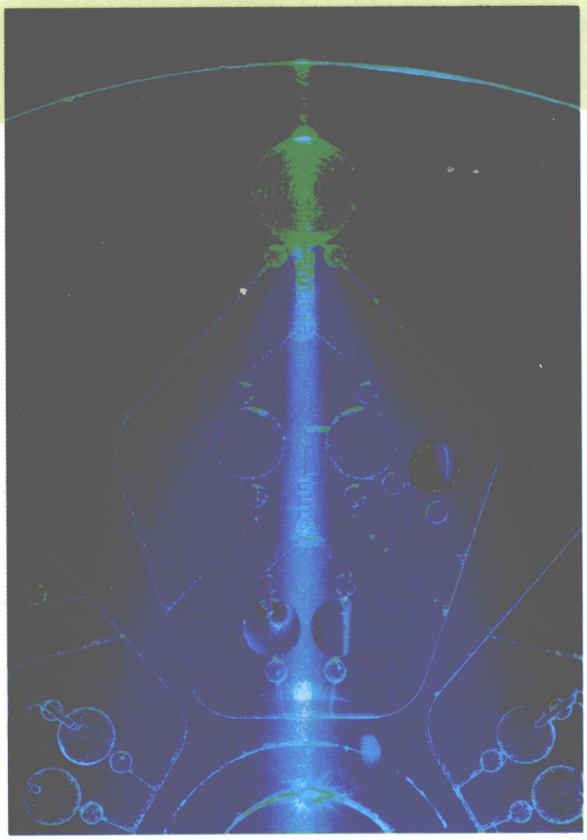
INTERNATIONAL STUDENT EDITION

# *Fundamentals of* Analytical Chemistry

EIGHTH EDITION



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*Fundamentals of*

# Analytical Chemistry

*Eighth Edition*


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Publisher, Chemistry: David Harris
Development Editor: Sandra Kiselica
Assistant Editor: Alyssa White
Editorial Assistants: Jessica Howard and Annie Mac
Technology Project Manager: Ericka Yeoman-Saler
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Marketing Assistant: Melanie Wagner
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Project Manager, Editorial Production: Lisa Weber
Print Buyer: Karen Hunt
Permissions Editor: Elizabeth Zuber

Production Service: Nesbitt Graphics, Inc.
Text Designer: Kim Menning
Photo Researcher: Jane Sanders
Copy Editors: Bonnie Boehme, Linda Van Pelt
Illustrators: Rolin Graphics, Inc., and Nesbitt Graphics, Inc.
Cover Designer: Stephen Rapley
Cover Image: Charles D. Winters
Cover Printer: The Lehigh Press, Inc.
Compositor: Nesbitt Graphics, Inc.
Printer: R.R. Donnelley/Willard

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**Library of Congress Control Number:** 2003105608

ISBN 0-03-035523-0

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**On the Cover:** Image of a plastic disc with micromachined channels and reservoirs used in a total microanalysis system based on a microfluidics centrifuge platform. Capillary burst valves provide control for the release of solutions from the reactant reservoirs (bottom and right) into the channels and reaction chambers (center), and the analyte is monitored optically in the green chamber at the top. For fabrication details, see M. J. Madou, L. J. Lee, S. Daunert, K. W. Koelling, S. Lai, and C-H Shih, "Design and Fabrication of CD-like Microfluidic Platforms for Diagnostics: Microfluidic Functions," *Biomed. Microdev.,* **2001,** *3,* 245–254. For applications of the device, see I. H. A. Badr, R. D. Johnson, M. J. Madou, and L. G. Bachas, "Fluorescent Ion-Selective Optode Membranes Incorporated onto a Centrifugal Microfluidics Platform," *Anal. Chem.,* **2002,** *74,* 5569–5575.

# PREFACE

The eighth edition of ***Fundamentals of Analytical Chemistry,*** like its predecessors, is an introductory textbook designed primarily for a one- or two-semester course for chemistry majors. Since the publication of the seventh edition, the scope of analytical chemistry has continued to evolve, and in this edition we have included many applications to biology, medicine, materials science, ecology, forensic science, and other related fields. The widespread use of computers for instructional purposes has led us to incorporate many spreadsheet applications, examples, and exercises. Our companion book, *Applications of Microsoft® Excel in Analytical Chemistry,* provides students with a tutorial guide for applying spreadsheets to analytical chemistry and introduces many additional spreadsheet operations. We also have added many current topics, such as atomic and molecular mass spectrometry, field-flow fractionation, and chiral chromatography. We have revised many older treatments to incorporate contemporary instrumentation and techniques. We recognize that courses in analytical chemistry vary from institution to institution and depend upon the available facilities, the time allocated to analytical chemistry in the chemistry curriculum, and the desires of individual instructors. We have therefore designed the eighth edition of *Fundamentals of Analytical Chemistry* so that instructors can tailor the text to meet their needs and students can encounter the material on several levels, in descriptions, pictorials, illustrations, and interesting features.

## Objectives

Our major objective of this text is to provide a thorough background in those chemical principles that are particularly important to analytical chemistry. Second, we want students to develop an appreciation for the difficult task of judging the accuracy and precision of experimental data and to show how these judgments can be sharpened by the application of statistical methods. Our third aim is to introduce a wide range of techniques that are useful in modern analytical chemistry. Additionally, our hope is that with the help of this book, students will develop the skills necessary to solve analytical problems in a quantitative manner, particularly with the aid of the spreadsheet tools that are so commonly available. Finally, we aim to teach those laboratory skills that will give students confidence in their ability to obtain high-quality analytical data.

## Coverage and Organization

The material in this text covers both fundamental and practical aspects of chemical analysis. Users of earlier editions will find that we have organized this edition in a somewhat different manner than its predecessors. In particular, we have organized

the chapters into Parts that group together related topics. There are seven major Parts to the text that follow the brief introduction in Chapter 1.

- **Part I** covers the tools of analytical chemistry and comprises seven chapters. Chapter 2 discusses the chemicals and equipment used in analytical laboratories and includes many photographs of analytical operations. A new Chapter 3, "Using Spreadsheets in Analytical Chemistry," is a tutorial introduction to the use of spreadsheets in analytical chemistry. Chapter 4 reviews the basic calculations of analytical chemistry, including expressions of chemical concentration and stoichiometric relationships. Chapters 5, 6, and 7 present topics in statistics and data analysis that are important in analytical chemistry and incorporate extensive use of spreadsheet calculations. Analysis of Variance, ANOVA, is a new topic included in Chapter 7. A new Chapter 8, "Sampling, Standardization, and Calibration," consolidates coverage of sampling, sample handling, external and internal standards, and standard additions, and includes new coverage of calibration and standardization.
- **Part II** covers the principles and application of chemical equilibrium systems in quantitative analysis. Chapter 9 covers the fundamentals of chemical equilibria. Chapter 10 discusses the effect of electrolytes on equilibrium systems. The systematic approach for attacking equilibrium problems in complex systems is the subject of Chapter 11.
- **Part III** brings together several chapters dealing with classical gravimetric and volumetric analytical chemistry. Chapter 12 covers gravimetric analysis. In Chapters 13 through 17, we consider the theory and practice of titrimetric methods of analysis, including acid/base titrations, precipitation titrations, and complexometric titrations. In these chapters, advantage is taken of the systematic approach to equilibria and the use of spreadsheets in calculations.
- **Part IV** is devoted to electrochemical methods. After an introduction to electrochemistry in Chapter 18, Chapter 19 describes the many uses of electrode potentials. Oxidation/reduction titrations are the subject of Chapter 20, while Chapter 21 presents the use of potentiometric methods to obtain concentrations of molecular and ionic species. Chapter 22 considers the bulk electrolytic methods of electrogravimetry and coulometry, while Chapter 23 discusses voltammetric methods including linear sweep and cyclic voltammetry, anodic stripping voltammetry, and polarography.
- **Part V** covers spectroscopic methods of analysis. Basic material on the nature of light and its interaction with matter is presented in Chapter 24. Spectroscopic instruments and their components are described in Chapter 25. The various applications of molecular absorption spectrometric methods are covered in some detail in Chapter 26, while Chapter 27 is concerned with molecular fluorescence spectroscopy. Chapter 28 discusses various atomic spectrometric methods, including atomic mass spectrometry, plasma emission spectrometry, and atomic absorption spectroscopy.
- **Part VI** comprises five chapters dealing with kinetics and analytical separations. Kinetic methods of analysis are covered in Chapter 29. Chapter 30 introduces analytical separations including the various chromatographic methods. Chapter 31 discusses gas chromatography, while high-performance liquid chromatography is presented in Chapter 32. The final chapter in this section, Chapter 33, "Miscellaneous Separation Methods," is new to this edition and includes coverage of supercritical fluid chromatography, capillary electrophoresis, and field-flow fractionation.

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- The final **Part VII** consists of four chapters dealing with the practical aspects of analytical chemistry. Real samples are considered and compared with ideal samples in Chapter 34. Methods for preparing samples are discussed in Chapter 35, while techniques for decomposing and dissolving samples are covered in Chapter 36. Chapter 37 provides detailed procedures for 57 laboratory experiments, covering many of the principles and applications discussed in previous chapters. This chapter is only available as an Adobe Acrobat® PDF file on the **Analytical Chemistry CD-ROM** enclosed in this book or on our Web site at **http://chemistry.brookscole.com/skoogfac/.**

## Flexibility

Because the text is divided into Parts, there is a good deal of flexibility in the use of material. Many of the Parts can stand alone or be taken in a different order. For example, some instructors may want to cover spectroscopic methods prior to electrochemical methods or separations prior to spectroscopic methods.

## Highlights

This edition incorporates many features and methods intended to enhance the learning experience for the student and to provide a versatile teaching tool for the instructor.

**Important Equations.** Equations that we feel are most important have been highlighted with a color screen for emphasis and ease of review.

**Mathematical Level.** Generally, the principles of chemical analysis developed here are based on college algebra. Some of the concepts presented require basic differential and integral calculus.

**Worked Examples.** A large number of worked examples serve as aids in understanding the concepts of analytical chemistry. As in the seventh edition, we follow the practice of including units in chemical calculations and using the factor-label method to check their correctness. The examples also are models for the solution of problems found at the end of most of the chapters. Many of these use spreadsheet calculations, as described next.

New! **Spreadsheet Calculations.** Throughout the book we have introduced spreadsheets for problem solving, graphical analysis, and many other applications. Microsoft® Excel has been adopted as the standard for these calculations, but the instructions could be readily adapted to other programs. Several chapters have tutorial discussions of how to enter values, formulas, and built-in functions. Many other examples worked in detail are presented in our companion book, *Applications of Microsoft® Excel in Analytical Chemistry.* We have attempted to document each stand-alone spreadsheet with working formulas and entries.

New! **Spreadsheet Summaries.** References to our companion book *Applications of Microsoft® Excel in Analytical Chemistry* are given as Spreadsheet Summaries in the text. These are intended to direct the user to examples, tutorials and elaborations of the text topics.

**Questions and Problems.** An extensive set of questions and problems is included at the end of most chapters. Answers to approximately half of the problems are given at the end of the book. Many of the problems are best solved using spreadsheets. These are identified by a spreadsheet icon placed in the margin next to the problem.

New! **Challenge Problems.** Most of the chapters have a challenge problem at the end of the regular questions and problems. Such problems are intended to be

open-ended, research-type problems that are more challenging than normal. These problems may consist of multiple steps, dependent on one another, or may involve library or Web searches to find information. We hope these challenge problems stimulate discussion and extend the topics of the chapter into new areas. We encourage instructors to use them in innovative ways, such as group projects, inquiry-driven learning assignments, and case study discussions.

**Features.** A series of boxed and highlighted Features are found throughout the text. These essays contain interesting applications of analytical chemistry to the modern world, derivation of equations, explanations of more difficult theoretical points, or historical notes. Examples include Breath Alcohol Analyzers (Chapter 7), Antioxidants (Chapter 20), Fourier Transform Spectroscopy (Chapter 25), LC/MS and LC/MS/MS (Chapter 32), and Capillary Electrophoresis in DNA Sequencing (Chapter 33).

**Illustrations and Photos.** We feel strongly that photographs, drawings, pictorials, and other visual aids greatly assist the learning process. Hence, we have included new and updated visual materials to aid the student. Most of the drawings are done in two colors to increase the information content and to highlight important aspects of the figures. Photographs and color plates taken exclusively for this book by renowned chemistry photographer Charles Winters are intended to illustrate concepts, equipment, and procedures that are difficult to illustrate with drawings.

**Expanded Figure Captions.** Where appropriate, we have attempted to make the figure captions quite descriptive so that reading the caption provides a second level of explanation for many of the concepts. In some cases, the figures can stand by themselves much in the manner of a *Scientific American* figure.

New! **Interviews.** Each Part begins with an interview of a noted analytical scientist: Dick Zare (Stanford University), Sylvia Daunert (University of Kentucky), Larry Faulkner (University of Texas), Allen Bard (University of Texas), Gary Hieftje (Indiana University), Isiah Warner (Lousiana State University), and Julie Leary (University of California, Berkeley). The interviews are informal question-and-answer sessions designed to provide information about the scientists and their backgrounds, their reasons for choosing analytical chemistry, their thoughts on the importance of the field, their research areas, and other interesting topics. It is hoped that these interviews will add interest to the subject matter by personalizing some of the topics covered.

New! **Web Works.** At the end of most of the chapters we have included a brief Web Works feature. In this feature, we ask the student to find information on the Web, do online searches, visit the Web sites of equipment manufacturers, or solve analytical problems. These Web Works and the links given are intended to stimulate student interest in exploring the information available on the World Wide Web. These links will be updated regularly on the Brooks/Cole Web site, **http://chemistry.brookscole.com/skoogfac/.**

**Glossary.** The glossary at the end of the book defines the most important terms, phrases, techniques, and operations used in the text. The glossary is intended to provide students with quick access to meanings, without having to search through the text.

**Appendixes and Endpapers.** Included in the appendixes are an updated guide to the literature of analytical chemistry, tables of chemical constants, electrode potentials, and recommended compounds for the preparation of standard materials; sections on the use of logarithms and exponential notation, and on normality and equivalents (terms that are not used in the text itself); and a derivation of the propagation of error equations. The inside front and back covers of this book provide a full-color chart of chemical indicators, a table of molar masses of com-

pounds of particular interest in analytical chemistry, a table of international atomic masses, and a periodic table. In addition, the book has a tear-out reference card for Microsoft® Excel.

## Changes in the Eighth Edition

Readers of the seventh edition will find that the eighth edition has numerous changes in content as well as style and format.

**Content.** Several changes in content have been made to strengthen the book.

- New and exciting chapter opening introductions, accompanied by applied photos, present a relevant example of one of the chapter topics. Examples include stalagmites and stalactites as an illustration of an equilibrium process (Chapter 9), the effects of acid rain (Chapter 16), and the oxidation/reduction properties of chlorophyll (Chapter 19).
- Many chapters have been strengthened by adding spreadsheet examples, applications, and problems. The new Chapter 3 gives tutorials on the construction and use of spreadsheets. Many other tutorials are included in our supplement, *Applications of Microsoft® Excel in Analytical Chemistry.*
- The chapters on statistics (Chapters 5–7) have been updated and brought into conformity with the terminology of modern statistics. Analysis of Variance (ANOVA) is included in Chapter 7. ANOVA is easy to perform with modern spreadsheet programs and quite useful in analytical problem solving.
- A new Chapter 8 consolidates material on sampling and integrates material on calibration and standardization. Methods such as external standards, internal standards, and standard additions are presented in this chapter, and their advantages and disadvantages are discussed.
- The chapter on precipitation titrimetry has been eliminated, and some of the material is included in Chapter 13 on titrimetric methods.
- Chapters 18, 19, 20, and 21 on electrochemical cells and cell potentials have been extensively revised to clarify the discussion and introduce the free energy of cell processes. Chapter 23 has been altered to decrease the emphasis on classical polarography. It now includes a discussion of cyclic voltammetry.
- Chapter 28 in this edition covers atomic mass spectrometry, including inductively coupled plasma mass spectrometry. Flame photometry has been deemphasized.
- In Part VI, Chapter 30 is now a general introduction to separations. It includes solvent extraction and precipitation methods, an introduction to chromatography, and a new section on solid-phase extraction. Chapter 31 contains new material on molecular mass spectrometry and gas chromatography/mass spectrometry. Chapter 32 includes new sections on affinity chromatography and chiral chromatography. A section on LC/MS has been added. A new Chapter 33, "Miscellaneous Separation Methods," has been included. It introduces capillary electrophoresis and field-flow fractionation.
- **Style and Format.** To make the text more readable and student-friendly, we have continued to change style and format.
- We have attempted to use shorter sentences, a more active voice, and a more conversational writing style in each chapter.
- More descriptive figure captions are used whenever appropriate to allow a student to understand the figure and its meaning without having to alternate between text and caption.
- Molecular models are liberally used in most chapters to stimulate interest in the beauty of molecular structures and to reinforce structural concepts and descriptive chemistry presented in general chemistry and upper-level courses.

- Photographs, taken specifically for this text, are used whenever appropriate to illustrate important techniques, apparatus, and operations.
- Marginal notes are used throughout to emphasize recently discussed concepts or to reinforce key information.
- A running marginal glossary reinforces key terminology.

## A Full Support Package for Students

- **Solutions Manual.** Written by Gary Kinsel, University of Texas, Arlington, the solutions manual contains worked-out solutions for all the starred problems in the text. For added value and convenience, the Student Solutions Manual can be packaged with the text. Contact your Thomson • Brooks/Cole sales representative for more information.
- **Spreadsheet Applications.** *Applications of Microsoft® Excel in Analytical Chemistry,* by Stanley R. Crouch and F. James Holler, treats in detail the spreadsheet approaches summarized in the text. This supplement contains 16 chapters that lead the student from basic concepts and operations to using spreadsheets for simulations, curve fitting, data smoothing, curve resolution, and many other topics. Topics in this companion book are correlated with topics in the text. See pages xvii and xviii for a correlation chart. Summaries in the text point to specific chapters and sections in the companion book. For added value and convenience, this ancillary can be packaged with the text. Contact your Thomson • Brooks/Cole representative for details.
- **Interactive Analytical Chemistry CD-ROM.** Developed by William J. Vining, University of Massachusetts, Amherst, in conjunction with the text authors, this CD-ROM is packaged free with every copy of the book. Prompted by icons with captions in the text, students explore the corresponding Intelligent Tutors, Guided Simulations, and Media-based Exercises. This CD-ROM includes tutorials on statistics, equilibria, spectrophotometry, electroanalytical chemistry, chromatography, atomic absorption spectroscopy, and gravimetric and combustion analysis. Also included on the CD-ROM as an Adobe Acrobat® PDF file is Chapter 37, "Selected Methods of Analysis." Students will be able to print only those experiments that they will perform, and the printed sheets can be easily used in the laboratory.
- **Brooks/Cole Book Companion Web Site** at **http://chemistry.brookscole.com/skoogfac/.** The Web site includes a set of updated links to the Web sites mentioned in the Web Works, problems, and other places in this text. Instructors may download spreadsheets developed in this book as well as those from *Applications of Microsoft® Excel in Analytical Chemistry.* Instructors may download graphics files containing all of the figures from the text to aid in preparing PowerPoint® presentations. The Chapter 37 PDF file is also included on the Web site.
- **InfoTrac® College Edition.** Every new copy of this book is packaged with four months of free access to InfoTrac College Edition. This online resource features a comprehensive database of reliable, full-length articles from thousands of top academic journals and popular sources.

## Additional Support for Professors

The following ancillaries are available to qualified adopters. Please consult your Thomson • Brooks/Cole sales representative for details.

- **Instructor's Manual.** Complete solutions to all of the problems in the text are available on the Instructor's password-protected companion site for this text located at **http://chemistry.brookscole.com/skoogfac.**
- **Multimedia Manager for *Fundamentals of Analytical Chemistry,* Eighth Edition: A Microsoft® PowerPoint® Link Tool.** The Multimedia Manager is a digital library and presentation, dual-platform CD-ROM. Included is a library of resources valuable to instructors, such as text art and tables, in a variety of e-formats that are easily exported into other software packages. You can also customize your own presentation by importing your personal lecture slides or other material you choose.
- **Overhead Transparencies.** A set of 100 color overhead transparencies is available to assist instructors in presenting student lectures.
- **MyCourse 2.1.** A new, free, online course builder that offers a simple solution to creating a custom course Web site where professors can assign, track, and report on student progress. Contact your Thomson • Brooks/Cole sales representative for details or visit **http://mycourse.thomsonlearning.com** for a free demo.
- ***Applications of Microsoft® Excel in Analytical Chemistry,*** a clear and concise companion to *Fundamentals of Analytical Chemistry,* eighth edition, and *Analytical Chemistry, An Introduction,* seventh edition, provides students and professors with a valuable resource of the most useful spreadsheet methods.
- **Correlation of Spreadsheet Supplement to Texts.** The following chart lists cross-references to *Fundamentals of Analytical Chemistry,* Eighth Edition, and *Analytical Chemistry: An Introduction,* Seventh Edition.

| *Applications of Microsoft® Excel in Analytical Chemistry* | *Fundamentals of Analytical Chemistry,* Eighth edition | *Analytical Chemistry, An Introduction,* Seventh edition |
|---|---|---|
| Chapter 1 Excel Basics | Chapter 3 Using Spreadsheets in Analytical Chemistry | Section 2J Using Spreadsheets in Analytical Chemistry |
| Chapter 2 Basic Statistical Analysis with Excel | Chapters 5, 6 Basic Statistics | Chapters 5, 6 Basic Statistics |
| Chapter 3 Statistical Tests with Excel | Chapter 7 Statistical Data Treatment | Chapter 7 Statistical Analysis |
| Chapter 4 Least Squares and Calibration Methods | Section 8C Standardization and Calibration | Section 7D The Least Squares Method |
| Chapter 5 Equilibrium Activity and Solving Equations | Section 9B Chemical Equilibrium<br>Chapter 10 Electrolyte Effects | Section 4B Chemical Equilibrium<br>Chapter 9 Electrolyte Effects |
| Chapter 6 The Systematic Approach to Equilibria: Solving Many Equations | Chapter 11 Complex Equilibrium Calculations | Chapter 10 Complex Equilibrium Calculations |
| Chapter 7 Titrations and Graphical Representations | Chapter 13 Titrimetric Methods and Precipitation Titrations<br>Chapter 14 Neutralization Titrations | Chapter 11 Titrations<br>Chapter 12 Precipitation Titrations<br>Section 15B-2 Neutralization Titrations |
| Chapter 8 Polyfunctional Acids and Bases | Chapter 15 Polyfunctional Acids and Bases | Chapter 13 Polyfunctional Acids and Bases |

*(continues)*

| *Applications of Microsoft® Excel in Analytical Chemistry* | *Fundamentals of Analytical Chemistry,* Eighth edition | *Analytical Chemistry, An Introduction,* Seventh edition |
|---|---|---|
| Chapter 9 Complexometric Titrations | Chapter 17 Complexation Reactions and Titrations | Chapter 15 Complexation Titrations |
| Chapter 10 Potentiometry and Redox Titrations | Chapter 18 Introduction to Electrochemistry<br>Chapter 19 Standard Electrode Potentials<br>Chapter 20 Oxidation/ReductionTitrations<br>Chapter 21 Potentiometry | Chapter 16 Elements of Electrochemistry<br>Chapter 17 Using Electrode Potentials<br>Chapter 18 Oxidation/Reduction Titrations<br>Chapter 19 Potentiometry |
| Chapter 11 Dynamic Electrochemistry | Chapter 22 Electrogravimetry and Coulometry<br>Chapter 23 Voltammetry | Chapter 20 Other Electro-analytical Methods |
| Chapter 12 Spectroscopic Methods | Chapter 24 Introduction to Spectrochemical Methods<br>Chapter 25 Optical Instrumentation<br>Chapter 26 Molecular Absorption Spectroscopy<br>Chapter 27 Molecular Fluorescence Spectroscopy | Chapter 21 Spectroscopic Methods of Analysis<br>Chapter 22 Instruments for Measuring Absorption<br>Chapter 23 Spectroscopic Methods |
| Chapter 13 Kinetic Methods | Chapter 29 Kinetic Methods of Analysis | Section 23A-2 Quantitative UV/Visible Spectrophotometry |
| Chapter 14 Chromatography | Chapter 30 Introduction to Analytical Separations<br>Section 31C-2 Quantitative GC | Chapter 24 Introduction to Analytical Separations<br>Section 25A-7 GC Applications |
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| Chapter 16 Data Processing with Excel | Chapter 7 Statistical Data Treatment | Chapter 7 Statistical Analysis |

## Acknowledgments

We wish to acknowledge with thanks the comments and suggestions of many reviewers who critiqued the seventh edition prior to our writing or who evaluated the current manuscript in various stages.

Joseph Aldstadt,
*University of Wisconsin, Milwaukee*
Stephen Brown,
*University of Delaware*
James Burlitch,
*Cornell University*
Michael DeGrandpre,
*University of Montana*
Simon Garrett,
*Michigan State University*
Carol Lasko,
*Humboldt State University*

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Tingyu Li,
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Peter Palmer,
*San Francisco State University*
Reginald Penner,
*University of California, Irvine*
Jeanette Rice,
*Georgia Southern University*
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*Washington State University*
Maria Schroeder,
*United States Naval Academy*
Manuel Soriaga,
*Texas A&M University*
Keith Stevenson,
*University of Texas*
Larry Taylor,
*Virginia Technical Institute*
Robert Thompson,
*Oberlin College*
Richard Vachet,
*University of Massachusetts*
Joseph Wang,
*New Mexico State University*

We especially acknowledge the assistance of Professor David Zellmer, California State University, Fresno, who reviewed several chapters and served as the accuracy reviewer for the entire manuscript. In addition, we appreciate the comments and suggestions of Professor Gary Kinsel of the University of Texas, Arlington, who prepared the solutions manual, and Professor Scott Van Bramer, of Widener University, who checked all the solutions to the problems. We are grateful to Professor Bill Vining of the University of Massachusetts, who prepared the accompanying CD-ROM, and we are fortunate to have worked with Charles D. Winters, who contributed many of the new photos in the text and in the color plates.

Our writing team enjoys the services of a superb technical reference librarian, Ms. Maggie Johnson. She assisted us in many ways in the production of this book, including checking references, performing literature searches, and providing background information for many of the Features. We appreciate her competence, enthusiasm, and good humor.

We are grateful to the many staff members of Brooks/Cole/Thomson Learning who provided excellent support during the production of this text. Senior Developmental Editor Sandi Kiselica has done a superb job of organizing this project, maintaining continuity, and making many important comments and suggestions. Bonnie Boehme of Nesbitt Graphics is simply the best copy editor that we have ever had. Her keen eye and consummate editorial skills have contributed greatly to the quality of the text. Alyssa White has done an excellent job coordinating the ancillary materials, and Jane Sanders, our photo researcher, has shown style and good humor in handling the various tasks associated with acquiring the many new photos in the book.

**Douglas A. Skoog**
**Donald M. West**
**F. James Holler**
**Stanley R. Crouch**

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