DETERMINATION OF THE CONCENTRATION OF ORGANIC COMPOUNDS USING AN ELECTROCHEMICAL TEST SYSTEM

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Abstract

The research paper looks at the possibility of using an electrochemical test system to determine the concentration of organic compounds. The experiments were based on the fact that each class of organic substances required a specific test system. Since we were interested in sulfurcontaining organic compounds, the electrochemical test system was a solution containing cations of zinc, gallium, and copper. These metals can form complex compounds with sulfur-containing organic substances. When inserted into such a test system, organic substances of this class significantly alter its electrochemical behavior, which is reflected in stripping voltammograms. The experimental procedure and software made it possible to obtain the required number of parameters, which enabled a multisensory analysis on a single working (indicative) electrode. The stripping voltammograms recorded before and after addition of organic matter to the electrochemical test system were digitized; then one voltammogram (recorded when the test system contained no admixtures) was deducted from the other one (recorded when organic matter was added to the test system). The resulting difference curve was divided into segments; experiments showed that the number of segments should not exceed 20 or 30. These digitized curved sections were integrated in order to obtain a set of informative parameters, which can be viewed as a set of vectors, i.e., a multi-dimensional vector representation of each analyte. To visualize the results of the electroanalytical study, we represent the

Keywords

Stripping voltammetry, sulfur-containing organic substances, identification, multi-sensors, electrochemical test system, concentration

multidimensional image of organic substances of various concentrations as a number of vectors arranged in a circlel; the number of vectors corresponds to the number of sections of the difference curves in each experiment. The results show that the length of the vectors characterizing the difference curves decreases as the concentration of the analyzed organic matter decreases. In the limit, the curve visualizing organic matter with zero concentration takes the form of a circle, which indicates that there are no deviations from the stripping voltammogram of the electrochemical test system. Therefore, it can be concluded that the electrochemical test system can be certainly used for determining the concentration of organic compounds, producing quite reliable estimated results. This conclusion is confirmed by comparing the vector representation of analytes with the vector representations of organic substances of different concentrations, which constitute the database containing the results of experimental studies. Such a comparison is given in the form of a histogram reflecting the degree of proximity of the vector representation of the analyzed organic matter to substances from the database based on an estimate of Euclidean distances between the corresponding multidimensional vectors

Introduction. Issues linked to identification and determining of the concentration of organic compounds in different objects are of great practical importance, since validating their contents is one of the critical parts of environmental challenges. It is worth noting that organic substances are widely used in different areas of the economy.

Using electrochemical methods of analysis [1], stripping voltammetry in particular, looks quite promising, as they are free of most drawbacks of such methods of identification and comparative analysis as chromatography, mass spectrometry and spot assay. Among these drawbacks are high percentage of false positives, large sample weight, sample preparation complexity, unwieldy equipment, need for highly skilled research personnel.

In order to increase validity of results, obtained in analytical testing of objects, containing organic compounds, it was suggested that the electrochemical multisensory analysis based on the concept, described by the term "electronic tongue", should be used.

To implement such a method it makes sense to take approach [2–6] of using a multisensory test system in the form of a solution containing ions of different

metals. These ions are able to form coordination compounds with organic substances. Metal cations, contained in the test system, fulfill a role of many sensors. There is no need for several work (indicative) electrodes, the number of which must determine the number of informative parameters. The required set of parameters is obtained from a single electrode in the process of acquiring stripping voltammograms.

The main purpose of the suggested test system is identification of organic substances based on results of research, which showed that each substance influences the electrochemical behaviour of the multi-sensory test system in different ways. There were virtually no systematic studies of influence of the amount of organic substance in the sample on behaviour of the test system. The aim of the research work was to determine the possibility of using of an electrochemical test system to determine the concentration of organic compounds.

Materials and methods of solving problems, assumptions. Experiments were carried out in a 15 ml glass electrochemical cell with the use of planar electrodes in a three-electrode design. Such electrodes (Fig. 1) form a structure in
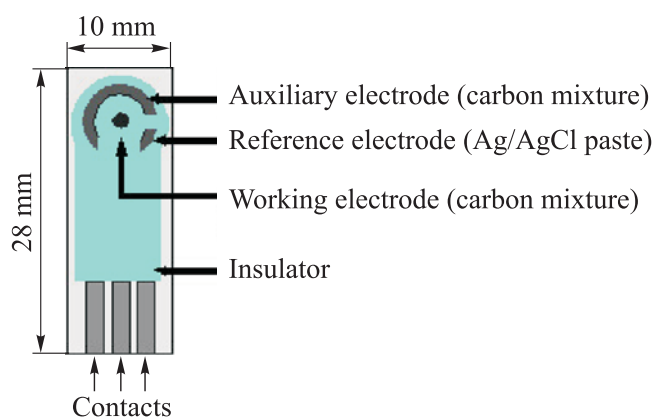
Fig. 1. Planar electrode design (three-electrode configuration)

which one plane (polyester film substrate) contains working (indicative) and auxiliary electrodes, and also a reference electrode. Working and auxiliary electrodes are made of carbon mixture, and the reference electrode is made of Ag/AgCl paste. Background electrolyte — into which cations of different metals were inserted for creating the electrochemical test system was a 0.05 M KCl solution.

A multifunction research appliance El-02 was used to set the necessary modes and measure electric parameters during the experiments.

The experiments were carried out in stripping voltammetry mode with accumulation. Accumulation potential is -1.55 V (relative to silver chloride reference electrode), accumulation time is 60 s, and speed of potential sweep is 1 V/s in anode direction towards the value of 0 V. The research was carried out in two stages. The first stage was used to obtain the voltammetry in a solution containing cations of test metals, without inserting the analyzed organic substance. The voltammetry of the second stage was obtained after addition of organic matter to the solution. Quantitative evaluation of experimental results represents the amount of change in the electrodissolution speed of test metals before and after addition of organic matter to the solution of the analyzed substance.

Results. Unitiol, thiamine and thiocarbamide were chosen as objects of electroanalytical study. These substances belong to sulfur-containing organic compounds. Consequently, the electrochemical test system containing cations of zinc, gallium, and copper [8] was used for the study. The test system was formed by adding nitrates of test metals listed above (concentration $5 \cdot 10^{-5}$ M) to background electrolyte (0.05 M KCl solution). Concentration of analyzed organic substances was set in the range of $5 \cdot 10^{-2}$–$1 \cdot 10^{-3}$ mg/ml.

The experimental study was carried out with the help of software algorithm digitizing stripping voltammograms of the electrochemical test system at the first stage of the electroanalysis. Digitization was performed also at the second stage of experiments after addition of analyzed organic matter to the electrochemical test system. Digitization of stripping voltammograms at both stages was performed using 4000 points. The resulting difference curve between stripping voltammograms of the test system and the test system with added analyzed substance also contained 4000 points. All obtained results were normalized to the value of peak current of anodic dissolution of copper in the electrochemical test system.

The previously mentioned concept of the multisensory test system was based on using metal cations in the test system as sensors. Supposedly it is possible to increase the number of informative parameters and treat each it as a sensor. To achieve this, the difference curves should be divided into certain number of segments; experiments showed that the number of segments should not exceed 20 or 30. These digitized curved sections were integrated in order to obtain a set of informative parameters, which can be viewed as a set of vectors, i.e., a multi-dimensional vector representation of each analyte.

The most informative representation of the results of the electroanalytical study can be produced in the form of circumferential vectors, corresponding to

the analyzed substance. Analytical results for different concentrations of unitiol, thiamine and thiocarbamide are shown in Fig. 2, *a–c*. The number of vectors, representing images of organic substances with different concentrations in the sample, corresponds to the number of sections of the difference curves in each experiment. As the concentration of the analyzed organic substance decreases, the length of vectors characterizing difference curves diminishes.
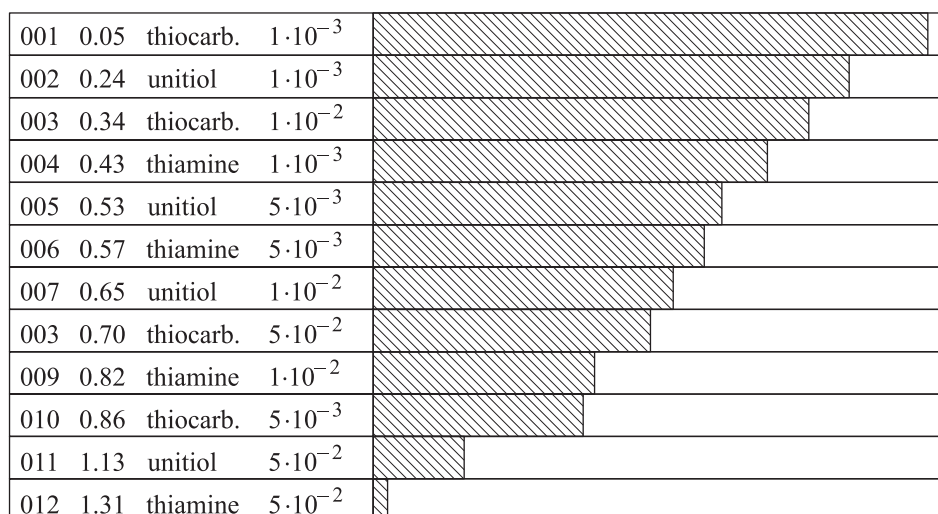

a   *b*   *c*   *d*
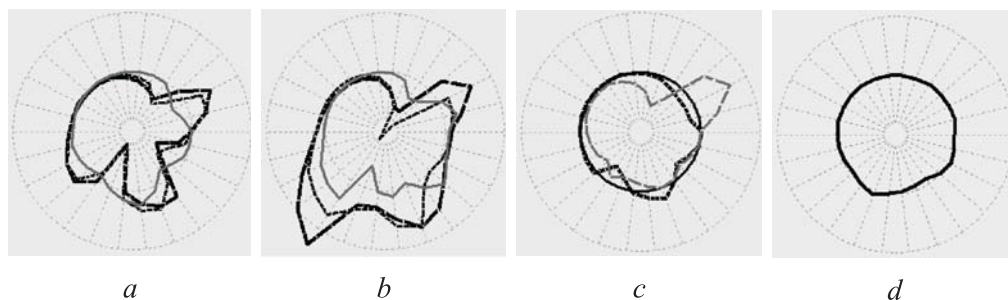
Fig. 2. Images of unitiol (*a*), thiamine (*b*), thiocarbamide (*c*) with different concentrations $5 \cdot 10^{-2}$ mg/ml ($----$), $1 \cdot 10^{-2}$ mg/ml ($------$), $1 \cdot 10^{-3}$ mg/ml (——), visualization of organic matter with zero concentration (*d*)

In the limit, the curve visualizing organic matter with zero concentration takes the form of a circle, which indicates that there are no deviations from the stripping voltammogram of the electrochemical test system. The example of such curve is shown on Fig. 2, *d*.

Some deviations of the perfect circle are caused by inevitable measurement error and do not exceed several percent.

Experimental studies based on electroanalysis of organic compounds with different concentrations led to creating the database containing results of these studies. Such a database allows not only to identify the analyzed organic substance but also to evaluate its concentration. Such evaluation is performed by comparing the vector representation of analytes with the vector representations of organic substances of different concentrations, which constitute the database. The evaluation is given in the form of the degree of proximity of multidimensional vectors based on Euclidean distances between them and can be shown on a histogram (Fig. 3).

Conclusion. The electroanalytical study show that the electrochemical test system in the form a solution containing cations of metals, able to form complex compounds with analyzed organic compounds, can be successfully used to determine concentrations of these compounds. Such a conclusion can be derived from experimental results, visualized as a multi-dimensional vector

001	0.05	thiocarb.	$1 \cdot 10^{-3}$	
002	0.24	unitiol	$1 \cdot 10^{-3}$	
003	0.34	thiocarb.	$1 \cdot 10^{-2}$	
004	0.43	thiamine	$1 \cdot 10^{-3}$	
005	0.53	unitiol	$5 \cdot 10^{-3}$	
006	0.57	thiamine	$5 \cdot 10^{-3}$	
007	0.65	unitiol	$1 \cdot 10^{-2}$	
003	0.70	thiocarb.	$5 \cdot 10^{-2}$	
009	0.82	thiamine	$1 \cdot 10^{-2}$	
010	0.86	thiocarb.	$5 \cdot 10^{-3}$	
011	1.13	unitiol	$5 \cdot 10^{-2}$	
012	1.31	thiamine	$5 \cdot 10^{-2}$	

Fig. 3. Example of a histogram, reflecting the degree of proximity of the thiocarbamide with concentration of $1 \cdot 10^{-3}$ mg/ml to substances from the database

representation of relevant substances. The electrochemical test system can be certainly used for determining the concentration of organic compounds, producing quite reliable estimated results. This conclusion is confirmed by comparing the vector representation of analytes with the vector representations of organic substances of different concentrations, which constitute the database containing the results of experimental studies.

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