MATHCAD FILE-WORKING SHEET FOR SIMULATION OF DIFFUSIONAL EC' catalytic mechanism (EC'=Electrochemical Mechanism Coupled with Regenerative Chemical Reaction) in SQUARE-WAVE VOLTAMMETRY

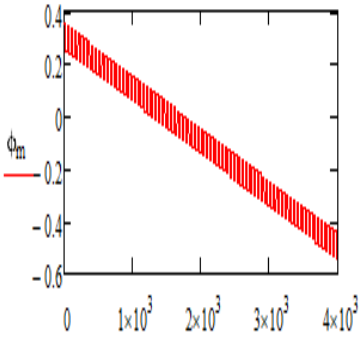
Rubin Gulaboski, Valentin Mirceski

$dE := 0.01$ $Esw := 0.05$ $\Delta E := 0.8$ $m := 1..\frac{\Delta E}{dE} \cdot 50$ $Es := 0.3$ $i := 1..1$

$f := 50$

$$relativenpot_m := \left(ceil\left(\frac{m}{25} \cdot \frac{1}{2}\right) \cdot dE + if\left(\frac{ceil\left(\frac{m}{25}\right)}{2} = ceil\left(\frac{m}{25} \cdot \frac{1}{2}\right), 1, -1\right) \cdot Esw + Esw \right) - dE \qquad \phi_m := Es + Esw - relativenpot_m$$

$D := 5 \cdot 10^{-6}$ $ks := 10^{-2}$



$$\lambda := \frac{ks}{\sqrt{D \cdot f}}$$

$\alpha := 0.5$

$log(\lambda) = -0.199$

$F := 96500$ $n := 1$ $R := 8.314$ $T := 298.15$ $\Phi_m := n \cdot \frac{F}{R \cdot T} \cdot \phi_m$

$kc := 10^{0.85}$

kc-konstanta na kataliza

$k := 1..\frac{\Delta E}{dE} \cdot 50$

$$z := \left(\frac{kc}{f}\right)$$

$z = 0.142$

$log(z) = -0.849$

$$S_k := erf\left(\frac{\sqrt{z} \cdot \sqrt{k}}{\sqrt{50}}\right) - erf\left(\frac{\sqrt{z} \cdot \sqrt{k-1}}{\sqrt{50}}\right)$$

$Ox + ne = Red$

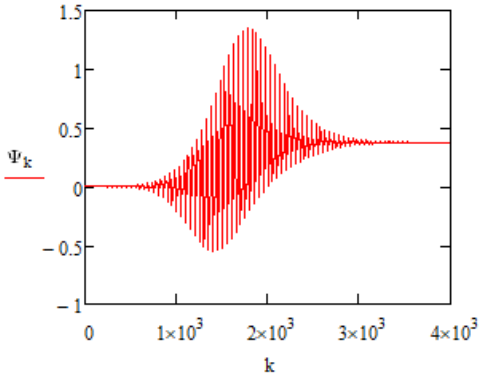
$Red + Y = Ox$

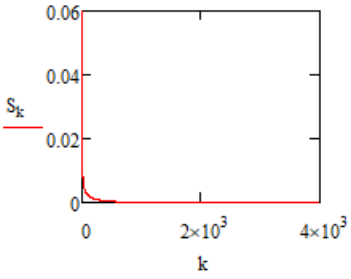
Diffusional EC' mechanism in Square-wave voltammetry

λ is dimensionless kinetic parameter related to electrode reaction
ks is rate constant of electrode reaction
kc is catalytic rate constant
z is dimensionless catalytic parameter related to regenerative reactions
α is electron transfer coefficient
Es is starting potential
Ef is final potential
dE is potential step
Ψ is symbol for dimensionless current
Em is cathodic potential ramp in cyclic voltammetry
En is anodic potential ramp
Sk is a numerical integration factor
τ is duration of potential steps
D is diffusion coefficient of Ox and Red

$$\Psi_1 := \lambda \cdot e^{-\alpha \cdot \Phi_1} \cdot \left[1 + \frac{\lambda \cdot S_1}{\sqrt{z}} + \frac{e^{(1-\alpha)\cdot \Phi_1} \cdot S_1}{\sqrt{z}} \right]^{-1}$$

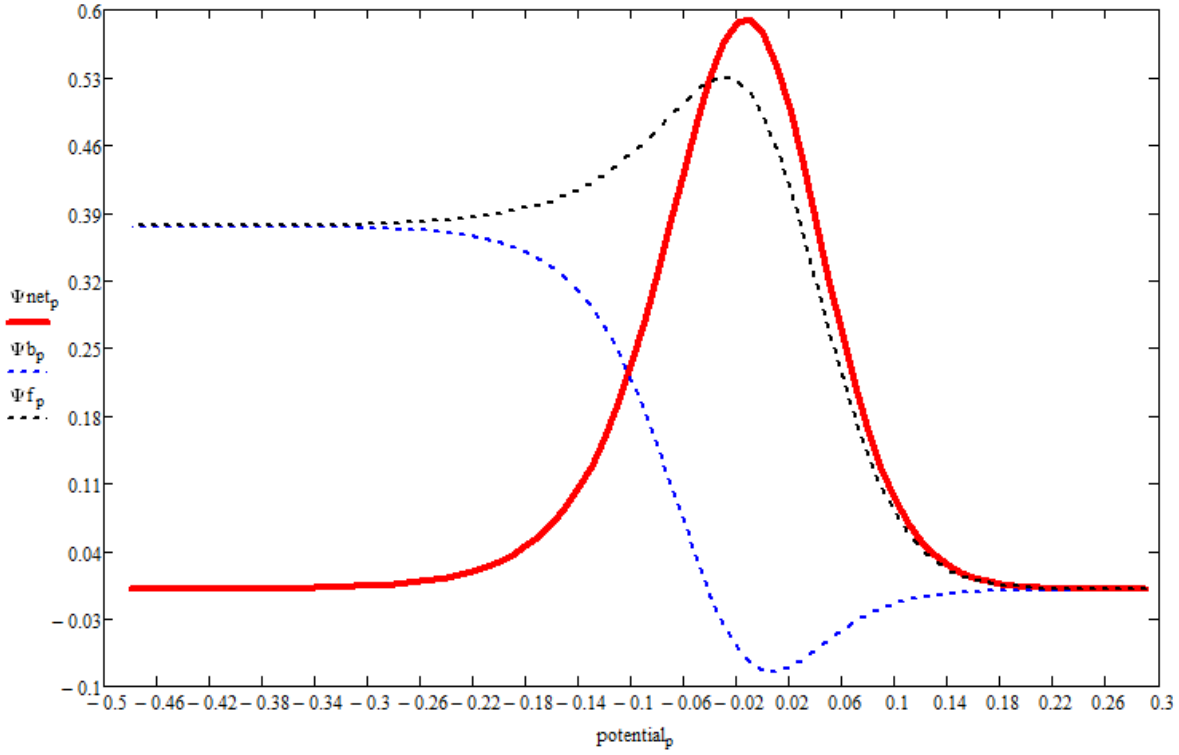
$$\Psi_k := \frac{\lambda \cdot e^{-\alpha \cdot \Phi_k} - \frac{\lambda \cdot e^{-\alpha \cdot \Phi_k}}{\sqrt{z}} \cdot \sum_{j=1}^{k-1} \left(\Psi_j \cdot S_{k-j+1} \right) - e^{\Phi_k \cdot (1-\alpha)} \cdot \lambda \cdot \frac{1}{\sqrt{z}} \cdot \sum_{j=1}^{k-1} \left(\Psi_j \cdot S_{k-j+1} \right)}{1 + \frac{\lambda \cdot e^{-\alpha \cdot \Phi_k} \cdot S_1}{\sqrt{z}} + \frac{\lambda \cdot e^{(1-\alpha)\cdot \Phi_k} \cdot S_1}{\sqrt{z}}}$$





$$p := 1 .. \frac{\Delta E}{dE} - 2 \qquad \Psi f_p := \Psi_{(p+1)\cdot 50} \qquad \Psi b_p := \Psi_{50 \cdot p + 25} \qquad \Psi net_p := \Psi f_p - \Psi b_p$$

$$potential_p := Es - (p) \cdot dE$$



REFERENCES

1. **R. Gulaboski** and V. Mirceski, New aspects of the electrochemical-catalytic (EC') mechanism in square-wave voltammetry, Electrochim. Acta, 167 (2015) 219-225.
2. V. Mirceski, S Komorsky Lovric, M. Lovric, Square-wave voltammetry, Theory and Application, 2007.
3. **R. Gulaboski** and L. Mihajlov, "Catalytic mechanism in successive two-step protein-film voltammetry—heoretical study in square-wave voltammetry", ***Biophys. Chem.***155 (2011) 1-9.
4. **R. Gulaboski**, M. Lovric, V. Mirceski, I. Bogeski and M. Hoth, Protein-film voltammetry: a theoretical study of the temperature effect using square-wave voltammetry., ***Biophys. Chem***. 137 (2008) 49-55.
5. **R. Gulaboski**, Surface ECE mechanism in protein film voltammetry—a theoretical study under conditions of square-wave voltammetry, ***J. Solid State Electrochem***. 13 (2009) 1015-1024.
6. Scholz, F.; Schroeder U.; **Gulaboski R**, *Electrochemistry of Immobilized Particles and Droplets*, Springer Verlag, New York, pp. 1-269, 2005
7. **Gulaboski, R.** Pereira, C. M. In Electrochemical Methods and Instrumentation in Food Analysis, in Handbook of Food Analysis Instruments, Otles, S. (ed.) Taylor & Francis, 2008 and 2015 2nd Edition
8. **R. Gulaboski**, Theoretical contribution towards understanding specific behaviour of "simple" protein-film reactions in square-wave voltammetry", ***Electroanalysis,*** 31 (2019) 545-553
9. **R. Gulaboski,** P. Kokoskarova, S. Petkovska, Time independent methodology to assess Michaelis Menten constant by exploring electrochemical-catalytic mechanism in protein-film cyclic staircase voltammetry, ***Croat. Chem. Acta***, 91 (2018) 377-382.
10. V. Mirceski, D. Guziejewski, L. Stojanov, **R. Gulaboski,** Differential Square-Wave Voltammetry, ***Analytical Chemistry*** (2019) https://pubs.acs.org/doi/abs/10.1021/acs.analchem.9b03035.
11. Scholz, F, Schroeder U, **Gulaboski R**, A Domenech-Carbo, *Electrochemistry of Immobilized Particles and Droplets, Experiments with Three-phase Electrode,* Springer Verlag, New York, pp. 2nd Edition, 2015
12. **R. Gulaboski**, V. Mirceski, R. Kappl, M. Hoth, M. Bozem, "Quantification of Hydrogen Peroxide by Electrochemical Methods and Electron Spin Resonance Spectroscopy" ***Journal of Electrochemical Society,*** 166 (2019) G82-G101.
13. **Rubin Gulaboski**, Valentin Mirceski, Milivoj Lovric, Square-wave protein-film voltammetry: new insights in the enzymatic electrode processes coupled with chemical reactions, ***Journal of Solid State Electrochemistry***, 23 (**2019) 2493-2506.**
14. Milkica Janeva, Pavlinka Kokoskarova, Viktorija Maksimova, **Rubin Gulaboski**, Square-wave voltammetry of two-step surface redox mechanisms coupled with chemical reactions-a theoretical overview, ***Electroanalysis, 31 (2019) 1488-1506***
    https://onlinelibrary.wiley.com/doi/10.1002/elan.201900416
15. **Gulaboski Rubin**, Milkica Janeva, Viktorija Maksimova, ***"***New Aspects of Protein-film Voltammetry of Redox Enzymes Coupled to Follow-up Reversible Chemical Reaction in Square-wave Voltammetry***", Electroanalysis***, 31 (2019) **946-956 .**

16. P. Kokoskarova, M. Janeva, V. Maksimova, **R. Gulaboski,** "Protein-film Voltammetry of Two-step Electrode Enzymatic Reactions Coupled with an Irreversible Chemical Reaction of a Final Product-a Theoretical Study in Square-wave Voltammetry", ***Electroanalysis 31*** (**2019**) 1454-1464, DOI: 10.1002/elan.201900225
17. P. Kokoskarova, **R. Gulaboski**, Theoretical Aspects of a Surface Electrode Reaction Coupled with Preceding and Regenerative Chemical Steps: Square-wave Voltammetry of a Surface CEC' Mechanism**,** ***Electroanalysis*** **(2019)**doi.org/10.1002/elan.201900491
https://onlinelibrary.wiley.com/doi/10.1002/elan.201900491
18. **R. Gulaboski,** I. Bogeski, P. Kokoskarova, H. H. Haeri, S. Mitrev, M. Stefova, Marina, J. Stanoeva-Petreska, V. Markovski, V. Mirceski, M. Hoth, and R. Kappl, *New insights into the chemistry of Coenzyme Q-0: A voltammetric and spectroscopic study.* ***Bioelectrochem.*** 111 (2016) 100-108.
19. **R. Gulaboski,** V. Markovski, and Z. Jihe, *Redox chemistry of coenzyme Q—a short overview of the voltammetric features*, ***J. Solid State Electrochem*****.** 20 (2016) 3229-3238.
20. Haeri, Haleh H. I. Bogeski, **R. Gulaboski,** V. Mirceski, M. Hoth, and R. Kappl, *An EPR and DFT study on the primary radical formed in hydroxylation reactions of 2,6-dimethoxy-1,4-benzoquinone.* ***Mol. Phys****.* 114 (2016) 1856-1866.
21. V. Mirceski, D. Guzijewski and **R. Gulaboski**, Electrode kinetics from a single square-wave voltammograms, ***Maced. J. Chem. Chem. Eng.*** 34 (2015) 1-12.
22. V. Mirceski, A. Aleksovska, B. Pejova, V. Ivanovski, B. Mitrova, N. Mitreska and **R. Gulaboski**, Thiol anchoring and catalysis of Gold nanoparticles at the liquid-liquid interface of thin-organic film modified electrodes", ***Electrochem Commun***. 39 (2014) 5-8
23. V. Mirceski, Valentin and **R. Gulaboski,** *Recent achievements in square-wave voltammetry (a review).* ***Maced. J. Chem. Chem. Eng.*** 33 (2014). 1-12.
24. V. Mirceski, **R. Gulaboski**, M. Lovric, I. Bogeski, R. Kappl and M. Hoth, Square-Wave Voltammetry: A Review on the Recent Progress, ***Electroanal.*** 25 (2013) 2411–2422.
25. **R. Gulaboski**, I. Bogeski, V. Mirčeski, S. Saul, B. Pasieka, H. H. Haeri, M. Stefova, J. Petreska Stanoeva, S. Mitrev, M. Hoth and R. Kappl, "Hydroxylated derivatives of dimethoxy-1,4-benzoquinone as redox switchable earth-alkaline metal ligands and radical scavengers" ***Sci. Reports***, 3 (2013) 1-8.
26. **R. Gulaboski**, V. Mirceski, I. Bogeski and M. Hoth, „Protein film voltammetry: electrochemical enzymatic spectroscopy. A review on recent progress„ ***J. Solid State Electrochem.*** 16 (2012) 2315-2328.
27. **R. Gulaboski,** P. Kokoskarova and S. Mitrev, "Theoretical aspects of several successive two-step redox mechanisms in protein-film cyclic staircase voltammetry" ***Electrochim. Acta*** 69 (2012) 86-96.
28. I. Bogeski, **R. Gulaboski***, R. Kappl, V. Mirceski, M. Stefova, J. Petreska and M. Hoth, „Calcium Binding and Transport by Coenzyme Q„ ***J. Am. Chem. Soc.*** 133 (2011) 9293-9303.
29. I. Bogeski, R. Kappl, C. Kumerow, **R. Gulaboski**, M. Hoth and B. A. Niemeyer "Redox regulation of calcium ion channels: Chemical and physiological aspects, ***Cell Calcium*** **50** (2011) 407-423.
30. **R. Gulaboski**, E. S. Ferreira, C. M. Pereira, M. N. D. S. Cordeiro, A. Garrau, V. Lippolis and A. F. Silva, Coupling of Cyclic Voltammetry and Electrochemical Impedance Spectroscopy for Probing the Thermodynamics of Facilitated Ion Transfer Reactions Exhibiting Chemical Kinetic Hindrances, ***J. Phys. Chem. C*** 112 (2008) 153-161.
31. **R. Gulaboski**, M. Lovric, V. Mirceski, I. Bogeski and M. Hoth, A new rapid and simple method to determine the kinetics of electrode reactions of biologically relevant

compounds from the half-peak width of the square-wave voltammograms., ***Biophys. Chem***. 138 (2008) 130-137.

32. **R. Gulaboski**, C. M. Pereira, M. N. D. S. Cordeiro, M. Hoth and I. Bogeski, Redox properties of the calcium chelator Fura-2 in mimetic biomembranes. ***Cell Calcium*** 43 (2008) 615-621.
33. **R. Gulaboski**, M. Chirea, C. M. Pereira, M. N. D. S. Cordeiro, R. B. Costa and A. F. Silva, Probing of the Voltammetric Features of Graphite Electrodes Modified with Mercaptoundecanoic Acid Stabilized Gold Nanoparticles, ***J. Phys. Chem.*** *C* 112 (2008) 2428-2435.
34. V. Mirceski, **R. Gulaboski**, I. Bogeski and M. Hoth, Redox Chemistry of Ca-Transporter 2-Palmitoylhydroquinone in an Artificial Thin Organic Film Membrane, ***J. Phys. Chem. C*** 111 (2007) 6068-6076.

35. **R. Gulaboski**, F. Borges, C. M. Pereira, M. N. D. S. Cordeiro, J. Garrido and A. F. Silva, Voltammetric insights in the transfer of ionizable drugs across biomimetic membranes: recent achievements., **Comb. Chem. High Throughput Screen.** 10 (2007) 514-526.

36. **R. Gulaboski**, V. Mirčeski, M. Lovrić and I. Bogeski, "Theoretical study of a surface electrode reaction preceded by a homogeneous chemical reaction under conditions of square-wave voltammetry." ***Electrochem. Commun***. 7 (2005) 515-522.

37. **R. Gulaboski**, M. N. D.S. Cordeiro, N. Milhazes, J. Garrido, F. Borges, M. Jorge, C. M. Pereira, I. Bogeski, A. Helguera Morales**,** B. Naumoski and A. F. Silva, "Evaluation of the lipophilic properties of opioids, amphetamine-like drugs, and metabolites through electrochemical studies at the interface between two immiscible solutions. ***Anal. Biochem***. 361 (2007) 236-243.

38. M. Jorge, **R. Gulaboski**, C. M. Pereira and M. N. D. S. Cordeiro, Molecular dynamics study of nitrobenzene and 2-nitrophenyloctyl ether saturated with water", ***Mol. Phys.*** 104 (2006) 3627-3634.

39. M. Jorge, **R. Gulaboski**, C. M. Pereira and M. N. D. S. Cordeiro "Molecular dynamics study of 2-nitrophenyl octyl ether and nitrobenzene." ***J. Phys. Chem. B*** 110 (2006) 12530-12538.

40. M. Chirea, V. Garcia-Morales , J. A. Manzanares, C, M. Pereira and A. F: Silva "Electrochemical characterization of polyelectrolyte/gold nanoparticle multilayers self-assembled on gold electrodes." ***J. Phys. Chem. B*** 109 (2005) 21808-21817.

41. V. Mirčeski and **R. Gulaboski**, "Simple electrochemical method for deposition and voltammetric inspection of silver particles at the liquid-liquid interface of a thin-film electrode." ***J. Phys. Chem. B*** 110 (2006) 2812-2820.

42. **R. Gulaboski**, V. Mirčeski, C. M. Pereira, M. N. D. S. Cordeiro, A. F Silva, F. Quentel, M. L'Her and M. Lovrić, "A comparative study of the anion transfer kinetics across a water/nitrobenzene interface by means of electrochemical impedance spectroscopy and square-wave voltammetry at thin organic film-modified electrodes." ***Langmuir*** 22 (2006) 3404-3412.

43. **R. Gulaboski**, C. M. Pereira. M. N. D. S. Cordeiro, I. Bogeski, E. Fereira, D. Ribeiro, M. Chirea and A. F. Silva, "Electrochemical study of ion transfer of acetylcholine across the interface of water and a lipid-modified 1,2-dichloroethane." ***J. Phys. Chem. B*** 109 (2005) 12549-12559.

44. **R. Gulaboski**, C. M. Pereira. M. N. D. S. Cordeiro, I. Bogeski and A. F. Silva "Enzymatic formation of ions and their detection at a three-phase electrode" ***J. Solid State Electrochem*.** 9 (2005) 469-474.

45. F. Scholz and **R. Gulaboski** "Determining the Gibbs energy of ion transfer across water-organic liquid interfaces with three-phase electrodes." ***Chem. Phys. Chem***., 6 (2005) 1-13.

46. F. Scholz and **R. Gulaboski** "Gibbs energies of transfer of chiral anions across the interface water/chiral organic solvent determined with the help of three-phase electrodes." ***Faraday Discussions*** 129 (2005) 169-177.

47. **R. Gulaboski**, A. Galland, G. Bouchard, K. Caban, A. Kretschmer, P.–A. Carrupt, H. H. Girault and F. Scholz, A Comparison of the Solvation Properties of 2-Nitrophenyloctyl Ether, Nitrobenzene, and *n*-Octanol as Assessed by Ion Transfer Experiments" ***J. Phys. Chem*. *B*.** 108 (2004) 4565-4572.

48. **R. Gulaboski** and F. Scholz, "Lipophilicity of Peptide Anions: An Experimental Data Set for Lipophilicity Calculations", ***J. Phys. Chem*. *B***. 107 (2003) 5650-5657.

49. **R. Gulaboski**, K. Caban, Z. Stojek and F. Scholz, "The determination of the standard Gibbs energies of ion transfer between water and heavy water by using the three-phase electrode approach", ***Electrochem. Commun***. 6 (2004) 215-218.

50. V. Mirčeski, **R. Gulaboski** and F. Scholz, "Square-wave thin-film voltammetry: influence of uncompensated resistance and charge transfer kinetics", ***J. Electroanal. Chem*.** 566 (2004) 351-360**.**

51. F. Scholz, **R. Gulaboski** and K. Caban, "The determination of standard Gibbs energies of transfer of cations across the nitrobenzene|water interface using a three-phase electrode.", ***Electrochem. Commun***., 5 (2003) 929-934.

52. G. Bouchard, A. Galland, P.-A. Carrupt, **R. Gulaboski**, V. Mirčeski, F. Scholz and H. Girault, "Standard partition coefficients of anionic drugs in the *n*-octanol/water system determined by voltammetry at three-phase electrodes**"**, ***Phys. Chem. Chem. Phys***. 5 (2003) 3748-3751.

53. **R. Gulaboski**, V. Mirčeski, Š. Komorsky-Lovrić and M. Lovrić, "Square-Wave Voltammetry of Cathodic Stipping Reactions. Diagnostic Criteria, Redox Kinetic Measurements, and Analytical Applications", ***Electroanal.*** 16 (2004) 832-842.

54. V. Mirčeski and **R. Gulaboski**, "A Theoretical and Experimental Study of Two-Step Quasireversible Surface Reaction by Square-Wave Voltammetry" ***Croat. Chem. Acta*** 76 (2003) 37-48.

55. V. Mirčeski and **R. Gulaboski**, "The surface catalytic mechanism: a comparative study with square-wave and staircase cyclic voltammetry ", ***J. Solid State Electrochem***. 7 (2003) 157-165.

56. **R. Gulaboski**, V. Mirčeski and Š. Komorsky-Lovrić, "Square-Wave Voltammetry of a Second Order Cathodic Stripping Process Coupled by Adsorption of the Reacting Ligand", ***Electroanalysis*** 14 (2002) 345-354.

57. V. Mirčeski, M. Lovrić and **R. Gulaboski**, “Theoretical and experimental study of the surface redox reaction involving interactions between the adsorbed particles.under conditions of square-wave voltammetry.”, ***J. Electroanal. Chem***., 515 (2001) 91-99.

58. V. Mirčeski and **R. Gulaboski**, “Surface Catalytic Mechanism in Square-Wave Voltammetry”, ***Electroanalysis*** 13 (2001) 1326-1334.

59. **R. Gulaboski**, K. Riedel and F. Scholz, **“**Standard Gibbs energies of transfer of halogenate and pseudohalogenate ions, halogen substituted acetates, and cycloalkyl carboxylate anions at the water|nitrobenzene interface**”**, ***Phys. Chem. Chem. Phys***. 5 (2003) 1284-1289.

60. **R. Gulaboski**, V. Mirčeski and F. Scholz, “Determination of the standard Gibbs energies of transfer of cations and anions of amino acids and small peptides across the water nitrobenzene interface.”, ***Amino Acids***, 24 (2003) 149-154

61. V. Mirčeski, **R. Gulaboski** and F. Scholz, “Determination of the standard Gibbs energies of transfer of cations across the nitrobenzene|water interface utilizing te reduction of Iodine in an immobilized dropplett“ ***Electrochem. Commun***., 4 (2002) 814-819.

62. **R. Gulaboski**, V. Mirčeski and F. Scholz, “An electrochemical method for determination of the standard Gibbs energy of anion transfer between water and n-octanol” ***Electrochem. Commun*****.** 4 (2002) 277-283.

63. V. Mirčeski, **R. Gulaboski** and I. Kuzmanovski, “Mathcad-a Tool for Numerical Calculation of Square-Wave Voltammograms”, ***Bull. Chem. Technol. Macedonia*****,** 18 (1999) 57-64.

64. V. Mirčeski, **R. Gulaboski**, B. Jordanoski and Š. Komorsky-Lovrić, „Square-wave voltammetry of 5-fluorouracil “, ***J. Electroanal. Chem****.,* 490 (2000) 37-47.