Enantioselective voltammetric sensor system based on mesoporous carbon black Carbopack X and cyclopentadiene derivatives for determination of clopidogrel enantiomers

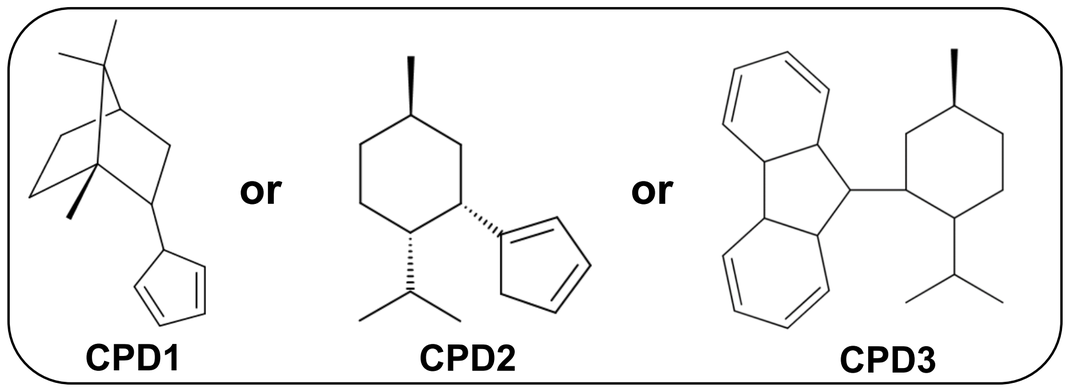
Nazyrov M.I., Yarkaeva Y.A.

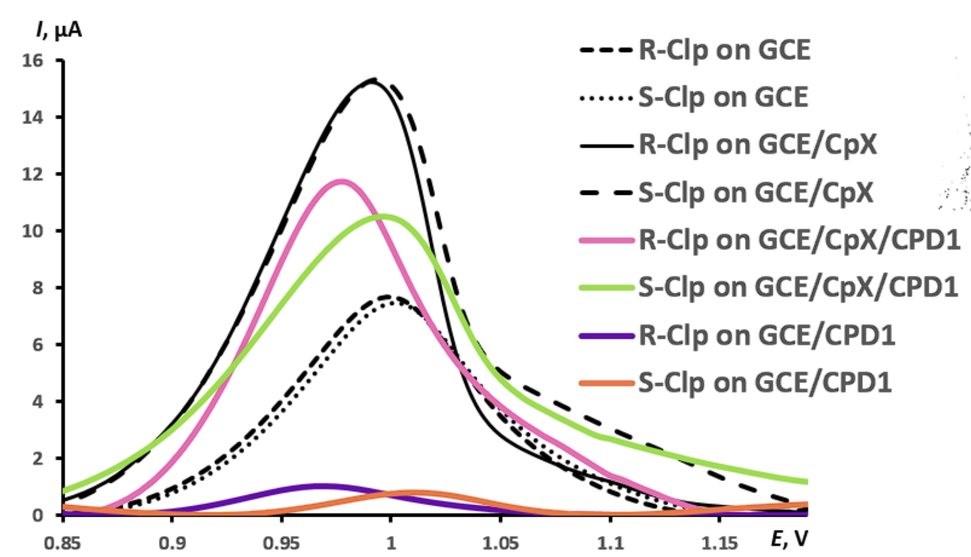
Ufa University of Science and Technology, Ufa, Russia

8 996 581 50 84 | mnazyrov@list.ru

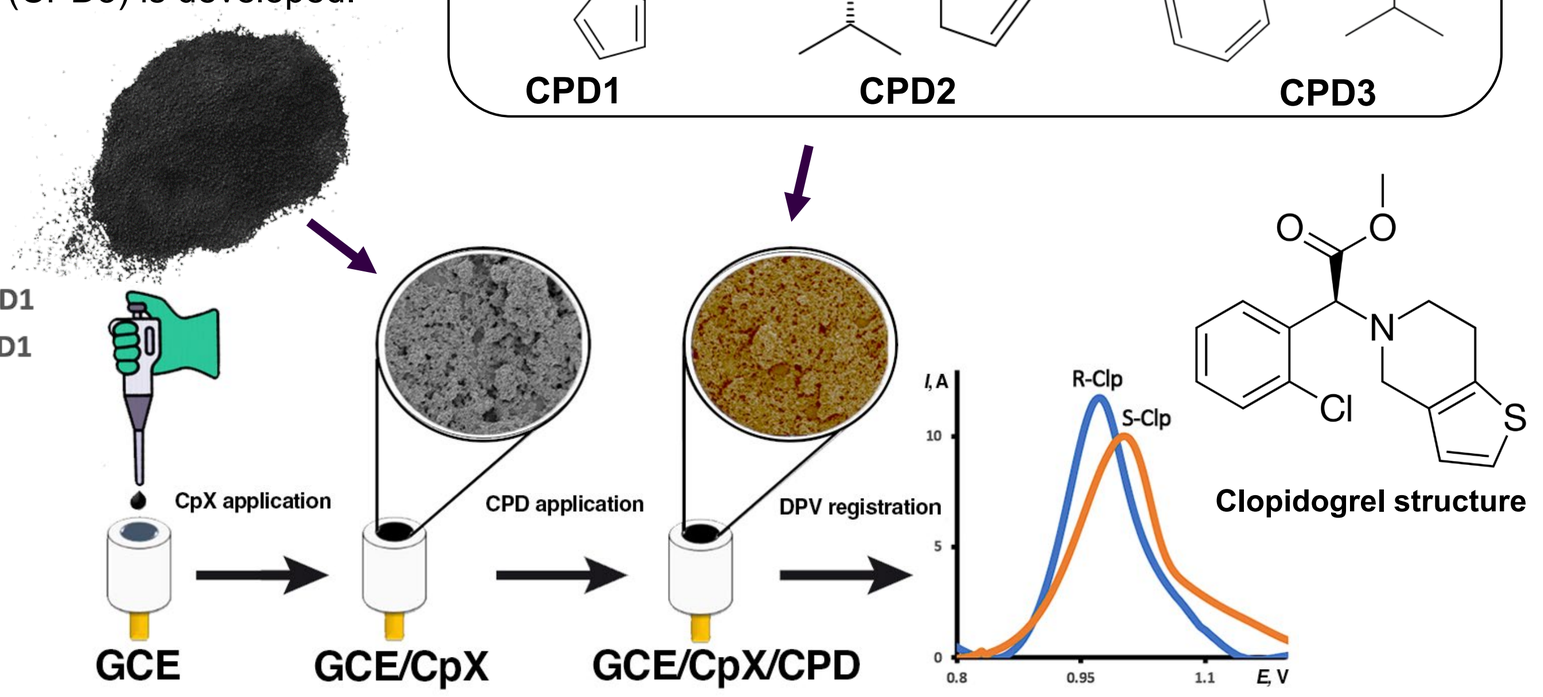
The recognition and determination of enantiomers plays an important role in modern medicine and pharmaceuticals, since living organisms react differently to their presence in medicines. Currently, chromatographic and spectrometric methods are often used to determine enantiomers, but the use of electrochemical methods can theoretically become a more cost-effective alternative due to their relative cheapness of instruments, rapidity, and low consumption of reagents. In this regard, enantioselective voltammetric sensors (EVS) are receiving increasing attention.

For the recognition and determination of clopidogrel (Clp) enantiomers sensor system based on a glassy carbon electrode (GCE) modified by mesoporous carbon black Carbopack X (CpX) and cyclopentadiene derivatives - (1S)-2-cyclopenta-2,4-dien-1-yl-1,7,7-trimethylbicyclo[2.2.1]heptane (CPD1), (1S, 2S, 4R)-2-cyclopenta-1,3-dien-1-yl-1-isopropyl-4-methylcyclohexane (CPD2); 9-[(1S,2S,5R)-2-isopropyl-5-methylcyclohexyl]-9H-fluorene (CPD3) is developed.



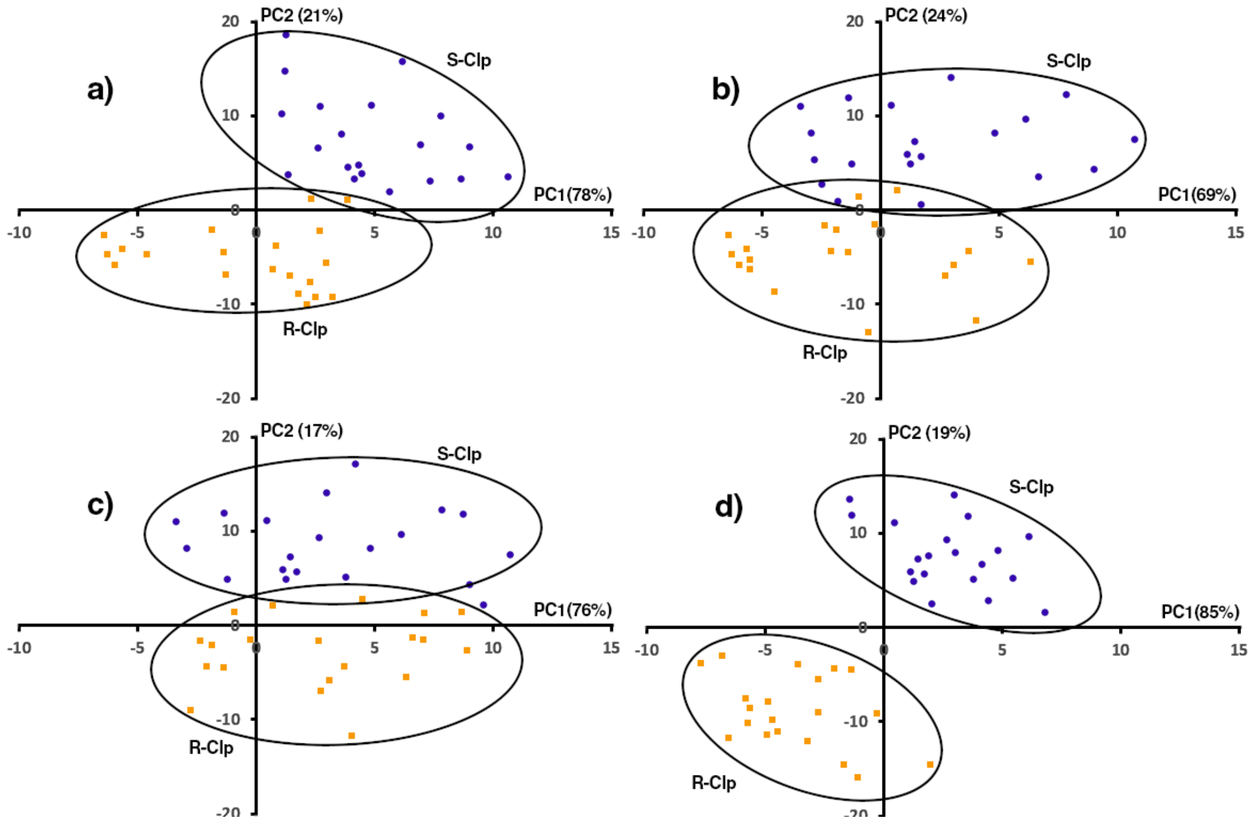


Differential-pulse voltammograms of clopidogrel enantiomers on various electrodes (concentration 0.5 mM)

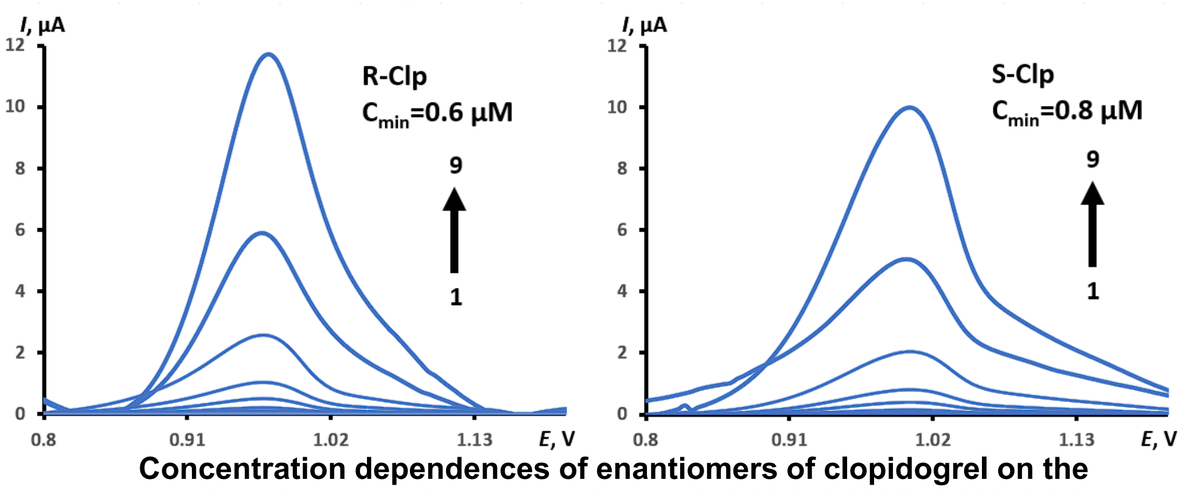


Clopidogrel structure

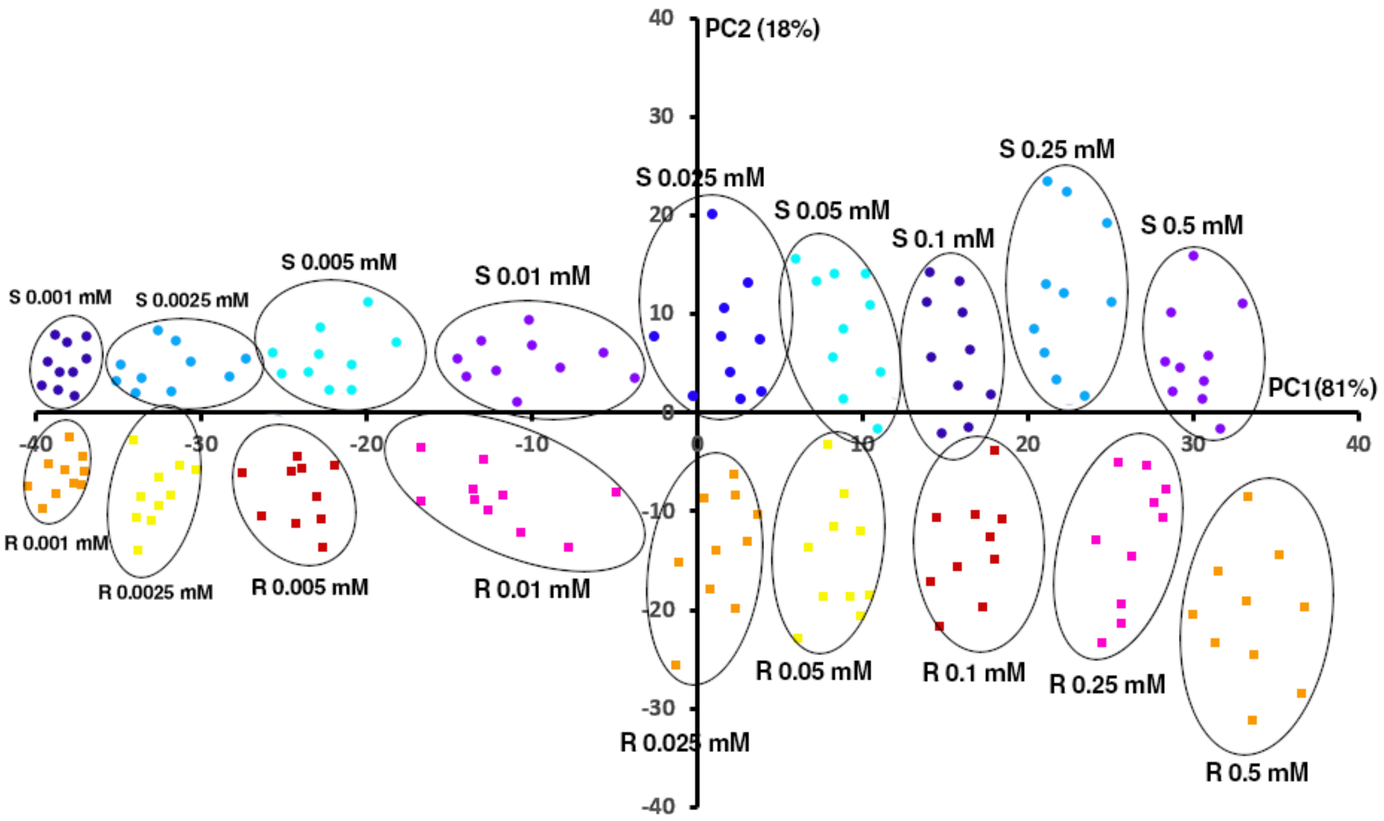
Sensor manufacturing scheme



Score plots of the PCA-modeling of the DPVs of Clp enantiomers obtained using GCE/CpX/CPD1 (a), GCE/CpX/CPD2 (b), GCE/CpX/CPD3 (c) and the sensor system (d).



Concentration dependences of enantiomers of clopidogrel on the developed sensors (concentrations 1-9: 0.001, 0.0025, 0.005, 0.01, 0.025, 0.05, 0.1, 0.25, 0.5 mM)



Score plots of the PCA-modeling of the DPVs obtained using the sensor system with different concentrations of Clp enantiomers

Equations of calibration curves of concentration dependences for R- and S-Clp:

Sensor	Enantiomer	Equation	R^2
GCE/CpX/CPD1	R	y=23.753x+0.0197	0.997
	S	y=19.926x-0.0396	0.998
GCE/CpX/CPD2	R	y=24.256x+0.0456	0.996
	S	y=20.655x+0.0265	0.998
GCE/CpX/CPD3	R	y=18.454x+0.0195	0.997
	S	y=21.153x+0.0201	0.998

It can be seen that, the use of GCE/CpX/CPD1 makes it possible to obtain R- and S-Clp DPV's differing from each other both in peak currents and potentials (I_{pR}/I_{pS}=1.15, ΔE_p= 20 mV). Similar results have been achieved on GCE/CpX/CPD2 (I_{pR}/I_{pS}=1.17, ΔE_p= 18 mV) and GCE/CpX/CPD3 (I_{pR}/I_{pS}=1.22, ΔE_p= 21 mV), what indicates the presence of cross-sensitivity to Clp enantiomers between sensors. It allows us to make a sensor system based on them with chemometric processing of analytical signals. The use of the sensor system leads to an increase in the probability of correctly recognized samples.

The work was supported by the Russian Science Foundation, Grant № 21-13-00169.