A VOLTAMMETRIC SENSORY SYSTEM FOR RECOGNITION OF TRYPTOPHAN ENANTIOMERS BASED ON GLASSY CARBON ELECTRODES MODIFIED BY POLYARYLENEPHTHALIDE COMPOSITES OF α-, β-, AND γ-CYCLODEXTRINS

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For a human, tryptophan (Trp) is an essential amino acid that enters the body with food proteins or nutritional supplements. The amino acids that make up proteins generally are in the L-configuration, whereas the D-amino acids do not participate in protein synthesis or even have an adverse effect on living organisms. These facts led researchers to develop methods for the recognition and determination of tryptophan enantiomers in medicines and food products.

An enantioselective voltammetric sensory system based on glassy carbon electrodes modified by polyarylenephthalide (PAP) composites of α-, β-, and γ-cyclodextrin was developed for selective detection of tryptophan enantiomers. The system uses the chemometric method of principal component analysis (PCA) and projection to latent structures discriminant analysis (PLS-DA). Results of chemometric processing of voltammograms of only one composite electrode (α-, β-, or γ-CD) not allowing for the reliable recognition of Trp enantiomers. To increase the probability of distinguishing between Trp enantiomers, a sensory system with three indicator electrodes modified by PAP composites of α-, β-, and γ-CD, with a cross sensitivity to the D- and L-enantiomers, was used. In this case, the array of experimental data containing the values of the instantaneous currents obtained during registration of the voltammograms on three indicator electrodes was chemometrically processed. The voltammograms using PCA were transformed into points on the principal component, constructed along the maximum dispersion of experimental data (PC1). Then, the next principal component (PC2) was constructed orthogonal to PC1 and directed along the next largest change in the measurement data, and so on. The number of principal components (from 2 to 5) allowing the structure of the initial array of experimental data and their direction in space was chosen on the basis of the explained variability (90 %). PCA shows that voltammogram clusters on the principal components plane do not intersect each other. Chemometric PLS-DA was then used for recognition of tryptophan enantiomers in real objects. Values of discriminant responses were calculated and the stereoisomer was determined. The closer the enantiomer discriminant response values were to unity, the higher the probability that they belonged to a given stereoisomer. Results were considered positive if an enantiomer was correctly assigned to the test sample and not assigned to the other enantiomer. The reference set and the test set were prepared independently. Use of separate GCEs modified by PAP composites of α-, β-, and γ-CD to recognise the Trp enantiomers resulted in large errors of the second kind (acceptance of the incorrect enantiomer) of up to 50 % in the case of α-CD and 40 % in the case of γ-CD. The smallest errors were observed for GCE modified by PAP composites of β-CD, which is supported by the fact that the binding constants of the tryptophan enantiomers with β-CD differ from each other. Using a sensory system with three GCEs modified by PAP composites of α-, β-, and γ-CD, errors of the first kind (incorrect assignment of the identified enantiomer) were not observed, and errors of the second kind were minimised. In this case, 99 % of samples were correctly recognised. The proposed sensory system, after additional studies, may be used to assess the enantiomeric purity of drugs containing tryptophan, the loss of activity of enantiomers due to improper storage and transportation, and drug expiration.

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