Methodological development of voltammetry: theory and application

Valentin Mirceski

[1] *Department of Inorganic and Analytical Chemistry, University of Lodz, Tamka 12, 91-403 Lodz, Poland*
[2] *Institute of Chemistry, Faculty of Natural Sciences and Mathematics, "Ss Cyril and Methodius" University in Skopje, P.O. Box 162, 1000 Skopje, North Macedonia*
[3] *Research Center for Environment and Materials, Macedonian Academy of Sciences and Arts, Bul. Krste Misirkov 2, 1000 Skopje, North Macedonia*
valentin@pmf.ukim.mk

This lecture explores the development of innovative electroanalytical techniques designed to advance applications in electroanalytical chemistry. After revisiting the foundational aspects of electrochemical experiments and the key factors influencing analytical sensitivity, several novel techniques are proposed, primarily from the perspective of square-wave voltammetry (SWV). Two new forms of SWV are introduced: double-sampled differential SWV and multi-sampled SWV, both based on a novel current sampling methodology. This approach is further expanded to simplify SWV into pulse-form chronoamperometry, resulting in square-wave chronoamperometry—a versatile technique enabling multi-frequency and multi-amplitude characterization of electrode reactions within a single experiment. Additionally, a new pulse-voltammetric technique is proposed, integrating elements of differential pulse voltammetry and SWV. Various electrode mechanisms are analyzed using these new techniques, with theoretical data critically evaluated to identify the optimal technique for specific mechanisms based on analytical performance and suitability for rapid, comprehensive kinetic and mechanistic characterization. Experimental data from model systems using these techniques are also presented.