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Electroanalytical Methods

Theory, Instrumentation and Application

RMC d.o.o., Zagreb, Croatia, 1995, 420 pp.

Electrochemical methods are included not only in a number of undergraduate and postgraduate courses at universities, but they are often useful methods applied in numerous research laboratories. Therefore, a book devoted to detailed theoretical, as well as practical, aspects of electroanalytical methods is more than welcome.

This textbook is derived from the author's course in Electrochemical Analysis at the University of Zagreb and represents a competent and comprehensive overview of the described methods. It is written in the Croatian language and, although it is aimed at graduate students, the book will be useful to those who use electroanalytical methods either in research or in product control, environment control *etc.* It will certainly be of help to those who often meet requirements for trace analysis, like food technologists, pharmacologists, biochemists, and to those who use electroanalytical methods as a routine. The content of the book is as follows:

Chapter 1 (64 pp.) gives an overview of the basic theories and it contains a description of: Galvanic cell. Diffusion potential. Electromotive force. Electrode potential. Nature of electrode potential. Standard electrode potential. Standard hydrogen electrode. Measurements of electrode potential. Standard free energy of the cell reaction. Activity and activity coefficient. Formal potential. Electrolysis, Faraday's law. Reference electrode(s). Calomel electrode(s). Silver-silver chloride electrode. Weston cell(s). Double layer. Electrode reaction rate. Effect of mass transfer on electrode current. Diffusion current. Current-potential curve. Electrode current in nonstationary condition. Overview of electroanalytical methods.

Chapter 2 (35 pp.) provides a coverage of the instrumentation used in electroanalytical methods: Operational amplifier(s). Inverter. Voltage adder. Voltage follower. Current follower. Integrator. Differentiator. Convertors of current to voltage. Sample and hold amplifier. Comparators. Precision volt-

age source. Potentiostat(s). Booster amplifier. Galvanostat(s). Digital instrumentation. Digital voltmeter.

Chapter 3 (86 pp.) is devoted to Potentiometry and Potentiometric Titrations and describes: Indicator electrode(s). Metallic indicator electrode(s). Selective electrode(s). Glass electrode. Glass electrode(s) for other cations. Homogeneous and heterogeneous solid-state membrane electrodes. Liquid-membrane electrode(s). Gas-sensors. Bio-sensors. Measuring the EMF of electrochemical cell. Laboratory potentiometer. pH meter and pIon meter. Potentiograph(s). Determination of activity by direct potentiometry. Determination of pH. Hydrogen electrode. Quinhydrone electrode. Metal-metal oxide electrodes. Glass electrode. ISFETs-sensors. Potentiometric titrations. Determination of the equivalent volume. Titration to a fixed potential or pH. Gran titrations. Linear titration plots. Acid-base titrations. Acid-base titrations in nonaqueous media. Precipitation titrations. Compleximetric titrations. Redox titrations.

Chapter 4 (68 pp.) brings in polarographic methods: Dropping mercury electrode. Capillary characteristics. Diffusion current. Ilkovič equation. Heyrovsky-Ilkovič equation. Residual and charging current. Migration current. Irregularities in limiting current-polarographic maxima. Effect of ohmic resistance on reversible reaction. Effect of pH on reversible waves. Quasi-reversible and irreversible waves. Multicomponent systems and multistep charge transfer. Kinetically controlled limiting current. Catalytic wave. ECE reaction. Limiting current controlled by adsorption or other surface phenomena. Instrumentation. Tast polarography. Pulse polarography. Differential pulse polarography.

Linear sweep voltammetry and cyclic voltammetry are described in chapter 5 (39 pp.): Principles. Voltammogram in terms of dimensionless current function. Peak current and potential. Cyclic voltammogram for reversible reaction. Effect of uncompensated resistance. Quasi-reversible reaction. Multicomponent systems and multistep charge transfer. Influence of coupled chemical reactions. CE reaction. ECE reactions. Influence of adsorption. Convolution or semi-integral techniques. Instrumentation. Working electrodes. Hydrodynamic methods. Rotating disk electrode. Rotating ring-disk electrode. Rotating cylindrical electrode.

Electrogravimetric methods and coulometric measurements are described in chapter 6 (17 pp.) and chapter 7 (21 pp.) with emphasis on: Deposition potential. Controlled potential methods. Current-time behaviour. Controlled current methods. Electroseparation. Controlled potential coulometric determinations. Controlled current coulometry. Electrolysis cells. Applications.

Chapter 8 (19 pp.) depicts electrometric end point detection: Potentiometric methods with one electrode. Two electrode potentiometry. Amperometric method with two indicator electrode. Amperometric methods with one indicator electrode.

Stripping analysis is described in chapter 9 (19 pp.) with emphasis on: Anodic stripping voltammetry. Principles and theory. Working electrodes. Instrumentation. Cathodic stripping voltammetry. Potentiometric stripping analysis. Adsorptive stripping voltammetry.

Chapter 10 (27 pp.) is devoted to conductometry with focus on: Electrolytic conduction. Ionic conductivity. Molar conductivity. Variation of molar conductivity with concentration. Transport numbers. Ionic conductivity of aqueous H^+ and OH^- . Conductivity cells. Instrumentation. Applications. Acid-base conductometric titrations. Other conductometric titrations. High-frequency methods.

All the chapters provide a useful summary of the recent work in the fields covered. The book is written at a level that undergraduate students can cope with. The mathematical content of the subjects is reduced to the level of putting one in the way of practical application of the method. The book is well illustrated and contains 148 figures and diagrams. Relevant literature on the specific subject is given at the end of each chapter.

The book has all the qualities that newcomers to the subject, and experienced alike, will find very useful.

Ljerka Duić