

Theory of Cathodic stripping square-wave voltammetry

M. LOVRIC, I. PIZETA and S. KOMORSKY-LOVRIC

Center for Marine Research, "Rudjer Boskovic" Institute, ZAGREB (Croatia)

Kinetic parameters for redox reactions of reactants immobilized at the working electrode surface are k_s/f , if a product is also immobilized, and $k_s/f^{0.75}$ if the product is soluble.

Cathodic stripping voltammetry is a valuable analytical method for the determination of traces of electroinactive anions which can form a thin film of insoluble salt on the surface of a mercury, or a silver working electrode (1-5). The method has been used to analyse traces of halides (1,3) sulfide (2,4), selenide (5) and some other substances (1). Detection limits reported for different anions vary from $5 \cdot 10^{-9}$ M to $5 \cdot 10^{-7}$ M, depending on the stripping technique applied. One of the most advanced electroanalytical techniques, the square-wave voltammetry, is especially sensitive to quasireversible redox reactions of reactants immobilized at the working electrode surface (6). The immobilization can be achieved by different processes, such as the direct, or anion-induced adsorption, the electrodeposition of metal atoms on solid electrodes and insoluble salts on the surface of mercury and silver electrodes, the amalgam formation within the thin mercury film covered glassy-carbon electrode, or by the abrasive transfer of traces of solid analyte onto a surface of a graphite rod. All these processes can serve as a preconcentration step of an electroanalytical method and usually are followed by the cathodic, or the anodic square-wave stripping scan. A model of cathodic stripping square-wave voltammetry of insoluble mercuric salt accumulated at the mercury drop electrode surface is developed.

Theoretical relationships between the properties of responses and the parameters of both the redox reaction and the SWV signal are analysed. Both reversible and quasireversible redox reactions are considered and the nature of the so called "quasireversible maximum" is discussed. Similarity between responses of reactants which are immobilized by different processes is demonstrated. The kinetic parameters of these redox reactions are shown to be k_s/f , if the product is also immobilized, and $k_s/f^{0.75}$ if the product is soluble. Here, K_s is the standard reaction rate constant and f is the SW frequency. Numerical simulations are compared qualitatively with the SW stripping voltammograms of electrodeposited Hg_2Cl_2 and Hg_2Br_2 . The application of the method to the measurements of halides in the seawater and S^{2-} in anaerobic waters is discussed.

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