STUDIES ON ELECTRODE PROCESSES IN STRIPPING ANALYSIS USING SQUARE-WAVE VOLTAMMETRY: THEORY AND APPLICATION

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This paper presents mechanistic studies on electrode processes in stripping trace and ultratrace analysis under square-wave voltammetry conditions from both theoretical and experimental points of view. Besides adsorptive stripping and cathodic stripping mechanisms [1], a special attention is given to the anodic stripping processes at bismuth-film electrodes [2]. Several electrode mechanisms are analyzed, including those coupled with adsorption equilibria and lateral interactions of selected metal analytes within the deposited electroactive film. An attempt is made to identify a critical set of voltammetric properties upon which diagnostic criteria can be established for differentiation between particular electrode mechanisms. Theoretical data are analyzed in terms of dimensionless critical voltammetric parameters related to electrode kinetics, mass transfer, adsorption equilibria, and possible lateral interactions. Several strategies for electrode kinetic measurements are presented. The study mainly focuses on the role of the height of the potential pulses used in square-wave voltammetry that enables kinetic measurements at a constant scan rate. Theoretical considerations outlined are illustrated using experimental data collected at bismuth-film electrodes.

[1] V. Mirceski, S. Komorsky Lovric, M. Lovric, Square-wave voltammetry: theory and application, (Ed.) F. Scholz, Springer Verlag, Heidelberg, 2007.

[2] V. Mirceski, S. B. Hocevar, B. Ogorevc, R. Gulaboski, I. Drangov, Anal. Chem., 84 (2012) 4429.