

## PCA-analysis of tryptophan enantiomers voltammetric time rows under continuous sensor functioning conditions

© Artem V. Sidelnikov,<sup>1\*</sup> Raoul R. Nigmatullin,<sup>2\*</sup> Valery N. Maystrenko,<sup>1</sup>  
Herman C. Budnikov,<sup>3\*</sup> Elza I. Maksyutova,<sup>1+</sup> and Anastasia A. Tikhonova<sup>1</sup>

<sup>1</sup>Analytical Chemistry Department. Chemistry faculty. Bashkir State University. Z. Validy St., 32. Ufa, 450076. Bashkortostan Republic. Russia. Phone: +7 (347) 229-97-12.

E-mail: artsid2000@gmail.com, v\_maystrenko@mail.ru, elzsha@gmail.com

<sup>2</sup>Radioelectronic and Informative-Measurements Techniques Department. Kazan National Research Technical University-KAI. K. Marx St., 10. Kazan, 420111. Tatarstan Republic. Russia.

Phone: +7 (843) 238-94-16. E-mail: renigmat@gmail.com

<sup>3</sup>Analytical Chemistry Department. Institute of Chemistry. Kazan Federal University.

Kremlyovskaya St., 18. Kazan, 420008. Tatarstan Republic. Russia.

Phone: +7 (843) 233-72-15. E-mail: herman.budnikov@kpfu.ru

\*Supervising author; +Corresponding author

**Keywords:** principal component analysis, voltammetric time rows, enantiomers, tryptophan, voltammetry.

### Abstract

In this paper the results of L- and D-tryptophan voltammetric time rows analysis by the method of principal components are presented. It is shown that in the case of continuous registration of tryptophan enantiomers oxidation voltammograms under cyclic electrochemical activation conditions of graphite electrode, clusters are formed in the space of the three principal components, the shape of which depends of the electrochemical activation duration of the graphite electrode and the nature of the depolarizer. It is found that for obtaining stable and independent of the experiment duration responses arrays of the sensor system, it is necessary to conduct from 180 or more cycles of electrode activation. In this case, the voltammetric time rows in the space of the two principle components are transformed into rings, mean radius of whose depends of the nature of the depolarizer. With the use of the transposed matrix of time rows, the selectivity factors of the sensor with respect to the tryptophan enantiomers are established. "Noise" in the voltammetric time rows, accumulated with more than 600 activation cycles, becomes ordered in time and has a latent structure. With the use of the PCA-transformation of the transposed time rows matrix, it is found that the spread of the currents values in time manifests a periodicity, and clusters of L- and D-tryptophans are formed in the spaces of the first, second and third principle components of the loadings plot, which are clearly distinguishable from each other. Proposed approaches to the obtaining and processing of voltammetric time rows, in our opinion, can serve as the basis for the functioning of enantioselective multisensor systems and sensors for medicines quality control in the pharmaceutical industry, the detection of counterfeit products and etc.

### References

- [1] H.C. Budnikov, G.A. Evtugin, V.N. Maystrenko. Modified electrodes for voltammetry in chemistry, biology and medicine. *Moscow: BINOM. Laboratoriya znaniy*. **2009**. 416p. (russian)
- [2] M. Su, M. Ma, Y. Ma. Electrochemical detection of tryptophan using carbon paste electrode modified silicium dioxide nanoparticles. *Electrochemistry*. **2012**. Vol.48. No.5. P.538-543. (russian)
- [3] L.-Y. Yu, Q. Liu, X.-W. Wu, X.-Y. Jiang, J.-G. Yu, X.-Q. Chen. Chiral electrochemical recognition of tryptophan enantiomers at a multi-walled carbon nanotube–chitosan composite modified glassy carbon electrode. *RSC Adv*. **2015**. No.5. P.98020-98025. DOI: 10.1039/c5ra20082b
- [4] C.G. Nan, Z.Z. Feng, W.X. Li, D.J. Ping, C.H. Qin. Electrochemical behavior of tryptophan and its derivatives at a glassy carbon electrode modified with hemin. *Anal. Chim. Acta*. **2002**. Vol.452. P.245-254. DOI: 10.1016/S0003-2670(01)01470-2
- [5] W. Feng, C. Liu, S. Lu, C. Zhang, X. Zhu, Y. Liang, J. Nan. Electrochemical chiral recognition of tryptophan using a glassy carbon electrode modified with  $\beta$ -cyclodextrin and grapheme. *Microchim. Acta*. **2014**. Vol.181. No.5-6. P.501-509. DOI: 10.1007/s00604-014-1174-0

- [6] Y. Tao, J. Dai, Y. Kong, Y. Sha. temperature-sensitive electrochemical recognition of tryptophan enantiomers based on  $\beta$ -cyclodextrin self-assembled on poly(L-glutamic acid). *Anal. Chem.* **2014**. Vol.86. P.2633-2639. DOI: 10.1021/ac403935s
- [7] Q. Xiao, S. Lu, C. Huang, W. Su, S. Huang. Novel N-doped carbon dots/ $\beta$ -cyclodextrin nanocomposites for enantioselective recognition of tryptophan enantiomers. *Sensors*. **2016**. Vol.16. No.11. P.1874. DOI: 10.3390/s16111874
- [8] J. Ou, Y. Tao, J. Xue, Y. Kong, J. Dai, L. Deng. Electrochemical enantioselective recognition of tryptophan enantiomers based on graphene quantum dots-chitosan composite film. *Electrochem. Commun.* **2015**. Vol.57. P.5-9. DOI: 10.1016/j.elecom.2015.04.004
- [9] B.B. Prasad, M.P. Tiwari, R. Madhuri, P.S. Sharma. Enantioselective separation and electrochemical sensing of D- and L-tryptophan at ultratrace level using molecularly imprinted micro-solid phase extraction fiber coupled with complementary molecularly imprinted polymer-fiber sensor. *J. Chromatogr. B.* **2011**. Vol.879. P.364-370. DOI: 10.1016/j.jchromb.2010.12.023
- [10] Y. Kong, W. Zhao, S. Yao, J. Xu, W. Wang, Z. Chen. Molecularly Imprinted Polypyrrole Prepared by Electrodeposition for the Selective Recognition of Tryptophan Enantiomers. *J. Appl. Polym. Sci.* **2010**. Vol.115. P.1952-1957. DOI: 10.1002/app.31165
- [11] A.L. Pomerantsev. *Chemometrics in Excel*. New York: Wiley. **2014**.
- [12] R.R. Nigmatullin, H.C. Budnikov, A.V. Sidelnikov. New approach for voltammetry near limit of detection: integrated voltammograms and reduction of measurements to an "ideal" experiment. *Electroanalysis*. **2015**. Vol.27. No.6. P.1416-1426. DOI: 10.1002/elan.201400735
- [13] R.R. Nigmatullin, H.C. Budnikov, A.V. Sidelnikov., Y.A. Yarkaeva. New quantitative methods of electrode evaluation under continuous voltammetric conditions. *New J. Chem.* **2017**. Vol.41. No.7. P.2561-2573. DOI: 10.1039/c6nj03743g
- [14] R.R. Nigmatullin, H.C. Budnikov, A.V. Sidelnikov., E.I. Maksyutova. Quantitative "reading" of the score matrix components in the PCA: new general tool for electrochemical data analysis. *CCC*. **2017**. Vol.5. No.3. P.12-32. DOIC: 2292-1036-2017-03-002-89