t_{b23} = \frac{|b_{23}|}{S_{bi}} = \frac{|5{,}008|}{2{,}65} = 1{,}889$$

$$t_{b123} = \frac{|b_{123}|}{S_{bi}} = \frac{|6{,}533|}{2{,}65} = 2{,}464$$

d) we check the significance condition of each of the regression coefficients, namely $t_{bi}>t_T$, the fulfillment of this condition gives reason to state the significance of the corresponding i-th coefficient. In our case, all regression coefficients are significant except for t_{b12} and t_{b23}.

We write the obtained regression equation in the final form in the form of a polynomial of the first order:

$$\hat{y} = 168{,}7 + 16{,}658x_1 + 9{,}833x_2 + 16{,}325x_3 + 13{,}917x_1x_3 + 6{,}533x_1x_2x_3$$

By substituting the value of each factor into the resulting regression equation, we obtain the calculated values of the function and compare them with the experimental values:

$$\widehat{y_1} = 168{,}7 + 16{,}658(-1) + 9{,}833(-1) + 16{,}325(-1) + 13{,}917(-1)(-1) + 6{,}533(-1)(-1)(-1) = 133{,}23$$

$$\widehat{y_2} = 168{,}7 + 16{,}658(+1) + 9{,}833(+1) + 16{,}325(-1) + 13{,}917(+1)(-1) + 6{,}533(+1)(+1)(-1) = 158{,}38$$

$$\widehat{y_3} = 157{,}72;\ \widehat{y_4} = 199{,}2;\ \widehat{y_5} = 151{,}12;\ \widehat{y_6} = 231{,}93;\ \widehat{y_7} = 165{,}97;\ \widehat{y_8} = 151{,}78$$

Testing the regression equation for adequacy

We check the obtained regression equation for the adequacy of the actual process

$$S_{gen}^2 = \frac{1}{N-l}\sum_{n=1}^{N}(\widehat{y_n} - \overline{y_n})^2 = \frac{1}{8-4}\left[\begin{array}{c}(133{,}23 - 142{,}733)^2 + (158{,}38 - 157{,}867)^2 + (157{,}72 - 158{,}233)^2 \\ +(199{,}2 - 189{,}7)^2 + (151{,}12 - 150{,}6)^2 + (231{,}93 - 241{,}433)^2 + \\ (165{,}97 - 156{,}467)^2 + (151{,}78 - 152{,}3)^2\end{array}\right] =90{,}517$$

b) calculate the value of the Fisher criterion:

$$F_p = \frac{S_{\text{gen}}^2}{S_0^2} = \frac{90{,}517}{56{,}25} = 1{,}61$$

c) according to the tables for the degree of freedom $f_1 = N - l = 8\text{-}4 = 4$ та $f_2 = N\ (m\ \text{-}1) = 8\ (3\text{-}1) = 16$ and for the level of significance α=5%; where l = 4 – the number of coefficients in the regression equation.

We select the tabular value of the Fisher criterion: $F_T=2{,}5911$

d) check the adequacy condition: $F_p=1{,}61< F_T =2{,}5911$

We conclude that the obtained regression equation is adequate for the investigated process, which is also proven by the comparison of variances.

To switch from coded to natural values, we use the formulas:

$$x_1 = \frac{C_1 - 15}{5}$$

$$x_2 = \frac{C_2 - 1{,}0}{0{,}5}$$

$$x_8 = \frac{t - 35}{25}$$

Then the mathematical model will look like this:

$$\hat{y} = 3{,}094 * C_1 + 74{,}547 * C_2 + 0{,}551 * t - 3{,}659 * C_1 * C_2 + 0{,}007 * C_1 * t - 1{,}568 * C_2 * t + 0{,}105 * C_1 * C_2 * t + 79{,}74$$

Now, substituting the values of the specified input parameters into the obtained mathematical model, we obtain mathematical calculations of the content of vitamin C in black currants: $\widehat{y_1} = 142{,}773$; $\widehat{y_2} = 157{,}867$; $\widehat{y_3} = 158{,}233$; $\widehat{y_4} = 189{,}7$; $\widehat{y_5} = 150{,}6$; $\widehat{y_6} = 241{,}433$; $\widehat{y_7} = 156{,}467$; $\widehat{y_8} = 152{,}3$.

We calculate the total error of the experiment:

$$\Delta = \frac{\sum_{i=1}^{N} \frac{|\widehat{y_i} - \overline{y_1}|}{\bar{y}}}{N}$$

The total error of the experiment Δ = 2,876 %

For a specific type of raw material (blackcurrant berries), the maximum preservation of ascorbic acid is achieved when using a combined cryoprotectant, the concentration of the components of which is 1% for a citric acid solution and 15% for a glucose solution with a duration of 35 minutes of processing the berries before freezing.

We built the response surfaces of this model - the content of vitamin C in blackcurrant berries in the planes of the investigated parameters of influence, which allow us to visually illustrate the dependence of this target function on them (Fig. 2-4).

Thus, the mathematical model for predicting the course of certain technological processes plays a large role in the conduct of scientific research, it helps to determine the optimal parameters of the experiment in the minimum time and save expendable resources.

Based on the results of experimental and theoretical research, a mathematical model of the dependence of vitamin C content in frozen berries pre-treated with a combined cryoprotectant (a mixture of glucose and citric acid in different concentrations) and for different durations of treatment in the form of a regression dependence was developed according to the planned matrix of the experiment; the response surfaces of this model were constructed – the content of vitamin C in blackcurrant berries in the planes of the studied influence parameters, which allow to visually illustrate the dependence of this target function on them.

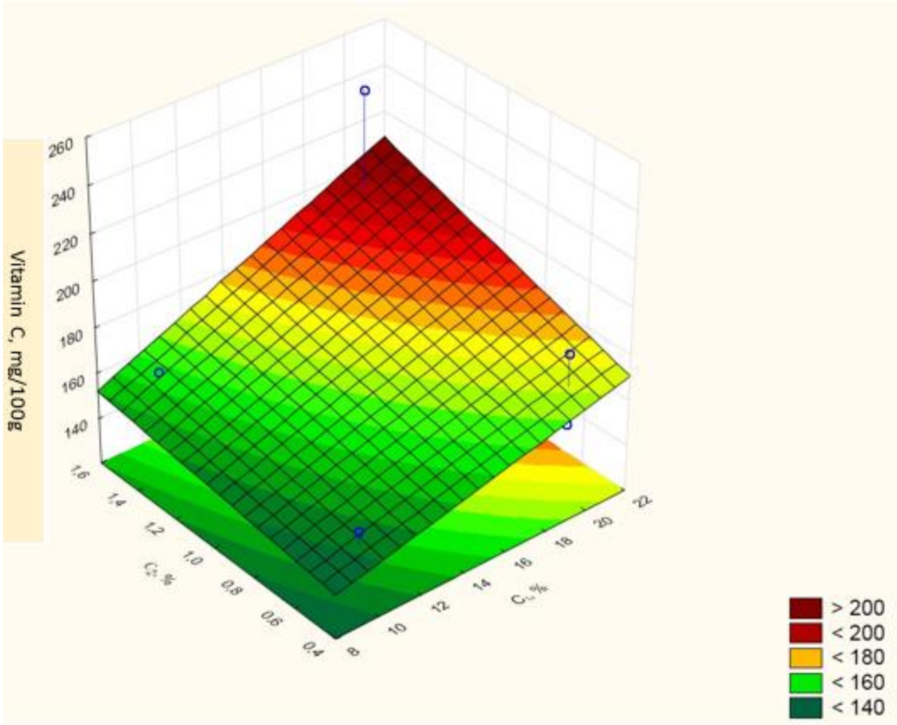

Fig. 2. The response surface of the mathematical model of content dependence of vitamin C from C1 and C2 at t=const=35 min

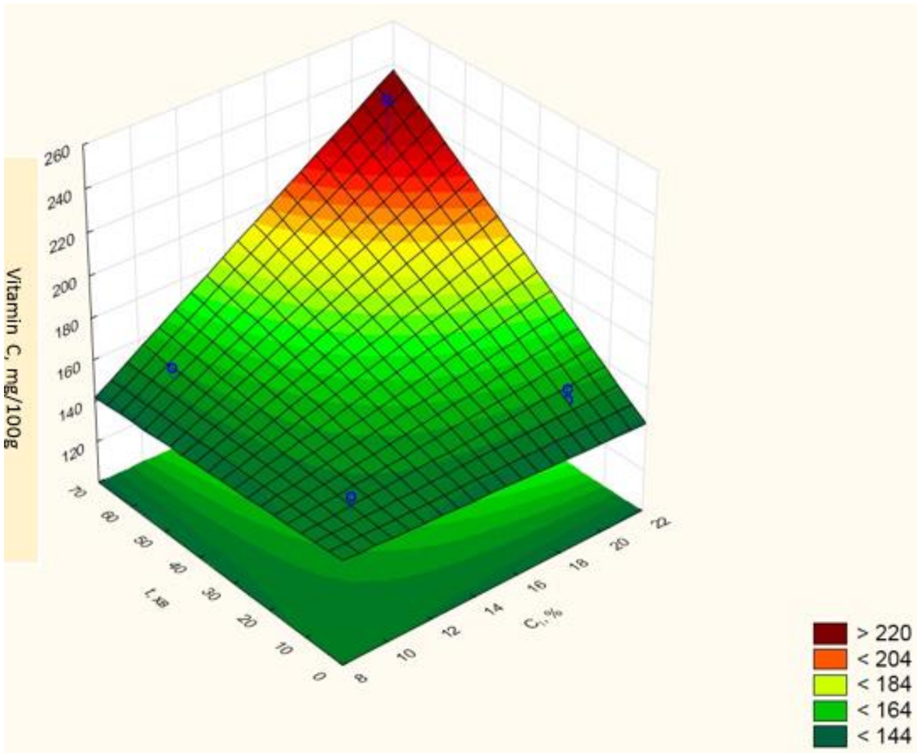

Fig. 3. The response surface of the mathematical model of content dependence of vitamin C from $C_1$and t at C_2=const=1,0%

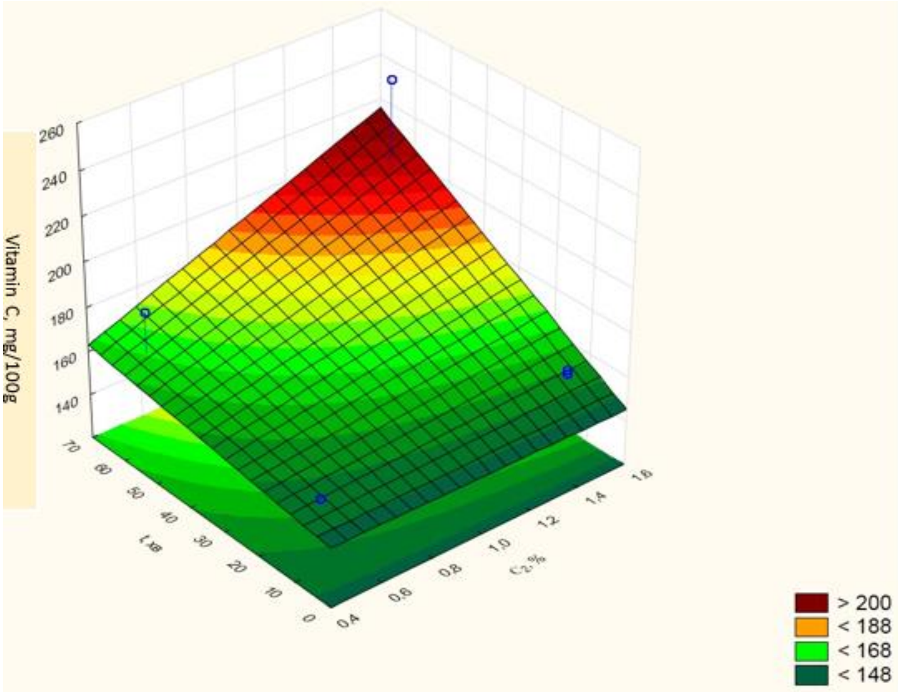

Fig. 4. The response surface of the mathematical model of content dependence of vitamin C from C_2 and t at C_1=const=15%

The implementation of theoretical knowledge of the features of mathematical modeling showed a positive effect of cryoprotection in freezing technologies, the evaluation criterion of which is the minimization of ascorbic acid losses during freezing, storage and defrosting of berries.

Conclusions. The use of mathematical modeling methods in conducting innovative research aimed at overcoming the shortcomings of traditional freezing technologies is a promising direction for improving the methods of preserving plant raw materials using artificial cold.

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