Multicomponent Analysis of Basic Physico-chemical Parameters of Bulgarian Yoghurt

Mariyana Sestrimska[1], Tanya Titova[2], Veselin Nachev[3] and Chavdar Damyanov[4]

Abstract – **In this paper are considered basic methods for research the properties of multicomponent mixtures based multifactor statistical regression models.**

Keywords – **regression models, mixture design, simplex centroid design, experiments with mixtures, principal component analysis**

I. Introduction

Modern food production is characterized with multiparametric composition on the technology of the product. Requirements for quality and safety of products require the compilation of reliable multifactor models. This requires the use of methods for assessing the parameters of the research object, optimization of specify qualitative and quantitative characteristics and study of their relationship with different instrumental and experimental factors.

The task of optimization of products focuses on modeling mixture through a finite number of experiments.

The purpose of modeling is to clarify the influence of individual components on the quality of food to provide for the nutritional properties of the finished product, and create a product with optimal quality characteristics [1,2].

In the present paper is committed multi-parameter study of mixtures in a specific task to investigate the effect of adding fruit mixture on basic physicochemical parameters of Bulgarian yoghurt.

II. Materials and Methods

A. Problem definition

Statistical optimization of products in the food industry, uses the analogy of the problem of the synthesis of multicomponent mixtures in many other areas - metallurgy, medicine, chemical industry and others. The research product is presented as the sum of its constituent components. The total quantity of mixture is taken to be equal to one (or 100%):

$$\sum_{i=1}^{q} x_1 = 1\,,\ 0 \le x_i \le 1\,,\ i = 1,2,\ldots,q\,, \qquad (1)$$

where: x_i is i– th component in the mixture, q– total of the components constituting the mixture.

These conditions determining factor space, require special coordinate system for presenting multicomponent mixture. It is called *barycentric coordinate system* or *simplex diagram* of the composition of the mixture. It consists of (q-1) - dimension simplex defined area of change components (factors). For a three-component mixture barycentric coordinate system is an equilateral triangle presented in Figure 1 [1, 6, 7].

Experimental-statistical, simplex centroid plan for a three-component mixture is presented in Table 1.

TABLE I
A SIMPLEX CENTROID DESIGN FOR A MIXTURE SYSTEM WITH THREE COMPONENTS

№	Components			Coordinates	Response
	x_1	x_2	x_3		y
1	1	0	0	(1, 0, 0)	y_1
2	0	1	0	(0, 1, 0)	y_2
3	0	0	1	(0, 0, 1)	y_3
4	0.5	0.5	0	(0.5, 0.5, 0)	y_{12}
5	0.5	0	0.5	(0.5, 0, 0.5)	y_{13}
6	0	0.5	0.5	(0, 0.5, 0.5)	y_{23}
7	0.33	0.33	0.34	(0.33, 0.33, 0.33)	y_{123}

Simplex-centroid plans are saturated plans, i.e. the number of coefficients of the model is equal to the number of experiments in the plan. On the basis of symmetrical coordinates of the model in barycentric coordinate system (Fig.1) are derived formulas for calculating the coefficients of the polynomial model.

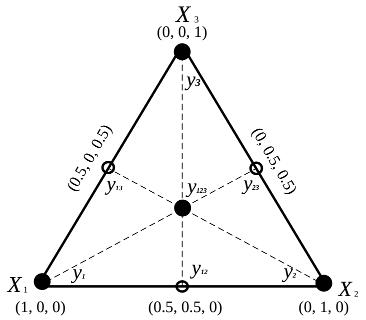

Fig.1 Simplex - centroid baricentrical diagram of a three-component mixture

[1]Mariyana Sestrimska, Department Automation and Control Systems University of Food Technologies, 26 Maritza Blvd, Plovdiv, 4002 Bulgaria, e-mail: mariana_brusova@abv.bg

[2]Tanya Titova, Department Automation and Control Systems University of Food Technologies, 26 Maritza Blvd, Plovdiv, 4002 Bulgaria, e-mail: t_titova@abv.bg

[3]Veselin Nachev, Department Automation and Control Systems University of Food Technologies, 26 Maritza Blvd, Plovdiv, 4002 Bulgaria, e-mail: v_nachevbg@yahoo.com

[4]Chavdar Damyanov, Department Automation and Control Systems University of Food Technologies, 26 Maritza Blvd, Plovdiv, 4002 Bulgaria, e-mail: chavdam@yahoo.com

The used model in our study is aligned cubic polynomial: i.e incomplete polynomial of third degree

$$\hat{y} = \sum_{i=1}^{q} b_i x_i + \sum_{1\le i<j\le q} b_{ij} x_i x_j + \sum_{1\le i<j<k\le q} b_{ijk} x_i x_j x_k \quad (2)$$

where: $\hat{y}$ a predicted value for research property, b_i,, b_{ij} and b_{ijk} are regression coefficients.

Coefficients of a mathematical model are obtained by replacing in equation (2) the coordinates of a point of the plan and the respective experimental value of the index *y* [4,5].

After obtaining regression equation is necessary to verification of the mathematical model. For this purpose they performed additional *L* (control) and the experience is determined experimentally properties of the mixture therein y_u (u=1,2,…,L). The number of control points *L* is usually chosen by 4 ÷ 6. The residual variance is determined by the expression:

$$S_{a\partial}^2 = \frac{1}{L}\sum_{u=1}^{L}(y_u - \hat{y}_u)^2, \quad (3)$$

where: y_u and $\hat{y}_u$ are respectively experience and modal value of the property of the mixture *y* in control points *u.*

For determining the variation of the experiment is carried out *n* parallel experience in one of the points of the plan or any of the additional points. Reproducibility variance is:

$$S_\varepsilon^2 = \frac{1}{n-1}\sum_{i=1}^{n}(y_i - \bar{y})^2; \quad (4)$$

$$\bar{y} = \frac{1}{n}\sum_{i=1}^{n} y_i. \quad (5)$$

Verification of adequacy is performed by Fisher criterion:

$$F = \frac{S_{a\partial}^2}{S_\varepsilon^2}. \quad (6)$$

B. Preparation of the samples.

Samples to be analyzed are structured in three separate groups. The first group is composed of the experimental samples, which consist of yoghurt (80%) and fruit pulp (20%) of the strawberries - x_1, raspberries - x_2 и blueberries - x_3. Yogurt and frozen fruits are bought from commercial supermarket in Bulgaria. The third group of 35 samples of different brands of fruit yogurts bought retail chain. The fruits are finely pureed and pasteurized.

For obtaining experimental data, according to the statistical plan are prepared seven types of mixtures. First three mixtures were prepared by adding each of the types of fruit puree separately. The next three mixtures satisfy the two-component mixture, i.e fruit ratio is 50:50% and the final mixture is a three-component, i.e. fruit puree were mixed in equal proportions 33: 33: 34%. The second group consists of 35 samples of different retail chain brands of yogurt that painted coloring food E122 (azorubine, carmoisine) which is authorized in Bulgaria. The third group of 35 samples of different brands of fruit yogurts bought from retail chain.

C. Measurement on soluble solids and pH.

Dry matter is related to the content of protein, fat, carbohydrates and minerals in the product. By definition Brix degrees represent percentages by weight extract identified as equivalent to the sucrose content in the solutions or mixtures, i.e .:

1°Brix=1g saccharose /100g solution=1% sugar solution.

In this study the total soluble solids, expressed as the equivalent of sucrose is determined by a digital refractometer HANNA, HI96-801, at a temperature of 20°C.

To determine the pH of the analyzed samples used digital pH-meter PH-201.

D. Determining the color characteristics

The color is the main organoleptic characteristics associated with quality and perception of food. To determine the color characteristics of the fruit yoghurts (L*, a*, b*, c*, h*) is used fiber-optic spectrophotometer USB4000 company Ocean Optics, equipped with a suitable sample holder, and the necessary optics.

The spectrophotometer is connected to a personal computer and specialized software (Spectra Suite), by which the data obtained are recorded in digital and graphic form. Software may change the number of repetitions waive the features, the number of averaged to obtain a spectrum step of scanning and frequency range.

III. Results and Discussion

Table 2 presents the values of the studied physico-chemical indicators of the fruit yogurt obtained according to accepted experimental and statistical plan (Table 1).

TABLE II
BASIC PHYSICO-CHEMICAL PARAMETERS OF FRUIT MIXTURE

	№ on sample	x_1	x_2	x_3	*pH*	*°Brix*	*L**	*a**	*b**	*c**	*h**
Group 1	1	1	0	0	4.24	7.94	37.96	1.56	23.85	23.9	1.51
	2	0	1	0	4.17	7.40	48.71	2.33	18.13	18.28	1.44
	3	0	0	1	4.22	7.40	46.33	0.18	16.72	16.72	1.56
	4	0.5	0.5	0	4.20	7.76	43.04	4.59	15.98	16.63	1.29
	5	0.5	0	0.5	4.28	7.72	33.74	4.58	10.18	11.16	1.15
	6	0	0.5	0.5	4.21	7.52	36.29	5,.03	12.68	13.64	1.19
	7	0.33	0.33	0.34	4.25	7.56	43.04	3.64	10.73	11.33	1.24

x_1 –strawberries puree; x_2 – raspberry puree; x_3 – puree of blueberries; a^* - color coordinates on the axis, corresponding to the red-green color, according to standard CIELAB; b^*- color coordinates on the axis corresponding to the yellow-blue; L^* - relative brightness (brightness), c^* - saturation, h^* - hue.

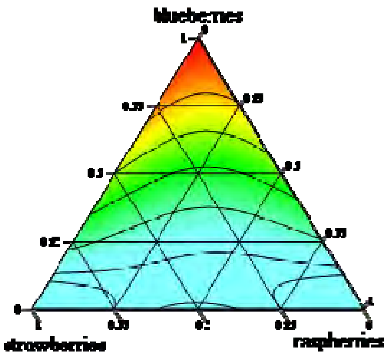

Fig.2 Mixture design for pH

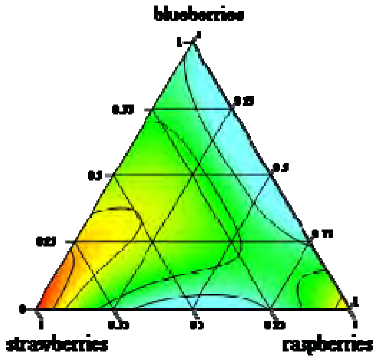

Fig.3 Mixture design for soluble solids

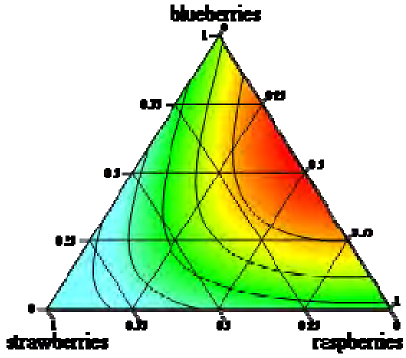

Fig.4 Mixture design for color descriptor L*

Fruit purees used to make fruit yogurts Group I, affect the pH and color characteristics In Fig. 2-4 show simplex isoliness for the characteristics of *pH, a* , b*, L** and soluble solids.

Physico-chemical parameters of other two groups also differ samples (Table 2). Total sucrose content trademarks fruit yogurts is the highest that could be explained by further adding sugar production conditions or a different sort the fruit. The acidity of the tested samples ranged in very small ranges.

On the basis of experimental-statistical plan and the experiments are derived mathematical regression models for the content of soluble solids, pH and color characteristics.

TABLE III
REGRESSION MODELS

$\hat{y}_1(pH)=4.24x_1+4.17x_2+4.22x_3+0.02x_1x_2+0.20x_1x_3+0.06x_2x_3+ +0.36x_1x_2x_3$
$\hat{y}_2(°Brix)=7.94x_1+7.40x_2+7.40x_3+0.36x_1x_2+0.20x_1x_3+0.48x_2x_3- -3.66x_1x_2x_3$
$\hat{y}_3(L^*)=37.96x_1+48.71x_2+46.33x_3-1.18x_1x_2-33.62x_1x_3-44.92x_2x_3 +204.24x_1x_2x_3$
$\hat{y}_4(a^*)=1.56x_1+2.33x_2+0.18x_3+10.58x_1x_2+14.84x_1x_3+15.10x_2x_3- -59.91x_1x_2x_3$
$\hat{y}_5(b^*)=23.85x_1+18.13x_2+16.72x_3-20.04x_1x_2-40.42x_1x_3-18.98x_2x_3 -0.27x_1x_2x_3$

The obtained coefficient of determination R^2 for the models from Table 3 is not less 0.97. These coefficients of determination shows that the selected factors significantly affect the resulted sign, which confirms the correctness of their inclusion in the experimental - statistical model. For the assessment of practical suitability of regression equations are been made additional attempts at random points experimentally-statistical plan. On the basis of conducted an additional experiment were obtained dispersion and dispersion adequacy of the experience as follows: $S^2_{aд}(pH)=3{,}25.10^{-4}$ and $S^2_{\varepsilon}(pH)=2{,}2.10^{-4}$; $S^2_{aд}(^oBrix)=0{,}00141$ and $S^2_{\varepsilon}(^oBrix)=0{,}012$ The calculated values *Fisher's criteria* are respectively $F(pH)=1{,}49$ and $F(^oBrix)=0{,}118$. Both values for *Fisher's criteria* are smaller than the critical ($F_{critical}=6{,}39$ for degrees of freedom $\upsilon_{aд}=4$ и $\upsilon_{\varepsilon}=4$ level of significance $\alpha=0{,}05$. Therefore deduced based on experimental-statistical plan regression models were adequate and could be used to predict the values of soluble solids and pH at fruit mixtures.

Results from the analysis of samples by the Principal Components Analysis (PCA) are shown in Figure 6 and 7.

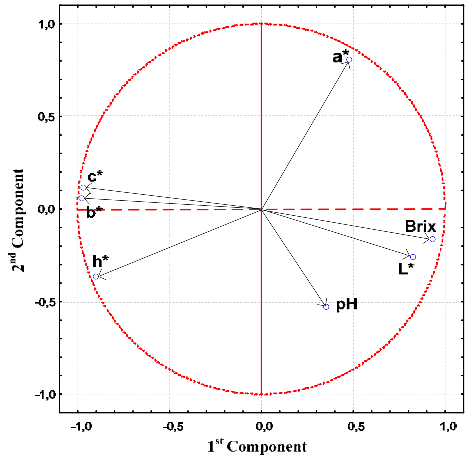

Fig.6

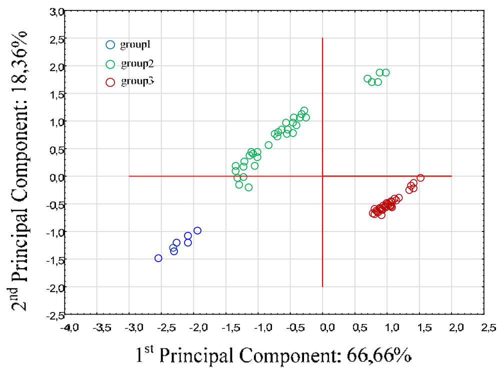

Fig.7

IV. Conclusion

In the present article discussed the influence of three types of fruit purees on basic physical-chemical parameters of Bulgarian yoghurt. Based on experimental and statistical simplex centroid plan for analyzing mixtures are derived adequate regression equations that could be applied to predict and obtain fruit yogurts with desired physico-chemical characteristics (pH, soluble solids, color).

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