SUPPLEMENTARY MATERIAL: Electrochemistry of Coenzyme Q-0: A voltammetric and antioxidative study

Rubin Gulaboski, Ivan Bogeski, Kokoskarova Pavlinka

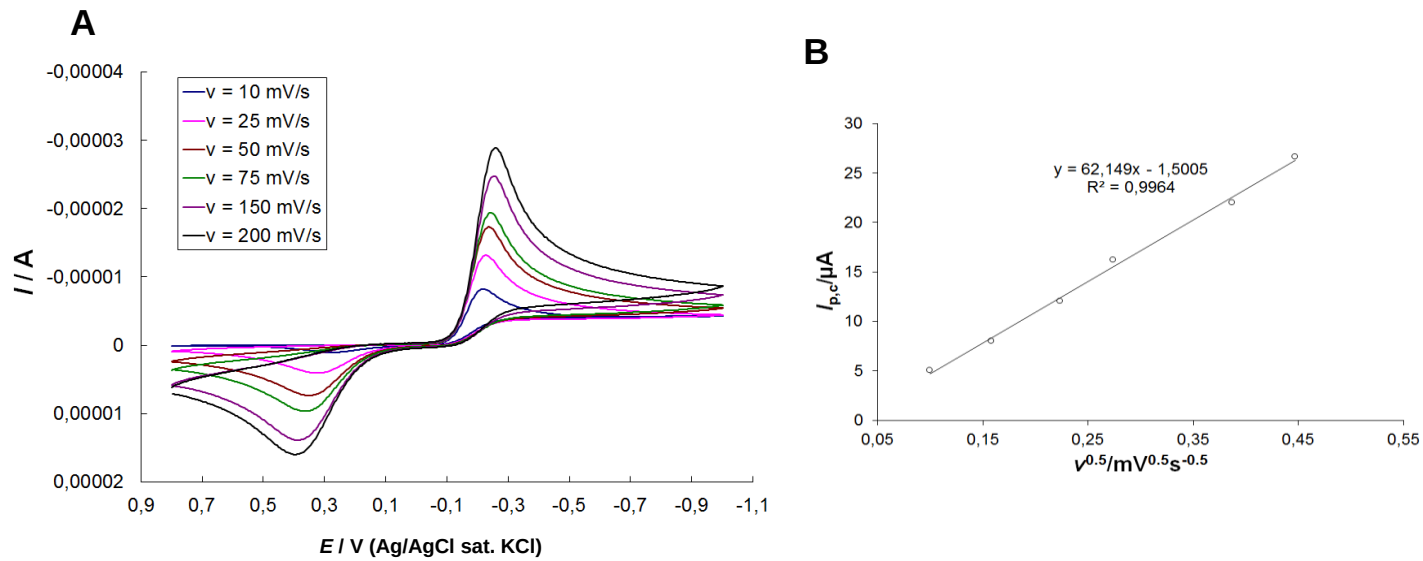
Related to work

Bioelectrochemistry 111 (2016) 100–108

http://dx.doi.org/10.1016/j.bioelechem.2016.05.008

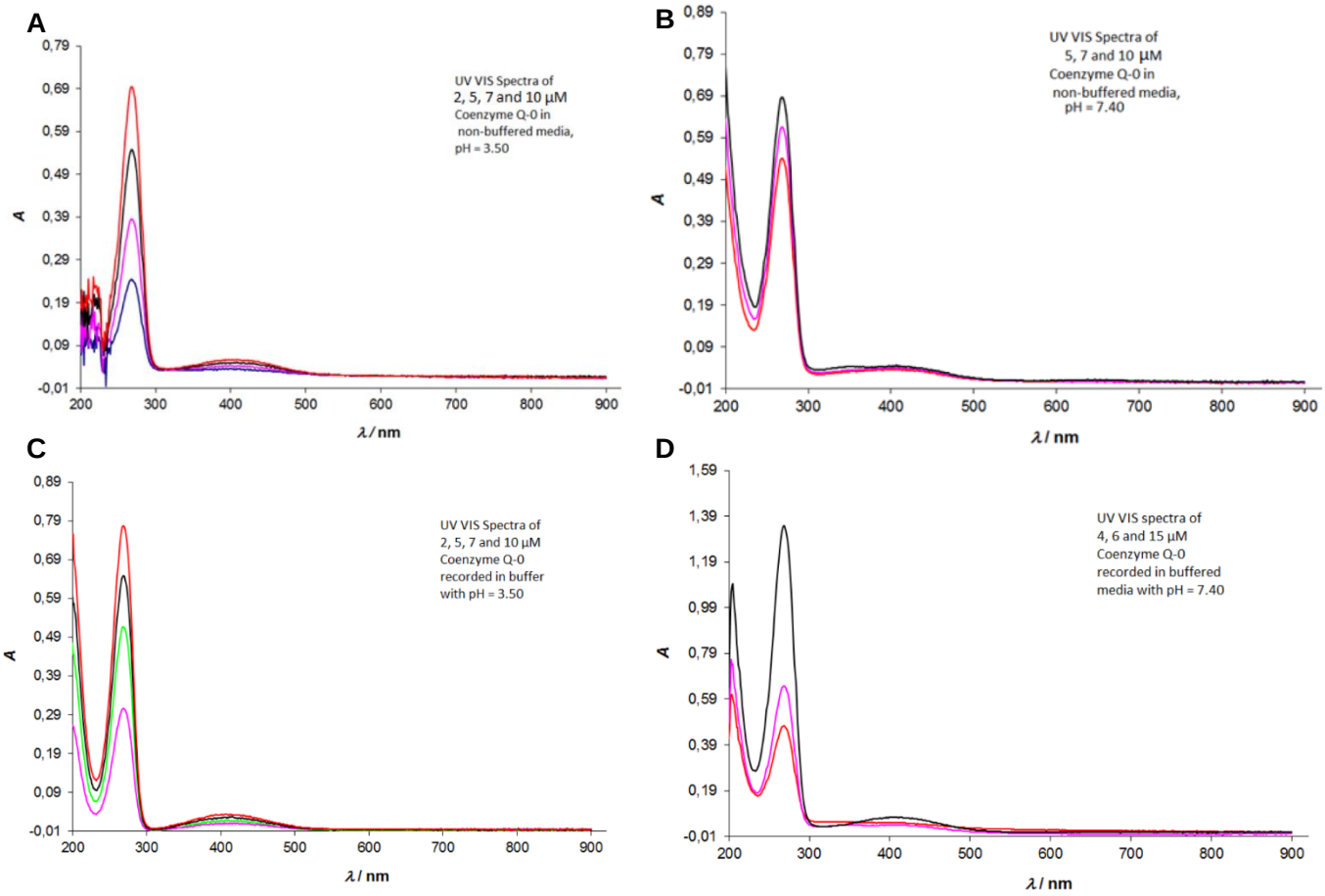
Abstract: we report in this work on redox features of CoQ-0 in buffered and non-buffered aqueous mediawas examined. In buffered aqueous media CoQ-0 redox chemistry can be described by a 2-electron–2-proton redox scheme, characteristic for all benzoquinones. In non-buffered media the number of electrons involved in the electrode reaction of CoQ-0 is still 2; however, the number of protons involved varies between 0 and 2. This results in two additional voltammetric signals, attributed to 2-electrons–1H+ and 2-electrons–0H+ redox processes, in which mono- and di-anionic compounds of CoQ-0 are formed. In addition, CoQ-0 exhibits a complex chemistry in strong alkaline environment. The reaction of CoQ-0 and OH− anions generates several hydroxyl derivatives as products. Their structures were identified with HPLC/MS. The prevailing radical reaction mechanism was analyzed by electron paramagnetic resonance spectroscopy. The hydroxyl derivatives of CoQ-0 have a strong antioxidative potential and form stable complexeswith Ca2+ ions. In summary, our results allowmechanistic insights into the redox properties of CoQ-0 and its hydroxylated derivatives and provide hints on possible applications.

The color of CoQ-0 solution (*c* = 1 mmol/L) directly after dissolving it in aqueous solution with pH = 7.00 (left), and after its reaction in 0.1 mol/L NaOH for 60 minutes followed by re-titration with HCl to pH = 7.00 (right).



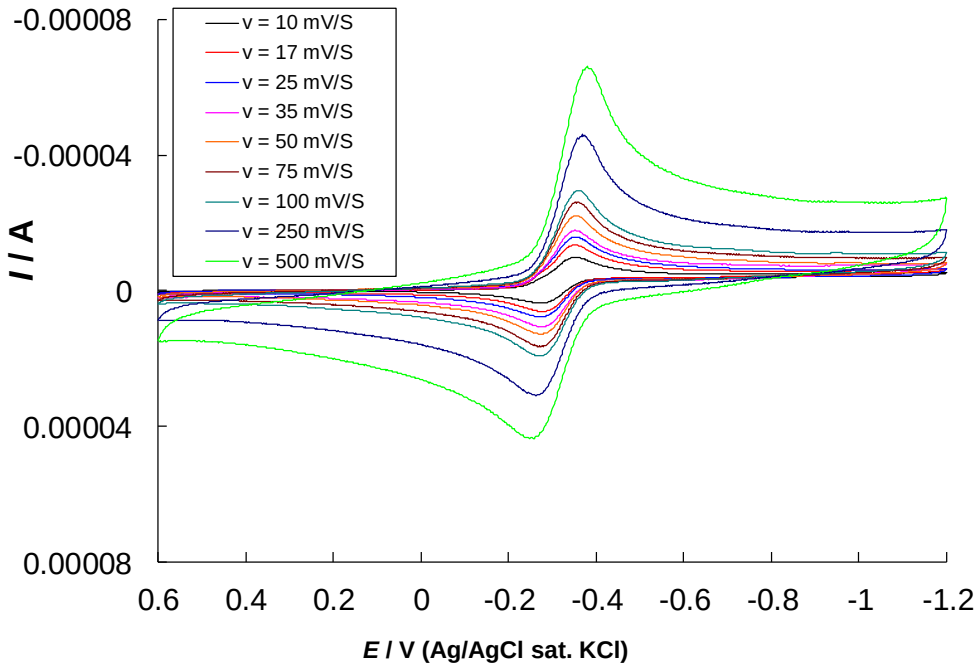
Supplementary figure 1: (A) Buffered water solutions: Cyclic voltammograms of Coenzyme Q-0 (*c* = 0.5 mmol/L) recorded in ammonia buffers with pH = 7.40 at several scan rates. **(B)** Dependence of the anodic peak currents of cyclic voltammograms of Coenzyme Q-0 recorded in ammonia buffers (pH = 7.40) on the square root of the applied scan rates.

Figure S1



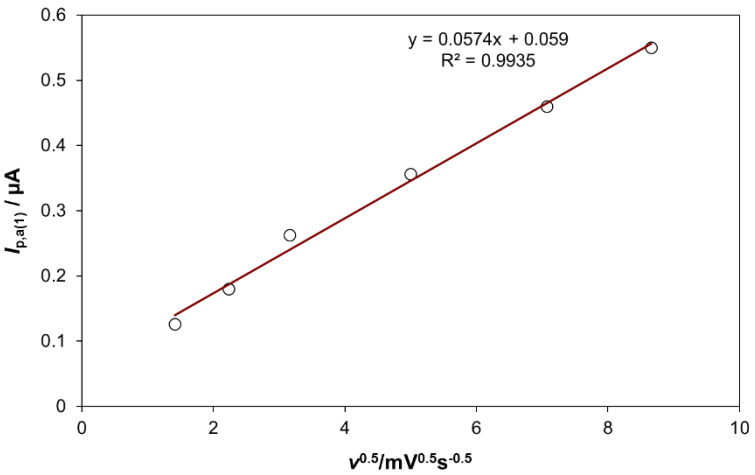
Supplementary figure 2: (A-D) UV-VIS spectra of CoQ-0 recorded in buffered and non-buffered aqueous solution with different pH values.

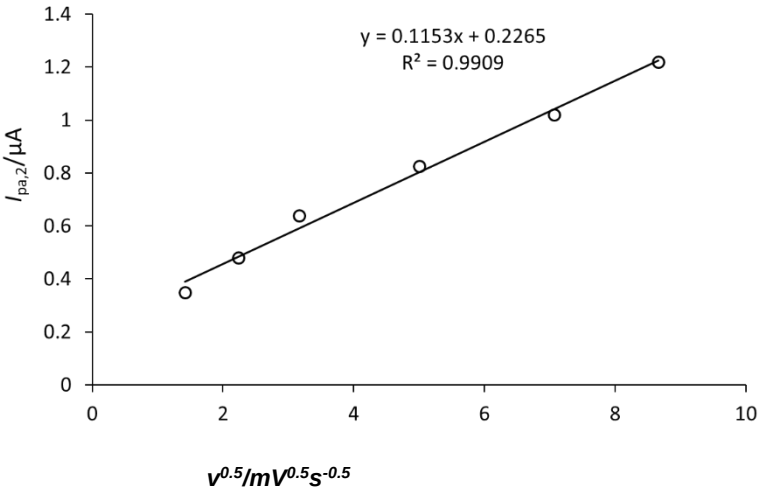
Figure S2



Supplementary figure 3: Scan rate analysis of 0.5 mmol/L Coenzyme Q-0 recorded in pH of 7.00 in non-buffered solutions

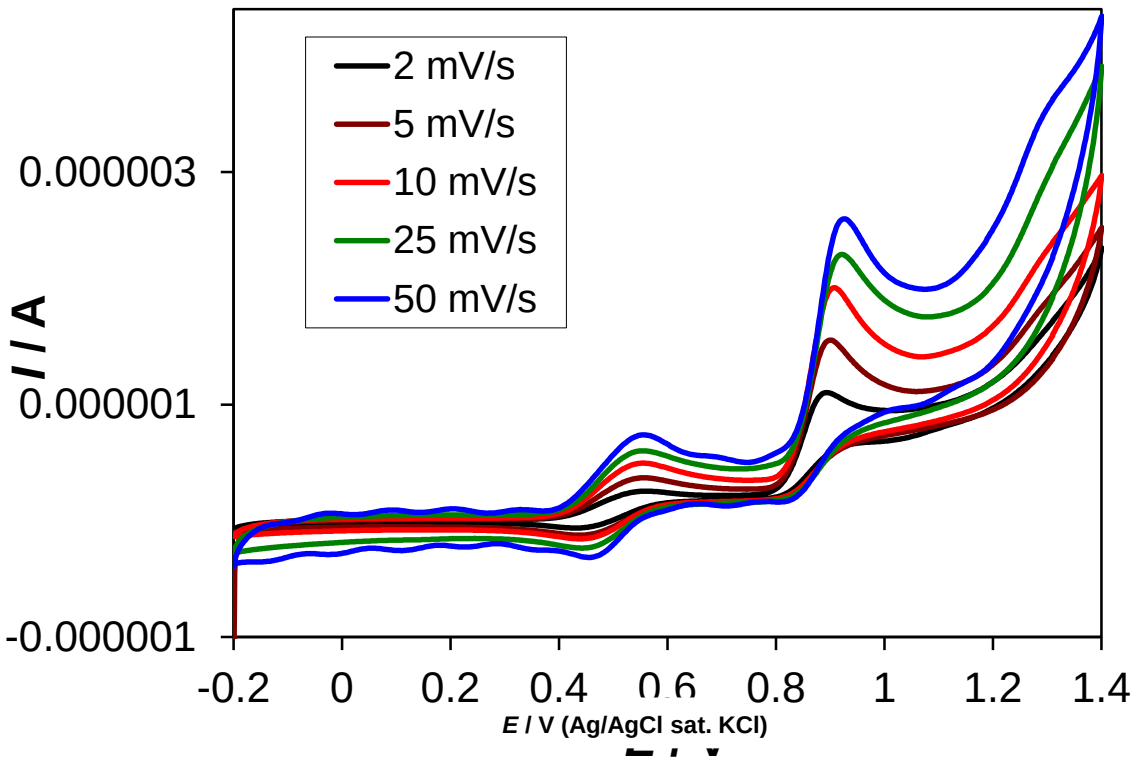
Figure S3


y = 0.0574x + 0.059
R² = 0.9935
$I_{p,a(1)}$ / µA
$v^{0.5}/mV^{0.5}s^{-0.5}$


y = 0.1153x + 0.2265
R² = 0.9909
$I_{pa,2}$/µA
$v^{0.5}/mV^{0.5}s^{-0.5}$

Supplementary figure 4: The color of CoQ-0 solution (*c* = 1 mmol/L) directly after dissolving it in aqueous solution with pH = 7.00 (left), and after its reaction in 0.1 mol/L NaOH for 60 minutes followed by re-titration with HCl to pH = 7.00 (right).

Figure S4



Supplementary figure 5: Cyclic voltammograms of 0.5 mmol/L ABTS recorded in pH of 7.00 at different scan rates.

Figure S5

REFERENCES

[1] B.L. Trumpower, Function of Quinones in Energy Conserving Systems, Academic Press Inc., New York, 1982.
[2] E.R. Price, S.C. Johnson, Quinones: Occurrence, Medicinal Use and Physiological Importance, Nova Science Pub Inc., 2013
[3] H. Nohl, W. Jordan, R.J. Youngman, Quinones in Biology: Functions in Electron Transfer and Oxygen Activation, Adv. Free Radic. Biol. Med. 2 (1986) 211–279.
[4] J. Swenton, Chemistry of Quinones, John Wiley, New York, 1988.
[5] R.L. Lester, F.L. Crane, Y. Hatefi, Coenzyme Q—a new group of quinones, J. Am. Chem. Soc. 80 (1958) 4751–4752.
[6] F.L. Crane, Biochemical functions of coenzyme Q10, J. Am. Coll. Nutr. 20 (2001) 591–598.
[7] A. Roetig, E.-L. Appelkvist, V. Geromel, D. Chretien, N. Kadhom, P. Edery, M. Lebideau, G. Dallner, A. Munnich, L. Ernster, P. Rustin, Quinone-responsive multiple respiratory-chain dysfunction due to widespread coenzyme Q10 deficiency, Lancet 356 (2000) 391–395.
[8] H.P. Indo, H.-C. Yen, I. Nakanishi, K.-i. Matsumoto, M. Tamura, Y. Nagano, H. Matsui, O. Gusev, R. Cornette, T. Okuda, Y. Minamiyama, H. Ichikawa, S. Suenaga, M. Oki, T. Sato, T. Ozawa, D.K.S. Clair, H.J. Majima, A mitochondrial superoxide theory for oxidative stress diseases and aging, J. Clin. Biochem. Nutr. 56 (2015) 1–7.
[9] D. Abdali, S.E. Samson, A.K. Grover, How effective are antioxidant supplements in obesity and diabetes? Med. Princ. Pract. 24 (2015) 201–215.
[10] A.K.S.A. Mortensen, P. Dolliner, K.J. Filipiak, D. Pella, U. Alehagen, G. Steurer, G.P. Littarru, F. Rosenfeldt, Oral abstract session clinical: the effect of coenzyme Q10 on morbidity and mortality in chronic heart failure. Results from the Q-SYMBIO study, Eur. J. Heart Fail. 12 (2013) S20.
[11] N. Gueven, K. Woolley, J. Smith, Border between natural product and drug: comparison of the related benzoquinones idebenone and coenzyme Q10, Redox Biol. 4 (2015) 289–295.
[12] H.H. Szeto, L.P. James, A.J. Atkinson, Mitochondrial pharmacology: its future is now, Clin. Pharmacol. Ther. 96 (2014) 629–633.
[13] S. Jaber, B.M. Polster, Idebenone and neuroprotection: antioxidant, pro-oxidant, or electron carrier? J. Bioenerg. Biomembr. 47 (2014) 111–118.
[14] J.Wang, S. Li, T. Yang, J. Yang, Synthesis and antioxidant activities of Coenzyme Q analogues, Eur. J. Med. Chem. 86 (2014) 710–713.

11] N. Gueven, K. Woolley, J. Smith, Border between natural product and drug: comparison of the related benzoquinones idebenone and coenzyme Q10, Redox Biol. 4 (2015) 289–295.
[12] H.H. Szeto, L.P. James, A.J. Atkinson, Mitochondrial pharmacology: its future is now, Clin. Pharmacol. Ther. 96 (2014) 629–633.
[13] S. Jaber, B.M. Polster, Idebenone and neuroprotection: antioxidant, pro-oxidant, or electron carrier? J. Bioenerg. Biomembr. 47 (2014) 111–118.
[14] J.Wang, S. Li, T. Yang, J. Yang, Synthesis and antioxidant activities of Coenzyme Q analogues, Eur. J. Med. Chem. 86 (2014) 710–713.
[15] L.N. Laredj, F. Licitra, H.M. Puccio, The molecular genetics of coenzyme Q biosynthesis in health and disease, Biochimie 100 (2014) 78–87.
[16] H.M. Cocheme, G.F. Kelso, A.M. James, M.F. Ross, J. Trnka, T. Mahendiran, J. Asin-Cayuela, F.H. Blaikie, A.R. Manas, C.M. Porteous, V.J. Adlam, R.A. Smith, M.P. Murphy, Mitochondrial targeting of quinones: therapeutic implications, Mitochondrion 7 (Suppl.) (2007) S94–102.
[17] D. Graham, N.N. Huynh, C.A. Hamilton, E. Beattie, R.A.J. Smith, H.M. Cochemé, M.P. Murphy, A.F. Dominiczak, Mitochondria-targeted antioxidantmitoq10 improves endothelial function and attenuates cardiac hypertrophy, Hypertension 54 (2009) 322–328.
[18] A.M. James, R.A.J. Smith,M.P. Murphy, Antioxidant and prooxidant properties ofmitochondrial Coenzyme Q, Arch. Biochem. Biophys. 423 (2004) 47–56.
[19] I. Bogeski, R. Gulaboski, R. Kappl, V. Mirceski, M. Stefova, J. Petreska, M. Hoth, Calcium binding and transport by coenzyme Q, J. Am. Chem. Soc. 133 (2011) 9293–9303.
[20] R. Gulaboski, I. Bogeski, V. Mirceski, S. Saul, B. Pasieka, H.H. Haeri, M. Stefova, J.P. Stanoeva, S. Mitrev, M. Hoth, R. Kappl, Hydroxylated derivatives of dimethoxy-1,4-benzoquinone as redox switchable earth-alkaline metal ligands and radical scavengers, Sci. Rep. 3 (2013).
[21] R. Petrucci, E. Giorgini, E. Damiani, P. Carloni, G. Marrosu, A. Trazza, G.P. Littarru, L. Greci, A study on the interactions between coenzyme Q 0 and superoxide anion. Could ubiquinones mimic superoxide dismutase (SOD)? Res. Chem. Intermed. 26 (2000) 269–282.
[22] K. Takehara, H. Takemura, Y. Ide, S. Okayama, Electrochemical-behavior of ubiquinone and vitamin-K incorporated into normal-alkanethiol molecular assemblies on a gold electrode, J. Electroanal. Chem. 308 (1991) 345–350.
[23] M.D. Greaves, A. Niemz, V.M. Rotello, Control of one- versus two-electron reduction of ubiquinone via redox-dependent recognition [11], J. Am. Chem. Soc. 121 (1999) 266–267.
[24] G.J. Gordillo, D.J. Schiffrin, Redox properties of ubiquinone (Uq10) adsorbed on a mercury-electrode, J. Chem. Soc. Faraday Trans. 90 (1994) 1913–1922.
[25] G.J. Gordillo, D.J. Schiffrin, The electrochemistry of ubiquinone-10 in a phospholipid model membrane, Faraday Discuss., (2000) 89-107; (discussion 171-190).
[26] P.S. Guin, S. Das, P.C. Mandal, Electrochemical reduction of quinones in different media: a review, Int. J. Electrochem. 2011 (2011) 22.

[28] A.A. Franke, C.M. Morrison, J.L. Bakke, L.J. Custer, X. Li, R.V. Cooney, Coenzyme Q10 in human blood: native levels and determinants of oxidation during processing and storage, Free Radic. Biol. Med. 48 (2010) 1610–1617.
[29] O.S. Ksenzhek, S.A. Petrova, M.V. Kolodyazhny, Redox properties of ubiquinones in aqueous-solutions, Bioelectrochem. Bioenerg. 9 (1982) 167–174.
[30] R.H. Crabtree, The Organometallic Chemistry of the Transition Metals, sixth ed., 2014.
[31] R.G. Pearson, Hard and soft acids and bases, J. Am. Chem. Soc. 85 (1963) 3533–3539.
[32] M. Witwicki, J. Jezierska, DFT insight into o-semiquinone radicals and Ca2+ion interaction:
structure, g tensor, and stability, Theor. Chem. Accounts 132 (2013).
[33] R.L. Compton, E, K.R. Ward, Understanding Voltammetry: Simulation of Electrode Processes, Imperial College Press, 2014.
[34] D.D. Deford, D.N. Hume, The determination of consecutive formation constants of complex ions from polarographic data, J. Am. Chem. Soc. 73 (1951) 5321–5322.
[35] V. Mirceski, R. Gulaboski, M. Lovric, I. Bogeski, R. Kappl, M. Hoth, Square-wave voltammetry:
a review on the recent progress, Electroanalysis 25 (2013) 2411–2422.
[36] U. Eisner, E. Gileadi, Anodic oxidation of hydrazine and its derivatives. Part I. The oxidation
of hydrazine on gold electrodes in acid solutions, J. Electroanal. Chem. 28 (1970) 81–92.
[37] R. Gulaboski, V. Mirceski, New aspects of the electrochemical-catalytic (EC') mechanism in square-wave voltammetry, Electrochim. Acta 167 (2015) 219–225.
[38] R. Gulaboski, V. Mirčeski, S. Mitrev, Development of a rapid and simple voltammetric method to determine total antioxidative capacity of edible oils, Food Chem. 138 (2013) 116–121.

REFERENCES

38. 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.

39. S. Petkovska, **R. Gulaboski*, "**Theoretical Analysis of a Surface Catalytic Mechanism Associated with Reversible Chemical Reaction Under Conditions of Cyclic Staircase Voltammetry**", *Electroanalysis*** 32 (**2020**) **10.1002/elan.201900698** https://onlinelibrary.wiley.com/doi/10.1002/elan.201900698

40. Rubin Gulaboski, Electrochemistry in 21st Century-Future Trends and Perspectives, ***Journal of Solid State Electrochemistry*** 24 (**2020) DOI: 10.1007/s10008-020-04550-0**

41. Rubin Gulaboski, Pavlinka Kokoskarova, Sofija Petkovska, "Analysis of Drug-Drug Interactions with Cyclic Voltammetry-An Overview of Relevant Theoretical Models and Recent Experimental Achievments", ***Analytical and Bioanalytical Electrochemistry*** 12 (**2020**) 345-364

42. 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.**

43. Sofija Petkovska, **Rubin Gulaboski***, "Diffusional Electrochemical Catalytic (EC') Mechanism Featuring Chemical Reversibility of Regenerative Reaction-Theoretical Analysis in Cyclic Voltammetry", ***Croatica Chemica Acta*** 92 (4) (**2019**) 1-8

44. 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)** 2488-2506.

45. **Rubin Gulaboski**, 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.**

46. S. Petkovska, **Rubin Gulaboski***, Theoretical Analysis of a Surface Catalytic Mechanism Associated with Reversible Chemical Reaction under Conditions of Cyclic Staircase Voltammetry, ***Electroanalysis*** 32 (**2020**).

47. 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

48. 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*** **32 (2020) 333-344.**

49. R. Gulaboski, "Theoretical contribution towards understanding specific behaviour of "simple" protein-film reactions in square-wave voltammetry", ***Electroanalysis,*** 31 (**2019**) 545-553 ISSN 1040-0397

50. **. 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.

51. **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.

52. **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.

53. **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

54. **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.

55. 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.