Analytical Chemistry

SECOND EDITION

DONALD J. PIETRZYK
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ACADEMIC PRESS

New York - San Francisco London
A Subsidiary of Harcourt Brace Jovanovich, Publishers

Cover photo by Sigrid Owen/D.P.I.

ACADEMIC PRESS, INC.
111 Fifth Avenue, New York, New York 10003

United Kingdom Edition published by
ACADEMIC PRESS, INC. (LONDON) LTD.
24/28 Oval Road, London NW1

ISBN: 0-12-555160-6
Library of Congress Catalog Card Number: 77-80792

PRINTED IN THE UNITED STATES OF AMERICA

Preface

This text is designed for introductory courses in analytical chemistry, especially those shorter courses servicing chemistry majors and life and health science majors.

Before undertaking this revision, we discussed the role of analytical chemistry with advisers from the various academic disciplines whose students traditionally require exposure to analytical courses. Two major objectives arose from these discussions: first, students should become acquainted with the fundamental principles encountered in modern chemical and instrumental methods of analysis, and second, students need to master the basic quantitative skills and techniques required to perform careful measurements in the laboratory. These are essentially the same goals one strives for in a course for chemistry majors.

Within the pages of this text, we attempt to present information that will accommodate both the chemistry major and students majoring in other disciplines without sacrificing the fundamentals of analytical chemistry. This was accomplished by using examples from related disciplines to illustrate the fundamental principles. In addition, most experiments involve procedures identical to those that would be used for real samples. We have not utilized real samples in the experiments, since students at this level need to know if they have obtained the correct answer. This is accomplished best by using well-characterized unknowns.

The text begins with a core of six chapters containing concepts basic to all of analytical chemistry. Five major areas are then emphasized. These include neutralization, potentiometry, spectroscopy, chromatography, and electrolysis methods. Each of these are subdivided into units. The first unit provides the fundamentals specific to that area, while the following units build by presenting additional concepts, applications, calculations, instrumentation, and chemical reactions specific to that particular area.

In neutralization, concepts relating to solutions of strong acids and bases, weak acids and bases, their salts, and buffer solutions are stressed. Final expressions are written when appropriate in a Henderson–Hasselbalch form. All approximations are clearly defined and discussed, while concepts necessary for exact calculations are introduced in chapters dealing with complexes in analytical chemistry.

Oxidation–reduction reactions and instrumental measurements of these reactions via cell potential determinations are discussed in several chapters. Accompanying this section is a broad development of the fundamental concepts and the utility of ion-selective electrodes.

In spectroscopy, atomic and molecular absorption, emission, and luminescence techniques are discussed. The first chapter of this unit provides the fundamental concepts, while subsequent chapters contain specific details for each technique including a discussion of the key components of the required instrumentation. Many practical examples are cited. For example, a comparison is made for the various ways of applying Beer's Law.

Separations are introduced in a series of six chapters with an emphasis on chromatography. The first of these chapters provides a brief survey of separation techniques and introduces the concepts common to all of chromatography. Subsequent chapters describe sheet and column methods, gas chromatography, ion-exchange chromatography, and solvent extraction. All the fundamentals are provided while stressing operational features for each technique.

Electrochemical techniques are introduced but not covered in depth. However, the principles discussed are sufficient to provide a background for understanding electrolysis, coulometry, and polarography.

Complementing these five areas are chapters devoted to the discussion of precipitation and complexes in analytical chemistry. Principles and applications and the relationship of these reactions to the other areas are stressed.

The remaining portion of the book is devoted to the laboratory. In one chapter, the basic laboratory operations are discussed with an emphasis on safety. This is followed by a series of experiments that are designed to reinforce the concepts developed in the chapters.

Many changes have been made in this second edition. Readily apparent ones are the omission of the chapter on radiochemistry and a restructuring of the chapter order. The first was done as a compromise due to the space needed for the many additions, while the second was based on user response. It should be emphasized that after the core of introductory chapters the presentation of the other areas is independent enough to allow instructors to assign chapters according to their own course outline.

Other changes in the second edition deal with improvements in the presentation, addition of new concepts or expansion of previously discussed concepts, and the inclusion of many new examples and problems. In the core of introductory chapters, Chapters 1 to 6, discussion of the problems of method

development and of obtaining standards and suitable samples has been broadened. Particularly noteworthy is that the chapter on Statistical Handling of Analytical Data has been broadened and introduces the concept of propagation of error.

In the chapters dealing with precipitation, neutralization, and oxidation–reduction in analytical chemistry (Chapters 7 to 12), several new examples have been introduced which illustrate typical calculations. Precipitation titrations (Chapter 14) has been separated from the chapter on precipitation methods (Chapter 7) and follows the chapter on ion-selective electrodes. Thus, its development is tied with cell potential measurements. The ion-selective electrode chapter has been broadened to contain more applications, including a discussion of gas-permeable membranes.

Additions in the chapter on spectroscopy include more practical examples and discussion of the instrumental requirements for measurement of atomic emission and related techniques. In chromatography, emphasis has been increased on the discussion of the chromatographic peak and how it is used in qualitative and quantitative determinations. Also, chromatographic detection techniques have been broadened. More examples have been introduced in the chapters on electrochemistry.

Throughout the presentation we have illustrated principles by often referring to biological, clinical, pharmaceutical, environmental, and industrial problems. Not only do they illustrate practical analytical chemistry but they also illustrate the mathematical steps, approximations, etc. encountered in analytical chemistry. Many new practical problems are also included at the end of each chapter.

We would like to thank the many students and colleagues at The University of Iowa for their timely advice, help in proofreading, and constructive criticism. Particularly valuable to us have been the many comments from students and faculty who used the first edition.

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Chapter One Introduction to Analytical Chemistry

TO THE STUDENT

For many of you, this course will be your first experience in analytical chemistry. The authors assume that you are here because you have an interest in chemistry, pharmacy, medical technology, medicine, the biological sciences, or a combination of these fields, and because you want to learn how analytical chemistry will be of use to you. For this reason, the presentation in this book is not designed just for the student majoring in chemistry. Instead, the emphasis is on the knowledge and experimental techniques of analytical chemistry that are most often encountered in the disciplines listed above.

The authors feel that there are four major areas of analytical chemistry that are of importance in their application to diverse scientific disciplines. These areas are spectroscopy, acid–base methods, potentiometry (ion selective electrodes, etc.), and chromatography. Therefore, much of this book is devoted to the background and techniques necessary to understand and carry out these analytical methods.

The goal of the authors in this book is to answer in a concise and logical way the following questions: What is analytical chemistry? What does an analytical chemist do? Where does analytical chemistry fit into the overall scheme of science?

ANALYTICAL CHEMISTRY

Analytical chemistry deals with the solving of qualitative and quantitative problems. In qualitative analysis the goal is to determine *what* the constituents are in the sample while in quantitative analysis the goal is to determine *how*