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New Way of "Electronic Nose" Informativity Increase in the Grape Wines Analysis

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ABSTRACT

The sorption of volatile organic compounds of the wine flavor has been studied on thin films of sorbents - modifiers of piezoelectric resonators electrodes which form sensors array of gas analyzer "electronic nose". The sensor array has been trained on the substances (ethanol, 1-butanol, 2-butanol, pentanol-2, ethanoic acid, ethyl acetate, water) and adapted to the wine flavor. It has been established the correlation between sugar content in wine and integral quantitative indicator of piezoelectric quartz crystal microbalance – the "visual print" area of the sensors array responses, reflecting the content of highly volatile substances in the equilibrium gas phase over wine. The parameters of rate and efficiency of highly volatile compounds sorption have been calculated, which could be used for estimation of wine samples quality. The connection of empirical physical and chemical characteristics and piezoelectric quartz crystal microbalance parameters of the wine samples has been studied by principal component analysis. The possibility of quality estimation, different physical and chemical parameters (content of sugar, alcohol), specified wine assortment, presence of artificial flavorings has been demonstrated as a results of the individual substance detection in the equilibrium gas phase over the wine samples by the array of the 7 piezosensors with different films. The new way of wine quality express estimation has been developed by the standard indicators and flavor, which can be an alternative to the preliminary examination in the routine analysis of detecting adulteration.

Keywords: *chemical piezosensors, detection of organic vapors (gases), wine quality, expert estimation.*

INTRODUCTION

The problem of natural wine production is urgent nowadays as adulterated wines can be dangerous for the consumer health as they can cause moral and material harm.

In Europe the control Regulations of adulterated products have been developed and they contain a list of more than 40 indicators, combinations of which give opportunity to estimate wine quality and authenticity quite objectively. But it's a long and expensive process; and, unfortunately, it is not compulsory today in many countries.

It's vital to develop perspective objective to highlight methods that make it possible to determine any kind of wine adulteration**,** artificial flavoring applications and natural raw materials replacements on the base of selected results as well as on their combinations or according to calculated criteria. Such methods include sensor analysis based on the arrays of different measuring elements in gases analyzer "electronic nose".

The sensors application in analysis of food products is based on operation of separate elements and intellectual multisensory systems (e-nose, e-toungue), which are adjusted on

detection of gas traces – quality indices of studied object. "Electronic nose "based on piezoelectric quartz resonators [7] is used to classify coffee mixture consisting of 12 sorts ("Espresso"). To determine the methanol impurity in whiskey samples the portable device like "electronic nose" based on gas sensors modified by carbon nano tubes and SnO_2 has been proposed [8]. System "electronic nose" with metal oxide transducers prepared by sol-gel method is used for analysis of air pollutants and food products (butter, milk, tomatos, wine, coffee), to classify olive oil [9], to estimate the freshness of fish [10] and meat [11]. Analysis of olive oil quality is carried out using the two type sensors system (quartz resonators and metalloxide chemoresistors) [12].

A multichannel gas analyzer "MAG-8" with software for data processing and construction of "visual prints" is developed for the analysis of quality of fruit and vegetable beverages, dairy and meat products etc. [13-18]. In Germany the device with optical sensors array has been designed for determination of water and other volatile compounds (ammonia, hydrogen sulfide) contents in thermally labile food products, for example, for sugar analysis [19]. Erik Borg with Philips [20] has developed the portable "electronic nose", which is able to differ the 8 products that can cause the allergic reactions. In the company Lapka Electronics the set from 4^{th} high sensitive sensors has been elaborated, that allows to determine the humidity of food products, presence of allergenes, nitrates concentarations [21].

These examples of application do not characterize all possibilities of "electronic nose" systems in food products analysis. The semiconductor (metal oxide), mass sensitive, generating bulk (OAW-type) or surface (SAW-type) acoustic waves and combinations of them have a wide application as transducers in such systems. The advantage of OAW-type piezo sensors is the easy regulation of selectivity and sensitivity by means of fast recycling of modifiers on the electrodes. It allows to select the most optimal sensors' combination for the solution to the certain analytical problem.

In case the determination of compounds group or qualitative comparison of several samples with one of them identified as standard is enough [22] for the problem solution, the chemical sensors are applied. To increase the informativity of multisensory systems the preliminary training of sensors array for individual test-substances, called quality indices of studied objects, in particular amines, alcohols, ketones, ethers etc. is usually employed.

Individual chemical sensors and their arrays (multisensory or polysensory) after a preliminary training for the test-substances are widely used for alcohol beverages quality assessment [23-25] and wine quality control [26]. The advantages of gas sensor arrays application have been determined in wine quality assessment in comparison with tasting analysis in 15 stages [27].

Researchers who use the chemometrics for processing multivariate data from e-nose propose different approaches in samples preparation. Recently in routine analysis not only individual components of the samples but their common profile (set of compounds), the so-called "image", which reflects the content of individual classes of compounds or ions, have been compared. In this case it is sufficient to determine the samples with the critical results that are unusual for the total sample and they are products of adulteration with high probability.

For objective quantitative estimation of volatile fraction of wine flavor ("the image of the first flavor tones" the application of piezosensors array with different selectivity and sensitivity to substances has been proposed to determine the nature of the raw material and the quality of the finished product.

The purpose of the research is to develop the way of the wine quality assessment by the image of flavor volatile fraction which is obtained using the piezo sensors array signals correlating with certain physical and chemical parameters of wine quality.

For the fulfillment of this purpose the following tasks were solved:

- The choice of the selective coating of the piezoelectric quartz resonators (PQR) electrodes, that sorbs substances-markers of wine volatile fraction differently, from the database;
- Training of the piezo sensors array using the main substances – the quality indices of wine (water, ethanol, butyl alcohol, ethanoic acid, ethyl acetate) and their mixtures;
- Development of the various calculation algorithms of the sorption rate parameters and efficiency of highly volatile substances (HVS) vapors which present analytical

information, in particular the identification parameters that correlate with the main physical and chemical indicators.

MATERIALS AND METHODS

Sensors Characteristics

The array of the 7 PQR bulk acoustic waves with Ag-electrodes, with the self-resonant frequency of F_0=10 MHz has been formed. From the database PQR selective coating have been chosen, they are standard chromatographic phase (Alfa Aesar, the USA) of different polarity and affinity to selected substances: polyethylene glycol adipinate**,** PEGA (sensor 1), polyoxyethylene - (21) – sorbitan - monooleate, Tween - 40 (sensor 2), octylpolyethoxysilane, Triton X-100, TX-100 (sensor 4), polyvinylpyrrolidone, PVP (sensor 7) and specific sorbents: dicyclohexan-18-crown-6, DCH-18-C-6, (sensor 3), di-β, β'-cyanetoxidiethyl ether, DCEDEE (sensor 6), trioctylphosphineoxide, TOPhO (synthesis IIC SB RAS**,** Novosibirsk) in the mixture with polystyrene (sensor 5). The weight of the films was 10-15 mcg. PQR electrodes modifiers were chosen in accordance with the previously defined selectivity and sensitivity parameters to the volatile organic compounds vapors using the database (methods of piezoelectric quartz crystal microbalance, gas chromatography) [13,14,28, 29].

The Selection of Optimal Modifiers Films of Piezosensors

Chemical composition of grape wine is the substances of different nature and polarity. However, a high selectivity and universal sorbent has not been recommended for many substances. The aroma composition of grape wine recognition could be done using piezo sensors array with at least 6 -8 PQR and with sorbents film of different polarity (by classification Rorshnaider for chromotographic phase) [29]. The most of grape aroma components belongs to polar compounds, that's why we inevitably choose polar phases (PEG-2000, PVP, TX-100, DCEDEE), medium polar one (PEGA, Tween-40), and specific sorbents (TOphO, DCH-18C6). The small polar substances are held by nonpolar sorbent (PS). These chromotographic phases are characterized as valuble and different selectivity to test - substances.

Formed piezo sensors array allows to detect a selected substance in the EGP over wine samples. However, in the method of quartz crystal microbalance (QCMB) this approach of the choice of PQR electrodes modifiers is not always effective due to the different conditions of sorbent interaction of the vapor in the column and on the surface. To establish quantitative and qualitative parameters of interaction we evaluated beforehand the sorption capacity of the films by the procedure [34], and the sorbents with the highest affinity for the test-substances were choosen. The 7 modifier films are selected - PEGA, Tween-40, DCH-18C6, TX-100, TOPhO, DCEDEE, PVP, they have a stable and reproducible signal; the time to complete sorption of volatile components of grape aroma does not exceed 30 seconds, the desorption – 120 s. We used mixtures TOPhO and PS, DCH-18C6 and PS in weight ratios of 2:1 respectively [14] to increase the mechanical stability and sensitivity to grape flavor of films based on TOPhO and DCH-18C6.

There are well reproducible quantitative (piezo sensors analytical signals) and kinetic interaction parameters of sorbents films with volatile substances from which the wine aroma consists. The studied PQR electrodes modifiers films are characterized to have high stability without refreshing (it's possible to carry out 100-150 cycles of sorption/desorption); the film loss weights after 100 sorption cycles does not exceed 0.5 %. The measurements' assessment of the results reproducibility was performed for the most informative and active films of modifiers which are universal sorbents. Measurement error on the selected piezosensors array does not exceed 4-5 % in the conditions recommended. It is typical for some mixtures sorption to have specific interaction between individual substances and modifiers films (for example, ethanoic acid and the TOPhO film) saving individuality of this interaction for multi-component samples. This feature gives opportunity to estimate individual quality indicator additionally, for example, acidity of the wine samples.

The Preparation of Detection Device "Electronic Nose"

The sensors array was formed from 7^{th} piezoelectric quartz crystals which electrodes had been modified by covering with uniform sorbents thin films using microsuringene (concentration 1-5 mg/cm^3): PEGA, Tween-40 and PVP in dimethylketone, DCEDEE and TX-100 in ethanol, DCH-18C6 and TOPhO in toluene for reaching the film mass 10-15 mcg. The weights of films of PQR modifiers and

sorbate were calculated by Sauerbrey equation [30]. Free solvents were removed in drying oven at temperature 50 ± 1 ºC during 20 min. Modified PQR were cooled to 20 ± 2 ºC in desiccator above dehumidifier layer. The completeness of solvents removing was controlled by stability of oscillation frequency of piezosensor with neglectable drift (F ± 3 Hz). The obtained piezosensors were fixed in holders of germetic chamber of device "electronic nose" with volume 60 cm^3 (Fig. 1). To regenerate the properties of modifiers after measurement the detection chamber was blown with dry air for approximately 5-7 min.

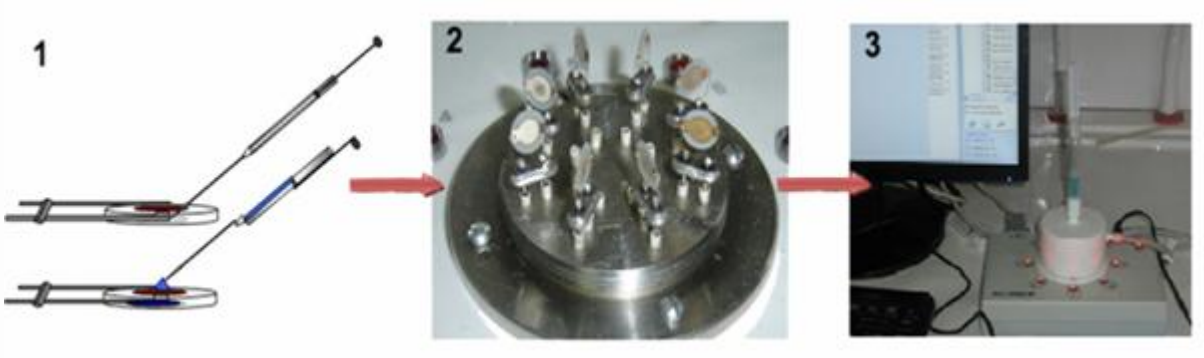


Fig1. *Preparation of detection device: 1 – modification of piezoelectric quartz resonators electrodes; 2 – forming of sensors array; 3 – airtight detection chamber*

Analytical Information from Sensors Array

Several types of piezosensors array signals and their derivatives have been used to obtain complete information about the qualitative and quantitative composition of the wine flavor volatile fraction, as well as the presence of the selected substances groups [28]:

- Maximum analytical signal of piezosensor (ΔF_i^{max}, Hz) characterizing organic compounds sorption efficiency on the thin sorbents films;
- Circular diagrams which are "visual prints" of piezosensors maximum response ΔF_{ii}^{max} in the equilibrium gas phase (EGP) over the samples for the certain measurement time, so called "visual prints" of maxima; they give opportunity to establish the identity degree of the composition;
- Kinetic "visual prints" which are circular diagrams, reflecting the dependence of all piezosensors signals on the time $\Delta F_i = f(\tau, s)$; the measurement time on the circle (s) and piezosensors response value on the radial axis ΔF_i, Hz was marked; piezosensors array responses were recorded with iteration of 1 s and processed with a special program for the experimental sample of the gas analyzer "MAG-8" (Russia). The small informative responses and their measurements are excluded from total data in programm;
- The geometric figure area of "visual print" $S_{«v.p.»}$, Hz·*s* is a criterion, which is determined by the total weight of HVS adsorbed by the sorbents thin films for measurement time and it is in proportion to their concentration in EGP over the sample. There was a stable dependence between the value of $S_{«v.p.»}$ and the substances vapors content in the detection cell. But it is correct if there are insignificant differences of the "visual print" geometry for the test substance vapors.
- Some new *identification parameters* have been proposed:
- The sorption rate parameter of the HVS vapor $\gamma_i = \frac{\Delta F_{\tau(1)}}{\Delta F_{\tau(2)}}$ is calculated as the ratio of the ΔF_i of this piezosensor at the maximum sorption moment $\tau(1)$ to the signal in the subsequent sorption time $\tau(2)$ which is close to equilibrium state or slight changes in the system (about 60 s)**;**
- The sorption efficiency parameter is $A(i/j)$ is calculated as the ratio of maximum responses of the individual sensors $A(i/j) = \frac{\Delta F^{max}{}_i}{\Delta F^{max}{}_j}$ (where i, j are different films of the electrodes modifiers); it allows to estimate the ratio of the various compounds' groups concentration in the sample and it is an affinity measure of 2 sorbents to the specific substance or the mixture.

Samples Characteristics

As the primary objects of the research the substances which characterize quality of wine: ethanol, butanol-1, butanol-2, pentanol-2,

ethanoic acid, ethyl acetate, water – have been selected so called quality indicies. The secondary objects of the analysis are samples of white and red wines of different brands and categories (dry, semi-sweet, semi-dessert, dessert, fortified) common in a trading network (14 samples) and private manufacturing (2 sample).

Manufacturer – company group "Vinnyi grad", Russia:

1 – "Chardonnay", dry white;

2 – "Isabella", dry red.

Manufacturer – LLD "Dolina", Krasnodar region, Russia:

3 – "Tatiana's day", semi-sweet white;

12 –"Muskatnoe", semi-sweet white.

Manufacturer – "KubanAlko", Krasnodar region, Russia:

4 – "Kovarstvo i lubov", semi-sweet red;

5 – "Muskatnoe Tamanskoe", semi-dessert white;

7 – "Anapa", fortified white.

Manufacturer – OAS APF "Fanagoriya", Krasnodar region, Russia:

6 – "Cahor", dessert red;

13 – "Chernyi lekar", semi-sweet red;

14 – "Ristling", semi-dry white.

Manufacturer – CAS "Lasurny", Krasnodar region, Russia:

8 – "Isabella", fortified red.

Manufacturer – NPAO "Massandra", Crimea:

9 – "Sedmoe nebo knyazya Golitsina", fortified dessert white;

15 – Muscate pink "Massandra", dessert liqueur.

Manufacturer – CAS APK "Gelendzhik", Krasnodar region, Russia:

16 – "Gelendzhik", strong white;

10 – "Lidia", semi-sweet white (private manufacturing);

11 – "Russkoe phioletovoe", semi-sweet pink (private manufacturing).

The sample 10,11,14-16 were applied to check the correctness of obtained correlation.

Preparation of Samples and Sampling of Equllibrium Gas Phase

The average sample of wine was placed for 15 min in germetic sampler. After gas phase had been saturated by wine vapors we selected the constant volume (2 cm^3) of EGP by syringe through soft membrane and injected fast in detection chamber with rate 1 cm^3/c. The volatile subtances, forming the wine aroma, were sorbed on surface of sorbents thin films, the oscillation frequency of piezosensor ΔF_i was decreased proportionally to sorbate weight. The responses of all sensors in array have been recorded during more than 60 s like the output curves with the resolution of 1 s.

Main physical and chemical wine quality parameters have been additionally determined: active (DSTU 4112.24-2002) and titratable (GOST 14252-73) acidity, solids content, sugar content (GOST 13192-73), density (GOST 14136-75) for all samples.

Chemometrics Method

In order to develop a model describing the relationship between empirical parameters and the analyzed wine samples properties principal component analysis (PCA) has been applied. Data matrix analysis by the PCA was performed in The Unscrambler v. 9.8 program with full cross-validation.

Results and Discussion

The EGP chemical composition which is the same as grape wine flavor consists of the aroma-forming substances of basic raw material (primary flavor), the fermentation process (secondary flavor), and then bouquet of aging (tertiary flavor) is added because of chemical reactions during wine aging process. In the wine flavor formation more than 300 highly volatile organic compounds: alcohols (ethanol, butanol, pentanol), organic acids (malic, lactic, acetic), ethers of acetic, capronic, caprylic acid (isopentyl acetate, hexyl acetate), aldehydes (ethanal, butanal, acetoxibutanal), terpenes (limonene, linalool), terpenoids (rose oxide, noroloxid), and many others [31, 32] are involved. Some components, such as ethanol, pentanol-2, butanol-2, ethyl ethers of fatty acids are the basis of the wine flavor. It is proved that the role of complex ethers can differ in formation of flavor and taste of wine and brandy and it has been determined by the type of ether and its quantity. For example, ethyl acetate, predominant over volatile ethers in large quantities is undesirable because of the fact that when its content in wines is more than 180 mg/dm^3 it causes taste of "sour wine"[33]. Based on the importance and informativity of various groups of wine volatile compounds as the quality indices of wine – ethanol, butanol-1, butanol-2, pentanol-2, ethanoic acid, ethyl acetate and water have been selected.

Analytes sorption kinetics on the thin modifiers films of PQR electrodes have been studied. Any deviation in the wine quality from the standard can be estimated using the sorption features of the test-substances on the modifiers films, which depend on compounds concentration in EGP.

Features of "Visual Prints"

The sensors array was trained by some individual test-substances, which are quality indices of natural wine. Analytical signals of the sensors array have been obtained during the HVS sorption process in the form of "visual prints" of the maxima.

Further EGP of 16 samples of red and white wines from different manufacturers and categories (see sample characteristic) have been tested. The maximum sensors response analysis allow to select several wine groups (for example, samples 1 and 10, samples 5 and 8, samples 7 and 12) for which the geometry of "visual prints" are noticeable difference (Fig. 2). At the same time the basic physical and chemical wine quality parameters have been determined (see Table 1).

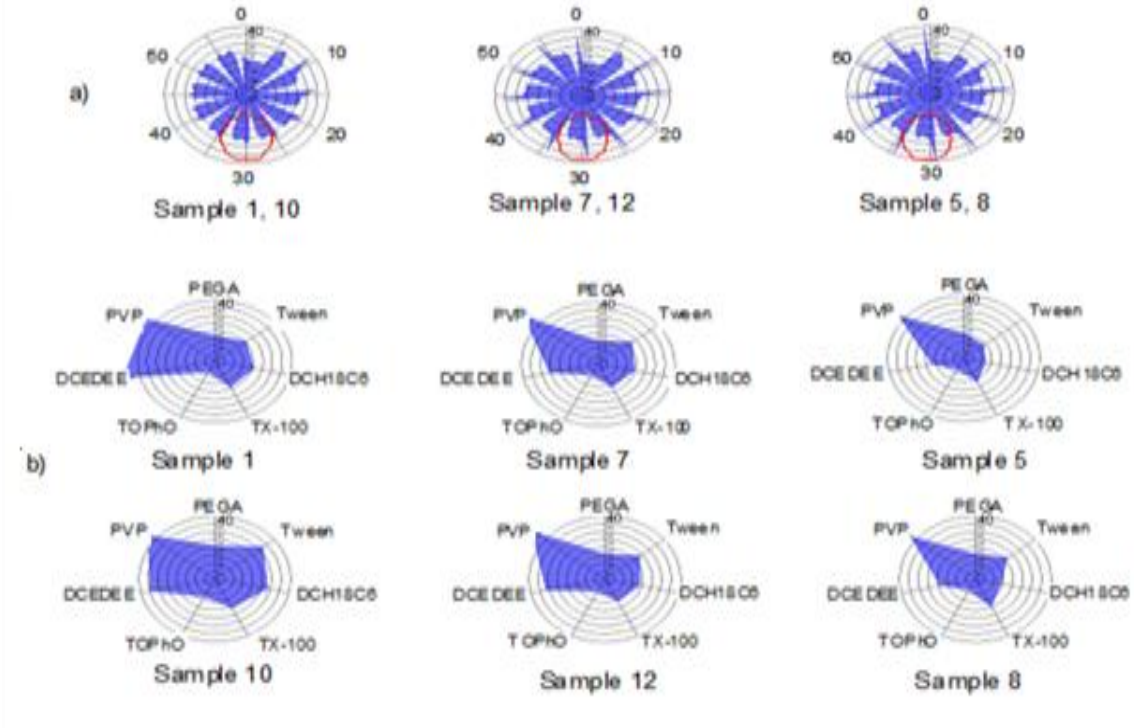


Fig2. «*Visual prints*» *of the sensor signals: kinetic (a) and maxima (b) in the EGP over samples. It is marked sorption time (s) on the circle of kinetic prints and sensor names on the circle of maxima prints*

Table1. *Results of PQM of EGP and physical and chemical indicators of wine quality (n=3; P=0,95)*

sample	$S_{«v.p.»}$, Hz·s	Alcohol content, % vol. (determined by the manufacturer)	Sugar content, g/dm^3	Solids content, %	Density, g/sm^3	Titratable acidity, g/dm^3	Active acidity (pH)
1	2340 ± 50	9–11	0	3.0	1.000	4.0	3.06
2	1620 ± 20	9–11	0	5.3	1.000	8.5	3.02
3	1680 ± 15	10–11	32	5.0	1.009	8.0	3.07
4	2010 ± 30	11–12	32	4.8	1.050	8.0	3.00
5	1050 ± 10	15–16	120	6.6	1.020	5.4	3.14
6	1120 ± 15	15–16	150	13.0	1.050	4.3	3.02
7	1570 ± 20	18	70	6.8	1.010	6.5	3.04
8	1320 ± 15	18	80	7.8	1.020	7.5	3.09
9	1070 ± 10	16	180	21.0	1.060	4.0	3.60
10	2200 ± 40	12–15	35	5.5	1.000	3.9	3.43
11	1750 ± 25	10–12	40	4.3	1.000	5.6	3.33
12	1910 ± 30	9–11	40	4.7	1.010	7.0	3.03
13	1720 ± 20	10–12	40	5.0	1.010	2.6	3.40

Informativity of the Area of "Visual Prints"

The most easily recorded quantitative indicator of the piezosensors array responses is the area of "visual print" $S_{«v.p.»}$, which reflects the HVS content in the EGP over wine. The complex composition of wine does not allow the researchers to conclude a definite correlation between the content of quality indices substances in the EGP and the liquid phase has been. For example, the surfactants have a significant impact on the HVS distribution between liquid and gas phases. Such substances in wines can include carbohydrates, which determine an important physical and chemical parameter. At the same time, sugar content increase in wine raises its viscosity and reduces the surface tension. In this case, at all other things being equal (the alcohol content and the total content of volatile compounds), the saturated vapor pressure of the polar HVS is decreased, and as a result, to the reduction of $S_{«v.p.»}$ of piezosensors array responses.

The correlation between sugar content in wine (x) and $S_{«v.p.»}$ (y) (Fig.3), described by the equation $y = 0{,}052x^2 - 16{,}4x + 2358$ ($R^2 = 0{,}9724$) has been determined, which allows to calculate the sugar content by the electronic nose information (S_i), and therefore estimate the quality and category of wine.

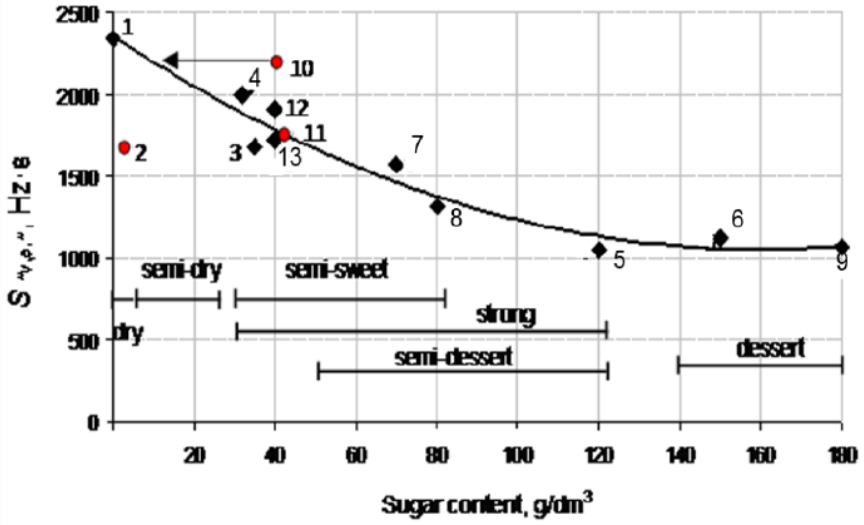


Fig3. *Dependence of sensor array responses «visual prints» on sugar content in wine*

Table 2 shows gradation for the wines categories studied according to integral quantitative indicator - $S_{«v.p.»}$. On the base of the data obtained it is possible to determine the rating of wines from the semi-dry category, which were not included in the sampling analyzed. The expected value of $S_{«v.p.»}$ for them will be 2000-2200 Hz•s.

Table2. *Interrelation of "visual prints" area of sensors array responses and specified wine category*

Wine Category According to the Classification	Alcohol Content, % vol.	Sugar Content, g/dm^3	$S_{«v.p.»}$, Hz·s
Natural:			
Dry	9 – 13	0 – 3	2200 – 2500
Semi-dry*	***9 – 13***	***5 – 25***	***2000 – 2200***
Semi-sweet	9 – 12	30 – 80	1500 – 2000
Spetial:			
Strong	17 – 20	30 – 120	1200 – 1500
Fortified:			
Semi-dessert,	14 – 16	50 – 120	
Dessert	15 – 17	140 – 200	900 – 1200

* *marked values for wine groups not engaged in the sampling studied*

The accuracy of this assumption has been verified by the results of analysis of the five wine samples declared as semi-sweet (samples 10 and 11), semi-dry (sample 14), dessert (sample 15) and strong (sample 16) which were not involved in the primary data processing. The sugar content in samples has been calculated using the correlation equation.

For the sample 10 the discrepancy between the values of $S_{«v.p.»}$ = 2200±40 Hz s has been revealed and sugar content manufacturer declared. On the base of the solid content in the sample it has been determined that it corresponds to the category "semi-sweet" (see Table 1), but it refers to the groups "dry"/"semi-dry" in accordance with the value of $S_{«v.p.»}$. This sample is characterized from the whole sampling by the maximum values of piezosensors response based on the Tween-40 and DCH-18C6 sensitive to the complex ethers and acids. However, this sample is also characterized with the presence of sugars and according to the sugar content it refers to the group of semi-dry wine. Thus, $S_{«v.p.»}$ and the sugar content correlate and they are more reliable parameters in wine categories determination than the solid content. The sample 10 must be rejected as inadequate to a certain category (informative falsification) or made in violation of the technological mode, as it leads to the high content of acids and ethers.

The sample 11 ($S_{«v.p.»}$ = 1750±10 Hz•s) corresponds to the group "semi-sweet" or "fortified" in relation to the sugar content (see Table 2, Fig.3**),** but according to the alcohol content it is a sample of semi-sweet wine that agrees with the requirements of GOST [35]. That's why to obtain reliable ranking of samples it is necessary to have 2 indicators: $S_{«v.p.»}$ and the alcohol content (vol. %) declared by the manufacturer.

From the value $S_{«v.p.»}$ = 2180 ± 25 Hz for sample 14 it has been established that wine is classified as semidry, the calculated value of sugar content 11.26 g/dm^3 (Table 3, Fig. 3), that corresponds to indicators declared by the manufacturer. Sample 15 is surely sweet wine by value $S_{«v.p.»}$ = 1065 ± 8Hz s with sugar content of 160 ± 1 g/dm3, which satisfies GOST (Table 2 and 3). Sample 16 ($S_{«v.p.»}$ = 1420 ± 10 Hz s) can be classified as "semi-sweet", "strong" or "semi-dessert" (Fig. 3). On the content of alcohol (17 vol. %) the wine is firmly ranked as "strong" (Table. 2), which corresponds to declared alcohol content by the manufacturer.

Table3. *The sugar content in wine samples by the results of piezoelectric quartz crystal microbalance (n=3; P=0.95)*

Sample	$S_{«v.p.»}$, *Hz·s*	Calculated sugar content, g/dm^3	Declared manufaturer wine category	Conformity with normal sugar content (see Table 2)
10	2200 ± 40	9.9	semi-sweet	does not correspond
11	1750 ± 25	42.9	semi-sweet	corresponds
14	2180 ± 25	11.3	semi-dry	corresponds
15	1065 ± 8	159.0	dessert	corresponds
16	1420 ± 10	75.1	strong	corresponds

The value of $S_{«v.p.»}$ for sample 2 (see Table 1) using established correlation does not correspond to the category "dry wine" to which the sample has been classified according to the physical and chemical parameters. Titratable acidity of the sample (8.5 g/dm^3) is higher than the standard rate that is connected with a high content of non-volatile acids. The solids content has been twice increased and the value of $S_{«v.p.»}$ is less in 1.5 times compared with the sample 1, which refers to the same category. This results allow researchers to conclude that the sample 2 does not meet requirements of dry wine and it is wine adulteration or wine of low quality.

It is proved that if the sample falls out of the correlation dependence (Fig. 3) by the value of $S_{«v.p.»}$, therefore, wine does not meet the standard requirements according to any physical and chemical indicator (sugar content or titratable acidity).

Informativity of Additional Parameters from Sensors Array

Parameter of Sorption Efficiency

An additional parameter of the vapor sorption efficiency *A(i/j)* gives opportunity to estimate the proportion of one HVS group in comparison to another. So, the ratio of the sensors signals with films from Tween-40 (sensor 2) and PVP (sensor 7) gives the possibility to estimate the portion of aliphatic acids among all polar HVS; the ratio of the sensors signals with the films from DCEDEE (sensor 6) and PVP (sensor 7) allows the researcher to determine the portion of phenolic compounds in the total amount of the polar substances; parameter *A(i/j)* calculated by sensors signals with films from DCH-18C6 (sensor 3) and DCEDEE (sensor 6) demonstrates the ratio of the polar compounds (acids, alcohols, ketones) to the phenolic ones. The parameters *A(2/7)*, *A(6/7)* and *A(3/6)* are

calculated for the samples of white, red and rose wines (see Table 4).

Table4. *Interralation of HVS sorption effectiveness parameters A(i/j) ± 0.02 and wine organaleptic indicators (n=3; P=0.95)*

Samples	Parameter *A(i/j)*			Flavor classification
	2/7*	3/6**	6/7**	
White wine				
1	0.47	0.43	1.10	soft oil and lemon flavor notes
3	**0.22**	**0.33**	**0.80**	light nutmeg and honey and flowery notes
5	0.32	**0.72**	**0.50**	nutmeg and honey with fruit and prune notes
7	0.46	0.77	0.48	pure with dry fruit notes
9	0.40	0.77	0.40	complex honey, notes of peach, apple-quince and medlar
10	0.73	0.83	0.77	delicate with strawberry notes
12	0.50	**0.56**	**0.65**	nutmeg and flowery with the notes of tea rose flavor
Red wine				
2	**0.22**	**0.31**	**0.66**	delectable flavor with nutmeg and flowery notes
4	**0.26**	**0.33**	**0.50**	flowery and nutmeg flavor
6	0.30	0.80	0.36	chocolate flavor with light notes of black currant and prune
8	0.50	0.74	0.43	strawberry notes; fruit notes
13	0.58	0.66	0.70	With notes of spices и cherry kernel
Rose Wine				
11	0.81	1.33	0.55	delectable flavor with fruit note

* *it is marked samples for which A(2/7) parameter is 2 times understated, it's high probability of dry substances replacement of natural raw material*

** *it is marked samples in which it has been determined nutmeg flavor according to A(3/6) and A(6/7) parameters*

The parameter *A(2/7)* does not allow reliably to determinate what sort (white or red) of wine sample is. However, using these parameters researcher can identify the presence of the substances determining nutmeg (muscat) flavor of wine. Earlier the possibility to identify wine nutmeg flavor has been proven using sensors array of "static electronic nose" according to other parameters of the system [36]. The parameter *A(3/6) < 0.58-0.60, A(6/7)* varies in the range of 0.50 - 0.82 for all samples with nutmeg notes. The proportion of the phenolic compounds in this flavor is larger than for flavors with fruit, and other complex tones for which the parameter *A(3/6)* > 0.6. Sample 5 (*A(3/6) = 0.72*) is an exception; it is characterized by a complex flavor of nutmeg, fruit and prunes. In the samples where both parameters correspond to the previously established values, there is a high probability of nutmeg tones determination by the experts (samples 2, 4, 12). If at least one of the parameters is not included in the range determined, it will be difficult to predict the presence of the nutmeg flavor when tasting (sample 1). The nutmeg flavor is predicted simultaneously by two parameters *A(3/6)* and *A(6/7)*.

It has been previously found that sucrose is a good salting-in agent of phenolic compounds [37]. Look into the dependence of the parameter *A(6/7)* connected with presence of phenolic substances in EGP, on the sugar content (Fig. 4, curve 1) and ethanol concentration (Fig. 4, curve 2) in wine.

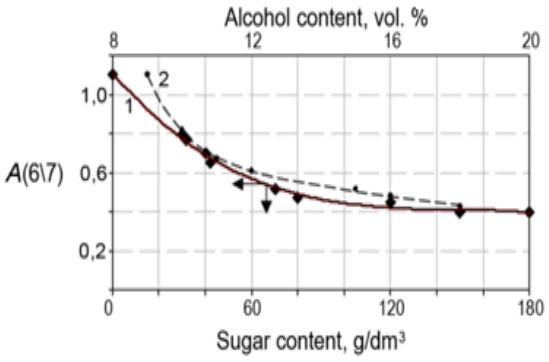


Fig4. *Dependence of A(6/7) HVS sorption effectiveness parameter on the content of sugar (1) and alcohol (2) in wine*

With carbohydrates content increase in wine there is a decrease in values of parameters *A(6/7)*. This is true to the previously established influence of the surfactants on the detection results of the HVS in EGP over wine. At the same time it has been found that sugar's

influence is less for the fortified wines with a high content of ethanol than for the wines with low alcohol content (dry, semi-dry). This type of the wine native components influence on the "electronic nose" analytical information should be taken into consideration when developing procedures of wine express-analysis.

Parameter of Sorption Rate

During components sorption from EGP over wines the differences in the interaction kinetics in comparison with the vapors sorption of the individual substances and their mixtures have been determined. So, the EGP of the sample 10, for example, is characterized by the HVS spontaneous desorption from the films of the most informative sensors (Tween-40, DCH-18C6, PVP, DCEDEE), cumulative sorption on the same films occur for the substances sorption from the EGP over the sample 6. Difference in the sorption kinetics of the HVS mixtures allows to apply the additional kinetic parameter γ_i, characterizing the relative sorption rate changes; it is determined by the nature of the sorbent and sorbate. Table 5 shows the parameter γ_i calculated for the most informative sensor with sensitive universal PVP film. According to the value of γ_{PVP} the main groups of wines have been distinguished: group I – the samples 1-4, 7, 11-13, group II – the samples 5, 6, 8, 9. Taking into account wine categories established by manufacturers, it was found that it is typical γ_{PVP} <1.0 (0.6-0.9) for low-alcohol wine (dry and sweet), and γ_{PVP} >1.0 (1.0-1.3) for specific and fortified wine. Abnormally low parameter γ_{PVP} has been obtained for the sample 10, which further confirms the significant difference of the EGP composition of this sample among all samples studied. This can be explained of its adulteration or violations in the production technology. Some recorded ($S_{«v.p.»}$) and calculated ($A(i/j)$, γ_i) parameters of "electronic nose" allow to determine a sample with critical values in sampling with a high degree of probability.

Table5. *Sorption rate parameter (γ ± 0,02) of sensor with PVP film in EGP over wine samples*

Wine group	**I (γ = 0.6 – 0.9)**						**II (γ =1.0 – 1.3)**				**Anomaly**
Sample №	1	3, 12	13	4	7, 11	2	9	6	8	5	10
γ	0.60	0.64	0.72	0.77	0.80	0.86	1.00	1.17	1.24	1.26	0.4

Classification of wine samples by PCA

To solve the problem of samples ranking the chemometrics method has been applied, that gives opportunity to estimate usefulness of "electronic nose" results and standard physical and chemical indicators. The principal component analysis can help to understand the correlation of standard parameters of the wine samples analyzed with PQR ones and to classify samples into groups by certain categories. The main advantage of this method is experimental data conversion in the coordinate system, which allows to consider the components as independent to each other and thus increasing their specificity for analytical evaluation of experimental data.

As variables it is selected physical and chemical standard indicators such as solid content (%), sugar content (g/dm^3), total acidity (pH), wine titratable acidity (g/dm^3), density, (g/cm^3) as well as wine flavor parameters obtained by PQM: the area of "visual print" ($S_{«v.p.»}$), the maximum responses of informative sensors (ΔF_i^{max}, Hz), kinetic parameter (γ_i), and the parameters of substances sorption efficiency $A(i/j)$.

Using Standard Indicators and PQM Results

A PCA model for the wine samples classification has been developed on the base of the multivariate data (standard and PQM indicators). The first principal component (PC1) describes the direction of maximum data change. If the data are not described completely (changes are significant), it is chosen one more direction perpendicular to PC1 that is the second component (PC2), etc. Components PC1 and PC2 make the greatest contribution to the data structure – 72 % (Fig. 5). Considering all variables on the scores plot it can be distinguished 2 groups of wines: group I are samples 2, 3, 4 (dry and sweet) and group II are samples 5, 6, 8, 9 (fortified, dessert).

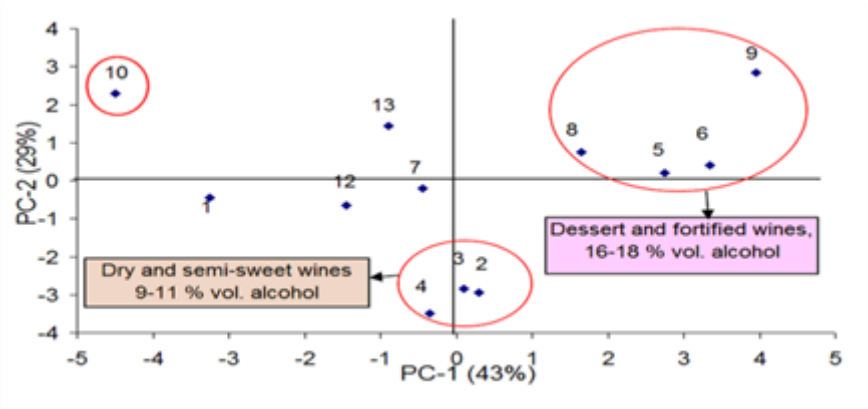


Fig5. *Scores plot from PCA of wine samples using all parameters*

The correlation between quality standard indicators of wine samples and sensors array parameters has been established. The total acidity correlates with signals of sensor with film from TX-100 ($\Delta F_{TX\text{-}100}^{max}$), titratable acidity – with ΔF_{PVP}^{max}, solid and sugar contents – with ΔF_{DCEDEE}^{max} and density – with γ_{PVP}.

Using PQM Parameters

The explained variance of new model, illustrated on Fig. 7, is 81 %, that is more than for previous model. As groups of wine samples are not changed using the model based on only the PQM parameters (Fig. 6) and with addition of standard physical and chemical characteristics (Fig. 5), therefore, analytical information of piezosensors array is enough for the wine samples ranking. According to loadings plot the parameters $S_{«v.p.»}$, γ_{PVP} and $\Delta F_{DCH\text{-}18\text{-}C\text{-}6}^{max}$ make the greatest contribution to the component PC1 and parameters of sorption efficiency *A(2/7)*, ΔF_{PVP}^{max} и $\Delta F_{TX\text{-}100}^{max}$ – to the component PC2.

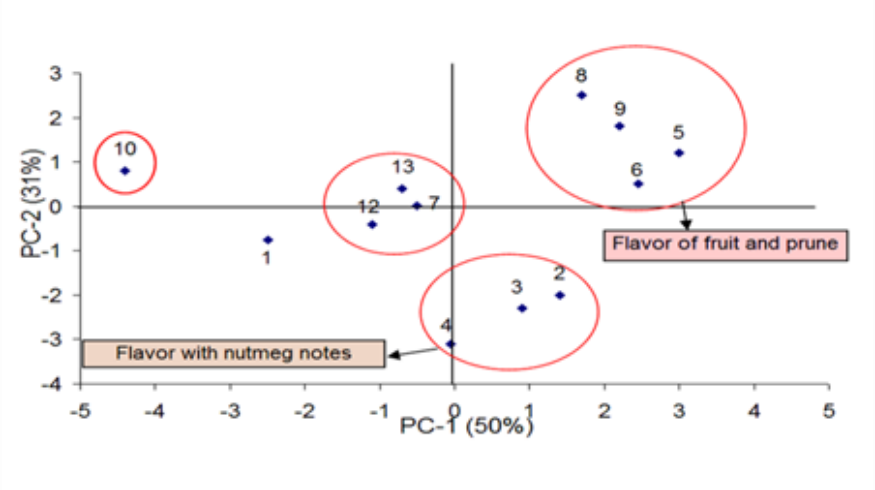


Fig6. *Scores plot from PCA of wine samples using piezoelectric quartz crystal microbalance parameters*

PCA allowed to classify wine samples according to aroma features. According to the new model (Fig. 6) it has been found that the first group consists of dry and semi-sweet wine with a volume fraction of alcohol 9-12%, group II includes dessert and fortified wines with a volume fraction of alcohol 16-18%. However, not all wine samples of this category were included in these groups. Therefore, there is another factor that unites samples selected by the model in the groups. This factor is sample's specific flavor: the first group consists of wine with flowery and different notes in flavor (nutmeg and honey, flowery and nutmeg), group II includes wines with a complex flavor of prunes or dry fruits ("Cahor", " Sedmoe nebo knyazya Golitsina" and others). The semi-sweet wines samples 7, 12 and 13 form another group, because of the substantial effect of sugars on the HVS distribution between liquid and gas phases. The sugar content in these samples is 40 – 70 g/dm^3. The obvious exception of any group is the sample 10.

Wine adulteration in all categories could be detected using all these indicators. The PCA model allows prediction of wine authenticity and quality based on the piezoelectric quartz

crystal microbalance results of EGP over samples. Even though the wine meets requirements of GOST according to the physical and chemical parameters, but it does not belong to the model group according to the parameter of PQM, there is a high probability of its adulteration or bad quality.

Identification of the Artificial Flavorings

It has been previously shown that the presence of artificial flavorings significantly alters the HVS sorption kinetics and therefore the parameter γ_i [38]. Using this parameter the artificial flavorings in dry and semi-dry wines can be identified with high probability.

To prove this hypothesis a sorption of artificial flavoring "Isabella", used in the production of wine and alcoholic beverages, has been studied on the previously selected sensors array. Parameters *A(2/7)* and *A(3/6)* have been calculated for flavor solutions of different concentrations of semi-dry natural wine "Isabella" and natural wine with flavoring addition (see Table 6). The sorption efficiency parameter *A(2/7)* of wine with the additives decreases in two times and it is surely connected with the artificial flavoring presence in the sample. Based on this parameter in Table 4 the samples 3, 4 were selected from the sampling studied. According to all physical and chemical parameters they meet the requirements of the declared categories, but with high probability they are adulterated by strengthening the flavor with artificial additives. In addition, it is true for sample 2 according to parameters (titratable acidity, solids content, $S_{«v.p.»}$ и *A(2/7)*) that it does not meet the requirements for dry wine, so it is adulterated by the replacement of natural raw material and by strengthening the flavor with artificial additives.

Table6. *Influence of artificial flavoring "Isabella" on the A(i/j) sorption effectiveness parameter of wine HVS (n=3; P=0.95)*

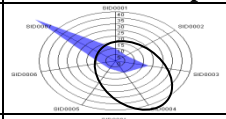
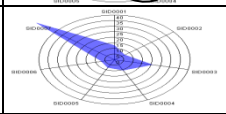
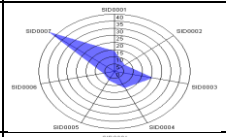
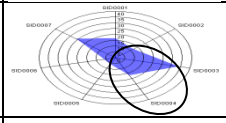
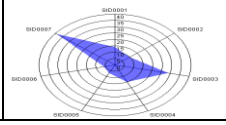
Research objects	*A(2/7)*	*A(3/6)*	«Visual print»
flavoring dilution ratio: 1:10	0.13 ± 0.02	0.47 ± 0.02	
1:100	0.14 ± 0.02	0.35 ± 0.05	
1:1000	0.16 ± 0.03	0.30 ± 0.010	
Semi-dry wine	0.46 ± 0.03	0.36 ± 0.015	
Semi-dry wine with flavor in volume ratio 1:1000	0.25 ± 0.015	0.21 ± 0.012	

Table 7 combined the experimental PQM parameters allowing to determine the samples belonging to the certain wine categories, to predict of the sugars content, to estimate of the identity of the production technology and to establish the presence of artificial flavorings.

Table7. *Parameters of HVS piezoelectric quartz microbalance in EGP over wine samples (n=3; P=0.95)*

Wine category	$S_{«v.p.»}$, *Hz·s*	Sugar content, g/dm^3	*A(3/6)*	*A(2/7)*	*γ*
Dry	2200 – 2500	0 – 3	0.30 – 0.45	0.45 – 0.49	0.6 – 0.86
Semi-dry	2000 – 2200	5 – 25	0.35–0.37	0.43 – 0.48	–
Semi-sweet	1600 – 2000	30 – 40	0.40 – 0.70	0.50 – 0.80	0.64 – 0.72
Specific strong wine	1200 – 1600	70 – 80	0.70 – 0.77	0.46 – 0.50	1.24 – 1.25
Fortified:					
Semi-dessert	900 – 1200	100 – 120	0.70 – 0.74		1.22 – 1.24
Dessert		120 – 180	0.77 – 0.80	0.3 – 0.4	1.00 – 1.20

CONCLUSION

Piezoelectric quartz crystal microbalance method gives an objective assessment of the wine organoleptic characteristics as opposed to physical and chemical ones. The model describing the correlation of empirical physical and chemical characteristics and the PQM parameters with the properties of analyzed wine samples has been developed using the principal component analysis. Based on the experimental results a way of wine quality rapid evaluation has been developed by the standard indicators and PQM parameters reflecting the flavor features, which can be the alternative to the preliminary examination in routine analysis in the determination of adulteration.

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