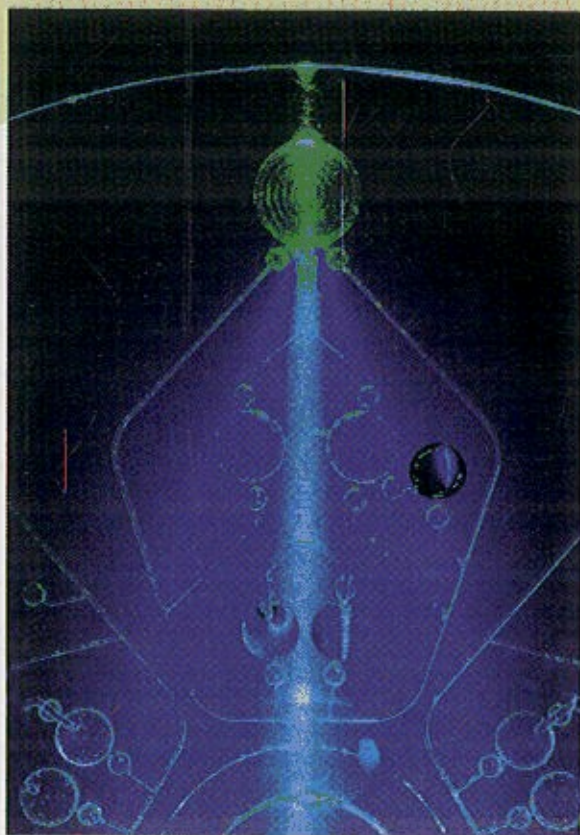


INTERNATIONAL STUDENT EDITION

*Fundamentals of*  
**Analytical Chemistry**

EIGHTH EDITION



SKOOG | WEST | HOLLER | CROUCH

Not for Sale in the  
United States

# CONTENTS

## **Chapter 1** The Nature of Analytical Chemistry 2

- 1A The Role of Analytical Chemistry 3
- 1B Quantitative Analytical Methods 4
- 1C A Typical Quantitative Analysis 5
- 1D An Integral Role for Chemical Analysis:  
Feedback Control Systems 10
- Feature 1-1** Deer Kill: A Case Study Illustrating the Use  
of Analytical Chemistry to Solve a Problem  
in Toxicology 12

## **PART I** Tools of Analytical Chemistry 17

### **A Conversation with Richard N. Zare** 18

## **Chapter 2** Chemicals, Apparatus, and Unit Operations of Analytical Chemistry 20

- 2A Selecting and Handling Reagents and Other  
Chemicals 21
- 2B Cleaning and Marking of Laboratory Ware 22
- 2C Evaporating Liquids 23
- 2D Measuring Mass 23
- 2E Equipment and Manipulations Associated with  
Weighing 30
- 2F Filtration and Ignition of Solids 33
- 2G Measuring Volume 39
- 2H Calibrating Volumetric Glassware 48
- 2I The Laboratory Notebook 51
- 2J Safety in the Laboratory 52

## **Chapter 3** Using Spreadsheets in Analytical Chemistry 54

- 3A Keeping Records and Making Calculations:  
Spreadsheet Exercise 1 55
- 3B Calculating Molar Masses Using Excel: Spreadsheet  
Exercise 2 60

## **Chapter 4** Calculations Used in Analytical Chemistry 71

- 4A Some Important Units of Measurement 71
- Feature 4-1** Atomic Mass Units and the Mole 73
- 4B Solutions and Their Concentrations 76
- 4C Chemical Stoichiometry 83

## **Chapter 5** Errors in Chemical Analyses 90

- 5A Some Important Terms 92
- 5B Systematic Errors 95

## **Chapter 6** Random Errors in Chemical Analysis 105

- 6A The Nature of Random Errors 105
- Feature 6-1** Flipping Coins: A Student Activity to  
Illustrate a Normal Distribution 109
- 6B Statistical Treatment of Random Error 110
- Feature 6-2** Calculating the Areas under the Gaussian  
Curve 113
- Feature 6-3** The Significance of the Number of Degrees  
of Freedom 116
- Feature 6-4** Equation for Calculating the Pooled  
Standard Deviation 124
- 6C Standard Deviation of Calculated Results 127
- 6D Reporting Computed Data 133

## **Chapter 7** Statistical Data Treatment and Evaluation 142

- 7A Confidence Intervals 143
- Feature 7-1** Breath Alcohol Analyzers 148
- 7B Statistical Aids to Hypothesis Testing 149
- 7C Analysis of Variance 160
- 7D Detection of Gross Errors 167

## **Chapter 8** Sampling, Standardization, and Calibration 175

- 8A Analytical Samples and Methods 175
- 8B Sampling and Sample Handling 178
- Feature 8-1** Lab-on-a-Chip 191
- 8C Standardization and Calibration 192
- Feature 8-2** A Comparison Method for Aflatoxins 192
- Feature 8-3** Multivariate Calibration 208
- 8D Figures of Merit for Analytical Methods 214

## **PART II** Chemical Equilibria 225

### **A Conversation with Sylvia Daunert** 226

## **Chapter 9** Aqueous Solutions and Chemical Equilibria 228

9A The Chemical Compositions of Aqueous Solutions	228	13C Volumetric Calculations	341
9B Chemical Equilibrium	233	Feature 13-1 Another Approach to Example 13-6(a)	346
Feature 9-1 Stepwise and Overall Formation Constants for Complex Ions	236	Feature 13-2 Rounding the Answer to Example 13-7	347
Feature 9-2 Why $[H_2O]$ Does Not Appear in Equilibrium-Constant Expressions for Aqueous Solutions	237	13D Gravimetric Titrimetry	349
Feature 9-3 Relative Strengths of Conjugate Acid/Base Pairs	244	13E Titration Curves in Titrimetric Methods	350
Feature 9-4 The Method of Successive Approximations	248	13F Precipitation Titrimetry	353
9C Buffer Solutions	251	Feature 13-3 Calculating the Concentration of Indicator Solutions	361
Feature 9-5 The Henderson-Hasselbalch Equation	252	<b>Chapter 14 Principles of Neutralization Titrations</b>	368
Feature 9-6 Acid Rain and the Buffer Capacity of Lakes	259	14A Solutions and Indicators for Acid/Base Titrations	368
<b>Chapter 10 Effect of Electrolytes on Chemical Equilibria</b>	267	14B Titration of Strong Acids and Strong Bases	372
10A The Effect of Electrolytes on Chemical Equilibria	267	Feature 14-1 Using the Charge-Balance Equation to Construct Titration Curves	375
10B Activity Coefficients	271	Feature 14-2 How Many Significant Figures Should We Retain in Titration Curve Calculations?	378
Feature 10-1 Mean Activity Coefficients	274	14C Titration Curves for Weak Acids	378
<b>Chapter 11 Solving Equilibrium Calculations for Complex Systems</b>	281	Feature 14-3 Determining Dissociation Constants for Weak Acids and Bases	381
11A Solving Multiple-Equilibrium Problems by a Systematic Method	282	14D Titration Curves for Weak Bases	383
11B Calculating Solubilities by the Systematic Method	287	Feature 14-4 Determining the $pK$ Values for Amino Acids	385
Feature 11-1 Algebraic Expressions Needed to Calculate the Solubility of $CaC_2O_4$ in Water	294	14E The Composition of Solutions During Acid/Base Titrations	387
11C Separation of Ions by Control of the Concentration of the Precipitating Agent	300	Feature 14-5 Locating Titration End Points from pH Measurements	388
Feature 11-2 Immunoassay: Equilibria in the Specific Determination of Drugs	304	<b>Chapter 15 Titration Curves for Complex Acid/Base Systems</b>	395
<b>PART III Classical Methods of Analysis</b>	311	15A Mixtures of Strong and Weak Acids or Strong and Weak Bases	398
<b>A Conversation with Larry R. Faulkner</b>	312	15B Polyfunctional Acids and Bases	399
<b>Chapter 12 Gravimetric Methods of Analysis</b>	314	15C Buffer Solutions Involving Polyprotic Acids	401
12A Precipitation Gravimetry	315	15D Calculation of the pH of Solutions of NaHA	403
Feature 12-1 Specific Surface Area of Colloids	322	15E Titration Curves for Polyfunctional Acids	407
12B Calculation of Results from Gravimetric Data	326	Feature 15-1 The Dissociation of Sulfuric Acid	415
12C Applications of Gravimetric Methods	329	15F Titration Curves for Polyfunctional Bases	416
<b>Chapter 13 Titrimetric Methods; Precipitation Titrimetry</b>	337	15G Titration Curves for Amphiprotic Species	417
13A Some Terms Used in Volumetric Titrimetry	338	Feature 15-2 Acid/Base Behavior of Amino Acids	418
13B Standard Solutions	340	15H The Composition of Solutions of a Polyprotic Acid as a Function of pH	419
		Feature 15-3 A General Expression for Alpha Values	420
		Feature 15-4 Logarithmic Concentration Diagrams	422
		<b>Chapter 16 Applications of Neutralization Titrations</b>	428
		16A Reagents for Neutralization Titrations	429



23C Pulse Polarographic and Voltammetric Methods	689	27C Fluorescence Instruments	830
<b>Feature 23-1</b> Voltammetric Instruments Based on Operational Amplifiers	668	27D Applications of Fluorescence Methods	831
23D Cyclic Voltammetry	694	<b>Feature 27-1</b> Use of Fluorescence Probes in Neurobiology: Probing the Enlightened Mind	832
<b>Feature 23-2</b> Modified Electrodes	697	27E Molecular Phosphorescence Spectroscopy	834
23E Stripping Methods	699	27F Chemiluminescence Methods	835
23F Voltammetry with Microelectrodes	703		
<b>PART V Spectrochemical Methods</b>	707	<b>Chapter 28 Atomic Spectroscopy</b>	839
<b>A Conversation with Gary M. Hieftje</b>	708	28A Origins of Atomic Spectra	840
<b>Chapter 24 Introduction to Spectrochemical Methods</b>	710	28B Production of Atoms and Ions	843
24A Properties of Electromagnetic Radiation	711	28C Atomic Emission Spectrometry	854
24B Interaction of Radiation and Matter	714	28D Atomic Absorption Spectrometry	858
<b>Feature 24-1</b> Spectroscopy and the Discovery of Elements	717	<b>Feature 28-1</b> Determining Mercury by Cold-Vapor Atomic Absorption Spectroscopy	865
24C Radiation Absorption	718	28E Atomic Fluorescence Spectrometry	868
<b>Feature 24-2</b> Deriving Beer's Law	720	28F Atomic Mass Spectrometry	868
<b>Feature 24-3</b> Why Is a Red Solution Red?	725		
24D Emission of Electromagnetic Radiation	734	<b>PART VI Kinetics and Separations</b>	875
<b>Chapter 25 Instruments for Optical Spectrometry</b>	744	<b>A Conversation with Isiah M. Warner</b>	876
25A Instrument Components	744	<b>Chapter 29 Kinetic Methods of Analysis</b>	878
<b>Feature 25-1</b> Laser Sources: The Light Fantastic	748	29A Rates of Chemical Reactions	879
<b>Feature 25-2</b> Derivation of Equation 25-1	754	<b>Feature 29-1</b> Enzymes	886
<b>Feature 25-3</b> Ruling Gratings	756	29B Determining Reaction Rates	892
<b>Feature 25-4</b> Deriving Equation 25-2	759	<b>Feature 29-2</b> Fast Reactions and Stopped-Flow Mixing	892
<b>Feature 25-5</b> Signals, Noise, and the Signal-to-Noise Ratio	761	29C Applications of Kinetic Methods	900
<b>Feature 25-6</b> Measuring Photocurrents with Operational Amplifiers	769	<b>Feature 29-3</b> The Enzymatic Determination of Urea	901
25B Ultraviolet-Visible Photometers and Spectrophotometers	771	<b>Chapter 30 Introduction to Analytical Separations</b>	906
25C Infrared Spectrophotometers		30A Separation by Precipitation	907
<b>Feature 25-7</b> How Does a Fourier Transform Infrared Spectrometer Work?	776	30B Separation of Species by Distillation	911
<b>Chapter 26 Molecular Absorption Spectrometry</b>	784	30C Separation by Extraction	911
26A Ultraviolet and Visible Molecular Absorption Spectroscopy	784	<b>Feature 30-1</b> Derivation of Equation 30-3	913
26B Automated Photometric and Spectrophotometric Methods	807	30D Separating Ions by Ion Exchange	916
26C Infrared Absorption Spectroscopy	811	<b>Feature 30-2</b> Home Water Softeners	919
<b>Feature 26-1</b> Using The Fourier Transform To Produce Infrared Spectra	818	30E Chromatographic Separations	920
<b>Chapter 27 Molecular Fluorescence Spectroscopy</b>	825	<b>Feature 30-3</b> What is the Source of the Terms <i>Plate</i> and <i>Plate Height</i> ?	930
27A Theory of Molecular Fluorescence	825	<b>Chapter 31 Gas Chromatography</b>	947
27B Effect of Concentration On Fluorescence Intensity	829	31A Instruments for Gas-Liquid Chromatography	948
		31B Gas Chromatography Columns and Stationary Phases	958
		31C Applications of Gas-Liquid Chromatography	963
		<b>Feature 31-1</b> Use of GC/MS to identify a Drug Metabolite in Blood	965
		<b>Feature 31-2</b> High-Speed Gas Chromatography	969
		31D Gas-Solid Chromatography	970

**Chapter 32** High-Performance Liquid Chromatography 973

31A Instrumentation 974

**Feature 32-1** Liquid Chromatography (LC)/Mass Spectrometry (MS) and LC/MS/MS 980

32B High-Performance Partition Chromatography 982

32C High-Performance Adsorption Chromatography 986

32D Ion-Exchange Chromatography 986

32E Size-Exclusion Chromatography 988

**Feature 32-2** Buckyballs: The Chromatographic Separation of Fullerenes 989

32F Affinity Chromatography 991

32G Chiral Chromatography 991

32H Comparison of High-Performance Liquid Chromatography and Gas Chromatography 992

**Chapter 33** Miscellaneous Separation Methods 996

33A Supercritical-Fluid Chromatography 996

33B Planar Chromatography 1000

33C Capillary Electrophoresis 1003

**Feature 33-1** Capillary Array Electrophoresis in DNA Sequencing 1010

33D Capillary Electrochromatography 1011

33E Field-Flow Fractionation 1013

**PART VII** Practical Aspects of Chemical Analysis 1021**A Conversation with Julie Leary** 1022**Chapter 34** Analysis of Real Samples 1024

34A Real Samples 1024

34B Choice of Analytical Method 1026

34C Accuracy in the Analysis of Complex Materials 1031

**Chapter 35** Preparing Samples for Analysis 1034

35A Preparing Laboratory Samples 1034

35B Moisture in Samples 1036

35C Determining Water in Samples 1039

**Chapter 36** Decomposing and Dissolving the Sample 1041

36A Sources of Error in Decomposition and Dissolution 1042

36B Decomposing Samples With Inorganic Acids in Open Vessels 1042

36C Microwave Decompositions 1044

36D Combustion Methods for Decomposing Organic Samples 1047

36E Decomposition of Inorganic Materials by Fluxes 1049

**Chapter 37** Selected Methods of Analysis

This chapter is only available as an Adobe Acrobat® PDF file on the **Analytical Chemistry CD-ROM** enclosed in this book or on our Web site at <http://chemistry.brookscole.com/skoogfac/>.

37A An Introductory Experiment

37B Gravimetric Methods of Analysis

37C Neutralization Titrations

37D Precipitation Titrations

37E Complex-Formation Titrations with EDTA

37F Titrations with Potassium Permanganate

37G Titrations with Iodine

37H Titrations with Sodium Thiosulfate

37I Titrations with Potassium Bromate

37J Potentiometric Methods

37K Electrogravimetric Methods

37L Coulometric Titrations

37M Voltammetry

37N Methods Based on the Absorption of Radiation

37O Molecular Fluorescence

37P Atomic Spectroscopy

37Q Application of Ion Exchange Resins

37R Gas-Liquid Chromatography

*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-27

**x**      Contents

**APPENDIX 9**   Derivation of Error Propagation  
Equations    A-29

*Answers to Selected Questions and Problems*    A-34

*Index*    I-1