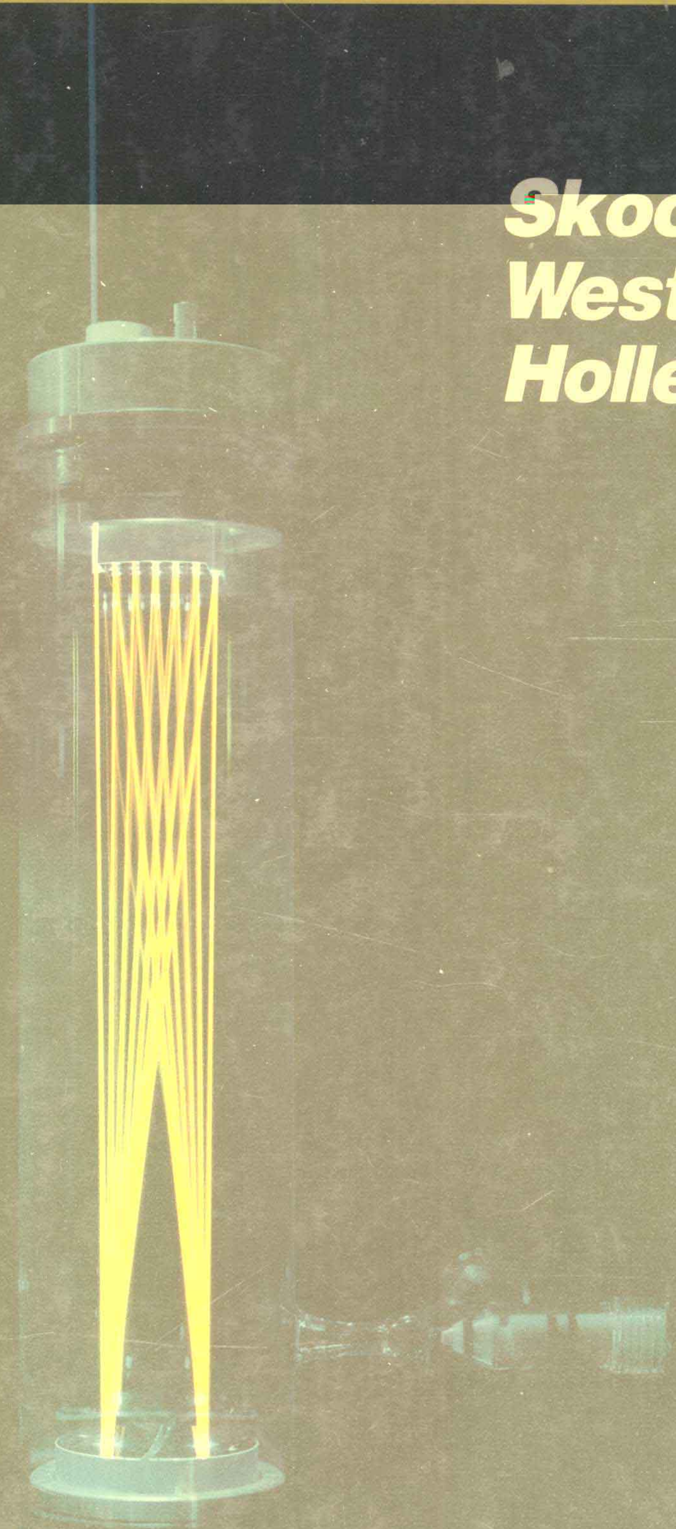
FUNDAMENTALS OF

Analytical Chemistry



Skoog
West
Holler

Fifth Edition

FUNDAMENTALS OF
Analytical Chemistry

FIFTH EDITION

DOUGLAS A. SKOOG
Stanford University

DONALD M. WEST
San Jose State University

F. JAMES HOLLER
University of Kentucky

Saunders Golden Sunburst Series
Saunders College Publishing
New York Chicago San Francisco
Philadelphia Montreal Toronto
London Sydney Tokyo

Requests for permission to make copies of any part of the work should be mailed to: Permissions, Holt, Rinehart and Winston, 111 Fifth Avenue, New York, New York 10003

Text Typeface: ITC New Baskerville
Compositor: General Graphic Services
Acquisitions Editor: John Vondeling
Project Editor: Merry Post
Copy Editor: Irene Nunes
Art Director: Carol Bleistine
Art Assistant: Doris Roessner
Text Designer: Tracy Baldwin
Cover Designer: Lawrence R. Didona
Text Artwork: Larry Ward, Tom Mallon
Production Manager: Harry Dean, Jr.
Assistant Production Manager: Jo Ann Melody

Cover credit: A blue (488.0 nm) beam from an argon-ion laser enters a cell containing a minute quantity of NO_2, a brown gas found in smog. The beam, which is directed through the sample several times by mirrors, is absorbed by the NO_2. The gas subsequently fluoresces to give the bright orange color characteristic of NO_2. The intensity of the color is a measure of the concentration of the pollutant. This is a dramatic illustration of the very sensitive technique of laser-induced fluorescence, which is discussed in Chapter 20. The photo is courtesy of Professor Dennis J. Clouthier of the University of Kentucky.

Printed in the United States of America

Fundamentals of Analytical Chemistry, 5th edition

ISBN 0-03-14828-6

Library of Congress Catalog Card Number: 87-24411

Preface

With the appearance of this edition—the fifth—*Fundamentals of Analytical Chemistry* enters its second quarter century as an introductory textbook on analytical chemistry designed primarily for a course for chemistry majors. During the lifetime of this text, the field of analytical chemistry has teemed with activity as never before: new instruments with previously unheard of sensitivities and selectivities have appeared; new methods for resolving the components of incredibly complex mixtures have been developed; and automation and computer control of the measurement process have become commonplace. Some of these developments have been incorporated in each new edition. Others have not, however, because the time alloted in most chemistry curricula for an introductory course in quantitative analysis is so limited.

In preparing each new edition, we have found ourselves facing the dilemma of what new developments to include and, equally important, what to delete from older editions to make space for the new. In making these decisions, we have adopted the general philosophy of avoiding superficiality by limiting the number of topics covered to those that we believe can be treated in sufficient depth so that the reader can develop a basic understanding of the principles upon which they are based.

Because disagreement is inevitable as to what topics should be included in an elementary analytical course, we have included more material than could possibly be covered in one or two semesters. We have tried to make chapters sufficiently independent so that some can be left out and the order of others changed without a loss in continuity. Thus, the text can be tailored to fit the tastes and prejudices of the individual instructor.

Much of the theoretical discussion in earlier editions of this text has centered on thermodynamics and the application of equilibrium calculations to analytical problems. With the appearance of automated instruments and the increasing importance of analytical methods for determining species of interest in medicine, biochemistry, and ecology, it is evident that a balanced analytical textbook must devote space not only to thermodynamic theory but also to the theory of reaction kinetics. Thus, the reader will find an entirely new chapter in this edition that deals with the kinetics and application of kinetic measurements in analytical chemistry.

Another significant change in this edition is the use of formula weights and molar concentrations in all volumetric calculations. The decision to abandon equivalent weights and normalities brings the text into line with current practice in most analytical journals. (We have, however, included a discussion of the use of normality and equivalent weight in Appendix 9.)

Other topics new to this edition include the operational definition of pH, modern voltammetric techniques including pulse polarography and stripping methods, diode array detectors and multichannel spectroscopic instruments, dc plasma sources for atomic spectroscopy, flow injection methods, fused silica columns for capillary gas chromatography, supercritical-fluid chromatography, and electronic balances. We have also introduced a short section and a laboratory experiment involving a very old technique—weight titrations. With modern top-loading balances and plastic reagent dispensers, a weight titration can be carried out more efficiently and accurately than one based on volumetric measurements.

To provide space for these new topics, we have had to condense or delete several parts of earlier editions. Thus, we have reduced the number of laboratory experiments from 53 to 34. In addition, we have eliminated the chapter devoted to nonaqueous titrations and substituted a brief discussion of this subject in the chapter on applications of acid/base titrations. We have also omitted the discussion of the use of mercury(II) for complex formation titrations and shortened the discussions devoted to the theory of membrane electrodes and to the applications of oxidation/reduction titrations.

In addition to updating the text, we have extensively reorganized the introductory chapters in order to remove redundancies and to present the material in a more logical and concise way. To this end, we have integrated the material dealing with stoichiometry and chemical calculations into two early chapters (3 and 4) dealing with gravimetry and titrimetry (including weight titrimetry). Chapter 5 is devoted to aqueous solution chemistry including simple equilibrium calculations of all types and the use of activities and activity coefficients in such calculations. Chapter 6 extends the discussion of equilibrium to complex systems involving several competing reactions. The chapters that follow dealing with precipitation, neutralization, and complex formation titrations retain the organizational pattern of earlier editions. Many parts of these chapters have been rewritten to improve their clarity and readability, however.

The introductory chapter on oxidation/reduction equilibrium and electrochemical theory (Chapter 12) has been completely rewritten. In addition, the material on polarization phenomena has been moved to the chapter on coulometry where it first becomes of importance. We believe that these changes provide a clearer and more logical presentation of electrochemical theory that will make it more readily absorbed and understood by students. Chapter 15 on potentiometric methods has also undergone reorganization and extensive rewriting with a particular emphasis on clarification of the sign conventions that are used for indicator and reference electrodes.

The organization of the chapters dealing with spectroscopy, chromatography, and preliminary steps in an analysis are substantially the same as in earlier editions. Much of the material in these chapters has also been rewritten for clarity and readability.

The problem sets at the ends of chapters have all been rewritten and, in addition, sets of questions have been introduced. Answers to approximately half of the questions and problems are found at the end of the text. A solutions manual is also available for instructors, and about 60 to 70 transparencies have been developed for use in lectures.

We wish to acknowledge with thanks the comments and suggestions of the following who have reviewed the manuscript for this edition at various stages in its production: Professor John Ganchoff of Elmhurst College; Professor Richard H. Hanson of the University of Arkansas at Little Rock; Professor T. J. Haupert of California State University, Sacramento; Professor John L. Plude of University of Wisconsin, Oshkosh; and Professor Joseph J. Topping of Towson State University. We also wish to thank Professor Elizabeth W. Kleppinger of Berea College, who was kind enough to read page proofs for the first 11 chapters. In addition, we want to thank Professor David K. Roe of Portland State University for bringing to our attention an inconsistency in the sign convention for electrodes that was present in our earlier editions as well as in other analytical textbooks. Finally, we offer particular thanks to Professor Alfred Armstrong of The College of William and Mary in Virginia for again reviewing the manuscript in detail and to Professor Peter F. Linde of San Francisco State University for his thoughtful and cogent comments.

Douglas A. Skoog
Donald M. West
F. James Holler

Contents Overview

Appendixes

Contents

CHAPTER 1

Introduction

Analytical chemistry is concerned with the separation, identification, and determination of the relative amounts of the components (the analytes) making up a sample of matter. A *qualitative analysis* provides information on the chemical identity of the analytes in the sample, whereas a *quantitative analysis* yields numerical information on the relative amount of one or more of these analytes. Generally, qualitative information is required before a quantitative analysis can be undertaken. A separation step is usually a necessary part of both a qualitative and a quantitative analysis.

The principal topics covered in this text are quantitative methods of analysis and methods of analytical separations, although references to qualitative methods appear from time to time.

1A The Role of Analytical Chemistry in the Sciences

Historically, analytical chemistry has played a vital role in the development of science. For example, in 1894 Wilhelm Ostwald wrote

> Analytical chemistry, or the art of recognizing different substances and determining their constituents, takes a prominent position among the applications of science, since the questions which it enables us to answer arise wherever chemical processes are employed for scientific or technical purposes. Its supreme importance has caused it to be assiduously cultivated from a very early period in the history of chemistry, and its records comprise a large part of the quantitative work which is spread over the whole domain of science.

Since 1894, analytical chemistry has evolved from an art to a science, due in no small part to the work of Ostwald himself, and its importance still spreads over all domains of science and technology. To cite but a few examples, consider the following: The effectiveness of smog-control devices is determined by measuring the parts per million of hydrocarbons, nitrogen oxides, and carbon monoxide in the exhaust gases of automobiles. Hyperparathyroidism in human patients is diagnosed by quantitative measurements of ionized calcium in blood serum. The protein content, and thus the nutritional value of foods, is ordinarily established by quantitative determination of their nitrogen content. Periodic analysis of steel during its production permits adjustment in the concentration of such elements as carbon, nickel, and chromium to give a product that has a desired strength, hardness, corrosion resistance, and ductility. Household gas supplies are continuously monitored for their mercaptan content in order to ensure sufficient levels of odorant to warn of leaks. Modern farmers tailor their fertilization and irrigation schedules to meet changing plant needs during the growing season; these needs are gauged from quantitative analyses of the plants and of the soil in which they grow.

In addition to everyday applications of the types just cited, quantitative analytical measurements play a vital role in many research areas in chemistry, biochemistry, biology, geology, and the other sciences. For example, chemists have learned much about mechanisms of chemical reactions through kinetic studies based upon periodic quantitative measurements that reveal the rates at which reactants are consumed or products are formed. Quantitative analyses for potassium, calcium, and sodium ions in the body fluids of animals have permitted physiologists to study the role these ions play in the conduction of nerve signals and the contraction and relaxation of muscles. Materials scientists, in their studies of the behavior of semiconductor devices, have relied heavily upon quantitative analyses of crystalline germanium and silicon for impurities in the concentration range from 1×10^{-6} to 1×10^{-10} percent. Archeologists have found it possible to identify sources of volcanic glasses (obsidian) based upon the concentrations of several minor elements in samples taken from various locations; this knowledge has made it possible to trace prehistoric trade routes for tools and weapons manufactured from obsidian.

Many chemists and biochemists devote a significant part of their time in the laboratory acquiring quantitative information about the systems in which they are interested. For such investigators, analytical chemistry serves as a tool in their scholarly efforts in much the same way that calculus and matrix algebra are tools of the theoretical physicist and ancient languages are tools of the classics scholar.

1B Classification of Quantitative Methods of Analysis

The results of a typical quantitative analysis are based upon two measurements. One is the weight or volume of sample to be analyzed. The second, which normally completes the analysis, is the measurement of some quantity that is proportional to the amount of analyte in that sample. Analytical methods are often classified according to the nature of this final measurement. In a *gravimetric method,* the mass of the analyte or that of some compound chemically related to the analyte is determined. In a *titrimetric method,* the quantity of reagent necessary to react completely with the analyte is measured. *Electroanalytical methods* involve the measurement of such properties as potential, current, resistance, and quantity of charge. *Spectroscopic methods* are based upon measurements of the interaction between electromagnetic radiation (including X-ray, ultraviolet, visible, infrared, microwave, and radio-frequency radiation) and analyte atoms or molecules or upon measurements of the amount of such radiation produced by analytes. Finally, there is a group of miscellaneous methods for completing analyses based upon measuring such properties as mass-to-charge ratio (mass spectrometry), rate of radioactive decay, heat of reaction, rate of reaction, thermal conductivity, optical activity, and refractive index.

1C Steps in a Typical Quantitative Analysis

A typical quantitative analysis involves a sequence of several steps:

1. Selecting a method of analysis
2. Sampling

3. Preparing a laboratory sample
4. Defining replicate samples
5. Preparing solutions of the sample
6. Eliminating interferences
7. Completing the analysis
8. Calculating results and estimating their reliability

In some instances, one or more of these steps can be dispensed with. Ordinarily, however, all play an important role in the success of an analysis.

The first 23 chapters of this text focus on the last two steps of this list. Step 7 involves measuring one of the physical properties mentioned in the previous section, preferably one that is proportional (in most cases) to the amount of analyte in a sample of known weight or volume. Step 8 consists of computing the relative amount of the analyte present in the samples and estimating the reliability of the results.

A brief description of each of these steps is provided at this juncture in order to give the reader an overall perspective on how quantitative chemical data are obtained.

1C-1 Selecting a Method of Analysis

Selecting which method will be used to solve an analytical problem is a vital first step in any quantitative analysis. The choice is sometimes difficult and requires experience as well as intuition on the part of the chemist. An important consideration in selection is the accuracy required. Unfortunately, high reliability nearly always entails a large expenditure of time; the method ultimately chosen may thus of necessity represent a compromise between accuracy and economics.

A second consideration, also related to economic factors, is the number of samples to be analyzed. If there are many, the chemist can afford to use a method that requires such preliminary operations as the assembling and calibrating of instrumental equipment and the preparing of standard solutions. On the other hand, with only a single sample or a few samples, it may be more expedient to select a procedure that avoids such preliminary steps.

Finally, the choice of method is always governed by the complexity of the sample being analyzed and by the number of components for which quantitative information is needed. Further details on choosing a method of analysis are given in Section 26A.

1C-2 Sampling

To produce meaningful information, an analysis must be performed on a sample whose composition faithfully reflects that of the bulk of material from which it is taken. Where the bulk is large and inhomogeneous, great effort is required to procure a representative sample. Consider, for example, a railroad car containing 25 tons of silver ore. Buyer and seller must come to agreement regarding the value of the shipment based primarily upon its silver content. The ore is inherently heterogeneous, consisting of lumps of various size as well as varying silver content. The assay of this shipment will be performed on a sample that has a mass of perhaps 1 g. For the analysis to have significance, it is essential that this small sample have a composition that is representative of the 25 tons (approximately 22,700,000 g) of ore in the shipment. The task of isolating 1 g with any confidence that its composition truly reflects the average composition of the nearly 23,000,000 g from which it is taken is clearly