Laboratory Techniques in Electroanalytical Chemistry

Second Edition, Revised and Expanded

edited by

Peter T. Kissinger

William R. Heineman

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Preface

The text that had the most influence on the education of American electrochemists between the late 1950s and the late 1960s was Delahay's *New Instrumental Methods in Electrochemistry* (1954). For well over a decade, this book played a dominant role in placing finite current electroanalytical chemistry on its modern course—beyond the titrations, coulometry, polarography, and electrogravimetry of an earlier age. The membrane-covered oxygen electrode developed by Clark in 1955 rapidly became one of the most important analytical tools. Modern engineering mathematics began to conquer mass transport problems in the 1950s, and toward the end of that decade, operational amplifiers revolutionized experimental electrochemistry.

In the 1960s, modern organic, inorganic, and biological electroanalytical chemistry advanced rapidly behind the advent of cyclic voltammetry, pulse chronoamperometry, rotating ring disk electrodes, and the use of electron spin resonance and optical measurements coupled to electrochemical experiments. After a burst of tremendous activity, it became clear during this period that chronopotentiometry was not competitive with controlled-potential techniques. In the second half of the 1960s, thin-layer electrochemistry had its heyday and electrodes other than mercury began to attract serious attention. It was discovered that platinum was surprisingly well behaved for studies in nonaqueous solvents, and even the likes of glassy carbon and carbon paste, to say nothing of thin films of metals and semiconductors deposited on glass, could actually solve chemical problems. Ralph Adams' book, *Electrochemistry at Solid Electrodes* (1969), surprised more than a few who did not believe it was possible. Anodic stripping voltammetry became a commercial reality and even was able to compete, for some elements, with atomic spectroscopy. Polarography gradually diminished in importance for practical analysis through the early 1960s. A little company in Princeton, New Jersey, brought it out of hibernation by making differential pulse polarography commercially available via the first significant op-amp-based electrochemical instruments.

The 1970s saw electroanalytical chemistry refine its fundamental basis and develop more powerful and more reliable instrumentation. Chemistry became more important than technique. For the first time, electrochemists had a significant clientele of users whose primary interest was not electrochemistry per se. Two important fundamental new directions in the 1970s were toward chemically modified electrodes and photoelectrochemistry. In addition, high-vacuum surface spectroscopies began to play a serious role in electrochemical investigations. A significant new development of practical analytical importance was the use of electrochemical flow cells for liquid chromatography, a development that introduced thousands of pharmacologists, clinical chemists, and toxicologists to electrochemistry for the first time. A small company in West Lafayette, Indiana, made this methodology easily accessible to non-electrochemists.

In the 1980s, it became widely recognized that there are advantages from doing electrochemistry at very small electrodes. In the 1990s, benefits from speed and access to electrochemistry in unusual media make microelectrodes quite routine. It is interesting that the microelectrodes of today are at least a thousand times smaller than the "microelectrodes" of the '30s, '40s, and '50s. What will the microelectrodes of tomorrow look like?

This book was conceived in 1970 by Peter Kissinger to provide a means of enabling a neophyte in electroanalytical chemistry to get started in the lab. During preparation of the first edition, the emphasis was expanded to include a pedagogical component. In the 12 years since the first edition, we've received a number of suggestions based on actual classroom experience. Many of these have been incorporated in this second edition.

These days, research papers are necessarily brief with respect to experimental insights. Review chapters are often replete with unexplained and generally confusing jargon and mathematics. Textbooks on instrumental methods have their good practical moments, but such moments are usually short, incomplete, and often out of date. None of these sources really does justice to the limited selection of material for the "bench chemist" wanting to get things moving in a hurry.

The emphasis of this book is entirely on analytical, mechanistic (homogeneous), kinetic (homogeneous), and synthetic (laboratory-scale) applications. Physical electrochemistry is not a direct concern, and equilibrium methods (potentiometry) are intentionally omitted. There is no attempt to include specific chemical examples except where they are particularly illustrative and have pedagogical value. No extensive review of the original literature is included, but references to key reviews and papers of historical interest are emphasized. Authors have selected experimental approaches that work best and have commented freely on outmoded or underdeveloped methods. The authors and editors have made value judgments that undoubtedly will disappoint some readers.

Electrochemistry is a very broad subject. Those interested in batteries, fuel cells, corrosion, membrane potentials, and so forth will not satisfy their needs here.

The organization of the book flows from principles through methodology to applications. Chapters 2–5 are devoted to what the editors perceive as the most commonly used techniques in electroanalytical chemistry today. These techniques have passed the development stage and can now be considered routine. The approach in these chapters is designed to give the readers an intuitive understanding of each technique without mathematical rigor. This is achieved by considering the excitation signal for each technique and the resulting concentration-distance profiles that determine the consequent response signal. Value judgments are given to permit an educated selection of techniques to use in a given situation. Chapter 2 provides the fundamental concepts that are important throughout the book. It is the editors' opinion that Chapters 2–5 are suitable for use in graduate-level introductory courses in electroanalytical chemistry.

Instrumentation for selected aspects of electroanalytical chemistry is covered in Chapters 6–8. Although computers have made a tremendous impact on electroanalytical instrumentation, many aspects of these chapters are timeless. The basic configurations of a potentiostat have not changed since the early 1960s, although the electronic components themselves are dramatically different! Learn to build your own potentiostat in Chapter 6, then see how to fine-tune it in Chapter 7.

Chapters 9–19 deal with some practical aspects of electroanalytical chemistry. These chapters are aimed at giving the novice some insight into the nuts and bolts of electrochemical cells and solutions. In this second edition, further emphasis has been given to obtaining and maintaining clean solutions, and new chapters have been added on chemically modified electrodes and electrochemical studies at reduced temperature.

In the early 1970s, many electrochemists learned about digital simulation from Steve Feldberg's papers and Joseph Maloy's "underground" chapter, which is now revised as Chapter 20. This field is 30 years old, and only recently has commercial software extended its reach to a wider audience.

Chapters 21–23 are for the neophyte trying to determine which technique can be useful for unraveling a mechanism and/or preparing a strategy for synthesis. The virtues of the key techniques described in Chapter 3 are illustrated here with specific chemical examples.

Chapters 24–29 are a potpourri of electroanalytical techniques and applications. Hybrid techniques in which electroanalytical chemistry is combined with luminescence, spectroscopy, or chromatography are discussed.

It is risky to predict the future, but the 1990s continue the trends of the 1970s: more chemistry; more practical organic, inorganic, and biochemical problem-solving; and more detailed knowledge of the chemical nature of the interface and how it can be manipulated to human advantage. Publication of the first edition in 1984 coincided with the 150th anniversary of Faraday's law; there seems no end of uses for this important principle describing the relationship between chemistry and electricity.

We hope that this book is of some use to you in the course of your research, for which we wish you good luck—it certainly helps.

Many people have assisted with this project. We would like to especially thank Peggy Sue Precup for her expertise in organizing numerous details, helping us overcome our English language deficiencies, and coordinating with the publisher. Rod Yoder and David Michell turned many rough figures into comprehensible art. Drs. Adrian Bott and Jon Howell helped refine several chapters and their suggestions were invaluable.

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