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HIGHLY EFFICIENT QUALITY CONTROL SYSTEMS FOR ENATHIOMER-PURE DRUGS ON THE BASIS OF SENSORS MODIFIED WITH TRANSITION METAL COMPLEX COMPOUNDS

Recognition and determination of optically pure medicinal and biologically active compounds that are in demand in medicine, pharmaceuticals, food industry and other areas of human activity is one of the most important tasks of analytical chemistry. Recently, the main efforts in this area have been focused on the development of affordable and inexpensive devices that allow rapid analysis of enantiomerically pure drugs. This is fully consistent with potentiostats/galvanostats using enantioselective voltammetric sensors (EVS). An increase in the availability, reliability of recognition of enantiomers, sensitivity, and other characteristics is primarily provided by chiral selectors used to construct such sensors [1]. The range of compounds used as chiral selectors is very diverse, but only a small part of them provides the required combination of characteristics - reliability of recognition of enantiomers, sensitivity, reproducibility, stability, availability, and most importantly, ease of manufacture of EMU. In the latter case, the use of transition metal complexes Cu(II), Ni(II), and Co(III) with organic chiral ligands seems promising [2].The structure of the chiral ligand with the coordination number of the complexing metal is of decisive importance for the selectivity and other characteristics of the EMU. At the same time, the cost of such complexes is much lower than that of modified cyclodextrins or chiral nanotubes. Thanks to the advances in synthetic organic chemistry, there are ample opportunities to control the properties of the resulting complexes by forming ligands of a given structure, geometry,

and the required chiral environment, which makes it possible to purposefully form highly selective, stable, and time-stable EMUs. Thus, the study of the properties of chiral transition metal complexes as enantioselectors in EMU has great prospects. We have developed two types of sensor platforms: composite ones based on GCE [2, 3] and paste electrodes made of carbon black Carboblack C modified with transition metal complexes. The proposed control systems have been tested for the determination of the enantiomers of tryptophan, tyrosine and propranolol, atenolol and naproxen. The developed sensor platforms have good analytical characteristics and allow the determination of enantiomers in biological fluids, in tablet forms, in a racemic mixture, and in a mixture with a predominance of one of the enantiomers [4, 5].The purpose of this work is to study the features of using sensor platforms based on chiral transition metal complexes for express recognition and detection of enantiomers of biologically active substances that are in demand in chemistry, biology, pharmaceuticals, food industry and related fields of science and practice.

A method for obtaining enantioselective voltammetric sensors based on transition metal complexes with chiral ligands (Carboblack C-based paste electrodes, composite sensors based on glassy carbon electrodes) has been developed and optimized. The questions of the analytical application of enantioselective voltammetric sensors for the recognition and detection of enantiomers of biologically active (pesticides) and medicinal compounds (naproxen, atenolol, amino acids) in model and real (blood plasma, urine, biological fluids, etc.) objects were studied, and the conditions for their recognition were optimized. and analysis, application of sensors, a comparison of the obtained results with the results for other sensors.

The possibilities of using "intelligent" methods of pattern recognition (neural networks, principal component analysis, discriminant and hierarchical cluster analysis, independent modeling based on the classification of SIMCA analogies, etc.) for the recognition of enantiomers in preparations of various manufacturers and in multicomponent solutions containing other analytes (with errors of the first kind not exceeding 5% and errors of the second kind not exceeding 20%).These approaches will make it possible to carry out not only the recognition of optically active biologically and medicinal compounds, but to establish their compliance with standard samples, control quality, determine the manufacturer and the presence of counterfeits. The developed devices were tested on real objects, the selectivity of the sensors was evaluated depending on the method of formation of the surface layer of the electrode and the nature of the chiral modifier, the composition of the electrode matrix and the object of analysis. To recognize and determine the enantiomers of tryptophan (Trp), tyrosine (Tyr) and

propranolol (Prp), it was found that the analytical signals of enantiomers on unmodified PEs coincide, and on modified PEs differences are observed in the potentials and currents of the oxidation peak:
- in the case of the PE/S-1 sensor, the highest selectivity is observed for Trp enantiomers, I_{pD} /I_{pL} =1.36, and E_p =35.25 mV;
- in the case of the PE/S-2 sensor, the highest selectivity is observed for Tyr enantiomers, I_{pD} / I_{pL} =1.14, and E_p =5.04 mV;
- in the case of the PE/C-3 sensor, the highest selectivity is observed for Trp enantiomers, I_{pD} / I_{pL} =1.15, and E_p =25.18 mV;
- in the case of the PE/S-4 sensor, the highest selectivity is observed for Prp enantiomers, I_{pS}/I_{pR}=1.24, and E_p =5.00 mV;
- in the case of the PE/S-5 sensor, the highest selectivity is observed for Trp enantiomers, I_{pD} / I_{pL} =1.21, and E_p =20.14 mV.

The PE/C-1 sensor has the highest enantioselectivity with respect to Trp enantiomers; therefore, the study of electrochemical and analytical characteristics was carried out for this sensor. According to the results of cyclic voltammetry and impedancemetry using a standard redox system based on potassium ferrocyanides, hindered electron transfer for the modified sensor was established. The effective surface area of the unmodified electrode was 5.64 ± 0.35 mm2, while that of the modified electrode was 2.75 ± 0.62 mm^2.
From the linear dependence $i_p/(v^{1/2})$ (R^2 =0.993÷0.999) it was established that the rate of diffusion of the electroactive substance to the electrode surface is the limiting stage of the electrode process (the value of the Semerano criterion is 0.55 and 0.58 for L- and D-Trp, respectively). The linear range of determined concentrations is 6×10–5 to 1×10^{-3} M, the limit of detection is 2.89 $\times10^{-6}$ for D-Trp and 3.87 ×10-6 for L-Trp. The sensor exhibits the highest sensitivity (11.30 μA/mM) to D-Trp. The relative standard deviation does not exceed 3.3%. The proposed sensor has been successfully tested for the determination of tryptophan enantiomers in mixtures, in the presence of interfering components (Sr = 0.2–14.0%), in biological fluids (urine Sr 1.4–5.1%, blood plasma Sr 1.4–5.4%), in tablet forms (Sr = 3.1–5.0 %).

According to the research data, the requirements for enantioselective sensor platforms based on the proposed chiral materials are formulated, the methods for their manufacture are specified, providing the required enantioselectivity (enantioselectivity coefficient ki/kj ≥ 1.3), analytical (detection limit up to 10-9 M) and operational characteristics (electrode modification time no more than 5 minutes, time of registration of voltammograms no more than 3 minutes, storage of the modified sensor for at least 72 hours).

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СРАВНЕНИЕ ЗАВИСИМОСТИ КОНСТАНТ УСТОЙЧИВОСТИ КОМПЛЕКСОВ КОБАЛЬТА С КОМПЛЕКСОНАМИ, ПРОИЗВОДНЫМИ УКСУСНОЙ И ЯНТАРНОЙ КИСЛОТ

Население Земли превысило 8 млрд. человек, поэтому актуальной задачей становится производство достаточного количества пищи для населения планеты. Это обстоятельство требует резкого увеличения урожайности культур, употребляемых в пищу. Создание эффективных и в то же время экологически безопасных стимуляторов роста и развития растений может содействовать решению этой задачи. Комплексонаты биометаллов с экологически безопасными комплексонами в полной мере удовлетворяют этим требованиям, т.к. не уступают традиционным комплексонам по комплексообразующей способности,