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VOLTAMMETRIC "ELECTRONIC TONGUE" FOR VODKA IDENTIFICATION

Summary. *In this work, a voltammetric "electronic tongue" is proposed for the identification of vodkas.*

Key words: *voltammetry, tube electrode, vodka, chemometrics.*

Introduction. Currently, there is an intensive growth in the production of alcoholic drinks, however, the quality and safety of these do not always meet the requirements of state standards. Manufacturers are trying to increase their volumes by diluting them with water or cheaper industrial alcohol. Therefore, the problem of determining the authenticity of alcoholic drinks remains relevant.

The quality of alcoholic drinks is usually assessed by qualified specialists or traditional chemical analysis. In recent years, multisensory systems of the "electronic tongue" type have become widely used for the analysis of alcoholic drinks (including the control of falsification, control of production processes). They consist of sensors arrays that recognize fingerprints of samples and can later be used to classify them.

Vodka is one of the most popular alcoholic drinks. In addition to pure vodkas, there are flavored vodkas, which are characterized by a specific taste that is different from the taste of the raw materials used in their production [1].

Measurement of alcohol content is traditionally performed using a hydrometric or pycnometric method. The analysis of the chemical composition is usually carried out using gas chromatography - determination of the content of methanol, acetaldehyde, diethyl phthalate, coumarin, ethyl acetate, and higher alcohols [2–8]. At present, in addition to the aforementioned analytical methods, studies of alcohol samples are carried out using ion chromatography and liquid chromatography, high-efficiency liquid chromatography, mass spectrometry, spectrophotometry, isotope analysis, etc. Methods for concentrating analytes are often used - solid-phase microextraction and extraction [2]. The study of the quality of ethanol used in the production of vodka was carried out using the "electronic tongue" and partial least squares regression [9].

In this work, a voltammetric "electronic tongue" is proposed for the identification of vodkas. Tubular electrodes are a sensor in which electrochemical reactions take place on the inside of the tube. This type of electrochemical cell enhances the mutual influence of chemical components on the shape of the voltammetric curve. As a result, the "electronic tongue", accumulating information during continuous oxidation/reduction cycles of the components of the electrode/solution phase interface, makes it possible, using chemometrics methods, to recognize the slightest differences in the composition of solutions.

Experimental part. All voltammetric measurements were performed using a two-electrode system using a potentiostat/galvanostat Elins-P-20X. Each sample included 100 measurements of voltammograms under conditions of continuous functioning of the tubular electrode (working potential range from –1.5 to +1.5 V, potential sweep rate 1 V/s). All measurement cycles were performed at room temperature. The analyzed samples were:

– pure commercial brand vodka (V);
– medical alcohol 95% (S);
– deionized water (W);
– a mixture of vodka + 10% vol. deionized water (V + W);
– a mixture of vodka + 10% vol. medical alcohol (V + S).

Results and its discussion. As a result of the experiment, arrays of voltammograms (VAGs) were obtained for samples of vodka, water, alcohol, and their mixtures. As an example, Fig. 1 shows a VAGs array of vodka.

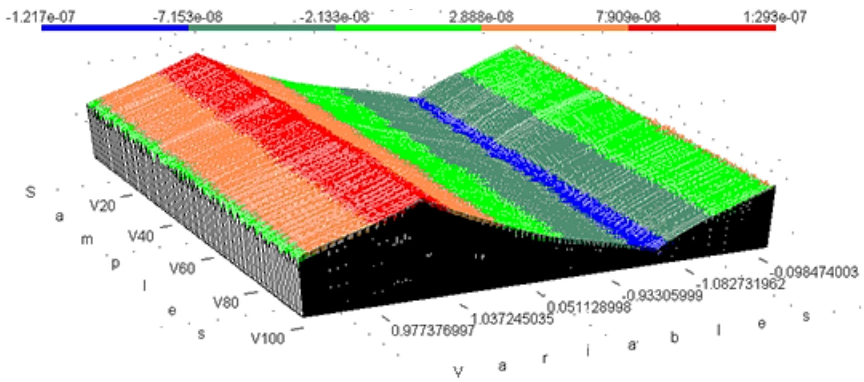

Fig. 1. VAGs array of the vodka sample

It is very difficult to see the difference in the samples from the VAGs arrays; one can only estimate the difference between the samples. In this regard, modeling of each VAGs array was carried out for all samples using the principal component analysis (PCA). The scores plot of the PCA-modeling is shown in Figs. 2–6.

On the scores plot of the PCA-modeling (Fig. 2), clusters of the studied samples are observed, where it is possible to clearly distinguish clusters of water and alcohol samples, which, despite the "signal drift", are well distinguishable and are in extreme positions. "Signal drift" interferes with a clear distinction between vodka samples, vodka mixtures with alcohol or water. This is due to the "memory effect" of the electrode - each previous impact on the electrode determines its behavior in the future. Taking into account these facts, further PCA-modeling was carried out for the last 20 measurements for each sample. The results are shown in Fig. 3. in the space of the principal components (PC) PC1-PC2.

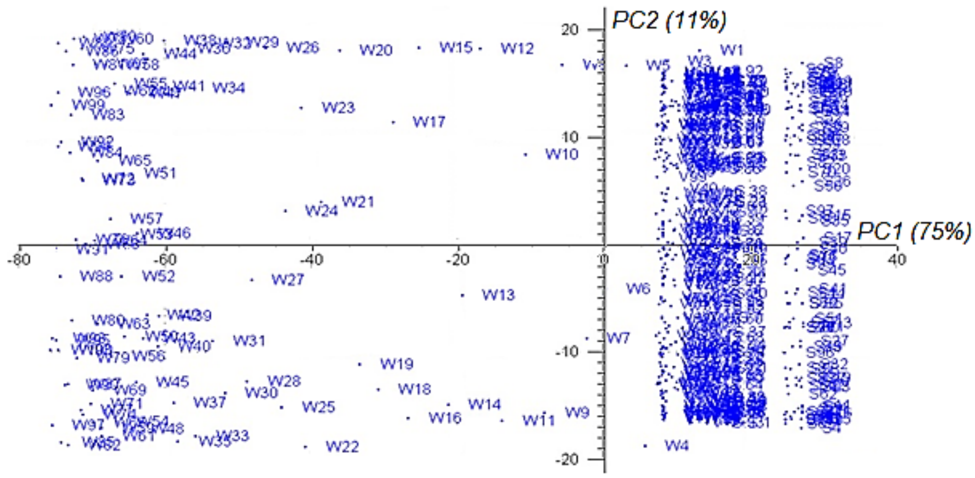

Fig. 2. The scores plot of the PCA-modeling of all samples VAGs

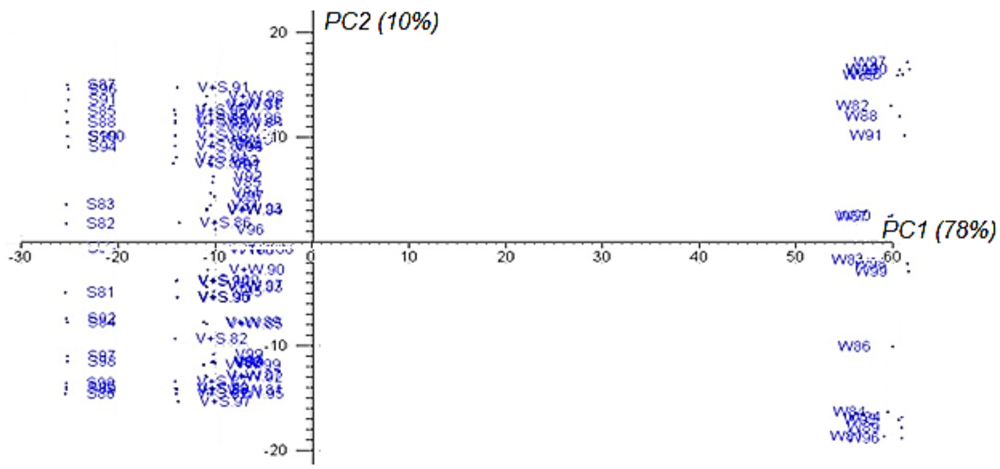

Fig. 3. The scores plot of the PCA-modeling for 81-100 measurements for each system (PC1-PC2)

In this case, the results will be more correct. Fig. 3. shows that the clusters of water and alcohol are very different from the other samples. Clusters can be distinguished for samples of vodka and its mixtures, but it is rather difficult to distinguish them from alcohol and water. Therefore, only samples of vodka and its mixtures are considered below. The scores plot of the PCA-modeling of vodka sample and its mixtures on the space of PC1-PC2 is shown in Fig. 4.

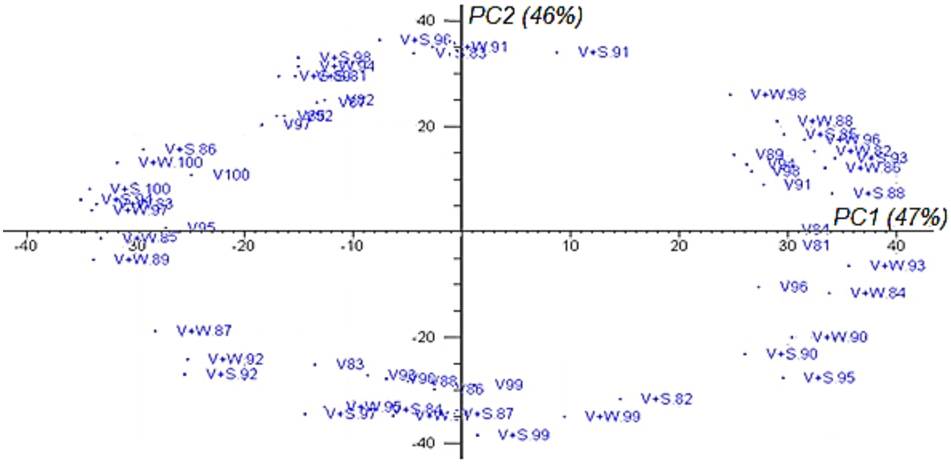

Fig. 4. The scores plot of the PCA-modeling for systems with vodka its mixture with alcohol and water (PC1-PC2)

As a result, it can be seen that the clusters of samples on the scores plot of the PCA-modeling have the form of an "ellipsoidal ring", the radius of which depends on the nature of the substance. However, it is difficult to distinguish between clusters for these samples. Subsequently, the PCA-modeling was carried out for these samples in the space of PC3-PC4 (Fig. 5).

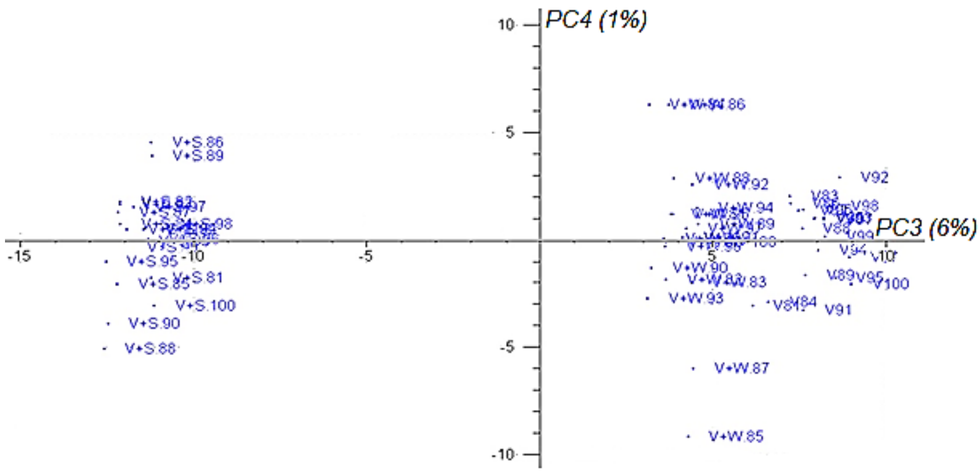

Fig. 5. The scores plot of the PCA-modeling for systems with vodka and its mixtures with alcohol and water (PC3-PC4)

In Fig. 5. there is a clear difference in the clusters of the vodka with alcohol mixture. For samples of vodka and its mixture with water, the differences are not so obvious. Next, we carried out the PCA-modeling of samples of vodka and its mixture with water (Fig. 6).

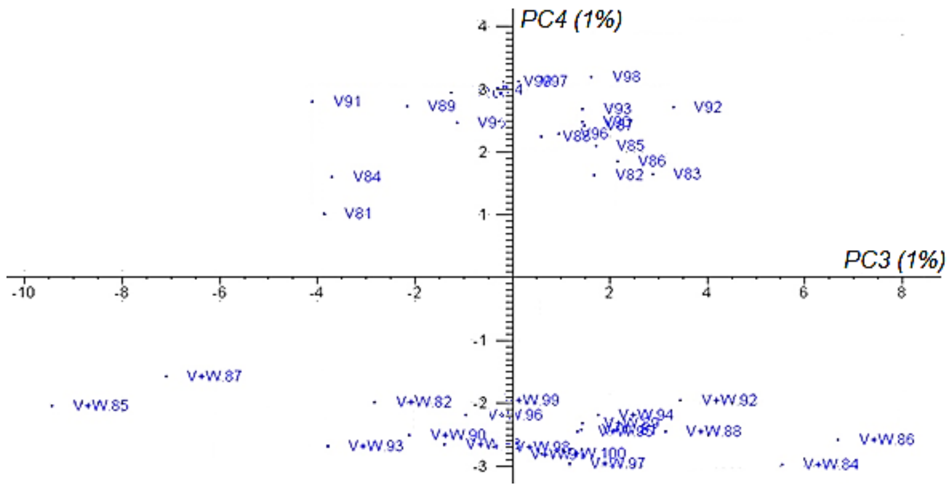

Fig. 6. The scores plot of the PCA-modeling for vodka and its mixture with water (PC3-PC4)

Thus, on the scores plot of the PCA-modeling, there is a clear separation of clusters for vodka and its mixture with water.

Conclusion. Summarizing all of the above, we can conclude that this tubular electrode, under conditions of electrochemical activation, senses the difference between all samples with a total explained dispersion of 99%. This method can be improved to recognize vodka falsification.

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