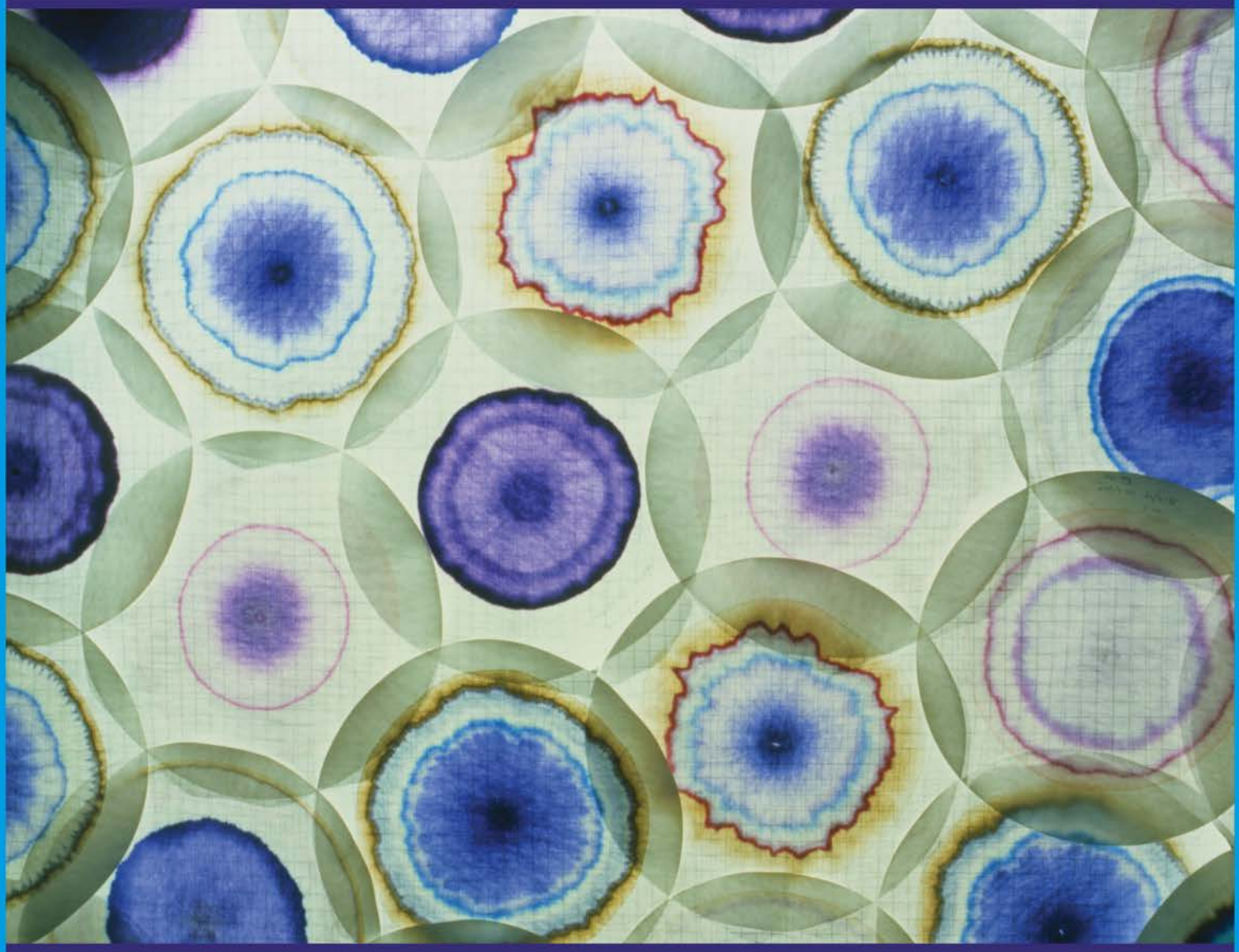
CENGAGE

SKOOG | WEST

Fundamentals of ANALYTICAL CHEMISTRY 10E



F. James Holler | Stanley R. Crouch

Fundamentals of Analytical Chemistry

Tenth Edition

Douglas A. Skoog
Stanford University

Donald M. West
San Jose State University

F. James Holler
University of Kentucky

Stanley R. Crouch
Michigan State University

CENGAGE

Australia • Brazil • Canada • Mexico • Singapore • United Kingdom • United States

Copyright 2022 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s). Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

This is an electronic version of the print textbook. Due to electronic rights restrictions, some third party content may be suppressed. Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. The publisher reserves the right to remove content from this title at any time if subsequent rights restrictions require it. For valuable information on pricing, previous editions, changes to current editions, and alternate formats, please visit www.cengage.com/highered to search by ISBN#, author, title, or keyword for materials in your areas of interest.

Important Notice: Media content referenced within the product description or the product text may not be available in the eBook version.

Copyright 2022 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s). Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

CENGAGE

***Fundamentals of Analytical Chemistry*, Tenth Edition**
Douglas A. Skoog, Donald M. West, F. James Holler, Stanley R. Crouch

SVP, Higher Education & Skills Product: Erin Joyner
VP, Higher Education & Skills Product: Thais Alencar
Product Managers: Helene Alfaro and Roxanne Wang
Product Assistant: Haley Hulett
Learning Designer: Mona Zeftel
Subject Matter Experts: Dakin Sharum and Theresa Dearborn
Senior Content Manager: Aileen Mason
Digital Delivery Lead: Beth McCracken
Director, Marketing: Janet del Mundo
Marketing Manager: Timothy Cali
Intellectual Property Analyst: Ann Hoffman
Intellectual Property Project Manager: Betsy Hathaway
Designer: Lizz Anderson
Cover Image: Geoff Tompkinson/Science Source

© 2022, 2014, Cengage, Inc.

WCN: 02-300

Unless otherwise noted, all content is © Cengage. ALL RIGHTS RESERVED. No part of this work covered by the copyright herein may be reproduced or distributed in any form or by any means, except as permitted by U.S. copyright law, without the prior written permission of the copyright owner.

For product information and technology assistance, contact us at **Cengage Customer & Sales Support, 1-800-354-9706** or **support.cengage.com**.

For permission to use material from this text or product, submit all requests online at **www.cengage.com/permissions**.

Library of Congress Control Number: 2020924523

Student Edition:
ISBN: 978-0-357-45039-0

Loose-leaf Edition
ISBN: 978-0-357-45041-3

Cengage
200 Pier 4 Boulevard
Boston, MA 02210
USA

Excel® screen captures are used courtesy of Microsoft® Corporation.

Cengage is a leading provider of customized learning solutions with employees residing in nearly 40 different countries and sales in more than 125 countries around the world. Find your local representative at **www.cengage.com**.

To learn more about Cengage platforms and services, register or access your online learning solution, or purchase materials for your course, visit **www.cengage.com**.

Printed in United States of America
Print Number: 01 Print Year: 2021

Copyright 2022 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s). Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

Contents in Brief

Chapter 1 The Nature of Analytical Chemistry 1

PART I QUALITY OF ANALYTICAL MEASUREMENTS 14

Chapter 2 Calculations Used in Analytical Chemistry 15
Chapter 3 Precision and Accuracy of Chemical Analyses 38
Chapter 4 Random Errors in Chemical Analysis 51
Chapter 5 Statistical Data Treatment and Evaluation 80
Chapter 6 Sampling, Standardization, and Calibration 113

PART II CHEMICAL EQUILIBRIA 159

Chapter 7 Aqueous Solutions and Chemical Equilibria 160
Chapter 8 Effect of Electrolytes on Chemical Equilibria 199
Chapter 9 Solving Equilibrium Problems for Complex Systems 214

PART III CLASSICAL METHODS OF ANALYSIS 243

Chapter 10 Gravimetric Methods of Analysis 244
Chapter 11 Titrations in Analytical Chemistry 267
Chapter 12 Principles of Neutralization Titrations 288
Chapter 13 Complex Acid-Base Systems 314
Chapter 14 Applications of Neutralization Titrations 345
Chapter 15 Complexation and Precipitation Reactions and Titrations 365

PART IV ELECTROCHEMICAL METHODS 406

Chapter 16 Introduction to Electrochemistry 407
Chapter 17 Applications of Standard Electrode Potentials 437
Chapter 18 Applications of Oxidation/Reduction Titrations 473
Chapter 19 Potentiometry 500
Chapter 20 Bulk Electrolysis: Electrogravimetry and Coulometry 544
Chapter 21 Voltammetry 575

PART V SPECTROCHEMICAL ANALYSIS 616

Chapter 22 Introduction to Spectrochemical Methods 617
Chapter 23 Instruments for Optical Spectrometry 649
Chapter 24 Molecular Absorption Spectrometry 689
Chapter 25 Molecular Fluorescence Spectroscopy 728
Chapter 26 Atomic Spectroscopy 742
Chapter 27 Mass Spectrometry 774

Copyright 2022 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s).
Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

PART VI KINETICS AND SEPARATIONS 791

Chapter 28 Kinetic Methods of Analysis 792
Chapter 29 Introduction to Analytical Separations 821
Chapter 30 Gas Chromatography 860
Chapter 31 High-Performance Liquid Chromatography 886
Chapter 32 Miscellaneous Separation Methods 910

PART VII PRACTICAL ASPECTS OF CHEMICAL ANALYSIS 934

Part VII chapters are available as Adobe Acrobat® PDF files, which are posted on the companion site for the book.

Chapter 33 The Analysis of Real Samples 935
Chapter 34 Preparing Samples for Analysis 945
Chapter 35 Decomposing and Dissolving the Sample 951
Chapter 36 Chemicals, Apparatus, and Unit Operations of Analytical Chemistry 961
Chapter 37 Selected Methods of Analysis 994

Glossary G-1

Appendix 1 The Literature of Analytical Chemistry A-1
Appendix 2 Solubility Product Constants at 25°C A-6
Appendix 3 Acid Dissociation Constants at 25°C A-8
Appendix 4 Formation Constants at 25°C A-10
Appendix 5 Standard and Formal Electrode Potentials A-12
Appendix 6 Use of Exponential Numbers and Logarithms A-15
Appendix 7 Volumetric Calculations Using Normality and Equivalent Weight A-19
Appendix 8 Compounds Recommended for the Preparation of Standard Solutions of Some Common Elements A-26
Appendix 9 Derivation of Error Propagation Equations A-28

Answers to Selected Questions and Problems A-33

Index I-1

Copyright 2022 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s).
Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

Contents

Chapter 1 The Nature of Analytical Chemistry 1

1A The Role of Analytical Chemistry 2
1B Quantitative Analytical Methods 4
1C A Typical Quantitative Analysis 4
1D An Integral Role for Chemical Analysis: Feedback Control Systems 8
Feature 1-1 Deer Kill: A Case Study Illustrating the Use of Analytical Chemistry to Solve a Problem in Toxicology 9

PART I QUALITY OF ANALYTICAL MEASUREMENTS 14

Chapter 2 Calculations Used in Analytical Chemistry 15

2A Some Important Units of Measurement 15
Feature 2-1 Unified Atomic Mass Units and the Mole 18
Feature 2-2 The Factor-Label Approach to Example 2-2 20
2B Solutions and Their Concentrations 20
2C Chemical Stoichiometry 28

Chapter 3 Precision and Accuracy of Chemical Analyses 38

3A Some Important Terms 39
3B Systematic Errors 43

Chapter 4 Random Errors in Chemical Analysis 51

4A The Nature of Random Errors 51
Feature 4-1 Flipping Coins: A Student Activity to Illustrate a Normal Distribution 55
4B Statistical Treatment of Random Errors 56
Feature 4-2 Areas under the Gaussian Curve 59
Feature 4-3 The Significance of the Number of Degrees of Freedom 60
Feature 4-4 Equation for Calculating the Pooled Standard Deviation 64
4C Standard Deviation of Calculated Results 66
4D Reporting Computed Data 71

Chapter 5 Statistical Data Treatment and Evaluation 80

5A Confidence Intervals 81
Feature 5-1 W. S. Gossett (Student) 85
5B Statistical Aids to Hypothesis Testing 86
5C Analysis of Variance 98
5D Detection of Gross Errors 105

Chapter 6 Sampling, Standardization, and Calibration 113

6A Analytical Samples and Methods 114
6B Sampling 116
6C Automated Sample Handling 126
6D Standardization and Calibration 128
Feature 6-1 Lab-on-a-Chip 129
Feature 6-2 A Comparison Method for Aflatoxins 130
Feature 6-3 Multivariate Calibration 141
6E Figures of Merit for Analytical Methods 146

PART II CHEMICAL EQUILIBRIA 159

Chapter 7 Aqueous Solutions and Chemical Equilibria 160

7A The Chemical Composition of Aqueous Solutions 160
7B Chemical Equilibrium 165
Feature 7-1 Stepwise and Overall Formation Constants for Complex Ions 169
Feature 7-2 Why $[H_2O]$ Does Not Appear in Equilibrium-Constant Expressions for Aqueous Solutions 170
Feature 7-3 Relative Strengths of Conjugate Acid-Base Pairs 176
Feature 7-4 The Method of Successive Approximations 181
7C Buffer Solutions 183
Feature 7-5 The Henderson-Hasselbalch Equation 185
Feature 7-6 Acid Rain and the Buffer Capacity of Lakes 191

Chapter 8 Effect of Electrolytes on Chemical Equilibria 199

8A The Effect of Electrolytes on Chemical Equilibria 200
8B Activity Coefficients 203
Feature 8-1 Mean Activity Coefficients 206

Chapter 9 Solving Equilibrium Problems for Complex Systems 214

9A Solving Multiple-Equilibrium Problems Using a Systematic Method 215
9B Calculating Solubilities by the Systematic Method 221
Feature 9-1 Algebraic Expressions Needed to Calculate the Solubility of CaC_2O_4 in Water 226
9C Separation of Ions by Control of the Concentration of the Precipitating Agent 231
Feature 9-2 Immunoassay: Equilibria in the Specific Determination of Drugs 235

PART III CLASSICAL METHODS OF ANALYSIS 243

Chapter 10 Gravimetric Methods of Analysis 244

10A Precipitation Gravimetry 244
Feature 10-1 Specific Surface Area of Colloids 252
10B Calculation of Results from Gravimetric Data 256
10C Applications of Gravimetric Methods 258

Chapter 11 Titrations in Analytical Chemistry 267

11A Some Terms Used in Volumetric Titrations 268
11B Standard Solutions 270
11C Volumetric Calculations 271

Copyright 2022 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s).
Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

Feature 11-1 Another Approach to Example 11-6(a) 276
Feature 11-2 Rounding the Answer to Example 11-7 277
11D Gravimetric Titrations 279
11E Titration Curves 280
Feature 11-3 Calculating the NaOH Volumes Shown in the First Column of Table 11-1 282

Chapter 12 Principles of Neutralization Titrations 288
12A Solutions and Indicators for Acid-Base Titrations 288
12B Titration of Strong Acids and Bases 293
Feature 12-1 Using the Charge-Balance Equation to Construct Titration Curves 295
Feature 12-2 Significant Figures in Titration Curve Calculations 297
12C Titration Curves for Weak Acids 298
Feature 12-3 Determining Dissociation Constants of Weak Acids and Bases 301
Feature 12-4 A Master Equation Approach to Weak Acid/Strong Base Titrations 302
12D Titration Curves for Weak Bases 303
Feature 12-5 Determining the p*K* Values for Amino Acids 305
12E The Composition of Solutions During Acid-Base Titrations 306
Feature 12-6 Locating Titration End Points from pH Measurements 307

Chapter 13 Complex Acid-Base Systems 314
13A Mixtures of Strong and Weak Acids or Strong and Weak Bases 314
13B Polyfunctional Acids and Bases 317
13C Buffer Solutions Involving Polyprotic Acids 320
13D Calculation of the pH of Solutions of NaHA 321
13E Titration Curves for Polyfunctional Acids 325
Feature 13-1 The Dissociation of Sulfuric Acid 333
13F Titration Curves for Polyfunctional Bases 334
13G Titration Curves for Amphiprotic Species 335
Feature 13-2 Acid-Base Behavior of Amino Acids 335
13H Composition of Polyprotic Acid Solutions as a Function of pH 336
Feature 13-3 A General Expression for Alpha Values 337
Feature 13-4 Logarithmic Concentration Diagrams 339

Chapter 14 Applications of Neutralization Titrations 345
14A Reagents for Neutralization Titrations 345
14B Typical Applications of Neutralization Titrations 351
Feature 14-1 Determining Total Serum Protein 352
Feature 14-2 Other Methods for Determining Organic Nitrogen 352
Feature 14-3 Equivalent Masses of Acids and Bases 358

Chapter 15 Complexation and Precipitation Reactions and Titrations 365
15A The Formation of Complexes 365
Feature 15-1 Calculation of Alpha Values for Metal Complexes 368
15B Titrations with Inorganic Complexing Agents 371
Feature 15-2 Determination of Hydrogen Cyanide in Acrylonitrile Plant Streams 372
15C Organic Complexing Agents 378
15D Aminocarboxylic Acid Titrations 379
Feature 15-3 Species Present in a Solution of EDTA 381
Feature 15-4 EDTA as a Preservative 383
Feature 15-5 EDTA Titration Curves When a Complexing Agent Is Present 393
Feature 15-6 Enhancing the Selectivity of EDTA Titrations with Masking and Demasking Agents 399
Feature 15-7 Test Kits for Water Hardness 401

PART IV ELECTROCHEMICAL METHODS 406

Chapter 16 Introduction to Electrochemistry 407
16A Characterizing Oxidation/Reduction Reactions 407
Feature 16-1 Balancing Redox Equations 408
16B Electrochemical Cells 412
Feature 16-2 The Daniell Gravity Cell 414
16C Electrode Potentials 417
Feature 16-3 Why We Cannot Measure Absolute Electrode Potentials 420
Feature 16-4 Sign Conventions in the Older Literature 427
Feature 16-5 Why Are There Two Electrode Potentials for Br_2 in Table 16-1? 430

Chapter 17 Applications of Standard Electrode Potentials 437
17A Calculating Potentials of Electrochemical Cells 437
17B Determining Standard Potentials Experimentally 444
Feature 17-1 Biological Redox Systems 446
17C Calculating Redox Equilibrium Constants 446
Feature 17-2 A General Expression for Calculating Equilibrium Constants from Standard Potentials 450
17D Constructing Redox Titration Curves 452
Feature 17-3 The Inverse Master Equation Approach for Redox Titration Curves 460
Feature 17-4 Reaction Rates and Electrode Potentials 465
17E Oxidation/Reduction Indicators 465
17F Potentiometric End Points 468

Chapter 18 Applications of Oxidation/Reduction Titrations 473
18A Auxiliary Oxidizing and Reducing Reagents 473
18B Applying Standard Reducing Agents 475
18C Applying Standard Oxidizing Agents 479
Feature 18-1 Determination of Chromium Species in Water Samples 481
Feature 18-2 Antioxidants 486

Chapter 19 Potentiometry 500
19A General Principles 501
19B Reference Electrodes 502
19C Liquid Junction Potentials 505
19D Indicator Electrodes 505
Feature 19-1 An Easily Constructed Liquid-Membrane Ion-Selective Electrode 517
Feature 19-2 The Structure and Performance of Ion-Sensitive Field Effect Transistors 519
Feature 19-3 Point-of-Care Testing: Blood Gases and Blood Electrolytes with Portable Instrumentation 523
19E Instruments for Measuring Cell Potential 525
Feature 19-4 The Loading Error in Potential Measurements 525

Copyright 2022 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s).
Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

Feature 19-5 Operational Amplifier Voltage Measurements 527
19F Direct Potentiometry 528
19G Potentiometric Titrations 534
19H Potentiometric Determination of Equilibrium Constants 538

Chapter 20 Bulk Electrolysis: Electrogravimetry and Coulometry 544
20A The Effect of Current on Cell Potential 545
Feature 20-1 Overvoltage and the Lead-Acid Battery 551
20B The Selectivity of Electrolytic Methods 552
20C Electrogravimetric Methods 553
20D Coulometric Methods 559
Feature 20-2 Coulometric Titration of Chloride in Biological Fluids 568

Chapter 21 Voltammetry 575
21A Excitation Signals in Voltammetry 576
21B Voltammetric Instrumentation 577
Feature 21-1 Voltammetric Instruments Based on Operational Amplifiers 578
21C Hydrodynamic Voltammetry 583
21D Polarography 598
21E Cyclic Voltammetry 601
21F Pulse Voltammetry 604
21G Applications of Voltammetry 607
21H Stripping Methods 608
21I Voltammetry with Microelectrodes 610

PART V SPECTROCHEMICAL ANALYSIS 616

Chapter 22 Introduction to Spectrochemical Methods 617
22A Properties of Electromagnetic Radiation 618
22B Interaction of Radiation and Matter 621
Feature 22-1 Spectroscopy and the Discovery of Elements 623
22C Absorption of Radiation 624
Feature 22-2 Deriving Beer's Law 627
Feature 22-3 Why Is a Red Solution Red? 631
22D Emission of Electromagnetic Radiation 639

Chapter 23 Instruments for Optical Spectrometry 649
23A Instrument Components 649
Feature 23-1 Laser Sources: The Light Fantastic 653
Feature 23-2 Origin of Equation 23-1 659
Feature 23-3 Producing Ruled and Holographic Gratings 661
Feature 23-4 Basis of Equation 23-2 664
Feature 23-5 Signals, Noise, and the Signal-to-Noise Ratio 666
Feature 23-6 Measuring Photocurrents with Operational Amplifiers 674
23B Ultraviolet/Visible Photometers and Spectrophotometers 676
23C Infrared Spectrophotometers 679
Feature 23-7 How Does a Fourier Transform Infrared Spectrometer Work? 681

Chapter 24 Molecular Absorption Spectrometry 689
24A Ultraviolet and Visible Molecular Absorption Spectroscopy 689
24B Automated Photometric and Spectrophotometric Methods 711
24C Infrared Absorption Spectroscopy 714
Feature 24-1 Producing Spectra with an FTIR Spectrometer 718

Chapter 25 Molecular Fluorescence Spectroscopy 728
25A Theory of Molecular Fluorescence 728
25B Effect of Concentration on Fluorescence Intensity 732
25C Fluorescence Instrumentation 733
25D Applications of Fluorescence Methods 734
Feature 25-1 Use of Fluorescence Probes in Neurobiology: Probing the Enlightened 735
25E Molecular Phosphorescence Spectroscopy 737
25F Chemiluminescence Methods 738

Chapter 26 Atomic Spectroscopy 742
26A Origins of Atomic Spectra 743
26B Production of Atoms and Ions 746
26C Atomic Emission Spectrometry 756
26D Atomic Absorption Spectrometry 760
Feature 26-1 Determining Mercury by Cold-Vapor Atomic Absorption Spectroscopy 767
26E Atomic Fluorescence Spectrometry 770

Chapter 27 Mass Spectrometry 774
27A Principles of Mass Spectrometry 774
27B Mass Spectrometers 776
27C Atomic Mass Spectrometry 780
27D Molecular Mass Spectrometry 783

PART VI KINETICS AND SEPARATIONS 791

Chapter 28 Kinetic Methods of Analysis 792
28A Rates of Chemical Reactions 793
Feature 28-1 Enzymes 800
28B Determining Reaction Rates 806
Feature 28-2 Fast Reactions and Stopped-Flow Mixing 806
28C Applications of Kinetic Methods 813
Feature 28-3 The Enzymatic Determination of Urea 815

Chapter 29 Introduction to Analytical Separations 821
29A Separation by Precipitation 822
29B Separation of Species by Distillation 826
29C Separation by Extraction 826
Feature 29-1 Derivation of Equation 29-3 828
29D Separating Ions by Ion Exchange 831
Feature 29-2 Home Water Softeners 833
29E Chromatographic Separations 835
Feature 29-3 What Is the Source of the Terms *Plate* and *Plate Height*? 843
Feature 29-4 Derivation of Equation 29-24 845

Copyright 2022 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s).
Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

Chapter 30 Gas Chromatography 860
30A Instruments for Gas-Liquid Chromatography 861
30B Gas Chromatographic Columns and Stationary Phases 870
30C Applications of Gas-Liquid Chromatography 874
Feature 30-1 Use of GC/MS to Identify a Drug Metabolite in Blood 876
30D Gas-Solid Chromatography 882

Chapter 31 High-Performance Liquid Chromatography 886
31A Instrumentation 887
Feature 31-1 LC/MS and LC/MS/MS 894
31B Partition Chromatography 895
31C Adsorption Chromatography 898
31D Ion Chromatography 899
31E Size-Exclusion Chromatography 901
Feature 31-2 Buckyballs: The Chromatographic Separation of Fullerenes 903
31F Affinity Chromatography 905
31G Chiral Chromatography 905
31H Comparison of High-Performance Liquid Chromatography and Gas Chromatography 906

Chapter 32 Miscellaneous Separation Methods 910
32A Supercritical Fluid Separations 910
32B Planar Chromatography 915
32C Capillary Electrophoresis 917
Feature 32-1 Capillary Array Electrophoresis in DNA Sequencing 924
32D Capillary Electrochromatography 924
32E Field-Flow Fractionation 927

PART VII PRACTICAL ASPECTS OF CHEMICAL ANALYSIS 934

The following chapters are available as Adobe Acrobat® PDF files on the companion site for the book.

Chapter 33 The Analysis of Real Samples 935
33A Real Samples 935
33B Choice of Analytical Method 937
33C Accuracy in the Analysis of Complex Materials 942

Chapter 34 Preparing Samples for Analysis 945
34A Preparing Laboratory Samples 945
34B Moisture in Samples 947
34C Determining Water in Samples 950

Chapter 35 Decomposing and Dissolving the Sample 951
35A Sources of Error in Decomposition and Dissolution 952
35B Decomposing Samples with Inorganic Acids in Open Vessels 952
35C Microwave Decompositions 954
35D Combustion Methods for Decomposing Organic Samples 957
35E Decomposing Inorganic Materials with Fluxes 959

Chapter 36 Chemicals, Apparatus, and Unit Operations of Analytical Chemistry 961
36A Selecting and Handling Reagents and Other Chemicals 962
36B Cleaning and Marking of Laboratory Ware 963
36C Evaporating Liquids 964
36D Measuring Mass 964
36E Equipment and Manipulations Associated with Weighing 971
36F Filtration and Ignition of Solids 974
36G Measuring Volume 980
36H Calibrating Volumetric Glassware 989
36I The Laboratory Notebook 991
36J Safety in the Laboratory 992

Chapter 37 Selected Methods of Analysis 994
37A An Introductory Experiment 995
37B Gravimetric Methods of Analysis 1004
37C Neutralization Titrations 1008
37D Precipitation Titrations 1017
37E Complex-Formation Titrations with EDTA 1020
37F Titrations with Potassium Permanganate 1023
37G Titrations with Iodine 1029
37H Titrations with Sodium Thiosulfate 1031
37I Titrations with Potassium Bromate 1034
37J Potentiometric Methods 1036
37K Electrogravimetric Methods 1040
37L Coulometric Titrations 1042
37M Voltammetry 1044
37N Methods Based on the Absorption of Radiation 1046
37O Molecular Fluorescence 1050
37P Atomic Spectroscopy 1051
37Q Application of Ion-Exchange Resins 1054
37R Gas-Liquid Chromatography 1056

Glossary G-1
APPENDIX 1 The Literature of Analytical Chemistry A-1
APPENDIX 2 Solubility Product Constants at 25°C A-6
APPENDIX 3 Acid Dissociation Constants at 25°C A-8
APPENDIX 4 Formation Constants at 25°C A-10
APPENDIX 5 Standard and Formal Electrode Potentials A-12
APPENDIX 6 Use of Exponential Numbers and Logarithms A-15
APPENDIX 7 Volumetric Calculations Using Normality and Equivalent Weight A-19
APPENDIX 8 Compounds Recommended for the Preparation of Standard Solutions of Some Common Elements A-26
APPENDIX 9 Derivation of Error Propagation Equations A-28

Answers to Selected Questions and Problems A-33

Index I-1

Copyright 2022 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s). Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

Preface

The tenth edition of *Fundamentals of Analytical Chemistry* is an introductory textbook designed primarily for a one- or two-semester course for chemistry majors. Since the publication of the ninth edition, the scope of analytical chemistry has continued to evolve, and thus, we have included many applications to biology, medicine, materials science, ecology, forensic science, and other related fields. As in previous editions, we have incorporated many spreadsheet applications, examples, and exercises. We have revised older treatments to incorporate contemporary instrumentation and techniques. Our companion supplement, *Applications of Microsoft® Excel® in Analytical Chemistry*, Fourth Edition, provides students with a tutorial guide for using spreadsheets in analytical chemistry and introduces many additional spreadsheet operations. Both instructors and students should sign in at **www.cengage.com** to access this supplement.

We recognize that courses in analytical chemistry vary from institution to institution and depend on the available facilities and instrumentation, the time allocated to analytical chemistry in the chemistry curriculum, and the unique instructional philosophies of teachers. We have, therefore, designed the tenth edition of *Fundamentals of Analytical Chemistry* so that instructors can tailor the text to meet their needs and students can learn the concepts of analytical chemistry on several levels: in descriptions, in pictorials, in illustrations, in interesting and relevant features, and in using online learning.

Since the production of the eighth edition of this text, the duties and responsibilities for planning and writing new editions have fallen to two of us (FJH and SRC). While making the many changes and improvements cited previously and in the remainder of the preface, we have maintained the basic philosophy and organization of the nine previous editions and endeavored to preserve the same high standards that characterized those texts.

Objectives

The primary objective of this text is to provide a thorough background in the 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 applying statistical methods to analytical data. Third, we aim to introduce a broad range of modern and classic techniques that are useful in analytical chemistry. Fourth, we hope that, with the help of this book, students will develop the skills necessary to solve quantitative analytical problems and, where appropriate, use powerful spreadsheet tools to solve problems, perform calculations, and create simulations of chemical phenomena. Finally, we aim to teach laboratory skills that will give students confidence in their ability to obtain high-quality analytical data and that will highlight the importance of attention to detail in acquiring these data.

Coverage and Organization

The material in this text covers both fundamental and practical aspects of chemical analysis. We have organized the chapters into Parts that group together

Copyright 2022 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s).
Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

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

- **Part I** covers the quality of analytical measurements and comprises five chapters. Chapter 2 reviews the basic calculations of analytical chemistry, including expressions of chemical concentration and stoichiometric relationships. Chapters 3–5 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 included in Chapter 5, and Chapter 6 provides details about acquiring samples, standardization, and calibration.
- **Part II** covers the principles and application of chemical equilibrium systems in quantitative analysis. Chapter 7 explores the fundamentals of chemical equilibria. Chapter 8 discusses the effect of electrolytes on equilibrium systems. The systematic approach for attacking equilibrium problems in complex systems is the subject of Chapter 9.
- **Part III** brings together six chapters dealing with classical gravimetric and volumetric analytical chemistry. Gravimetric analysis is described in Chapter 10. In Chapters 11–5, we consider the theory and practice of titrimetric methods of analysis, including acid-base titrations, precipitation titrations, and complexometric titrations. We take advantage of the systematic approach to equilibria and the use of spreadsheets in the calculations.
- **Part IV** is devoted to electrochemical methods. After an introduction to electrochemistry in Chapter 16, Chapter 17 describes the many uses of electrode potentials. Oxidation/reduction titrations are the subject of Chapter 18, while Chapter 19 presents the use of potentiometric methods to measure concentrations of molecular and ionic species. Chapter 20 considers the bulk electrolytic methods of electrogravimetry and coulometry, and Chapter 21 discusses voltammetric methods, including linear sweep and cyclic voltammetry, anodic stripping voltammetry, and polarography.
- **Part V** presents spectroscopic methods of analysis. The nature of light and its interaction with matter are explored in Chapter 22. Spectroscopic instruments and their components are the topics covered in Chapter 23. The various applications of molecular absorption spectrometric methods are discussed in some detail in Chapter 24, while Chapter 25 is concerned with molecular fluorescence spectroscopy. Chapter 26 covers various atomic spectrometric methods, including plasma and flame emission methods and electrothermal and flame atomic absorption spectroscopy. Chapter 27 on mass spectrometry provides an introduction to ionization sources, mass analyzers, and ion detectors. Both atomic and molecular mass spectrometry are included.
- **Part VI** includes five chapters dealing with kinetics and analytical separations. We investigate kinetic methods of analysis in Chapter 28. Chapter 29 introduces analytical separations including ion exchange and the various chromatographic methods. Chapter 30 discusses gas chromatography, while high-performance liquid chromatography is covered in Chapter 31. The final chapter in this Part, Chapter 32, introduces several miscellaneous separation methods, including supercritical fluid chromatography, capillary electrophoresis, and field-flow fractionation.
- The final **Part VII** consists of five chapters dealing with the practical aspects of analytical chemistry. These chapters are posted on the companion site for the book. We consider real samples and compare them to ideal samples in Chapter 33. Methods for preparing samples are discussed in Chapter 34, while techniques for decomposing and dissolving samples are covered in Chapter 35. Chapter 36 discusses the chemicals and

Copyright 2022 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s).
Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

equipment used in analytical laboratories and includes many photographs of analytical operations. The text ends with Chapter 37, which provides detailed procedures for laboratory experiments that cover many of the principles and applications discussed in previous chapters.

Flexibility

Because the text is divided into Parts, there is substantial flexibility in the use of the 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 the most important have been highlighted with a light blue screen for emphasis and ease of review.

Mathematical Level. Generally the principles of chemical analysis developed here are based on college algebra. A few 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. In this edition, we title the examples for easier identification. As in the ninth edition, we follow the practice of including units in chemical calculations and using the factor-label method to check 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. Where appropriate, solutions to the worked examples are clearly marked with the word **Solution** for ease in identification.

Spreadsheet Calculations. Throughout the book we have introduced spreadsheets for problem solving, graphical analysis, and many other applications. Microsoft Excel on the PC has been adopted as the standard for these calculations, but the instructions can be easily adapted to other spreadsheet programs and platforms. Many other detailed examples are presented in our companion supplement, *Applications of Microsoft® Excel® in Analytical Chemistry*, Fourth Edition. We have attempted to document each stand-alone spreadsheet with working formulas and entries.

Exercises in Excel. References to our supplement *Applications of Microsoft® Excel® in Analytical Chemistry*, Fourth Edition, are given as Exercises in Excel in the text. These are intended to direct students 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.

Challenge Problems. Most 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 require library or Web

Copyright 2022 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s). Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

searches to find information. We hope that 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 for group projects, inquiry-driven learning assignments, and case study discussions. Because many challenge problems are open-ended and may have multiple solutions, we do not provide answers or explanations for them.

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 "W. S. Gosset (Student)" (Chapter 5), "Antioxidants" (Chapter 18), "Fourier Transform Spectroscopy" (Chapter 23), "LC/MS/MS" (Chapter 31), and "Capillary Electrophoresis in DNA Sequencing" (Chapter 32).

Illustrations and Photos. We feel strongly that color photographs, drawings, pictorials, full-color molecular models, and other visual aids greatly assist the learning process. Hence, we have included new and updated visual materials to aid students. Full-color photographs 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* illustration.

Analytical Chemistry Online. In most chapters we have included a brief Analytical Chemistry Online feature at the end of the chapter. In these features, we ask the student to find information on the web, do online searches, visit the websites of equipment manufacturers, or solve analytical problems. These Analytical Chemistry Online features and the links given are intended to stimulate student interest in exploring the information available on the internet.

Glossary. Near the end of the book we have included a glossary that defines the most important terms, phrases, techniques, and operations used in the text. The glossary is intended to provide students with a means for rapidly determining a meaning 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 normality and equivalents (terms that are not used in the text itself); and a derivation of the propagation of error equations. The endpapers of this book provide a full-color chart of chemical indicators, a periodic table, a full-color diagram illustrating the important regions of the electromagnetic spectrum, a 2019 IUPAC table of atomic masses, and a table of molar masses of compounds of particular interest in analytical chemistry based on the 2019 atomic masses.

Digital Object Identifiers (DOIs). DOIs have been added to most references to the primary literature. These universal identifiers greatly simplify the task of locating articles by a link on the website **www.doi.org**. A DOI may be typed into a form on the home page, and when the identifier is submitted, the browser transfers directly to the article on the publisher's website. For example, 10.1351/goldbook.C01222 can be typed into the form, and the browser is directed to the IUPAC article on concentration. Alternatively, DOIs may be entered directly into the URL blank of any

Copyright 2022 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s).
Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

browser as http://dx.doi.org/10.1351/goldbook.C01222. Please note that students or instructors must have authorized access to the publication of interest.

What's New in the Tenth Edition

Readers of the ninth edition will find numerous changes in the tenth edition in content as well as in style and format.

Chapter Summaries, Key Terms, and Important Equations. Each chapter now ends with a Chapter Summary, Key Terms, and Important Equations to help students better focus on what they have learned from the chapter.

Careers in Chemistry. Inclusive and diverse analytical chemists from a variety of careers are featured in many chapters so that all students can see what types of careers they might pursue after studying analytical chemistry.

Currency. All techniques and instrumentation, including photographs, have been updated for this edition to preserve the currency of the text.

Full Color. Skoog is now printed fully in color, to ensure that all images and figures are visible for students and to improve the readability and clarity for students.

Accessibility. Figures and colors have been reviewed for accessibility, and alt text has been added to all digital content and the PowerPoint slides.

Revised Exercises. About 40% of end-of-chapter exercises have been revised with new numbers and variables.

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

- Chapter 2 provides a basic introduction to the construction and use of spreadsheets. Many detailed tutorials are included in our supplement, *Applications of Microsoft® Excel® in Analytical Chemistry*, Fourth Edition.
- The chapters on statistics (Chapters 3–5) have been updated and brought into conformity with the terminology of modern statistics. Analysis of variance (ANOVA) has been included in Chapter 5. ANOVA is very easy to perform with modern spreadsheet programs and quite useful in analytical problem solving. These chapters are closely linked to our Excel supplement through Examples, Features, and Summaries.
- References to the analytical chemistry literature have been updated and corrected as necessary.

Style and Format. Our style and format have continued to evolve to make the text more readable and student friendly.

- 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 alternating between text and caption.
- Full-color molecular models are used liberally 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.
- New figures have replaced obsolete figures of past editions.
- 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, to reinforce key information, or to serve as study aids.

Copyright 2022 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s). Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

OWLv2

Move students beyond memorization of chemistry concepts to a higher level of thinking with OWLv2. This powerful platform empowers students to learn chemistry through richly dynamic problems, detailed feedback, and interactive learning modules. With OWLv2, students practice at their own pace, receive meaningful feedback, and access learning resources to help them achieve better grades.

- **Master chemistry one concept at a time.** OWLv2 Algorithmic Mastery learning activities enable students to work at their own pace to promote understanding over memorization.
- **Learning tools for every type of student.** Adaptive review modules guide remediation, while interactive study tools and resources aid conceptualization, practice, and review.
- With OWLv2, students have access to exam preparation tools; detailed, step-by-step explanations; a mobile-compatible MindTap eReader; and real-time grades and progress.
- **Access analytics in real time.** Track course progress using detailed analytics alongside detailed student progress insights with the comprehensive OWLv2 gradebook.
- **Learning Management System (LMS) integration.** OWLv2 integrates with Blackboard, Brightspace, Canvas, Moodle, and other common LMSs to provide seamless integrations.

Skoog OWLv2 Course. The Skoog OWLv2 course has been revised for the tenth edition.

- **Targeted feedback.** Over thirty percent of Skoog problems in OWL now come with targeted feedback on common errors that students make. The targeted feedback explains why the student's answer is incorrect and guides them toward a correct solution.
- **Content audit.** All Skoog OWL exercises and activities were reviewed and updated to ensure that they relate directly to the text.
- **Solutions in OWL.** All OWL end-of-chapter exercises now show the complete solution after the student answers a question wrong two times.
- **Laddered Assessments.** Conceptual mastery modules are combined with more traditional homework questions into one structured learning path, organized by topic at the chapter level.
- **OWLv2 Help.** Resources have been streamlined and improved to make it easier for instructors and students to master OWL.

Instructor and Student Resources

Additional instructor and student resources are available online. Instructor assets include the following:

- **Part VII: Practical Aspects of Chemical Analysis** (Chapters 33–37)
- **Guide to Teaching Online**
- a **Transition Guide** from the ninth edition to the tenth edition
- an **Educator's Guide**
- **Lecture Notes PowerPoint®** slides
- **Image Library PowerPoints®**
- an updated and accuracy-checked **Solutions and Answer Guide** (formerly the Instructor Solutions Manual)
- the supplement *Applications of Microsoft® Excel® in Analytical Chemistry*, Fourth Edition

Copyright 2022 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s).
Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

Student assets include the following:

- **Part VII: Practical Aspects of Chemical Analysis** (Chapters 33–37)
- the supplement *Applications of Microsoft® Excel® in Analytical Chemistry*, Fourth Edition
- a **Student Solutions Manual**

Both instructors and students should sign in at **www.cengage.com** to access the online resources.

Acknowledgments

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

Reviewers for the Tenth Edition

Carolyn J. Cassady,
University of Alabama
Michael R. Columbia,
Purdue University
Jason W. Coym,
University of South Alabama
Chester Dabalos,
University of Hawaii at Manoa
Darwin Dahl,
Western Kentucky University
Wujian Miao,
University of Southern Mississippi
Robert Richter,
Chicago State University
Maria A. Soria,
Fresno Pacific University
Tarek Trad,
Sam Houston State University
Trent P. Vorlicek,
Minnesota State University, Mankato
Darcey Wayment,
Nicholls State University
Justyna Widera-Kalinowska,
Adelphi University

Our writing team enjoys the services of a superb technical reference librarian, Ms. Janette Carver of the University of Kentucky Science Library. She assisted us in many ways in the production of this book, including checking references, performing literature searches, and arranging for interlibrary loans. We appreciate her competence, enthusiasm, and good humor.

We are grateful to the many staff members of Cengage and Lumina Datamatics, as well as the freelance experts, who provided solid support during the production of this text and its supplementary material. Product Manager Helene Alfaro provided excellent leadership and encouragement throughout the course of this project. Our Learning Designer, Mona Zeftel, made many useful suggestions for improving this text. Senior Content Manager Aileen Mason kept the project moving with frequent reminders, weekly to-do lists, and timely schedule updates while coordinating the entire production process. We are deeply grateful to Aileen and Mona for their dedication, skill, and attention to detail. Associate Program Manager Valarmathy Munuswamy did a stellar job managing the project at Lumina Datamatics. We thank subject matter expert Trent Vorlicek for his many suggestions and corrections, as well as accuracy checkers Andrea Kelley and Jon Booze. We are grateful to our copy editor, Pooja Gaonkar, for her consistency and attention to detail. Her keen eye and excellent editorial skills have contributed significantly to the quality of the text. We also thank proofreader Jananee Sekar, who caught errors before the book went to press. Photo researcher Anjali Kambli handled many tasks associated with acquiring new photos and securing permissions for graphics, and Sheeba Baskar reviewed and secured text permissions.

Copyright 2022 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s).
Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

This is the second edition of *Fundamentals of Analytical Chemistry* written without the skill, guidance, and counsel of our senior coauthors Douglas A. Skoog and Donald M. West. Doug died in 2008, and Don followed in 2011. Doug was Don's preceptor while he was a graduate student at Stanford University, and they began writing analytical chemistry textbooks together in the 1950s. They produced twenty editions of three best-selling textbooks over a period of 45 years. Doug's vast knowledge of analytical chemistry and consummate writing skill coupled with Don's organizational expertise and attention to detail formed an outstanding writing team. We aspire to maintain the high standard of excellence of Skoog and West as we continue to build on their legacy. In honor of their manifest contributions to the philosophy, organization, and writing of this book and many others, we have chosen to list their names above the title.

Finally, we are deeply grateful to our wives Vicki Holler and Nicky Crouch for their counsel, patience, and support during the several years of writing this text and preparing it for production. Unfortunately, Nicky passed away from pancreatic cancer in 2016.

F. James Holler
Stanley R. Crouch

Copyright 2022 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s).
Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

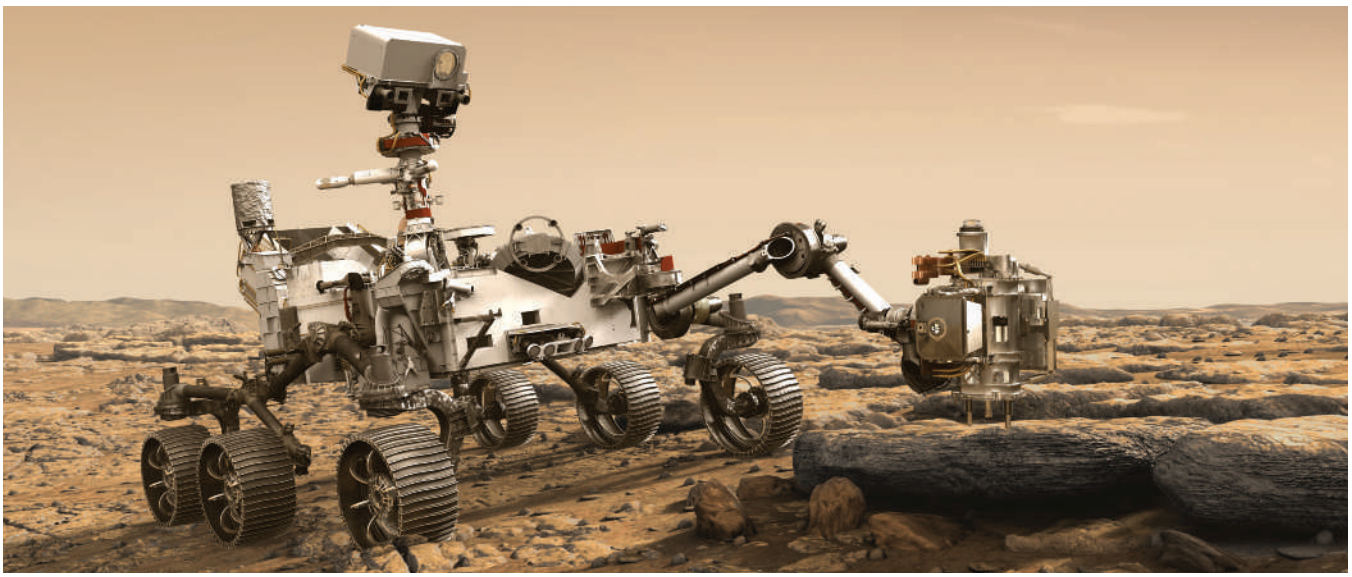
CHAPTER

1

The Nature of Analytical Chemistry

Analytical chemistry is a measurement science consisting of a set of powerful ideas and methods that are useful in all fields of science, engineering, and medicine. Some exciting illustrations of the power and significance of analytical chemistry have occurred, are occurring, and will occur during NASA's rover explorations of the planet Mars. On July 4, 1997, the Pathfinder spacecraft delivered the Sojourner rover to the Martian surface. Analytical instruments returned information on the chemical composition of rocks and soil. Investigations by the lander and rover suggested that Mars was at one time in its past warm and wet with liquid water on the surface and water vapor in the atmosphere. In January 2004, the Mars rovers Spirit and Opportunity arrived on Mars for a 3-month mission. A major result from Spirit's alpha particle X-ray spectrometer (APXS) and Mossbauer spectrometer was finding concentrated deposits of silica and, at a different site, high concentrations of carbonate. Spirit continued to explore and transmit data until 2010, outliving even the most optimistic predictions. Even more amazing, Opportunity continued to travel the surface of Mars and, by March, 2012, had covered more than 21 miles exploring and transmitting images of craters, small hills, and other features.

In late 2011, the Mars Science Laboratory aboard the rover Curiosity was launched. It arrived on August 6, 2012, with a host of analytical instruments on board. The Chemistry and Camera package includes a laser-induced breakdown spectrometer (LIBS, see Chapter 26) and a remote microimager. The LIBS instrument will provide determination of many elements with no sample preparation. It can determine the identity and amounts of major, minor, and trace elements and can detect hydrated minerals. The sample analysis package contains a quadrupole mass spectrometer (Chapter 27), a gas chromatograph (Chapter 30), and a tunable laser spectrometer (Chapter 23). Its goals are to survey carbon compound sources, search for organic compounds important to life, reveal the chemical and



NASA/JPL-Caltech

Perseverance Rover using drill and robotic arm to collect samples.

Copyright 2022 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s).
Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

isotopic states of several elements, determine the composition of the Martian atmosphere, and search for noble gas and light element isotopes.[1]

At the end of July 2020, the Mars 2020 Rover mission was launched. The Perseverance Rover that is part of this mission will focus on questions concerning the potential for life on Mars. It will seek signs of conditions on Mars in the past that indicate the presence of life. Core samples taken by the rover drill will be collected and stored for possible return to Earth for analysis in the future. The mission will also obtain information relevant to future human Mars explorations including possible habitation of the planet. It will explore producing oxygen from the Martian atmosphere, finding subsurface water, and characterizing Martian weather and other environmental conditions that could influence living and working on the planet. Perseverance successfully landed on Mars on February 18, 2021.

Qualitative analysis reveals the *identity* of the elements and compounds in a sample.

Quantitative analysis indicates the *amount* of each substance in a sample.

Analytes are the components of a sample that are determined.

These examples demonstrate that both qualitative and quantitative information are required in an analysis. **Qualitative analysis** establishes the chemical identity of the species in the sample. **Quantitative analysis** determines the relative amounts of these species, or **analytes**, in numerical terms. The data from the various spectrometers on the rovers contain both types of information. As is common with many analytical instruments, the gas chromatograph and mass spectrometer incorporate a separation step as a necessary part of the analytical process. With a few analytical tools, exemplified here by the APXS and LIBS experiments, chemical separation of the various elements contained in the rocks is unnecessary since the methods provide highly selective information. This text explores quantitative methods of analysis, separation methods, and the principles behind their operation. A qualitative analysis is often an integral part of the separation step, and determining the identity of the analytes is an essential adjunct to quantitative analysis.

1A The Role of Analytical Chemistry

Analytical chemistry is applied throughout industry, medicine, and all the sciences. To illustrate, consider a few examples. The concentrations of oxygen and of carbon dioxide are determined in millions of blood samples every day and used to diagnose and treat illnesses. Quantities of hydrocarbons, nitrogen oxides, and carbon monoxide present in automobile exhaust gases are measured to determine the effectiveness of emission-control devices. Quantitative measurements of ionized calcium in blood serum help diagnose parathyroid disease in humans. Quantitative determination of nitrogen in foods establishes their protein content and thus their nutritional value. Analysis of steel during its production permits adjustment in the concentrations of such elements as carbon, nickel, and chromium to achieve a desired strength, hardness, corrosion resistance, and ductility. The mercaptan content of household gas supplies is monitored continually to ensure that the gas has a sufficiently obnoxious odor to warn of dangerous leaks. Farmers tailor fertilization and irrigation schedules to meet changing plant needs during the growing season, gauging these needs from quantitative analyses of plants and soil.

Quantitative analytical measurements also play a vital role in many research areas in chemistry, biochemistry, biology, geology, physics, and the other sciences. For example, quantitative measurements of potassium, calcium, and sodium ions

[1]For details on the Mars Science missions and the rovers Curiosity, see http://www.nasa.gov.

Copyright 2022 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s). Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

in the body fluids of animals permit physiologists to study the role these ions play in nerve-signal conduction as well as muscle contraction and relaxation. Chemists unravel the mechanisms of chemical reactions through reaction rate studies. The rate of consumption of reactants or formation of products in a chemical reaction can be calculated from quantitative measurements made at precise time intervals. Materials scientists rely heavily on quantitative analyses of crystalline germanium and silicon in their studies of semiconductor devices whose impurities lie in the concentration range of 1×10^{-6} to 1×10^{-9} percent. Archaeologists identify the sources of volcanic glasses (obsidian) by measuring concentrations of minor elements in samples taken from various locations. This knowledge in turn makes it possible to trace prehistoric trade routes for tools and weapons fashioned from obsidian.

Many chemists, biochemists, and medicinal chemists devote much time in the laboratory gathering quantitative information about systems that are important and interesting to them. The central role of analytical chemistry in this enterprise and many others is illustrated in **Figure 1-1**. All branches of chemistry draw on the ideas and techniques of analytical chemistry. Analytical chemistry has a similar function

FIGURE 1-1 The relationship between analytical chemistry, other branches of chemistry, and the other sciences. The central location of analytical chemistry in the diagram signifies its importance and the breadth of its interactions with many other disciplines.

Copyright 2022 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s). Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

with respect to the many other scientific fields listed in the diagram. Chemistry is often called *the central science*; its top-center position and the central position of analytical chemistry in the figure emphasize this importance. The interdisciplinary nature of chemical analysis makes it a vital tool in medical, industrial, government, and academic laboratories throughout the world.

1B Quantitative Analytical Methods

We compute the results of a typical quantitative analysis from two measurements. One is the mass or the volume of sample being analyzed. The second measurement is of some quantity that is proportional to the amount of analyte in the sample such as mass, volume, intensity of light, or electrical charge. This second measurement usually completes the analysis, and we usually classify analytical methods according to the nature of this final measurement. **Gravimetric methods** determine the mass of the analyte or some compound chemically related to it. A **volumetric method** measures the volume of a solution containing sufficient reagent to react completely with the analyte. **Electroanalytical methods** measure electrical properties such as potential, current, resistance, and quantity of electrical charge. **Spectroscopic methods** explore the interaction between electromagnetic radiation and analyte atoms or molecules or the emission of radiation by analytes. Finally, in a group of miscellaneous methods, we measure such quantities as mass-to-charge ratio of ions by mass spectrometry, rate of radioactive decay, heat of reaction, rate of reaction, sample thermal conductivity, optical activity, and refractive index.

EPA (Environmental Protection Agency)

Dr. Ann Richard completed her Ph.D. at the University of North Carolina at Chapel Hill, specializing in physical chemistry. Using her computational chemistry skill set, she accepted a postdoctoral position at the U.S. Environmental Protection Agency (EPA), where she has worked since 1984. Dr. Richard is currently a researcher for the EPA's Center for Computational Toxicology and Exposure where one of her roles is to use computer models to predict the toxicity of molecules toward both humans and animals. She also combines chemistry, computer science, and data management in the area known as cheminformatics. Dr. Richard manages a large toxicity database and oversees a toxicity testing system utilizing testing plates the size of an iPhone. This system can analyze over 1,500 chemical compounds at one time. Computational toxicology has changed testing procedures, reducing testing of these compounds on animals.

1C A Typical Quantitative Analysis

A typical quantitative analysis includes the sequence of steps shown in the flow diagram of **Figure 1-2**. In some instances, one or more of these steps can be omitted. For example, if the sample is already a liquid, we can avoid the dissolution step. Chapters 1 through 32 focus on the last three steps in Figure 1-2. In the measurement step, we measure one of the physical properties mentioned in Section 1B. In the calculation step, we find the relative amount of the analyte present in the samples. In the final step, we evaluate the quality of the results and estimate their reliability.

In the paragraphs that follow, you will find a brief overview of each of the nine steps shown in Figure 1-2. We then present a case study to illustrate the use of these steps in solving an important and practical analytical problem. The details of this study foreshadow many of the methods and ideas you will explore as you study analytical chemistry.

1C-1 Choosing a Method

The essential first step in any quantitative analysis is the selection of a method as depicted in Figure 1-2. The choice is sometimes difficult and requires experience as well as intuition. One of the first questions that must be considered in the selection process is the level of accuracy required. Unfortunately, high reliability nearly always requires a large investment of time. The selected method usually represents a compromise between the accuracy required and the time and money available for the analysis.

A second consideration related to economic factors is the number of samples that will be analyzed. If there are many samples, we can afford to spend a significant

Copyright 2022 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s).
Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

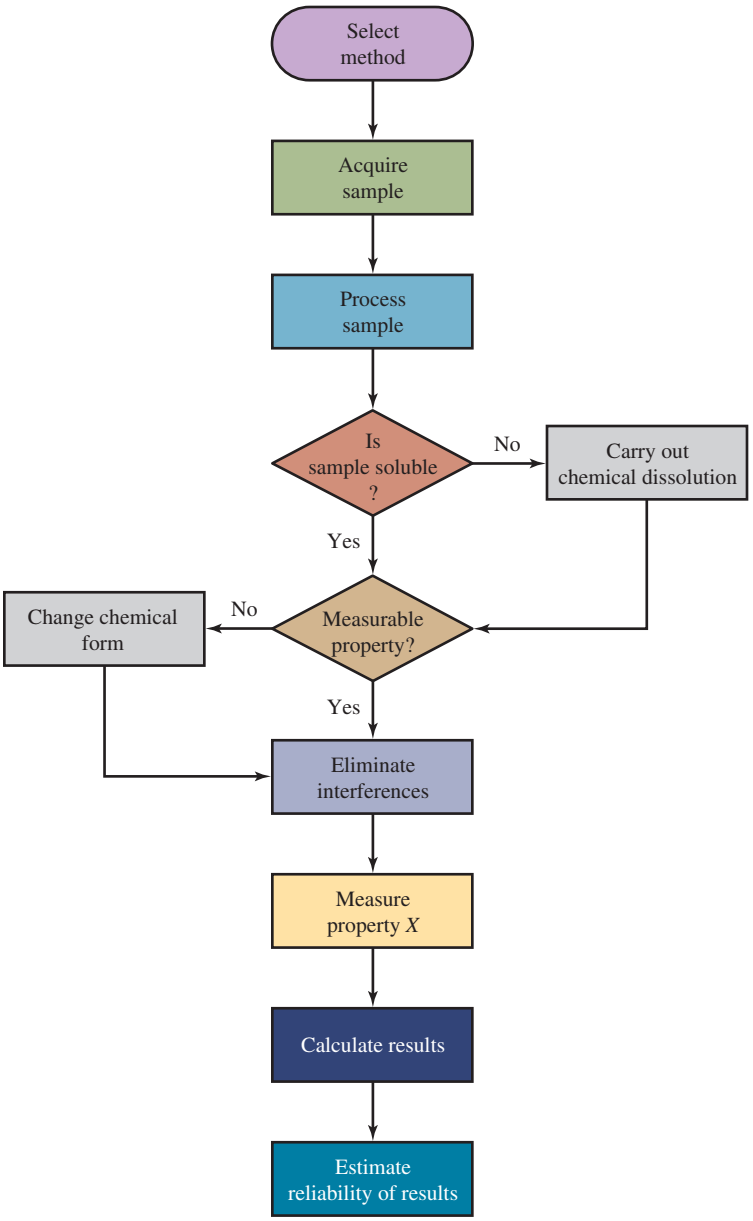


FIGURE 1-2
Flow diagram showing the steps in a quantitative analysis. There are a number of possible paths through these steps. In the simplest example represented by the central vertical pathway, we select a method, acquire and process the sample, dissolve the sample in a suitable solvent, measure a property of the analyte, calculate the results, and estimate the reliability of the results. Depending on the complexity of the sample and the chosen method, various other pathways may be necessary.

amount of time in preliminary operations such as assembling and calibrating instruments and equipment and preparing standard solutions. If we have only a single sample or a just a few samples, it may be more appropriate to select a procedure that avoids or minimizes such preliminary steps.

Finally, the complexity of the sample and the number of components in the sample always influence the choice of method to some degree.

1C-2 Acquiring the Sample

As illustrated in Figure 1-2, the second step in a quantitative analysis is to acquire the sample. To produce meaningful information, an analysis must be performed on a sample that has the same composition as the bulk of material from which it was taken. When the bulk is large and **heterogeneous**, great effort is required to get a representative sample. Consider, for example, a railroad car containing 25 tons

A material is **heterogeneous** if its constituent parts can be distinguished visually or with the aid of a microscope. Coal, animal tissue, and soil are heterogeneous.

Copyright 2022 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s).
Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

of silver ore. The buyer and seller of the ore must agree on a price, which will be based primarily on the silver content of the shipment. The ore itself is inherently heterogeneous, consisting of many lumps that vary in size as well as in silver content. The **assay** of this shipment will be performed on a sample that weighs about 1 gram. For the analysis to have significance, the composition of this small sample must be representative of the 25 tons (or approximately 22,700,000 g) of ore in the shipment. Isolation of 1 gram of material that accurately represents the average composition of the nearly 23,000,000 g of bulk sample is a difficult undertaking that requires a careful, systematic manipulation of the entire shipment. **Sampling** is the process of collecting a small mass of a material whose composition accurately represents the bulk of the material being sampled. Sampling is discussed in more detail in Chapter 6.

An **assay** is the process of determining how much of a given sample is the material by its indicated name. For example, a zinc alloy is assayed for its zinc content, and its assay is a particular numerical value.

We *analyze* samples, and we *determine* substances. For example, a blood sample is analyzed to determine the concentrations of various substances such as blood gases and glucose. We, therefore, speak of the determination of blood gases or glucose, *not* the analysis of blood gases or glucose.

The collection of specimens from biological sources represents a second type of sampling problem. Sampling of human blood for the determination of blood gases illustrates the difficulty of acquiring a representative sample from a complex biological system. The concentration of oxygen and carbon dioxide in blood depends on a variety of physiological and environmental variables. For example, applying a tourniquet incorrectly or hand flexing by the patient may cause the blood oxygen concentration to fluctuate. Because physicians make life-and-death decisions based on results of blood gas analyses, strict procedures have been developed for sampling and transporting specimens to the clinical laboratory. These procedures ensure that the sample is representative of the patient at the time it is collected and that its integrity is preserved until the sample can be analyzed.

Many sampling problems are easier to solve than the two just described. Whether sampling is simple or complex, however, the analyst must be sure that the laboratory sample is representative of the whole before proceeding. Sampling is frequently the most difficult step in an analysis and the source of greatest error. The final analytical result will never be any more reliable than the reliability of the sampling step.

1C-3 Processing the Sample

As shown in Figure 1-2, the third step in an analysis is to process the sample. Under certain circumstances, no sample processing is required prior to the measurement step. For example, once a water sample is withdrawn from a stream, a lake, or an ocean, the pH of the sample can be measured directly. Under most circumstances, the sample is processed in one of the several different ways. The first step in processing the sample is often the preparation of a laboratory sample.

Preparing a Laboratory Sample

A solid laboratory sample is ground to decrease particle size, mixed to ensure homogeneity, and stored for various lengths of time before analysis begins. Absorption or desorption of water may occur during each step, depending on the humidity of the environment. Because any loss or gain of water changes the chemical composition of solids, it is a good idea to dry samples just before starting an analysis. Alternatively, the moisture content of the sample can be determined at the time of the analysis in a separate analytical procedure.

Liquid samples present a slightly different but related set of problems during the preparation step. If such samples are allowed to stand in open containers, the solvent may evaporate and change the concentration of the analyte. If the analyte is a gas dissolved in a liquid, as in our blood gas example, the sample container must be kept inside a second sealed container, perhaps during the entire analytical procedure, to prevent contamination by atmospheric gases. Extraordinary measures, including

Copyright 2022 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s).
Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

sample manipulation and measurement in an inert atmosphere, may be required to preserve the integrity of the sample.

Defining Replicate Samples

Most chemical analyses are performed on **replicate samples** whose masses or volumes have been determined by careful measurements with an analytical balance or with a precise volumetric device. Replication improves the quality of the results and provides a measure of their reliability. Quantitative measurements on replicates are usually averaged, and various statistical tests are performed on the results to establish their reliability.

Replicate samples, or **replicates**, are portions of a material of approximately the same size that are carried through an analytical procedure at the same time and in the same way.

Preparing Solutions: Physical and Chemical Changes

Because many classical methods and most instrumental techniques use solution samples, most analyses are performed on solutions of the sample made with a suitable solvent. Ideally, the solvent should dissolve the entire sample, including the analyte, rapidly and completely. The conditions of dissolution should be sufficiently mild that loss of the analyte cannot occur. In our flow diagram of Figure 1-2, we ask whether the sample is soluble in the solvent of choice. Unfortunately, many materials that must be analyzed are insoluble in common solvents. Examples include silicate minerals, high-molecular-mass polymers, and specimens of animal tissue. With such substances, the analyst follows the flow diagram to the box on the right and performs some rather harsh chemistry. Converting the analyte in such materials into a soluble form is often the most difficult and time-consuming task in the analytical process. The sample may require heating with aqueous solutions of strong acids, strong bases, oxidizing agents, reducing agents, or some combination of such reagents. It may be necessary to ignite the sample in air or oxygen or to perform a high-temperature fusion of the sample in the presence of various fluxes. Once the analyte is made soluble, then ask whether the sample has a property that is proportional to analyte concentration and that we can measure. If it does not, other chemical steps may be necessary, as shown in Figure 1-2, to convert the analyte to a form that is suitable for the measurement step. For example, in the determination of manganese in steel, the element must be oxidized to MnO_4^- before the absorbance of the colored solution is measured (see Chapter 24). At this point in the analysis, it may be possible to proceed directly to the measurement step, but more often than not, eliminate interferences in the sample before making measurements, as illustrated in the flow diagram.

A **flux** is a material, often an alkali metal salt, that is mixed with the sample and heated to form a fused salt.

1C-4 Eliminating Interferences

Once we have the sample in solution and converted the analyte to an appropriate form for measurement, the next step is to eliminate substances from the sample that may interfere with measurement (see Figure 1-2). Few chemical or physical properties of importance in chemical analysis are unique to a single chemical species. Instead, the reactions used and the properties measured are characteristic of a group of elements of compounds. Species other than the analyte that affect the final measurement are called **interferences**, or **interferents**. A scheme must be devised to isolate the analytes from interferences before the final measurement is made. No hard and fast rules can be given for eliminating interference. This problem can certainly be the most demanding aspect of an analysis. Chapters 29–32 describe separation methods in detail.

An **interference** or **interferent** is a species that causes an error in an analysis by enhancing or attenuating (making smaller) the quantity being measured.

Copyright 2022 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s).
Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

1C-5 Calibrating and Measuring Concentration

The **matrix**, or **sample matrix**, is the collection of all the components in the sample containing an analyte.

All analytical results depend on a final measurement X of a physical or chemical property of the analyte, as shown in Figure 1-2. This property must vary in a known and reproducible way with the concentration c_A of the analyte. Ideally, the measurement of the property is directly proportional to the concentration, that is,

$$c_A = kX$$

Techniques or reactions that work for only one analyte are said to be **specific**. Techniques or reactions that apply to only a few analytes are **selective**.

where k is a proportionality constant. With a few exceptions, analytical methods require the empirical determination of k with chemical standards for which c_A is known.[2] The process of determining k is thus an important step in most analyses; this step is called a **calibration**. Calibration methods are discussed in some detail in Chapter 6.

Calibration is the process of determining the proportionality between analyte concentration and a measured quantity.

1C-6 Calculating Results

Computing analyte concentrations from experimental data is usually relatively easy, particularly with computers. This step is depicted in the next-to-last block of the flow diagram of Figure 1-2. These computations are based on the raw experimental data collected in the measurement step, the characteristics of the measurement instruments, and the stoichiometry of the analytical reaction. Samples of these calculations appear throughout this book.

1C-7 Evaluating Results by Estimating Reliability

As the final step in Figure 1-2 shows, analytical results are complete only when their reliability has been estimated. The experimenter must provide some measure of the uncertainties associated with computed results if the data are to have any value. Chapters 3–5 present detailed methods for carrying out this important final step in the analytical process.

An analytical result without an estimate of reliability is of no value.

1D An Integral Role for Chemical Analysis: Feedback Control Systems

Analytical chemistry is usually not an end in itself but is part of a bigger picture in which the analytical results may be used to help control a patient's health, to control the amount of mercury in fish, to control the quality of a product, to determine the status of a synthesis, or to find out whether there is life on Mars. Chemical analysis is the measurement element in all these examples and in many other cases. Consider the role of quantitative analysis in the determination and control of the concentration of glucose in blood. The system flow diagram of **Figure 1-3** illustrates the process. Patients suffering from insulin-dependent diabetes mellitus develop hyperglycemia, which manifests itself in a blood glucose concentration above the normal concentration range of 65 to 100 mg/dL. We begin our example by determining that the desired state is a blood glucose level below 100 mg/dL. Many patients must monitor their blood glucose levels by periodically submitting samples to a clinical laboratory for analysis or by measuring the levels themselves using a handheld electronic glucose monitor.

[2]Two exceptions are gravimetric methods, discussed in Chapter 10, and coulometric methods, considered in Chapter 20. In both these methods, k can be computed from known physical constants.

Copyright 2022 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s). Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

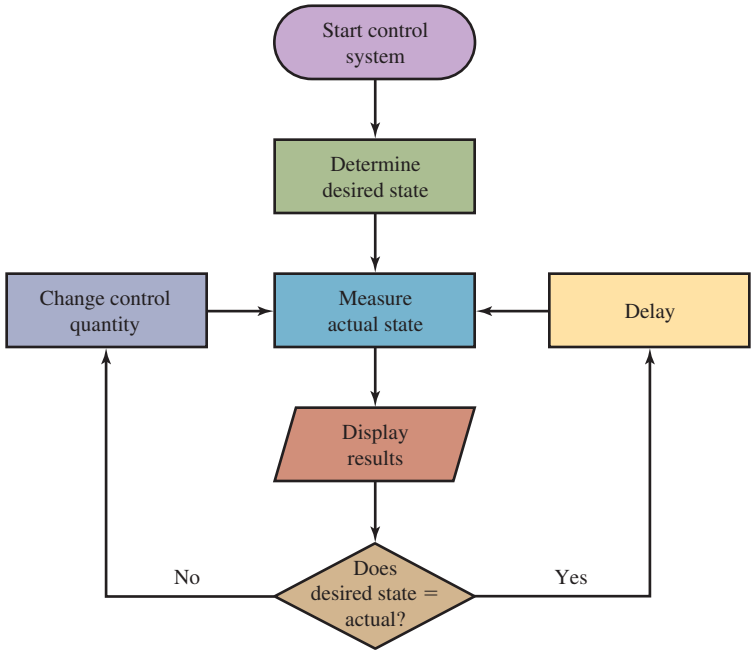


FIGURE 1-3
Feedback system flow diagram. The desired system state is defined, the actual state of the system is measured, and the two states are compared. The difference between the two states is used to change a controllable quantity that results in a change in the state of the system. Quantitative measurements are again performed on the system, and the comparison is repeated. The new difference between the desired state and the actual state is again used to change the state of the system if necessary. The process provides continuous monitoring and feedback to maintain the controllable quantity, and thus the actual state, at the proper level. The text describes the monitoring and control of blood glucose as an example of a feedback control system.

The first step in the monitoring process is to determine the actual state by collecting a blood sample from the patient and measuring the blood glucose level. The results are displayed, and then the actual state is compared to the desired state, as shown in Figure 1-3. If the measured blood glucose level is above 100 mg/dL, the patient's insulin level, which is a controllable quantity, is increased by injection or oral administration. After a delay to allow the insulin time to take effect, the glucose level is measured again to determine if the desired state has been achieved. If the level is below the threshold, the insulin level has been maintained, so no insulin is required. After a suitable delay time, the blood glucose level is measured again, and the cycle is repeated. In this way, the insulin level in the patient's blood, and thus the blood glucose level, is maintained at or below the critical threshold, which keeps the metabolism of the patient under control.

The process of continuous measurement and control is often referred to as a **feedback system**, and the cycle of measurement, comparison, and control is called a **feedback loop**. These ideas are widely applied in biological and biomedical systems, mechanical systems, and electronics. From the measurement and control of the concentration of manganese in steel to maintaining the proper level of chlorine in a swimming pool, chemical analysis plays a central role in a broad range of systems.

FEATURE 1-1

Deer Kill: A Case Study Illustrating the Use of Analytical Chemistry to Solve a Problem in Toxicology

Analytical chemistry is a powerful tool in environmental investigations. This feature describes a case study in which quantitative analysis was used to determine the agent that caused deaths in a population of white-tailed deer in a wildlife area of a national recreational area in Kentucky. We begin with a description of the problem and then show how the steps illustrated in Figure 1-2 were used to solve the analytical problem. This case study also shows how chemical analysis is used in a broad context as an integral part of the feedback control system depicted in Figure 1-3.

The Problem

The incident began when a park ranger found a dead white-tailed deer near a pond in the Land Between the Lakes National Recreation Area in western Kentucky. The ranger enlisted the help of a

(*continued*)

Copyright 2022 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s).
Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.