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ОРИГИНАЛЬНАЯ СТАТЬЯ / ORIGINAL ARTICLE

THE INFLUENCE OF THE JAPANESE MILLET FLOUR AND THE METHOD OF DOUGH PREPARATION ON THE FORMATION OF THE AROMA OF BAKERY PRODUCTS

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Abstract. The article presents the results of a study of the formation of aroma-forming substances in bakery products with the addition of paize flour to the recipe. Instrumental assessment of the smell of products was carried out on the smell analyzer «MAG-8» with the methodology «electronic nose». The variants of the experiment differ in the content of paize flour 15–20%, according to the method of preparing the dough: the biological method of loosening – bread, bread sticks, unleavened dough – bread skewers. With the help of an «electronic nose», it was instrumentally proved on the MAG-8 odor analyzer that for the samples submitted for testing, the smell is correct and not pronounced, aromatic additives and odor enhancers, as well as the presence of destructive processes and mold formation are absent. When comparing the volatile compounds in the samples quantitatively, it should be noted that since the semi-finished bread undergoes longer fermentation than breadsticks, the content of alcohols and ketones is 22% higher, and compared with bread skewers, where there is no fermentation process, they are 93% more, a similar picture with acids. However, when comparing the content of individual components in samples, especially oxygen-containing compounds, they are almost twice as large in the absence of a biological method of loosening in bread skewers. For consumer evaluation, such changes are not significant for those samples in the formulation of which the content of paize flour is no more than 15% and recognized by consumers according to organoleptic indicators.

Keywords: paize flour, chronochastogram, electronic nose, sensors, volatile compounds, «visual imprint», Fractions, Medicinal mixtures

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Introduction. The quality of food products, including bread, is understood as a set of characteristics that determine the consumer properties of the finished product and ensure its safety for humans. However, it would be completely wrong to assess the

nutritional value of bread only from the point of view of its chemical composition, without taking into account such properties as taste, aroma, porosity of the crumb and the appearance of bread, since according to Academician I.P. Pavlov, only that food is useful that is pleasant [Egorova].

Consumer acceptability is an expression of the consumer's attitude to the product. Consumer recognition is the most important information of interest to marketers and developers. There are many methods that make it possible to evaluate the impression of the product and determine the preference of consumers [kisel].

The problem of nutrition correction is relevant and defines as a priority the increase in the production of nutrient-enriched mass-consumption food products, including bakery products. Bakery products consistently maintain their positions in the list of food products of mass consumption.

In our country, the issues of providing the population with not only high-quality, but also healthy food are very relevant. Rector of MGUPP M.G. Balykhin (2019) speaking at the 3rd International scientific and practical conference «Functional food: scientific foundations of development, production and consumption» noted that «today our science is ready to implement developments related to functional and healthy nutrition, and the buyer is ready to buy healthy food» [2].

In this paper, as an enriching additive in the recipe of bakery products, paize flour is proposed.

Paize (Japanese millet, Chinese millet, millet) – Echinochloa frumentaceae – belongs to the group of millet-like crops of the cereal family. Paize in chemical composition and nutritional value is close to the grain of chumiz and sugar sorghum, but much cheaper.

Korzun O.S. [et al.] (2011) claim that the grain of paiza is not inferior in composition and nutritional value to barley and oats (table 1) [korz].

Paize is recognized as an ecologically clean culture. Thanks to the research conducted in the conditions of the Polesie of Ukraine and in the Mogilev branch of the Institute of Radiology, it has been proved that it is advisable to replace corn with paize on soils contaminated with radionuclides, since it has a low level of accumulation of 137 caesium [korz].

However, the use of unconventional raw materials affects the consumer properties of the product. One piece of bread contains more than 540 aromatic substances. The flavor is determined by their number and combination.

The purpose of the work: to study the influence of paize flour and the method of dough preparation on the formation of the aroma of bakery products.

Research methodology. Instrumental assessment of the smell of products was carried out in the NIL on a laboratory odor analyzer «MAG-8» with the methodology «electronic nose» (manufactured in Russia). The experience options are presented in table 2.

Sensors based on piezo-quartz resonators of the OAV type with a base oscillation frequency of 10.0–14.0 MHz with different sorbents on the electrodes were used [1; 2]. Coatings were selected in accordance with the test task (possible emission from samples of different classes of organic compounds).

Sensors are measuring sensitive elements in the electronic nose device, on which thin films of sorbents are applied. Thin films are selected so as to sorb (extract) certain groups of organic volatile compounds from the air in the near sensor

Table 1

Chemical composition of Paize grain (% per absolutely dry substance)

Crude	Protein	Fat	Fiber	BEV	Ash Sugar
14,21	4,25	10,87	80,04	1,88	0,82

space in the detection cell. As a result of the interaction, the oscillation frequency of the sensors changes, which is fixed in the software. The greater the change in the oscillation frequency, the more compounds were in the sample and, accordingly, in the sample. To ensure different selectivity and detection of the largest number of volatile compounds (drugs) emitting from samples, 8 different sensors with frontal spontaneous diffusion of volatile compounds from samples into the detection cell of the electronic nose «Aquastock» (produced by LLC «SNT», Russia) were used. All sensors are manufactured, trained and stabilized in pairs of drugs of different nature.

Sensor 1 – Polyethylene Glycol PEG-2000, PEG-2000

Sensor 2 – Dicyclohexane-18-Crown-6, DCG18K6

Sensor 3 – Methyl orange on a substrate of multilayer carbon nanotubes, MO/MUNT

Sensor 4 – Triton X-100, TH100

Sensor 5 – Bromocresol blue on a substrate of multilayer carbon nanotubes, BCS/MUNT

Sensor 6 – Carboxylated Multi-layer Carbon Nanotubes, MUNTsoon

Sensor 7 – Polyethylene Glycol succinate, PDEGS

Sensor 8 – Trioctyl phosphinoxide, TOFO. Twin-40, Tween

Table 2

Variants of experience

Bakery product	Variants	Baking wheat flour of the first grade	Pise flour	Flaxseed flour	Sunflower oil	Pumpkin seed oil	Dough preparation method
Bread	Control	100	–	–	–	–	Straight dough, yeast dough
	1	85	15	–	–	–	
	2	80	15	5	–	–	
Breadsticks	Control	100	–	–	+	–	
	1	85	15	–	–	+	
	2	80	20	–	–	+	
Breadskewers	Control	100	–	–	+	–	Unleavened dough
	1	85	15	–	–	+	
	2	80	20	–	–	+	

Sample preparation for analysis: samples weighing 10.0 g were placed in glass samplers, kept at room temperature (20 ± 1°C). After the sensors are stabilized, a sampler is brought close to the open detection cell and the measurement is started. Volatile substances from the sample spontaneously diffuse into the near sensory space and are sorbed by sensor modifiers. After 60 seconds, the sampler is removed and desorption occurs. Background of sensor array from 300 to 500 Hz.s.

Measurement mode: The measurement time is 120 s, the mode of recording sensor responses is uniform in increments of 1 s, 60 s is the load of sensors in pairs, 60 s is spontaneous desorption of substances from sensors in an open detection cell. The optimal algorithm for presenting responses is based on the maximum responses of individual sensors. The measurement error is 5–10%.

The total analytical signal of the sensor array:

Quantitative characteristics:

1) SΣ, Hz.s – the total area of the «visual imprint» – estimates the overall intensity of the odor, proportional to the concentration of volatile substances – built on all signals of all sensors for the full measurement time;

2) Smax, Hz 2 – the area of the «visual imprint» of the maximum signals, built on the largest signals of all sensors during the load – estimates the greatest intensity of the smell, proportional to the discrete concentration of substances;

3) the maximum signals of sensors with the most active or specific films of sorbents Fi, Hz – to assess the content of individual classes of organic compounds in the RGF by the normalization method [3].

Qualitative characteristics:

4) For recognition in a mixture of individual classes of compounds, the Ai/j identification parameter was used, calculated from sensor signals in the analyzed samples (table 4). A new approach in comparing the qualitative composition of the odor of samples or their parts is to compare not individual Ai/j parameters, but a set of the most stable and informative. The proximity of the composition of a part of the recorded volatile compounds of samples is estimated by the proportion of matching within the margin of error from the set of parameters [4; 5]. Samples are considered to have a close (identical flavor with a difference of no more than 30% of the parameters).

5) The form of the «visual imprint» of the maximum sensor signals – the degree of similarity (identity of the form) allows us to talk about the close nature of the composition of the smell. Presented and compared by similarity parameter.

The sensor responses are recorded, processed and compared in the software of the «MAG Soft» analyzer.

Results and their discussion. To establish differences in the composition and content of volatile compounds in the presented products compare primary information «electronic nose» – the magnitude of the responses of

Table 3

Sensor responses (Hz) and the area of the «visual imprint» of the maximum sensor signals above the samples

Variants	S1 – PEG-2000	S2 – DCG18K6	S3 – MO/ MUNT	S4 – TH100	S5 – BCS/ MUNT	S6 – MUNTsoon	S7 – PDEGS	S8 – Tween	S_{sum}Hz.s
Bread									
1 Control	360	39	575	198	42	13	101	564	191916
2 Sample 2	560	55	930	278	82	–48	122	692	260872
3 Sample 1	399	40	652	212	68	–44	121	655	182334
Bread sticks									
1 control	143	17	239	70	24	16	40	210	31140
2 Sample 1 (oily a little)	281	27	433	132	39	20	74	409	70932
3 Sample 2	22	3	28	8	4	6	6	33	585
Bread skewers									
1 Control	25	4	33	13	5	9	7	40	803
2 Sample 1	–57	–8	–85	–28	–11	–18	–17	–73	23053
3 Sample 2	14	3	17	6	2	5	3	26	857

selected sensors in the array and the value of integrated quantitative signal of «electronic nose» – square «visual print» maximum responses (table 1).

The signals of all the selected sensors meaningful, so they are considered to evaluate the contribution of different classes of compounds in odor and its intensity.

According to the general parameter associated with the content and nature of volatile odor compounds (the area of «visual prints» of the maximum sensor signals for 60 seconds of load), the samples differ both among themselves and from the standard sample (1 Control) within each group of products.

Let's consider the peculiarities of changing the composition of the volatile odor fraction when changing the formulation relative to the control.

First of all, we will analyze the uniformity of the data of various sensors in the set of «electronic nose» in the frontal mode of vapor input (table 3). It was found that the selected sensors react differently to the drug samples. Specific reactions of sensors with negative values were also established – for products from the «Bread skewers» group, as well as for sensor 6 in the «Bread» group. Such changes can be explained by a sharp difference in the humidity of the samples,

Bread

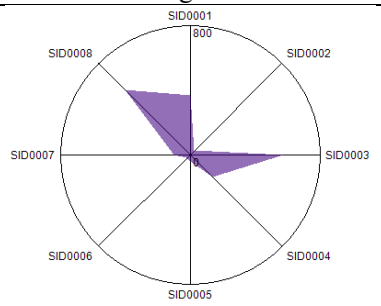
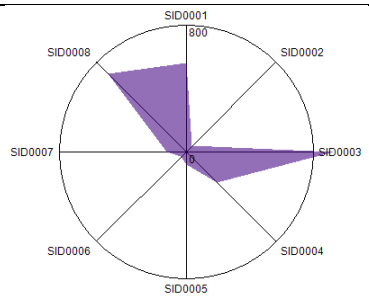
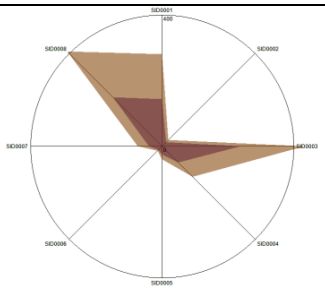
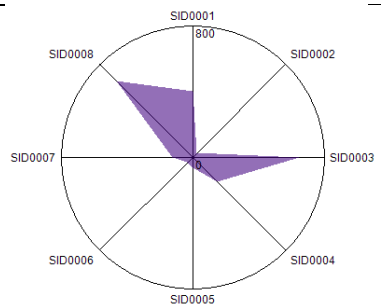
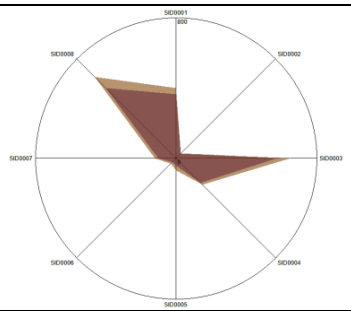
№	«Visual prints» of maximum signals	Comparison of «visual fingerprints» of signals for the standard and the analyzed sample (brown)
1		Standard (Control)
2	 	Absolute area difference, Hz 2:56898 The relative difference between the areas of control and sample 2: 46.0% The differences are very significant.
3	 	Absolute area difference, Hz 2:6839 The relative difference between the control and sample areas is 3:5.5% The differences are insignificant.

Fig. 1. *«Visual prints» of the maximum sensor signals in the RGF above the samples. The axes are indicated: on the circular axis – the sensor number in the array. Vertically – the maximum sensor response during measurement (ΔFmax, Hz)*

Bread sticks

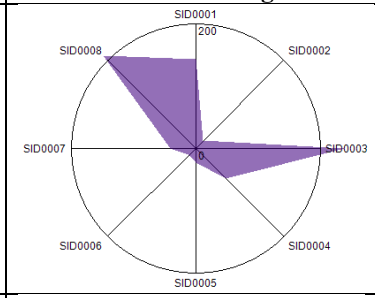
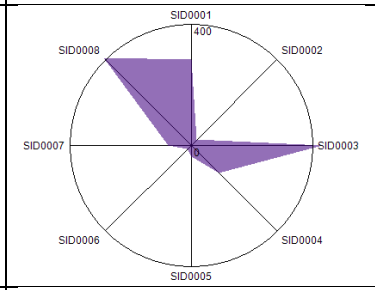
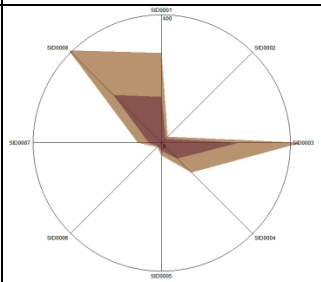
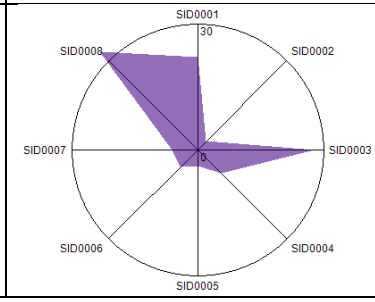
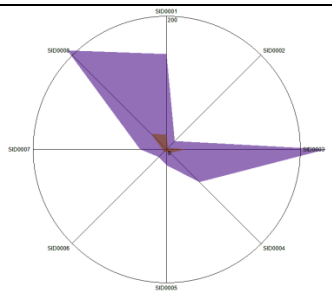
№	«Visual prints» of maximum signals	Comparison of «visual fingerprints» of signals for the standard and the analyzed sample (brown)
1		Standard (Control)
2	 	Absolute area difference, Hz 2: 30872 The relative difference between the control and sample areas is 2: 199% Very significant differences.
3	 	Absolute area difference, Hz 2: 12952 The relative difference between the control and sample areas is 3:83.5% The differences are significant.

Fig. 2. *«Visual prints» of the maximum sensor signals in the RGF above the samples. The axes are indicated: on the circular axis – the sensor number in the array. Vertically – the maximum sensor response during measurement (ΔFmax, Hz)*

when highly dried samples sorb hydrophilic compounds on their surface, reducing their concentration in the near-sensory space. It can also serve as analytical information for comparison. However, in order to reduce data interpretation errors, we consider it advisable to exclude from the data set when calculating qualitative and quantitative indicators the values of sensor responses 6. The results of comparing absolute analytical signals – figures of «visual prints» of the maximum sensor signals (fig. 2) – the exclusion of the readings of this sensor does not affect the results of comparing absolute analytical signals.

Group 1. BREAD: Sample 1 – Control; Sample 2; Sample 3.

Relative to the standard (Control) in Sample 1, the composition of volatile compounds diffusing from the crumb does not change significantly, within the margin of error. While flour, a change in the formulation for Sample 2 leads to a significant change in odor and an increase in the content of drugs in the finished product. We are talking here and further only about the connections that register the selected sensors of the «electronic nose».

Group 2. Bread sticks. Sample 1 – Control; Sample 2; Sample 3.

With respect to the standard (Control), the samples presented differ in oil content and humidity. This significantly affected the measurement results. Sample 2 is not

Bread Skewers

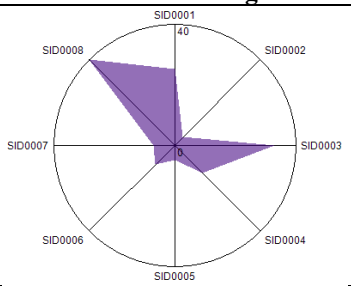
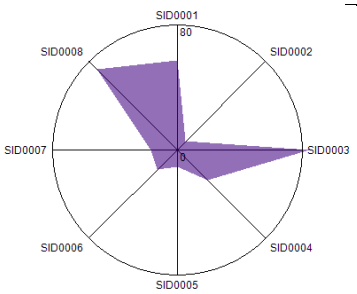
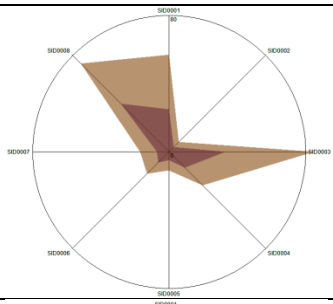
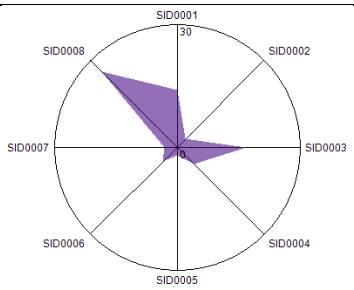
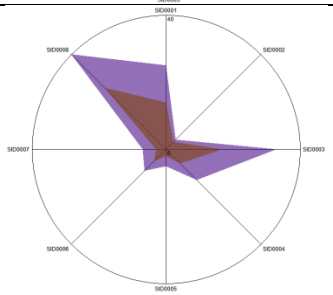
№	«Visual prints» of maximum signals	Comparison of «visual fingerprints» of signals for the standard and the analyzed sample (brown)
1		Standard (Control)
2		 Absolute area difference, Hz 2 164 The relative difference between the control and sample areas is 2: 20.4% The differences are significant.
3		 Absolute area difference, Hz 2:633 The relative difference between the control and sample areas is 3:78.8% The differences are noticeable.

Fig. 3. *«Visual prints» of the maximum sensor signals in the RGF above the samples. The axes are indicated: on the circular axis – the sensor number in the array. Vertically – the maximum sensor response during measurement (ΔFmax, Hz)*

correctly compared within the group due to the significant difference from the Control and Sample 1. The group is not homogeneous.

Group 3. Bread skewers: Sample 1 – Control, Sample 2; Sample 3.

Sample 2 is closest to the sample of the standard (Control), sample 1 is not correctly compared with the standard due to a critically different moisture (or a violation of the uniformity of manufacturing technology).

To establish differences in the composition (qualitative and quantitative) of the volatile odor fraction, we will trace the change in the total content of volatile components in the samples (fig. 1–3)

Differences in the composition of volatile compounds of products in the group are not equivalent relative to the Standard.

For this group, the displacement of the aroma is maximum, can be attributed to different names of products during organoleptic evaluation.

According to the shape of the sensor signal prints, it was found that all samples with a change in the formulation have a different flavor in terms of qualitative composition, and in terms of its intensity, samples 2 and 3 have different amounts of volatile compounds compared to the Standard.

Table 4

Relative content of components in samples, ω % (± 1%) by weight

№ Samples	S1 – PEG-2000	S2 – DCG18K6	S3 - MO/ MUNT	S4 – TH100	S5 – BCS/ MUNT	S6 – MUNTsoon	S7 – PDEGS	S8 – Tween
	Alcohols, ketones	O-content. soedin.	Acids, alcohols	Mid-polar, S-containing	Amines	Alcohols, light gases	Amines	Acids
Bread								
Control	19,16	2,08	30,60	10,54	2,24	0,00	5,38	30,02
Sample 2 mod. 2	**20,60***	2,02	**34,20**	10,22	3,02	0,00	4,49	**25,45**
Sample 3 mod. 1	18,58	1,86	30,37	9,87	3,17	0,00	5,64	30,51
Bread sticks								
Control	19,25	2,29	32,17	9,42	3,23	0,00	5,38	28,26
Sample 2	20,14	1,94	31,04	9,46	2,80	0,00	5,30	29,32
Sample 3	**21,15**	2,88	**26,92**	**7,69**	3,85	0,00	5,77	**31,73**
Bread skewers								
Control	19,69	3,15	25,98	10,24	3,94	0,00	5,51	31,50
Sample 2	20,43	2,87	**30,47**	10,04	3,94	0,00	6,09	26,16
Sample 3	19,72	**4,23**	23,94	**8,45**	**2,82**	0,00	**4,23**	**36,62**

* the parameters with the maximum deviation from the standard (control) are highlighted.

For this group, the flavor shift is more noticeable, and can be evaluated as markedly different from the control during organoleptic evaluation by experienced tasters.

We will conduct a detailed comparison of the quantitative and qualitative fractional composition of volatile compounds in the samples.

Let us trace the changes in the quantitative composition of the air above samples of all types by the relative content of the main classes of volatile compounds to which the sensor array is configured, estimated by the normalization method (table 4).

It was found that the change in the formulation leads to a slight redistribution of individual classes of compounds in the equilibrium gas phase over all samples within the groups, compared with the corresponding Standards. In the «Bread» group, Sample 1 has an identical quantitative composition of volatile compounds, Sample 2 contains fewer acids, more alcohols than the Standard.

In the Breadsticks group, Sample 1 has an identical quantitative composition of volatile compounds, Sample 2 contains fewer alcohols, S-containing, srednepolar substances, more ketones and acids than the Standard.

In the «Bread skewers» group, sample 1 emits more alcohols, but less acids than the standard. And Sample 2 has significant differences in the quantitative composition of the mixture of volatile compounds, compared with the Standard (table 2).

The Ai/j parameter allows us to trace changes in the qualitative composition of RGF over samples and the appearance/disappearance of compounds of the volatile fraction. It shows the constancy of the ratio of concentrations of individual classes of volatile compounds diffusing spontaneously from samples in 60 seconds (table 3) [3; 4]. If the Ai/j values for the samples are close or coincide, then it can be assumed that the ratio of the content

Table 5

Ratio of signals of several sensors in the matrix for the tested samples

Variants	*Stability index of the composition Ai/j, (± (0.5 – 0.02))*										
	Parameters on the charts										
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI
	1/3	1/4	1/8	2/4	2/5	2/7	3/4	4/8	5/7	5/8	7/8
Bread											
Control	0,63	1,82	0,64	0,20	0,93	0,39	2,90	0,35	0,42	0,07	0,18
Sample 2	0,60	2,01	**0,81***	0,20	**0,67**	**0,45**	3,35	0,40	**0,67**	0,12	0,18
Sample 3	0,61	1,88	0,61	0,19	**0,59**	0,33	3,08	0,32	**0,56**	0,10	0,18
Bread stiks											
Conrtrol	0,60	2,04	0,68	0,24	0,71	0,43	3,41	0,33	0,60	0,11	0,19
Sample 2	0,65	2,13	0,69	0,20	0,69	**0,36**	3,28	0,32	**0,53**	0,10	0,18
Sample 3	**0,79**	2,75	0,67	**0,38**	0,75	**0,50**	3,50	**0,24**	**0,67**	0,12	0,18
Bread skewers											
Control	0,76	1,92	0,63	0,31	0,80	0,57	2,54	0,33	0,71	0,13	0,18
Sample 2	**0,67**	2,04	**0,78**	0,29	**0,73**	**0,47**	**3,04**	0,38	0,65	0,15	0,23
Sample 3	**0,82**	2,33	**0,54**	**0,50**	**1,50**	**1,00**	**2,83**	**0,23**	0,67	**0,08**	**0,12**

* the parameters with the maximum deviation from the standard (control) are highlighted.

of these compounds in the samples is the same. If the ratio of signals differs for samples, then the ratio of the concentration of these groups of compounds is different, compared with the corresponding standard, and the smell of the samples differs significantly. The more the number of Ai/j parameters for the samples differs, the more significant the differences in the smell of the samples, which are recorded with a high degree of probability during the organoleptic evaluation by the consumer and tasters [3]. Taking into account the reliability of the signals and all the calculated parameters, 11 of the 21 (without sensor readings 6) possible parameters are selected (table 5). This is a noticeable proportion of the indicators of the qualitative composition, changing in the experiment.

In the «Bread» group, Sample 1 has an identical qualitative composition of volatile compounds and differs from the Standard by no more than 10% (according to the set of compounds), Sample 2 – by 20%. In the «Bread sticks» group, Sample 1 differs from the standard by 10%, Sample 2 – by 25%. In the «Bread skewers» group, Sample 1 differs in a set of compounds from the volatile fraction of the Standard by 25%. And Sample 2 – by 43%, which does not allow them to be assigned to the same flavor group (table 3).

About 50% of the parameters of the qualitative composition differ for samples within all groups. These are noticeable changes. Let's follow in detail how the composition changes relative to the Standards for different groups.

To assess the proximity of the qualitative composition of drugs in groups, consider the contour diagrams of their parameters (fig. 4–6). They combine the parameters from table 3 for individual groups. If their values coincide for the samples and the entire set, the composition of the drug mixture is identical. The displacement of individual parameters relative to each other in the diagram indicates a difference in the composition of drugs.

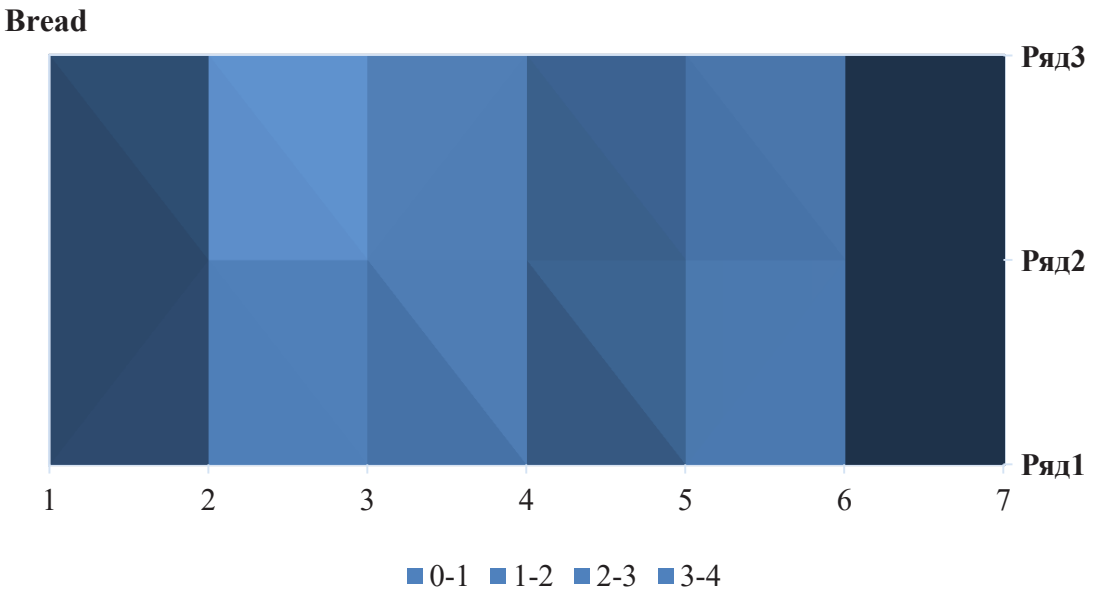


Fig. 4. *Contour diagram of the qualitative parameters of the «electronic nose» for bread samples: Standard (row 1), Sample 2 (row 2), Sample 1 (row 3)*

It was found that sample 3 (sample 1) is closer to the Control sample. For a set of qualitative parameters, we calculate the coefficients of difference of samples with additives relative to the standard:

	Sample 2	Sample 3
Parameter	0,109	0,0094

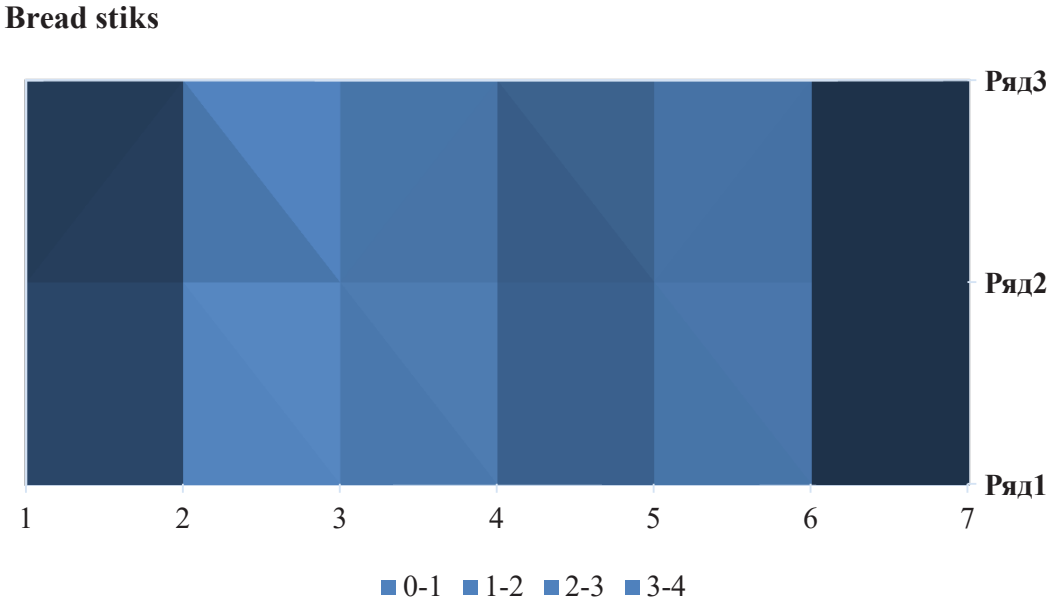


Fig. 5. *Contour diagram of the quality parameters of the «electronic nose» for Gressini samples: Standard (row 1), Sample 1 (row 2), Sample 2 (row 3)*

The smaller the number, the more samples are close in terms of a set of qualitative parameters, and therefore in terms of the composition of the drug. The differences

within the group are less significant than in the following two.

For a set of the most different qualitative parameters, we calculate the coefficients of difference of samples with additives relative to the standard:

	Sample 2	Sample 3
Parameter	0,022	0,130

Sample 2 is as close as possible in terms of the qualitative composition of

Bread skewers

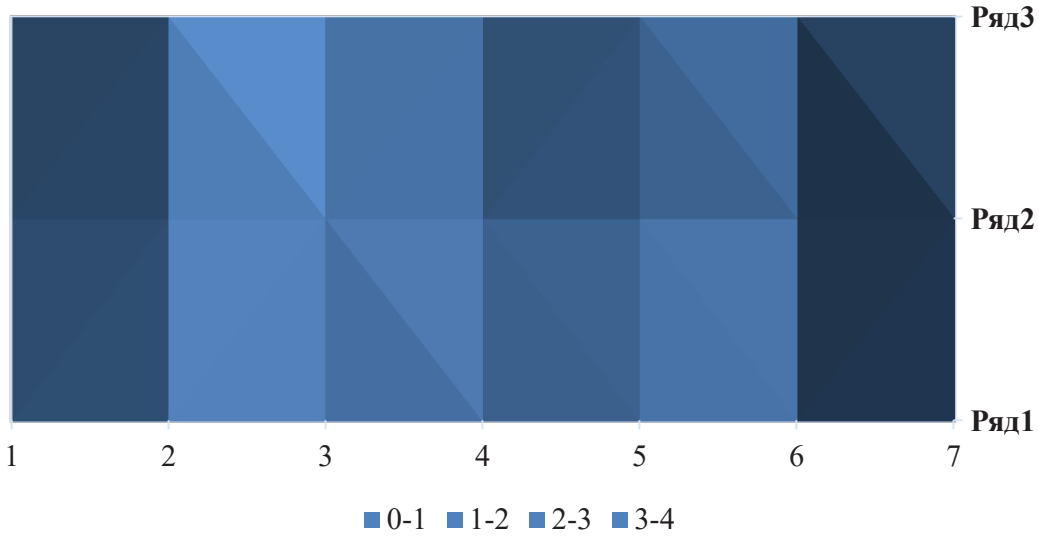


Fig. 6. *Contour diagram of the qualitative parameters of the «electronic nose» for bread stick samples: Standard (row 1), Sample 1 (row 2), Sample 2 (row 3)*

the volatile fraction to the Control sample. The differences in the group are significant.

For a set of the most different qualitative parameters, we calculate the coefficients of difference of samples with additives relative to the standard:

	Sample 2	Sample 3
Parameter	0,062	0,196

Sample 2 is close to the Control sample in terms of the qualitative composition of the volatile fraction. In this group, the samples differ more from each other in the qualitative composition of the drug mixture than in the others.

Taking into account the fact that 50% of the most strongly differing qualitative parameters were compared with each other, the following conclusions can be drawn that 1 or 2 samples with a significant change in the composition of volatile crumb compounds are allocated in all groups.

When comparing the volatile compounds in the samples quantitatively, it should be noted that since the semi-finished bread undergoes longer fermentation than breadsticks, the content of alcohols and ketones is 22% higher, and compared with bread skewers, where there is no fermentation process, they are 93% more, a similar picture with acids. However, when comparing the content of individual components in samples, especially oxygen-containing compounds, they are almost twice as large in the absence of a biological method of loosening in bread skewers.

For consumer evaluation, such changes are not significant for those samples in the formulation of which the content of paize flour is no more than 15% and recognized by consumers according to organoleptic indicators.

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