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IDENTIFICATION AND COMPARATIVE ANALYSIS OF ALKALOIDS BY INVERSION VOLTAMMETRY METHOD

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Abstract

The alkaloids concurrent detection and identification in the samples by the method of multisensory inversion voltammetry is the purpose of the work. To achieve this goal, the proposed method has been substantiated, the composition of the electrochemical test system has been optimized taking into account the specifics of the detected substances, and informative signs that characterize the presence of alkaloids in the studied sample have been found. A new approach, consisting in the use of an electro-chemical multisensor test system in the form of a solution containing a set of metal ions that can form complex compounds with organic substances, has been developed and scientifically approved. The results showed that each organic substance has a different effect on the electrochemical behavior of the multisensory test system. The use of such a test system made it possible to model the principle currently defined by the term “Electronic tongue”. An electronic database has been prepared according to the results of the electroanalytical studies, which made it possible to identify the detected substance by comparing it with analyzed sample. The proposed electrochemical method, which is based on multi-sensor inversion voltammetry, allows the detection and identification of both narcotic drugs and psychotropic substances with high confidence for a small mass of the sample

Keywords

Inversion voltammetry, identification, multisensors, electrochemical test system, alkaloids

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Introduction. Express detection and identification of alkaloids is an important part of a range of activities for illicit trafficking of narcotic drugs and psychotropic substances [1, 2]. Spot test [3], thin-layer chromatography [4, 5], mass spectroscopy [6, 7] are widely used nowadays, but have several disadvantages, the main is that they are multi-stage. In this regard, the development and implementation of a special method, which makes it possible to detect and identify alkaloids with high reliability during express analysis, is highly relevant [8, 9].

The inversion voltammetry method is one of the most informative among the electrochemical methods of analysis [10, 11]. The implementation of this method requires careful sample preparation, since the presence of organic substances in the analyzed sample significantly affects the type of analytical voltammograms [12]. The research results showed that each organic substance has a different effect on the electrochemical behavior of the multisensory test system; therefore it is proposed to use this feature for the analysis of alkaloids.

It has been proposed to use metal cations with partially filled *d*-orbitals as a sensor line, because they can form complex compounds with alkaloids and, thus, form a multisensor test system [13]. These metals are well defined by the method of inverse voltammetry, which allows the identification of various alkaloids based on the analysis of the characteristic changes in the current-voltage curves resulting from the introduction of various alkaloids into the initial test system.

The experimental technique. The experimental part of the work was performed on a portable programmable multifunctional device EL-02 (IPCE RAS) [14].

The test systems were formed to detect and identify alkaloids. The solutions of the following salts were used in the systems: mercury, zinc, cadmium, and lead, gallium, and cobalt nitrates. 12 ml of 0.05 M KCl solution have been poured into the cell, Hg^{2+} ions have been added to a concentration of 10^{-4} M and metal ions Zn^{2+}, Cd^{2+}, Pb^{2+}, Co^{3+}. The concentration of metals was $5 \cdot 10^{-5}$ M.

Real samples, in which alkaloids have to be determined, usually contain impurities of various substances, to which electrode reactions are sensitive. In this regard, the studies have been conducted. The results showed the possibility of alkaloids disengagement from the sample by extraction with chloroform, which allows separating substances that prevent receiving reliable results.

The studies were conducted on planar electrodes (KolorEtectronics, LLC), which are three-electrode circuits. Since planar electrodes are disposable, the surface preparation of the indicator electrode is not required.

The measurements have been carried out in two stages:

1) the deposition of the test system metals, the subsequent dissolution and registration of the corresponding dissolution currents;

2) carrying out the same operations, but with alkaloids added to the solution; the presence of alkaloids in the solution changes the values of the dissolution currents of metals.

Results and discussion. Such narcotic substances as heroin, cocaine, and hingamine have been the objects of research in this work.

To develop conditions for the alkaloids detection in the inversion voltammetry mode, the solutions, in which various combinations of zinc, cadmium, lead and cobalt cations have been used as indicators of the presence of alkaloids, have been studied. It should be noted that the dissolution potentials of these metals differ from each other significantly.

An important criterion for choosing a background electrolyte is the degree of influence of alkaloids on the peaks of dissolution currents of metals in the test system. The studies have shown that for cadmium and lead, with a decrease in their concentration, the influence of alkaloids increases, while for cobalt, the maximum effect is observed at its highest concentration ($1 \cdot 10^{-4}$ M). Since it is convenient to have the same metal concentrations in solution to study the influence of alkaloids, a compromise concentration value of $5 \cdot 10^{-5}$ M has been taken for them.

The concentration of hydrogen ions also plays an important role in the process of complex formation. Alkaloids are bases and, therefore, are easily protonated. In this regard, the concentration of free alkaloid capable of forming complexes with metals will depend on pH. To find the optimum pH of the background electrolyte, at which the influence of alkaloids is maximum, experiments with papaverine in the pH range 1–8 have been carried out [15]. The results are shown in the Table.

The effect of papaverine on the peaks of dissolution currents of metals(change in peak currents *I*,%) depending on pH

pH	*I*, %			
	Zn	Cd	Pb	Co
1	0	0	0	0
3	−52	−59	0	−100
3.5–4.0	−43	−57	−18	−100
4.5–5.0	−60	−45	−15	−100
5.5–6.0	0	0	0	0
7.5–8.0	0	0	0	0

Note. The sign "–" indicates a decrease in the peaks of metal dissolution currents, the "+" sign indicates an increase in the peaks of metal dissolution currents, the "0" sign indicates there is no change in the peaks of metal dissolution current.

In the acidic solution (pH = 1) there are no effects of alkaloids, since metals with alkaloids do not form complexes. In the range of pH = 3.5–5.0, the effect of papaverine has its maximum. At pH > 6, papaverine did not affect the dissolution currents of metals, since metal ions are hydrolyzed in alkaline solutions. Based on the studies, 0.05 M KCl with a pH = 5 has been selected as the background solution.

Inversion voltammograms obtained in an electrochemical test system in the presence of heroin at a concentration of $2{\cdot}10^{-2}$ g/l are shown in Fig. 1. The peaks of the cobalt dissolution currents decrease to zero, and the peak of the zinc dissolution current increases with the introduction of heroin into the background electrolyte. The peaks of the dissolution currents of cadmium and lead slightly reduce.

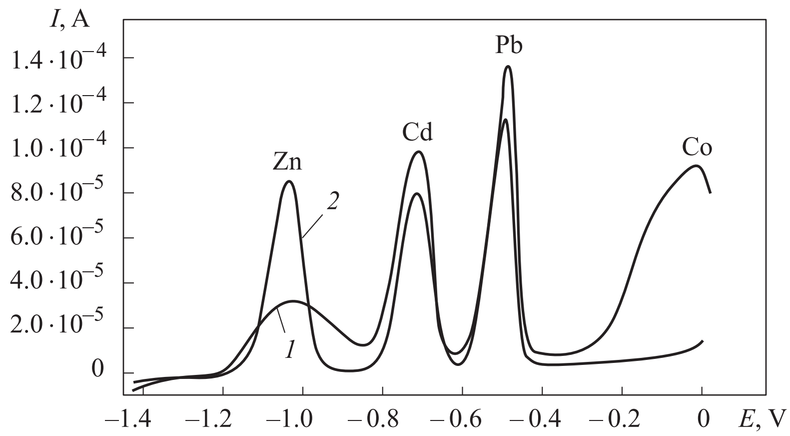

Fig. 1. Inversion voltammograms obtained in the electrochemical test system (Zn, Cd, Pb, Co) in the absence of heroin (*1*) and in the presence of heroin (*2*) ($C = 2{\cdot}10^{-2}$ g/l)

The cocaine as well as heroin changes the peaks of the dissolution currents of metals (Fig. 2). However, cocaine and heroin differ in magnitude of effects.

Inversion voltammograms obtained in an electrochemical test system in the presence of chingamine with a concentration of $2{\cdot}10^{-2}$ g/l are shown in Fig. 3. The peaks of the dissolution currents of cadmium and lead in the presence of chingamine with a concentration of $5{\cdot}10^{-2}$ mg/ml decrease by 10 % (see Fig. 3). The peak of the cobalt dissolution current disappears. The peak current dissolution of zinc increases. The nature of the effect of hingamine on the zinc current dissolution differs from the effect on the cocaine and heroin concentration current.

The introduction of alkaloids into the solution affects the metals electrodissolution currents, which are electrodeposited from the volume on the electrode surface solution, significantly. The presence of one or another alkaloid in the solution can be estimated by the magnitude of the changes in these currents.

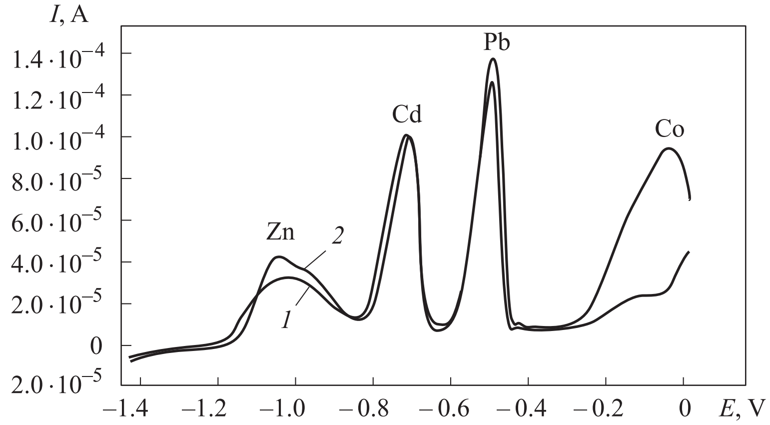

Fig. 2. Inversion voltammograms obtained in the electrochemical test system (Zn, Cd, Pb, Co) in the absence of cocaine (*1*) and in its presence (*2*) ($C = 2{\cdot}10^{-2}$ g/l)

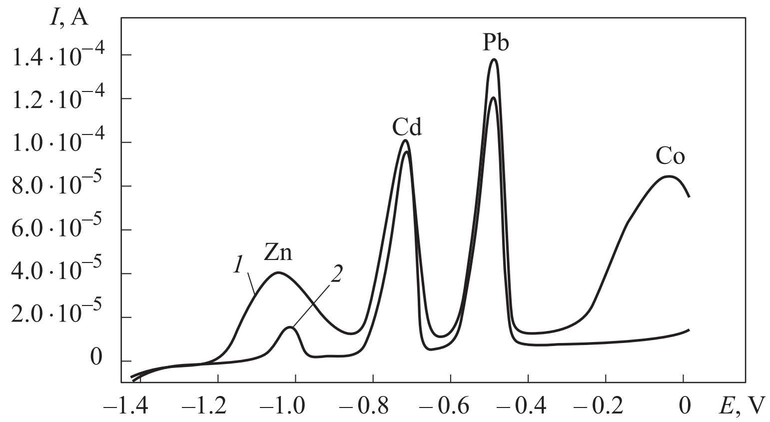

Fig. 3. Inversion voltammograms obtained in the electrochemical test system (Zn, Cd, Pb, Co) in the absence of chingamine (*1*) and in its presence (*2*) ($C = 2{\cdot}10^{-2}$ g/l)

The influence of alkaloids on the dissolution currents of metals in the test system can be explained by two reasons. The first is the ability of alkaloids to form complexes with metals; the second is the adsorption of alkaloids on the electrode and, therefore, the difficulty of the processes of metals electroreduction and electrooxidation.

The conducted experimental studies become the basis for preparing a database for the narcotic drugs and psychotropic substances detection and identification. The preparation of the database has been carried out according to the results of a vector representation of experiments conducted with some set of known narcotic drugs.

The primary measurement results are sets of 4000 points, which have been used for digitizing the solution analytical curve, which is the electrochemical test system, and the analytical curve obtained after introducing the corresponding sample into this solution, have been normalized to the peak value of the current of the lead anodic dissolution in the electrochemical test system. This peak has been chosen for normalization due to the minimal effect on its amplitude and potential of the analyzed alkaloids. After that the difference between the curves of the electrochemical test system and the curves obtained after the introduction of the sample has been calculated. Such difference dependences, also consisting of 4000 points, have been divided into N intervals over which integration has been performed to present information about each experiment in the form of an N-dimensional vector. Such a representation can be considered as the result of multisensor analysis, in which N is the number of sensors, since each of the N intervals carries information about the specific effect on the electrochemical test system of the analyte. According to the experimental results, the optimal value of N is 25 intervals.

Identification of a previously unknown substance is carried out by comparing its vector representation with the vector representations of narcotic drugs and psychotropic substances from a previously prepared database.

The comparison results are presented in the form of a histogram, which consists of horizontally spaced segments corresponding to known substances from the database, and shows their relative proximity to the analyzed one. An example of a histogram obtained by comparing heroin ($2 \cdot 10^{-2}$ g/l) with a database is shown in Fig. 4.

The created database also contains information on the alkaloids, taking into account the difference in their concentration in the sample. According to the histogram, the degree of deviation of heroin with a concentration of $2 \cdot 10^{-2}$ g/l from the data entered in the database — $5 \cdot 10^{-2}$ g/l (the first line) has 0.05 % deviation, and $1 \cdot 10^{-1}$ g/l (second line) for 0.19 %. This makes it possible to detect and identify substances with unknown concentration.

The proposed electrochemical method, which is based on multisensory inversion voltammetry, allows the detection and identification of both narcotic drugs and psychotropic substances for a small mass of the test sample with high reliability.

Conclusion. The possibility of experimental determination of parameter values providing a rational approach to the problem of detecting and identifying narcotic drugs and psychotropic substances has been shown.

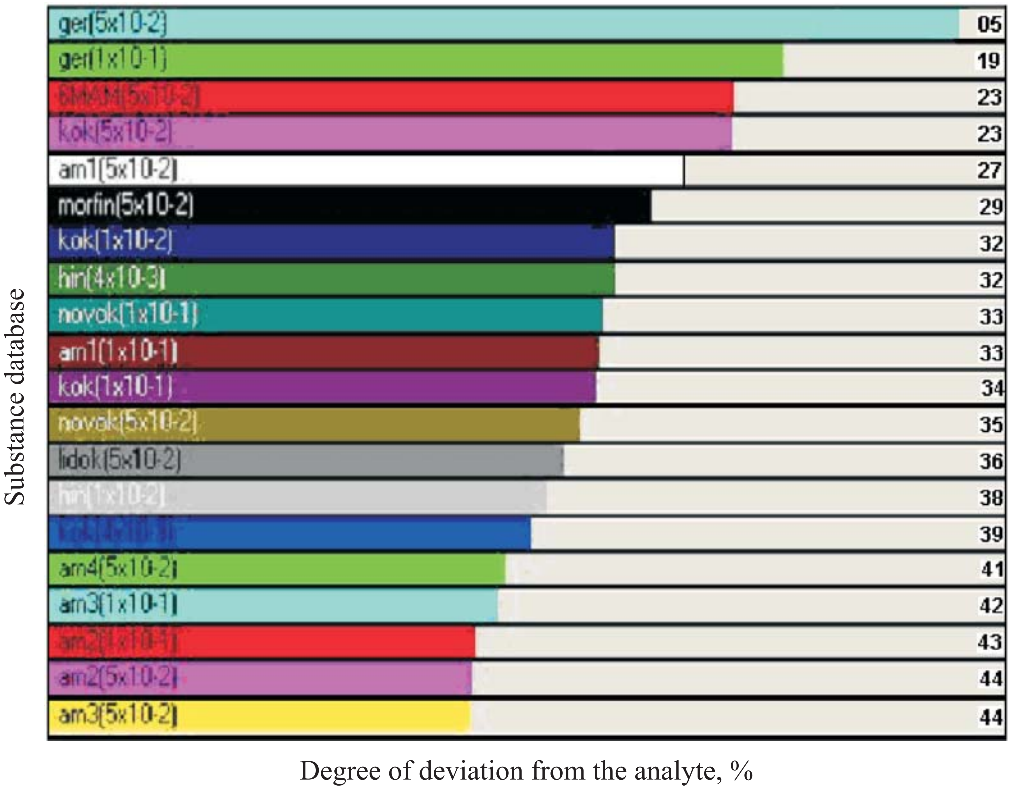

Fig. 4. The example of a histogram resulting from comparisons of heroin ($2 \cdot 10^{-2}$ g/l) with the database

A new approach to the analysis of alkaloids has been presented. It is based on the registration and quantification of the complexation effect of organic ligands on a multisensor electrochemical test system, which is a solution of metal salts with partially filled *d*-orbitals.

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