

Analytical Chemistry and Quantitative Analysis

David S. Hage • James D. Carr

CONTENTS

Preface xiii

Chapter 1	An Overview of Analytical Chemistry 1	
	1.1 Introduction: The Case of the Mysterious Chemist 1	
	1.2 The History of Chemical Analysis 2	
	1.2A Origins of Chemical Analysis 2	
	1.2B Chemical Analysis in the Modern World 3	
	1.3 General Terms Used in Chemical Analysis 4	
	1.3A Sample-Related Terms 4	
	1.3B Method-Related Terms 5	
	1.4 Information Provided by Chemical Analysis 7	
	1.5 Overview of Text 9	
	Key Words 9 • Other Terms 9 • Questions 9 • References 11	
Chapter 2	Good Laboratory Practices 12	
	2.1 Introduction: A Question of Quality 12	
	2.1A What Are Good Laboratory Practices? 12	
	2.1B Establishing Good Laboratory Practices 13	
	■ BOX 2.1: The Polymerase Chain Reaction 14	
	2.2 Laboratory Safety 16	
	2.2A Common Components of Laboratory Safety 16	
	2.2B Identifying Chemical Hazards 16	
	BOX 2.2: Determining the Safety of Chemicals 18	
	2.2C Sources of Information on Chemicals 19	
	2.2D Proper Handling of Chemicals 21	
	2.3 The Laboratory Notebook 22	
	2.3A Recommended Notebook Practices 22	
	2.3B Electronic Notebooks and Spreadsheets 23	
	2.4 Reporting Experimental Data 25	
	2.4A The SI System of Measurements 25	
	2.4B Significant Figures 29	
	Key Words 31 • Other Terms 31 • Questions 31 References 34	•
Chapter 3	Mass and Volume Measurements 36	
	3.1 Introduction: J. J. Berzelius 36	
	3.2 Mass Measurements 37	
	3.2A The Determination of Mass 37	
	3.2B Types of Laboratory Balances 38	
	■ BOX 3.1: Atomic Force Microscopy 39	
	3.2C Recommended Procedures for Mass Measurements	41

	3.3 Volume Measurements 43
	3.3A The Determination of Volume 44
	3.3B Types of Volumetric Equipment 45
	3.3C Recommended Procedures for Volume Measurements 48
	3.4 Samples, Reagents, and Solutions 50
	3.4A Describing Sample and Reagent Composition 50
	3.4B Solution Preparation 54 Key Words 58 • Other Terms 58 • Questions 58 • References 63
Chapter 4	Making Decisions with Data 64
•	4.1 Introduction: Take Me Out to the Ball Game? 64
	4.1A Types of Laboratory Errors 65
	4.1B Accuracy and Precision 65
	4.2 Describing Experimental Results 66
	4.2A Determining the Most Representative Value 66
	4.2B Reporting the Variation in a Group of Results 67
	4.3 The Propagation of Errors 68
	4.3A Addition and Subtraction 68
	4.3B Multiplication and Division 69
	4.3C Logarithms, Antilogarithms, and Exponents 70
	4.3D Mixed Calculations 71
	4.4 Sample Distributions and Confidence Intervals 71
	4.4A Describing the Variation in Large Data Sets 72
	4.4B Describing the Variation in Small Data Sets 73
	BOX 4.1: Who Was "Student"? 75
	4.5 Comparing Experimental Results 76
	4.5A General Requirements for the Comparison of Data 76
	4.5B Comparing an Experimental Result with a Reference Value 76
	4.5C Comparing Two or More Experimental Results 77
	BOX 4.2: Selecting a Confidence Level 78
	4.5D Comparing the Variation in Results 80
	4.6 Detecting Outliers 81
	4.6A General Strategy in Handling Outliers 81
	4.6B Statistical Tests for Outliers 81
	4.7 Fitting Experimental Results 83
	4.7A Linear Regression 83
	4.7B Testing the Goodness of a Fit 84 Key Words 87 • Other Terms 88 • Questions 88 • References 94
Chapter 5	Characterization and Selection of Analytical Methods 95
	5.1 Introduction: The Vinland Map 95
	5.2 Method Characterization and Validation 96
	5.2A Accuracy and Precision 96
·	■ BOX 5.1: A Closer Look at Small Samples 97

	5.2B Assay Response 99
	5.2C Other Properties of Analytical Methods 103
	5.3 Quality Control 103
	5.3A General Requirements for Quality Control 103
	5.3B Preparing and Using Control Charts 103
	5.4 Sample Collection and Preparation 104
	5.4A Sample Collection 105
	5.4B Sample Preparation 106 Key Words 109 • Other Terms 109 • Questions 109 •
Chapter 6	References 113 Chemical Activity and Chemical Equilibrium 115
	6.1 Introduction: "And the Long-Range Forecast Is" 115
	6.1A Types of Chemical Reactions and Transitions 115
	6.1B Describing Chemical Reactions 116
	6.2 Chemical Activity 117
	6.2A What Is Chemical Activity? 117
	■ BOX 6.1: Carbon-14 Dating 118
	6.2B Chemical Activity in Analytical Methods 121
	6.3 Chemical Equilibrium 125
	6.3A What is a Chemical Equilibrium? 125
	6.3B Solving Chemical Equilibrium Problems 130
	Key Words 136 • Other Terms 136 • Questions 136 • References 139
Chapter 7	Chemical Solubility and Precipitation 141
•	- ,
•	7.1 Introduction: Fighting Stomach Cancer 141
•	7.1 Introduction: Fighting Stomach Cancer 141 7.1A What Is Solubility? 141
·	7.1 Introduction: Fighting Stomach Cancer 141 7.1A What Is Solubility? 141 7.1B What Is Precipitation? 142
·	7.1 Introduction: Fighting Stomach Cancer 141 7.1A What Is Solubility? 141
·	 7.1 Introduction: Fighting Stomach Cancer 141 7.1A What Is Solubility? 141 7.1B What Is Precipitation? 142 7.1C Why Are Solubility and Precipitation Important in Chemical Analysis? 143 7.2 Chemical Solubility 144
·	 7.1 Introduction: Fighting Stomach Cancer 141 7.1A What Is Solubility? 141 7.1B What Is Precipitation? 142 7.1C Why Are Solubility and Precipitation Important in Chemical Analysis? 143 7.2 Chemical Solubility 144 7.2A What Determines Chemical Solubility? 144
·	 7.1 Introduction: Fighting Stomach Cancer 141 7.1A What Is Solubility? 141 7.1B What Is Precipitation? 142 7.1C Why Are Solubility and Precipitation Important in Chemical Analysis? 143 7.2 Chemical Solubility 144 7.2A What Determines Chemical Solubility? 144 BOX 7.1: X-Ray Crystallography 145
	 7.1 Introduction: Fighting Stomach Cancer 141 7.1A What Is Solubility? 141 7.1B What Is Precipitation? 142 7.1C Why Are Solubility and Precipitation Important in Chemical Analysis? 143 7.2 Chemical Solubility 144 7.2A What Determines Chemical Solubility? 144 BOX 7.1: X-Ray Crystallography 145 7.2B How Can We Describe Chemical Solubility? 147
	 7.1 Introduction: Fighting Stomach Cancer 141 7.1A What Is Solubility? 141 7.1B What Is Precipitation? 142 7.1C Why Are Solubility and Precipitation Important in Chemical Analysis? 143 7.2 Chemical Solubility 144 7.2A What Determines Chemical Solubility? 144 BOX 7.1: X-Ray Crystallography 145
	 7.1 Introduction: Fighting Stomach Cancer 141 7.1A What Is Solubility? 141 7.1B What Is Precipitation? 142 7.1C Why Are Solubility and Precipitation Important in Chemical Analysis? 143 7.2 Chemical Solubility 144 7.2A What Determines Chemical Solubility? 144 BOX 7.1: X-Ray Crystallography 145 7.2B How Can We Describe Chemical Solubility? 147 7.2C How Can We Determine the Solubility of a Chemical? 153 7.3 Chemical Precipitation 154
	 7.1 Introduction: Fighting Stomach Cancer 141 7.1A What Is Solubility? 141 7.1B What Is Precipitation? 142 7.1C Why Are Solubility and Precipitation Important in Chemical Analysis? 143 7.2 Chemical Solubility 144 7.2A What Determines Chemical Solubility? 144 BOX 7.1: X-Ray Crystallography 145 7.2B How Can We Describe Chemical Solubility? 147 7.2C How Can We Determine the Solubility of a Chemical? 153 7.3 Chemical Precipitation 154 7.3A The Process of Precipitation 154
	 7.1 Introduction: Fighting Stomach Cancer 141 7.1A What Is Solubility? 141 7.1B What Is Precipitation? 142 7.1C Why Are Solubility and Precipitation Important in Chemical Analysis? 143 7.2 Chemical Solubility 144 7.2A What Determines Chemical Solubility? 144 BOX 7.1: X-Ray Crystallography 145 7.2B How Can We Describe Chemical Solubility? 147 7.2C How Can We Determine the Solubility of a Chemical? 153 7.3 Chemical Precipitation 154 7.3A The Process of Precipitation 154 7.3B Using Solubility Products to Examine Precipitation 155
	 7.1 Introduction: Fighting Stomach Cancer 141 7.1A What Is Solubility? 141 7.1B What Is Precipitation? 142 7.1C Why Are Solubility and Precipitation Important in Chemical Analysis? 143 7.2 Chemical Solubility 144 7.2A What Determines Chemical Solubility? 144 BOX 7.1: X-Ray Crystallography 145 7.2B How Can We Describe Chemical Solubility? 147 7.2C How Can We Determine the Solubility of a Chemical? 153 7.3 Chemical Precipitation 154 7.3A The Process of Precipitation 154 7.3B Using Solubility Products to Examine Precipitation 155 7.3C Effects of Other Chemicals and Reactions on
	 7.1 Introduction: Fighting Stomach Cancer 141 7.1A What Is Solubility? 141 7.1B What Is Precipitation? 142 7.1C Why Are Solubility and Precipitation Important in Chemical Analysis? 143 7.2 Chemical Solubility 144 7.2A What Determines Chemical Solubility? 144 BOX 7.1: X-Ray Crystallography 145 7.2B How Can We Describe Chemical Solubility? 147 7.2C How Can We Determine the Solubility of a Chemical? 153 7.3 Chemical Precipitation 154 7.3A The Process of Precipitation 154 7.3B Using Solubility Products to Examine Precipitation 155
Chapter 8	 7.1 Introduction: Fighting Stomach Cancer 141 7.1A What Is Solubility? 141 7.1B What Is Precipitation? 142 7.1C Why Are Solubility and Precipitation Important in Chemical Analysis? 143 7.2 Chemical Solubility 144 7.2A What Determines Chemical Solubility? 144 BOX 7.1: X-Ray Crystallography 145 7.2B How Can We Describe Chemical Solubility? 147 7.2C How Can We Determine the Solubility of a Chemical? 153 7.3 Chemical Precipitation 154 7.3A The Process of Precipitation 154 7.3B Using Solubility Products to Examine Precipitation 155 7.3C Effects of Other Chemicals and Reactions on Precipitation 157 Key Words 159 • Other Terms 159 • Questions 159 • References 164
	 7.1 Introduction: Fighting Stomach Cancer 141 7.1A What Is Solubility? 141 7.1B What Is Precipitation? 142 7.1C Why Are Solubility and Precipitation Important in Chemical Analysis? 143 7.2 Chemical Solubility 144 7.2A What Determines Chemical Solubility? 144 BOX 7.1: X-Ray Crystallography 145 7.2B How Can We Describe Chemical Solubility? 147 7.2C How Can We Determine the Solubility of a Chemical? 153 7.3 Chemical Precipitation 154 7.3A The Process of Precipitation 154 7.3B Using Solubility Products to Examine Precipitation 155 7.3C Effects of Other Chemicals and Reactions on Precipitation 157 Key Words 159 • Other Terms 159 • Questions 159 • References 164
	 7.1 Introduction: Fighting Stomach Cancer 141 7.1A What Is Solubility? 141 7.1B What Is Precipitation? 142 7.1C Why Are Solubility and Precipitation Important in Chemical Analysis? 143 7.2 Chemical Solubility 144 7.2A What Determines Chemical Solubility? 144 BOX 7.1: X-Ray Crystallography 145 7.2B How Can We Describe Chemical Solubility? 147 7.2C How Can We Determine the Solubility of a Chemical? 153 7.3 Chemical Precipitation 154 7.3A The Process of Precipitation 154 7.3B Using Solubility Products to Examine Precipitation 155 7.3C Effects of Other Chemicals and Reactions on Precipitation 157 Key Words 159 Other Terms 159 Questions 159 References 164 Acid-Base Reactions 165

	8.2 Describing Acids and Bases 169
	8.2A Strong and Weak Acids 169
	8.2B Strong and Weak Bases 170
	8.2C The Acid and Base Properties of Water 171
	8.3 The Acid or Base Properties of a Solution 173
	8.3A What Is pH? 173
	8.3B Factors that Affect pH 175
	8.4 Estimating the pH of Simple Acid-Base Solutions 176
	8.4A Monoprotic Strong Acids and Bases 176
	8.4B Monoprotic Weak Acids and Bases 178
	8.5 Buffers and Polyprotic Acid–Base Systems 181
	8.5A Buffer Solutions 181
	BOX 8.1: Preparing Buffers 182
	8.5B Polyprotic Acid–Base Systems 185
	8.5C Zwitterions 190
	Key Words 195 • Other Terms 195 • Questions 195 • References 201
Chapter 9	Complex Formation 203
	9.1 Introduction: What's in My Mayo? 203
	9.1A What Is Complex Formation? 203
	9.1B What Are Some Analytical Applications of Complex Formation? 204
	9.2 Simple Metal-Ligand Complexes 204
	9.2A What Is a Metal–Ligand Complex? 205
	9.2B Formation Constants for Metal–Ligand Complexes 207
	9.2C Predicting the Distribution of Metal–Ligand Complexes 208
	BOX 9.1: A Closer Look at Metal–Ligand Complex Formation 209
	9.3 Complexes of Chelating Agents with Metal lons 213
	9.3A What Is a Chelating Agent? 213
	9.3B The Chelate Effect 214
	9.3C Ethylenediaminetetraacetic Acid 214
	9.3D Dealing with Side Reactions 217
	9.4 Other Types of Complexes 220
	9.4A A General Description of Complex Formation 220
	9.48 Examples of Alternative Complexes 221
	BOX 9.2: Immunoassays 222
	Key Words 223 • Other Terms 223 • Questions 223 • References 228
Chapter 10	Oxidation–Reduction Reactions 230
_	10.1 Introduction: Saving the <i>Arizona</i> 230
	10.1A What Are Oxidation-Reduction Reactions? 230
	10.1B How Are Oxidation–Reduction Reactions Used in
	Analytical Chemistry? 232
	10.2 General Principles of Oxidation–Reduction Reactions 232
	10.2A Describing Oxidation Reduction Reactions 232
	10.2B Identifying Oxidation-Reduction Reactions 233

	10.2C Predicting the Extent of Oxidation–Reduction Reactions 235
	10.3 Electrochemical Cells 238
	10.3A Describing Electrochemical Cells 238
	■ BOX 10.1: A Shorthand Description of Electrochemical Cells 240
	10.3B Predicting the Behavior of Electrochemical Cells 241
	10.4 The Nernst Equation 243
	10.4A Working with the Nernst Equation 243
	■ BOX 10.2: A Closer Look at the Nernst Equation 244
	10.4B Calculating Potentials for Oxidation-Reduction Reactions 245
	10.4C Effects of the Sample Matrix and Side Reactions 247
	Key Words 251 • Other Terms 251 • Questions 252 • References 258
Chapter 11	Gravimetric Analysis 259
	11.1 Introduction: Fixing the Periodic Table 259
	11.1A What Is Gravimetric Analysis? 259
	11.1B How Is Gravimetric Analysis Used in Analytical Chemistry? 260
	11.2 Performing a Traditional Gravimetric Analysis 261
	11.2A General Strategies and Methods 261
	11.2B Filtering Precipitates 262
	11.2C Drying and Weighing Precipitates 266
	11.2D Methods for Obtaining High-Quality Precipitates 266
	11.3 Examples of Gravimetric Methods 269
	11.3A Precipitation of Silver with Chloride 269
	11.3B Precipitation of Iron with Hydroxide 271
	11.3C Precipitation of Nickel with Dimethylglyoxime 272
	11.3D Combustion Analysis 273
	11.3E Thermogravimetric Analysis 275
	BOX 11.1: Combustion Analysis, Then and Now 276
	Key Words 277 • Other Terms 278 • Questions 278 • References 282
Chapter 12	Acid-Base Titrations 283
	12.1 Introduction: Rise of the Titrations 283
	12.1A What Is an Acid–Base Titration? 283
	12.1B How Are Acid-Base Titrations Used in Analytical Chemistry? 284
	BOX 12.1: The Kjeldahl Method 288
	12.2 Performing an Acid–Base Titration 289
	12.2A Preparing Titrant and Sample Solutions 289
	12.2B Performing a Titration 292
	12.2C Determining the End Point 293
	12.3 Predicting and Optimizing Acid–Base Titrations 296
	12.3A Describing Acid–Base Titrations 296
	12.3B Titration Curves for Strong Acids and Bases 298

	12.3C Titration Curves for Weak Acids and Bases 302
	12.3D A Closer Look at Acid–Base Titrations 306
	Key Words 312 • Other Terms 312 • Questions 312 • References 318
Chapter 13	Complexometric and Precipitation Titrations 319
-	13.1 Introduction: How Hard Is the Water? 319
	13.1A What Is a Complexometric or Precipitation Titration? 319
	13.1B How Are Complexometric and Precipitation Titrations Used in Analytical Chemistry? 322
	13.2 Performing a Complexometric Titration 322
	13.2A Titrants and Standard Solutions 322
	13.2B Using Auxiliary Ligands and Masking Agents 326
	13.2C Determining the End Point。327
	13.20 Predicting and Optimizing Complexometric Titrations 329
	13.3 Performing a Precipitation 1333
	13.3A Titrants and Standard Solutions 333
	13.3B Determining the End Point 334
	BOX 13.1: A King with a Problem 335
	13.3C Predicting and Optimizing Precipitation Titrations 337
	Key Words 341 • Other Terms 341 • Questions 341 • References 347
Chapter 14	An Introduction to Electrochemical Analysis 348
	14.1 Introduction: Getting a Brighter Smile 348
	14.1A Units of Electrical Measurements 348
	14.1B Methods for Electrochemical Analysis 351
	14.2 General Principles of Potentiometry 351
	•
	14.2A Cell Potentials and the Nernst Equation 351
	14.2A Cell Potentials and the Nernst Equation 351 14.2B Cell Components in Potentiometry 352
	14.2A Cell Potentials and the Nernst Equation 351 14.2B Cell Components in Potentiometry 352 14.2C Applications of Potentiometry 356
	14.2A Cell Potentials and the Nernst Equation 351 14.2B Cell Components in Potentiametry 352 14.2C Applications of Potentiametry 356 14.3 Ion-Selective Electrodes and Related Devices 356
	14.2A Cell Potentials and the Nernst Equation 351 14.2B Cell Components in Potentiometry 352 14.2C Applications of Potentiometry 356 14.3 Ion-Selective Electrodes and Related Devices 356 14.3A Glass Membrane Electrodes 357
	14.2A Cell Potentials and the Nernst Equation 351 14.2B Cell Components in Potentiometry 352 14.2C Applications of Potentiometry 356 14.3 ion-Selective Electrodes and Related Devices 356 14.3A Glass Membrane Electrodes 357 ■ BOX 14.1: Creation of the pH Meter 357
	14.2A Cell Potentials and the Nernst Equation 351 14.2B Cell Components in Potentiometry 352 14.2C Applications of Potentiometry 356 14.3 (on-Selective Electrodes and Related Devices 356 14.3A Glass Membrane Electrodes 357 ■ BOX 14.1: Creation of the pH Meter 357 14.3B Solid-State Ion-Selective Electrodes 359
	14.2A Cell Potentials and the Nernst Equation 351 14.2B Cell Components in Potentiometry 352 14.2C Applications of Potentiometry 356 14.3 ion-Selective Electrodes and Related Devices 356 14.3A Glass Membrane Electrodes 357 ■ BOX 14.1: Creation of the pH Meter 357 14.3B Solid-State Ion-Selective Electrodes 359 14.3C Compound Electrodes 360
Chanday 45	14.2A Cell Potentials and the Nernst Equation 351 14.2B Cell Components in Potentiometry 352 14.2C Applications of Potentiometry 356 14.3 (on-Selective Electrodes and Related Devices 356 14.3A Glass Membrane Electrodes 357 ■ BOX 14.1: Creation of the pH Meter 357 14.3B Solid-State Ion-Selective Electrodes 359 14.3C Compound Electrodes 360 Key Words 361 • Other Terms 361 • Questions 361 • References 364
Chapter 15	14.2A Cell Potentials and the Nernst Equation 351 14.2B Cell Components in Potentiometry 352 14.2C Applications of Potentiometry 356 14.3 ion-Selective Electrodes and Related Devices 356 14.3A Glass Membrane Electrodes 357 ■ BOX 14.1: Creation of the pH Meter 357 14.3B Solid-State Ion-Selective Electrodes 359 14.3C Compound Electrodes 360 Key Words 361 • Other Terms 361 • Questions 361 • References 364 Redox Titrations 365
Chapter 15	14.2A Cell Potentials and the Nernst Equation 351 14.2B Cell Components in Potentiometry 352 14.2C Applications of Potentiometry 356 14.3 ion-Selective Electrodes and Related Devices 356 14.3A Glass Membrane Electrodes 357 ■ BOX 14.1: Creation of the pH Meter 357 14.3B Solid-State Ion-Selective Electrodes 359 14.3C Compound Electrodes 360 Key Words 361 • Other Terms 361 • Questions 361 • References 364 Redox Titrations 365 15.1 Introduction: Chemical Oxygen Demand 365
Chapter 15	14.2A Cell Potentials and the Nernst Equation 351 14.2B Cell Components in Potentiometry 352 14.2C Applications of Potentiometry 356 i.4.3 ion-Selective Electrodes and Related Devices 356 14.3A Glass Membrane Electrodes 357 ■ BOX 14.1: Creation of the pH Meter 357 14.3B Solid-State Ion-Selective Electrodes 359 14.3C Compound Electrodes 360 Key Words 361 • Other Terms 361 • Questions 361 • References 364 Redox Titrations 365 15.1 Introduction: Chemical Oxygen Demand 365 15.1A What Is a Redox Titration? 365
Chapter 15	14.2A Cell Potentials and the Nernst Equation 351 14.2B Cell Components in Potentiometry 352 14.2C Applications of Potentiometry 356 14.3 ion-Selective Electrodes and Related Devices 356 14.3A Glass Membrane Electrodes 357 ■ BOX 14.1: Creation of the pH Meter 357 14.3B Solid-State Ion-Selective Electrodes 359 14.3C Compound Electrodes 360 Key Words 361 • Other Terms 361 • Questions 361 • References 364 Redox Titrations 365 15.1 Introduction: Chemical Oxygen Demand 365
Chapter 15	14.2A Cell Potentials and the Nernst Equation 351 14.2B Cell Components in Potentiometry 352 14.2C Applications of Potentiometry 356 14.3 ion-Selective Electrodes and Related Devices 356 14.3A Glass Membrane Electrodes 357 ■ BOX 14.1: Creation of the pH Meter 357 14.3B Solid-State Ion-Selective Electrodes 359 14.3C Compound Electrodes 360 Key Words 361 • Other Terms 361 • Questions 361 • References 364 Redox Titrations 365 15.1 Introduction: Chemical Oxygen Demand 365 15.1A What Is a Redox Titration? 365 15.1B How Are Redox Titrations Used in Analytical
Chapter 15	14.2A Cell Potentials and the Nernst Equation 351 14.2B Cell Components in Potentiometry 352 14.2C Applications of Potentiometry 356 14.3 ion-Selective Electrodes and Related Devices 356 14.3A Glass Membrane Electrodes 357 ■ BOX 14.1: Creation of the pH Meter 357 14.3B Solid-State Ion-Selective Electrodes 359 14.3C Compound Electrodes 360 Key Words 361 • Other Terms 361 • Questions 361 • References 364 Redox Titrations 365 15.1 Introduction: Chemical Oxygen Demand 365 15.1A What Is a Redox Titration? 365 15.1B How Are Redox Titrations Used in Analytical Chemistry? 367

```
15.3 Predicting and Optimizing Redox Titrations 373
                   15.3A General Approach to Calculations for Redox
                     Titrations 373
                   15.3B Estimating the Shape of a Redox Titration Curve 374
                   15.3C Using the Fraction of Titration 377
              15.4 Examples of Redox Titrations 378
                   15.4A Titrations Involving Cerate 378
                   15.4B Titrations Involving Permanganate 378
                   15.4C Titrations Involving Dichromate 382
                   15.4D Titrations Involving Iodine 383
                   BOX 15.1: The Karl Fischer Method 385
                   Key Words 386 • Other Terms 386 • Questions 386 •
                   References 390
Chapter 16 Coulometry, Voltammetry, and Related Methods 392
              16.1 Introduction: The Dead Zone 392
              16.2 Electrogravimetry 392
              16.3 Coulometry 394
                   16.3A Direct Coulometry 395
                   16.3B Coulometric Titrations 395
                   16.3C Constant Potential Coulometry 397
              16.4 Voltammetry and Amperometry 397
                   16.4A Direct Current Voltammetry 397
                   16.4B Amperometry 399
                   BOX 16.1: Cyclic Voltammetry 400
                  16.4C Anodic Stripping Voltammetry 401
                   Key Words 402 • Other Terms 402 • Questions 402 •
                   References 404
Chapter 17 An Introduction to Spectroscopy 405
              17.1 Introduction: The View from Above 405
                   17.1A What Is Spectroscopy? 405
                   17.1B How Is Spectroscopy Used in Analytical
                     Chemistry? 407
              17.2 The Properties of Light 407
                   17.2A What Is Light? 408
                   BOX 17.1: NMR: Tuning into Chemical Structure 412
                   17.2B Uptake and Release of Light by Matter 413
                   17.2C Physical Interactions of Light with Matter 416
              17.3 Quantitative Analysis Based on Spectroscopy 421
                   17.3A Analysis Based on Emission 421
                   17.3B Analysis Based on Absorption 421
                   ■ BOX 17.2: A Closer Look at Beer's Law 423
                   Key Words 427 • Other Terms 427 • Questions 427 •
                   References 433
Chapter 18 Molecular Spectroscopy 434
              18.1 Introduction: The Good, the Bad, and the Ugly 434
                   18.1A What Is Molecular Spectroscopy? 434
                   18.1B How Is Molecular Spectroscopy Used in Chemical
                     Analysis? 435
```

	18.2 Ultraviolet-Visible Spectroscopy 435
	18.2A General Principles of Ultraviolet-Visible Spectroscopy 435
	18.2B Instrumentation for Ultraviolet-Visible Spectroscopy 437
	18.2C Applications of Ultraviolet-Visible Spectroscopy 440
	18.3 Infrared Spectroscopy 445
	18.3A General Principles of Infrared Spectroscopy 445
	18.3B Instrumentation for Infrared Spectroscopy 446 BOX 18.1: Raman Spectroscopy 447
	18.3C Applications of Infrared Spectroscopy 448
	18.4 Molecular Luminescence 450
	18.4A General Principles of Luminescence 450
	18.4B Instrumentation for Luminescence Measurements 452
	18.4C Applications of Molecular Luminescence 452
	Key Words 453 • Other Terms 453 • Questians 453 • References 457
Chapter 19	Atomic Spectroscopý 459
	19.1 Introduction: Star Light, Star Bright 459
	19.1A What Is Atomic Spectroscopy? 459
	19.1B How Is Atomic Spectroscopy Used in Chemical Analysis? 460
	19.2 Principles of Atomic Spectroscopy 461
	19.2A Sample Atomization 461
	19.2B Sample Excitation 461
	19.2C Properties of Flames 461
	19.2D Analyte Measurement 463
	19.3 Atomic Absorption Spectrometry 464
	BOX 19.1: Tuning into Lasers 464
	19.3A Laminar Flow Instruments 465
	19.3B Graphite-Furnace Instruments 466
	19.3C Optimizing Atomic Absorption Spectroscopy 467
	19.4 Atomic Emission Spectroscopy 470
	19.4A Flame Instruments 470
	19.4B Plasma Instruments 470 Key Words 472 • Other Terms 472 • Questions 472 • References 475
Chapter 20	An Introduction to Chemical Separations 476
•	20.1 Introduction: The Green Revolution 476
	20.1A What Is a Chemical Separation? 476
	20.1B How Are Chemical Separations Used in Analytical Chemistry? 477
	20.2 Chemical Separations Based on Extractions 478
	20.2A What Is an Extraction? 478
	20.2B Using and Describing Extractions 480
	BOX 20.1: Supercritical Fluid Extractions 480
	20.2C A Closer Look at Extractions 482

	20.3 Chemical Separations Based on Chromatography 485
	20.3A What Is Chromatography? 485
	20.3B Using and Describing Chromatography 487
	20.4 A Closer Look at Chromatography 488
	20.4A Analyte Retention in Chromatography 488
	20.4B Chromatographic Band-Broadening 490
	BOX 20.2: A Closer Look at the van Deemter Equation 495
	20.4C Controlling Chromatographic Separations 496 Key Words 498 • Other Terms 498 • Questions 499 • References 505
Chapter 21	Gas Chromatography 507
_	21.1 Introduction: There's Something in the Air 507
	21.1A What Is Gas Chromatography? 507
	21.1B How Is Gas Chromatography Performed? 508
	21.2 Factors that Affect Gas Chromatography 510
	21.2A Requirements for the Analyte 510
	21.2B Factors that Determine Retention in Gas Chromatography 512
	21.2C Column Efficiency in Gas Chromatography 515
	■ BOX 21.1: Comparing Gas Chromatography Stationary Phases 515
	21.3 Gas Chromatography, Mobile Phases, and Elution Methods 515
	21.3A Common Mobile Phases in Gas Chromatography 515
	21.3B Elution Methods in Gas Chromatography 516
	21.4 Gas Chromatography Supports and Stationary Phases 517
	21.4A Gas Chromatography Support Materials 517 BOX 21.2: Analytical Chemistry in Space 518
	21.4B Gas Chromatography Stationary Phases 519
	21.5 Gas Chromatography Detectors and Sample Handling 522
	21.5A Types of Gas Chromatography Detectors 522
	21.5B Sample Injection and Pretreatment 527 Key Words 530 • Other Terms 530 • Questions 531 • References 535
Chapter 22	Liquid Chromatography 537
	22.1 Introduction: Battling a Modern Epidemic 537
	22.1A What Is Liquid Chromatography? 537
	22.1B How Is Liquid Chromatography Performed? 538
	22.2 Factors that Affect Liquid Chromatography 539
	22.2A Requirements for the Analyte 539
	22.2B Column Efficiency in Liquid Chromatography 540
	22.2C Role of the Mobile Phase in Liquid Chromatography 540
	■ BOX 22.1: Paper Chromatography and TLC 542
	22.3 Types of Liquid Chromatography 543
	22.3A Adsorption Chromatography 543

22.3B Partition Chromatography 54522.3C Ion-Exchange Chromatography 548

- 22.3D Size-Exclusion Chromatography 55222.3E Affinity Chromatography 553
- 22.4 Liquid Chromatography Detectors and Sample
 - Pretreatment 556
 - 22.4A Types of Liquid Chromatography Detectors 556
 - **BOX 2.2:** Chiral Separations 557
 - 22.4B Liquid Chromatography Equipment and Sample Pretreatment 561

Key Words 564 • Other Terms 564 • Questions 564 • References 569

Chapter 23 Electrophoresis 571

- 23.1 Introduction: The Human Genome Project 571
 - 23.1A What Is Electrophoresis? 571
 - 23.1B How is Electrophoresis Performed? 573
 - 23.2 General Principles of Electrophoresis 57423.2A Factors Affecting Analyte Migration 574
 - 23.2B Factors Affecting Band-Broadening 576
 - 23.3 Gel Electrophoresis 577
 23.3A What Is Gel Electrophoresis? 577
 - 22.20 Neverla Cal Flanting Income in Device and 12
 - 23.3B How Is Gel Electrophoresis Performed? 57823.3C What Are Some Special Types of Gel
 - Electrophoresis? 579
 BOX 23.1: Matrix-Assisted Laser Description/Jonization Time
 - BOX 23.1: Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrometry 580
 - 23.4 Capillary Electrophoresis 582
 - 23.4A What Is Capillary Electrophoresis? 582
 - 23.4B How Is Capillary Electrophoresis Performed? 583
 - 23.4C What Are Some Special Types of Capillary Electrophoresis? 587
 - **BOX 23.2**: Analytical Chemistry on a Chip 587

Key Words 590 • Other Terms 590 • Questions 590 • References 595

Appendices 597

Answers to Selected Questions 635

Glossary 645