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"SMART" POLYMERS AS MODIFIERS FOR CREATING VOLTAMMETRIC SENSORS AND SENSORY SYSTEMS

Methionine (Met) - 2-amino-4-methylthiobutanoic acid - one of the essential amino acids, is the main source of sulfur, which is necessary in the human diet for normal metabolism and growth. Its main task in the human body is biological methylation [1]. An important component of electrochemical systems is the indicator electrode, the specificity of which with respect to the drug being determined is achieved by modifying. When determining Met by voltammetric methods, mainly carbon-paste and glassy carbon electrodes modified by metal nanoparticles and metal complexes are used, since Met, being a sulfur-containing amino acid, can bind with metals through strong interaction. This property of Met also makes it possible to use the gold electrode to determine it [2].

In this scientific work, voltammetric sensors and a sensor system based on gold electrodes modified with “smart” polymers have been proposed for recognition of Met containing preparations from various manufacturers. As such polymers, polyphthalidylidenefluorene (PPF) and polyphthalidylidene diphenyls (PPD) containing various functional groups and substituents in the phenylene rings of the main chain and phthalide rings are used. To modify the electrodes used chlorinated (in position 4) poly (phthalidylidenefluorene) (PPF-Cl) and poly (phthalidylidene diphenyl) (PPD-Cl), brominated poly (phthalidylidene diphenyl) (PPD-Br), which is a mixture of brominated products substituted into various phthalide cycle positions. Polymer samples (99%) were obtained at the Ufa Institute of Chemistry, Russian Academy of Sciences (Ufa, Russia) [3].

From the literature [4] it is known that methionine is electrochemically oxidized to methionine sulfone. Fig. 1 shows that the voltammograms of the gold electrode modified with PPD-Cl, PFD-Br, PPP-Cl, in the solution of Met differ in the shape and peak oxidation current. This indicates that the proposed sensors, modified by “smart” polymers, have cross-sensitivity, which allows to use their in sensor system such as “electronic tongue”.

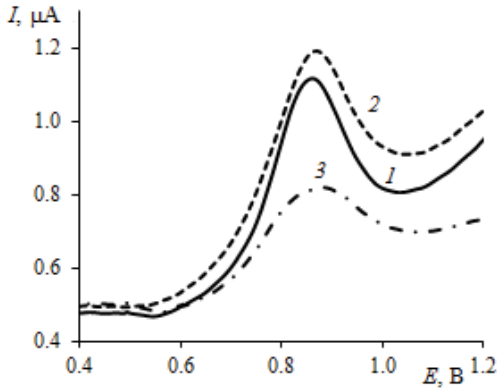

Fig. 1. Linear voltammograms of a gold electrode modified with PPD-Cl (1), PPD-Br (2), PPF-Cl (3) in 1 mM Met solution (Na_2HPO_4 + KH_2PO_4, pH 6.86, 100 mV / s)

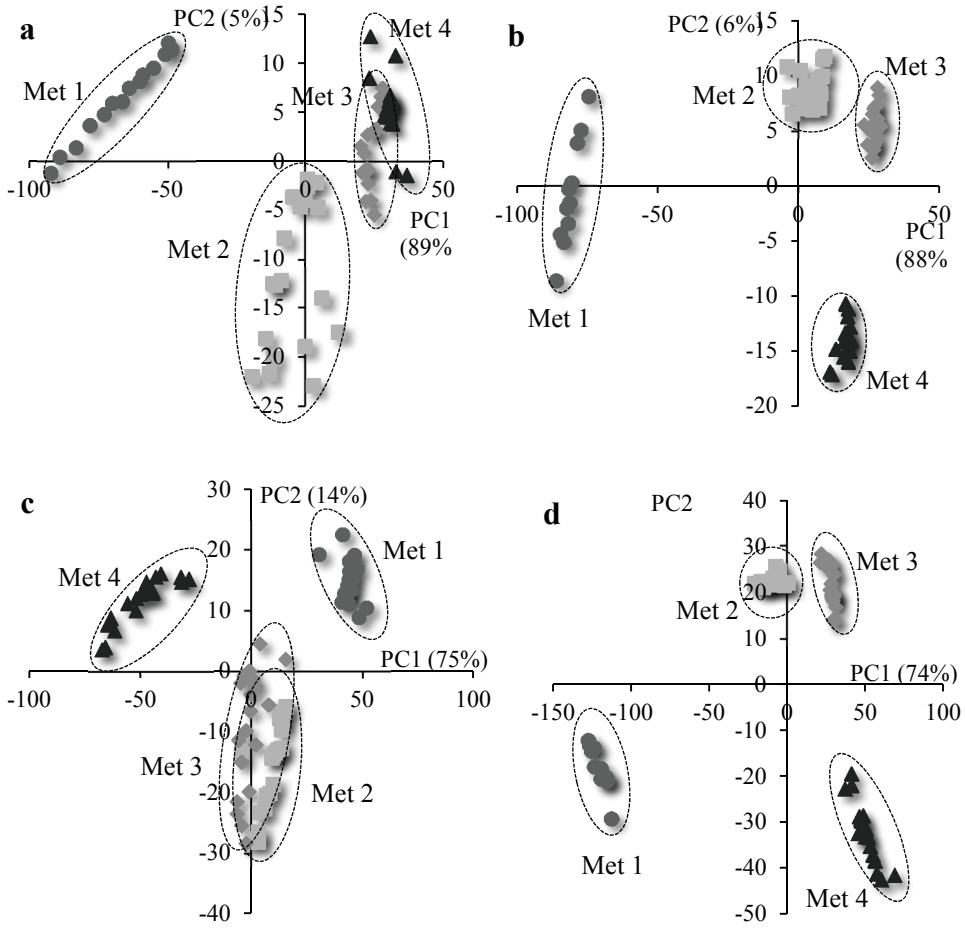

Fig. 2. Score plots of PCA modelling of voltammograms for 1 mM solutions of Met using Au/PPD-Cl (a), Au/PPD-Br (b), Au / PPD-Cl (c), and the sensory system (d)

Table 1. Results of SIMCA-classification of solutions of real samples containing Met from various manufacturers on modified electrodes and sensor system (n = 5; P = 0.95).

TS / OC	Мет1	Мет2	Мет3	Мет4
	The share of recognized samples,%			
Au/PPD-Cl				
Мет1	100	0	0	0
Мет2	0	100	**52.6**	0
Мет3	0	0	100	0
Мет4	0	**5.3**	**57.9**	100
Au/PPD-Br				
Мет1	100	0	0	0
Мет2	0	100	**26.3**	0
Мет3	0	**36.8**	100	0
Мет4	0	0	0	100
Au/PPF-Cl				
Мет1	100	0	0	0
Мет2	0	94.7	**84.2**	0
Мет3	0	**36.8**	100	0
Мет4	0	**47.4**	0	100
Sensor system				
Мет1	100	0	0	0
Мет2	0	100	0	0
Мет3	0	0	100	0
Мет4	0	0	0	100

To assess the possibility of recognizing dietary supplements containing Met from various manufacturers, chemometric data processing wasperformed using the proposed sensors. The voltammograms were transformed by the principal component analysis (PCA) and transferred to a new coordinate system, which is called the principal component system (PC), where each voltamogram is represented by one point (Fig. 2). It can be seen that the voltammograms of real samples belong to different clusters on the graphs of the accounts of PCA-models, while on the Au/PPD-Cl sensor clusters of samples Met 3 and Met 4 (Fig. 3a). As well as on the sensor Au/PPF-Cl clusters of samples Met 2 and Met 3 (Fig. 3c) intersect, that make it difficult to recognize the samples under investigation by manufacturer. From the results of the SIMCA classification, it can be seen that on the Au/PPD-Cl sensor, in about 50% of cases, Met 3 is recognized as Met 2 or Met 4, and on Au/PPF-Cl, samples of Met 2 and Met 3 are mistakenly recognized. Au/PPD-Br (Fig. 3b) sample clusters do not overlap, but the SIMCA classification results show erroneous recognition of Met 2 and Met

3. When using the sensory system, clusters of real samples do not intersect with each other; in 100% of cases, all samples are uniquely recognized.

For a quantitative assessment of the correctness of recognition of methionine preparations from various manufacturers, the soft independent modeling of class analogies (SIMCA) was used. It is shown that the use of the sensory system such as “electronic tongue” significantly increases the percentage of correctly recognized samples compared to the registration of voltammograms on the single sensor.

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СИНТЕЗ НОВЫХ СОПОЛИМЕРОВ НА ОСНОВЕ 4-МЕТИЛСТИРОЛА, 4-МЕТОКСИСТИРОЛА И α-МЕТИЛСТИРОЛА МЕТОДОМ ЭМУЛЬСИОННОЙ ПОЛИМЕРИЗАЦИИ

В настоящее время весьма актуальным является производство материалов на основе высокомолекулярных соединений. Преимущество таких материалов заключается в широкой области применения, небольшом весе, нетоксичности, особым спектром физико-химических и механических свойств. В данной работе представлены новые сополимеры на основе производных стирола и α-