

# Contents

List of Experiments.....	xvii
Preface.....	xix
Acknowledgments.....	xxi
Author .....	xxiii
Introduction to Laboratory Work .....	XXV
<b>Chapter 1</b> Introduction to Analytical Science.....	1
1.1    Analytical Science Defined .....	1
1.2    Classifications of Analysis.....	2
1.3    The Sample.....	3
1.4    The Analytical Process.....	3
1.5    Analytical Technique and Skills .....	4
1.6    Elementary Statistics .....	5
1.6.1    Errors.....	5
1.6.2    Definitions .....	6
1.6.3    Distribution of Measurements.....	8
1.6.4    Student's t .....	10
1.6.5    Rejection of Data.....	12
1.6.6    Final Comments on Statistics.....	13
1.7    Precision, Accuracy, and Calibration .....	13
<b>Chapter 2</b> Sampling and Sample Preparation .....	19
2.1    Introduction .....	19
2.2    Obtaining the Sample.....	19
2.3    Statistics of Sampling .....	20
2.4    Sample Handling .....	21
2.4.1    Chain of Custody.....	21
2.4.2    Maintaining Sample Integrity .....	22
2.5    Sample Preparation—Solid Materials.....	23
2.5.1    Particle Size Reduction .....	23
2.5.2    Sample Homogenization and Division .....	23
2.5.3    Solid–Liquid Extraction.....	24
2.5.4    Other Extractions from Solids.....	24
2.6    Water Purification and Use.....	25
2.6.1    Purifying Water by Distillation.....	25
2.6.2    Purifying Water by Deionization .....	26
2.7    Total Sample Dissolution and Other Considerations.....	26
2.7.1    Hydrochloric Acid .....	27
2.7.2    Sulfuric Acid .....	27
2.7.3    Nitric Acid .....	28
2.7.4    Hydrofluoric Acid.....	28
2.7.5    Perchloric Acid .....	28
2.7.6    “ <i>Aqua Regia</i> ” .....	28
2.7.7    Acetic Acid.....	28
2.7.8    Ammonium Hydroxide .....	29

2.8	Fusion .....	30
2.9	Sample Preparation: Liquid Samples, Extracts, and Solutions of Solids .....	30
2.9.1	Extraction from Liquid Solutions.....	30
2.9.2	Dilution, Concentration, and Solvent Exchange.....	32
2.9.3	Sample Stability .....	32
2.10	Liquid-Liquid Extraction .....	32
2.10.1	Introduction .....	32
2.10.2	The Separatory Funnel .....	33
2.10.3	Theory .....	34
2.10.4	Calculations Involving Equation 2.2 .....	35
2.10.5	Calculations Involving Equation 2.3 .....	36
2.10.6	Calculations Involving a Combination of Equations 2.3 (or 2.7) and 2.4 .....	37
2.10.7	Calculation of Percent Extracted (Equation 2.5) .....	37
2.10.8	Evaporators.....	38
2.11	Solid-Liquid Extraction .....	38
2.12	Distillation of a Mixture of Liquids .....	39
2.13	Reagents Used in Sample Preparation.....	41
2.14	Labeling and Record Keeping.....	41
<b>Chapter 3</b>	<b>Gravimetric Analysis .....</b>	<b>49</b>
3.1	Introduction .....	49
3.2	Weight vs. Mass.....	49
3.3	The Balance.....	49
3.4	The Desiccator.....	51
3.5	Calibration and Care of Balances.....	52
3.6	When to Use Which Balance .....	52
3.7	Details of Gravimetric Methods.....	53
3.7.1	Physical Separation Methods and Calculations .....	53
3.7.1.1	Loss on Drying .....	55
3.7.1.2	Loss on Ignition .....	55
3.7.1.3	Residue on Ignition .....	56
3.7.1.4	Insoluble Matter in Reagents .....	56
3.7.1.5	Solids in Water and Wastewater .....	56
3.7.1.6	Particle Size by Analytical Sieving .....	57
3.7.2	Chemical Alteration/Separation of the Analyte.....	58
3.7.3	Gravimetric Factors.....	59
3.7.4	Using Gravimetric Factors .....	61
3.8	Experimental Considerations .....	63
3.8.1	Weighing Bottles .....	63
3.8.2	Weighing by Difference .....	63
3.8.3	Isolating and Weighing Precipitates.....	64
<b>Chapter 4</b>	<b>Introduction to Titrimetric Analysis .....</b>	<b>73</b>
4.1	Introduction .....	73
4.2	Terminology .....	73
4.3	Review of Solution Concentration .....	75
4.3.1	Molarity .....	75
4.3.2	Normality .....	77

4.4	Review of Solution Preparation .....	79
4.4.1	Solid Solute and Molarity .....	80
4.4.2	Solid Solute and Normality .....	81
4.4.3	Solution Preparation by Dilution.....	82
4.5	Stoichiometry of Titration Reactions .....	82
4.6	Standardization.....	84
4.6.1	Standardization Using a Standard Solution.....	84
4.6.2	Standardization Using a Primary Standard .....	86
4.6.3	Titer .....	88
4.7	Percentage Analyte Calculations.....	88
4.8	Volumetric Glassware.....	91
4.8.1	Volumetric Flask .....	91
4.8.2	Pipet.....	94
4.8.3	Buret .....	98
4.8.4	Cleaning and Storing Procedures.....	100
4.9	Pipettors, Automatic Titrators, and Other Devices .....	100
4.9.1	Pipettors.....	100
4.9.2	Bottle-Top Dispensers .....	102
4.9.3	Digital Burets and Automatic Titrators.....	102
4.10	Calibration of Glassware and Devices .....	103
4.11	Analytical Technique.....	103
<b>Chapter 5</b>	<b>Applications of Titrimetric Analysis.....</b>	<b>113</b>
5.1	Introduction .....	113
5.2	Acid–Base Titrations and Titration Curves.....	113
5.2.1	Titration of Hydrochloric Acid.....	113
5.2.2	Titration of Weak Monoprotic Acids .....	115
5.2.3	Titration of Monobasic Strong and Weak Bases .....	116
5.2.4	Equivalence Point Detection .....	116
5.2.5	Titration of Polyprotic Acids: Sulfuric Acid and Phosphoric Acid.....	118
5.2.6	Titration of Potassium Biphthalate .....	121
5.2.7	Titration of Tris-(Hydroxymethyl)Amino Methane.....	122
5.2.8	Titration of Sodium Carbonate.....	122
5.3	Examples of Acid/Base Determinations .....	123
5.3.1	Alkalinity of Water or Wastewater.....	124
5.3.2	Back Titration Applications .....	124
5.3.3	Indirect Titration Applications.....	126
5.4	Other Acid/Base Applications.....	127
5.5	Buffer Solution Applications .....	127
5.5.1	Conjugate Acids and Bases .....	128
5.5.2	Henderson–Hasselbalch Equation .....	129
5.6	Complex Ion Formation Reactions .....	133
5.6.1	Introduction .....	133
5.6.2	Complex Ion Terminology.....	133
5.6.3	EDTA and Water Hardness .....	135
5.6.4	Expressing Concentration Using Parts per Million.....	138
5.6.4.1	Solution Preparation .....	139
5.6.5	Water Hardness Calculations .....	141
5.6.6	Other Uses of EDTA Titrations.....	143

5.7	Oxidation–Reduction Reactions.....	144
5.7.1	Review of Basic Concepts and Terminology .....	144
5.7.2	The Ion-Electron Method for Balancing Equations.....	147
5.7.3	Analytical Calculations .....	148
5.7.4	Applications.....	150
5.7.4.1	Potassium Permanganate .....	150
5.7.4.2	Iodometry: An Indirect Method .....	150
5.7.4.3	Prereduction and Preoxidation .....	152
5.8	Other Examples .....	152
<b>Chapter 6</b>	<b>Introduction to Instrumental Analysis .....</b>	<b>165</b>
6.1	Review of the Analytical Process.....	165
6.2	Instrumental Analysis Methods .....	166
6.3	Basics of Instrumental Measurement.....	167
6.3.1	Sensors, Signal Processors, Readouts, and Power Supplies.....	168
6.3.2	Calibration of an Analytical Instrument .....	168
6.3.3	Mathematics of Linear Relationships.....	170
6.3.4	Method of Least Squares.....	171
6.3.5	The Correlation Coefficient.....	172
6.4	Preparation of Standards .....	172
6.5	Blanks and Controls .....	173
6.5.1	Reagent Blanks.....	173
6.5.2	Sample Blanks.....	174
6.5.3	Controls .....	174
6.6	Post-Run Calculations in Instrumental Analysis.....	174
6.6.1	Calculation of ppm Analyte in a Solution Given Mass and Volume Data.....	175
6.6.2	Calculation of ppm Analyte in a Solid Sample Given Mass Data.....	175
6.6.3	Calculation of the Mass of Analyte Found in an Extract.....	175
6.6.4	Calculation of ppm Analyte in a Liquid or Solid That Was Extracted .....	176
6.6.5	Calculation When a Dilution Is Involved.....	176
6.7	Laboratory Data Acquisition and Information Management .....	178
6.7.1	Data Acquisition.....	178
6.7.2	Laboratory Information Management.....	179
<b>Chapter 7</b>	<b>Introduction to Spectrochemical Methods .....</b>	<b>185</b>
7.1	Introduction .....	185
7.2	Characterizing Light.....	185
7.2.1	Wavelength, Speed, Frequency, Energy, and Wavenumber .....	186
7.3	The Electromagnetic Spectrum.....	189
7.4	Refractometry .....	190
7.5	Absorption and Emission of Light.....	193
7.5.1	Brief Summary .....	193
7.5.2	Atoms vs. Molecules and Complex Ions .....	196
7.5.3	Absorption Spectra.....	197
7.5.4	Light Emission .....	201
7.6	Absorbance, Transmittance, and Beer's Law .....	202
7.7	Effect of Concentration on Spectra .....	207

<b>Chapter 8</b>	UV-Vis and IR Molecular Spectrometry.....	215
8.1	Review .....	215
8.2	UV-Vis Instrumentation .....	215
8.2.1	Sources .....	215
8.2.1.1	Tungsten Filament Lamp .....	215
8.2.1.2	Deuterium Lamp.....	216
8.2.1.3	Xenon Arc Lamp .....	216
8.2.2	Wavelength Selection .....	216
8.2.2.1	Absorption Filters .....	217
8.2.2.2	Monochromators.....	217
8.2.3	Sample Compartment.....	220
8.2.3.1	Single-Beam Spectrophotometer.....	220
8.2.3.2	Beam Splitting and Chopping .....	221
8.2.3.3	Double-Beam Designs .....	222
8.2.3.4	Diode Array Design.....	223
8.2.3.5	Summary .....	225
8.2.4	Detectors .....	226
8.2.4.1	Photomultiplier Tube .....	226
8.2.4.2	Photodiodes.....	228
8.3	Cuvette Selection and Handling .....	228
8.4	Interferences, Deviations, Maintenance, and Troubleshooting .....	229
8.4.1	Interferences .....	229
8.4.2	Deviations.....	229
8.4.3	Maintenance .....	230
8.4.4	Troubleshooting.....	230
8.5	Fluorometry .....	231
8.6	Introduction to IR Spectrometry .....	233
8.7	IR Instrumentation .....	234
8.8	Sampling.....	235
8.8.1	Liquid Sampling .....	235
8.9	Solid Sampling .....	240
8.9.1	Solution Prepared and Placed in a Liquid Sampling Cell .....	240
8.9.2	Thin Film Formed by Solvent Evaporation.....	240
8.9.3	KBr Pellet.....	240
8.9.4	Nujol Mull .....	242
8.9.5	Reflectance Methods .....	242
8.9.5.1	Specular Reflectance .....	242
8.9.5.2	Internal Reflectance.....	242
8.9.5.3	Diffuse Reflectance .....	244
8.9.6	Gas Sampling .....	244
8.10	Basic IR Spectra Interpretation .....	244
8.11	Quantitative Analysis .....	247
<b>Chapter 9</b>	Atomic Spectroscopy .....	259
9.1	Review and Comparisons .....	259
9.2	Brief Summary of Techniques and Instrument Designs .....	260
9.3	Flame Atomic Absorption.....	262
9.3.1	Flames and Flame Processes .....	262
9.3.2	Spectral Line Sources .....	263

9.3.2.1	Hollow Cathode Lamp.....	264
9.3.2.2	Electrodeless Discharge Lamp .....	265
9.3.3	Premix Burner.....	265
9.3.4	Optical Path.....	267
9.3.5	Practical Matters and Applications .....	268
9.3.5.1	Slits and Spectral Lines .....	268
9.3.5.2	Linear and Nonlinear Standard Curves.....	269
9.3.5.3	Hollow Cathode Lamp Current.....	271
9.3.5.4	Lamp Alignment.....	271
9.3.5.5	Aspiration Rate .....	271
9.3.5.6	Burner Head Position.....	271
9.3.5.7	Fuel and Oxidant Sources and Flow Rates.....	271
9.3.6	Interferences .....	271
9.3.6.1	Chemical Interferences.....	272
9.3.6.2	Spectral Interferences.....	273
9.3.7	Safety and Maintenance .....	274
9.4	Graphite Furnace Atomic Absorption.....	275
9.4.1	General Description .....	275
9.4.2	Advantages and Disadvantages .....	277
9.5	Inductively Coupled Plasma .....	278
9.6	Miscellaneous Atomic Techniques.....	281
9.6.1	Flame Photometry .....	281
9.6.2	Cold Vapor Mercury.....	282
9.6.3	Hydride Generation .....	282
9.6.4	Spark Emission.....	282
9.6.5	Atomic Fluorescence.....	282
9.7	Summary of Atomic Techniques.....	282
<b>Chapter 10</b>	<b>Introduction to Chromatography .....</b>	<b>291</b>
10.1	Introduction .....	291
10.2	Chromatography .....	291
10.3	"Types" of Chromatography .....	292
10.3.1	Partition Chromatography .....	292
10.3.2	Adsorption Chromatography.....	293
10.3.3	Ion-Exchange Chromatography .....	294
10.3.4	Size Exclusion Chromatography .....	295
10.4	Chromatography Configurations .....	295
10.4.1	Paper and Thin-Layer Chromatography .....	296
10.4.2	Classical Open-Column Chromatography .....	298
10.4.3	Instrumental Chromatography .....	301
10.4.4	Instrumental Chromatogram.....	301
10.4.5	Quantitative Analysis with GC and HPLC .....	305
10.5	Electrophoresis .....	306
<b>Chapter 11</b>	<b>Gas Chromatography .....</b>	<b>311</b>
11.1	Overview .....	311
11.2	Vapor Pressure and Solubility .....	311
11.3	Instrument Components .....	312
11.4	Sample Injection.....	314

11.5	Column Details.....	316
11.5.1	Instrument Logistics.....	316
11.5.2	Packed, Open Tubular, and Preparative Columns.....	317
11.5.3	The Nature and Selection of the Stationary Phase.....	318
11.5.4	Column Temperature.....	319
11.5.5	Carrier Gas Flow Rate .....	320
11.6	Detectors.....	321
11.6.1	Flame Ionization Detector (FID) .....	321
11.6.2	Thermal Conductivity Detector (TCD) .....	322
11.6.3	Electron Capture Detector (ECD) .....	323
11.6.4	Nitrogen/Phosphorus Detector (NPD) .....	324
11.6.5	Flame Photometric Detector (FPD) .....	324
11.6.6	Electrolytic Conductivity (Hall Detector) .....	324
11.6.7	Gas Chromatography–Mass Spectrometry (GC–MS) .....	324
11.6.8	Photoionization Detector (PID).....	325
11.7	Qualitative Analysis .....	325
11.8	Quantitative Analysis .....	326
11.8.1	Quantitation Methods.....	326
11.8.2	Response Factor Method .....	326
11.8.3	Internal Standard Method .....	327
11.8.4	Standard Additions Method .....	328
11.9	Troubleshooting .....	329
11.9.1	Diminished Peak Size .....	329
11.9.2	Unsymmetrical Peak Shapes .....	329
11.9.3	Altered Retention Times .....	330
11.9.4	Baseline Drift .....	330
11.9.5	Baseline Perturbations.....	330
11.9.6	Appearance of Unexpected Peaks.....	330

**Chapter 12 High-Performance Liquid Chromatography and Electrophoresis ..... 341**

12.1	Introduction .....	341
12.1.1	Summary of Method .....	341
12.1.2	Comparisons with GC.....	341
12.2	Mobile Phase Considerations .....	342
12.3	Solvent Delivery .....	344
12.3.1	Pumps.....	344
12.3.2	Gradient vs. Isocratic Elution.....	345
12.4	Sample Injection .....	346
12.5	Column Selection .....	348
12.5.1	Normal Phase Columns.....	348
12.5.2	Reverse-Phase Columns .....	348
12.5.3	Adsorption Columns .....	349
12.5.4	Ion Exchange and Size Exclusion Columns .....	349
12.5.5	The Size of the Stationary Phase Particles.....	349
12.5.6	Column Selection .....	349
12.6	Detectors.....	350
12.6.1	UV Absorption .....	350
12.6.2	Diode Array.....	351
12.6.3	Fluorescence .....	351
12.6.4	Refractive Index .....	353

12.6.5	Electrochemical.....	354
12.6.5.1	Conductivity.....	354
12.6.5.2	Amperometric.....	354
12.7	Qualitative and Quantitative Analysis.....	355
12.8	Troubleshooting.....	356
12.8.1	Unusually High Pressure.....	356
12.8.2	Unusually Low Pressure.....	356
12.8.2.1	System Leaks.....	356
12.8.2.2	Air Bubbles.....	357
12.8.2.3	Column "Channeling".....	357
12.8.2.4	Decreased Retention Time.....	357
12.8.2.5	Baseline Drift .....	357
12.9	Electrophoresis .....	357
12.9.1	Introduction .....	357
12.9.2	Capillary Electrophoresis .....	359
12.9.2.1	Electroosmotic Flow.....	361
12.9.2.2	Sample Introduction.....	361
12.9.2.3	Analyte Detection.....	361
<b>Chapter 13</b>	<b>Mass Spectrometry.....</b>	<b>371</b>
13.1	Basic Principles .....	371
13.2	Sample Inlet Systems and Ion Sources.....	372
13.3	Mass Analyzers .....	373
13.4	The Ion Detector.....	376
13.5	Mass Spectra.....	377
13.6	ICP-MS .....	378
13.7	GC-MS .....	378
13.8	LC-MS.....	380
13.9	Tandem Mass Spectrometry .....	381
<b>Chapter 14</b>	<b>Electroanalytical Methods .....</b>	<b>387</b>
14.1	Introduction .....	387
14.2	Transfer Tendencies: Standard Reduction Potentials .....	391
14.3	Determination of Overall Redox Reaction Tendency: $E_{\text{cell}}^{\circ}$ .....	393
14.4	The Nernst Equation.....	394
14.5	Potentiometry .....	396
14.5.1	Reference Electrodes .....	396
14.5.1.1	The Saturated Calomel Reference Electrode (SCE) .....	396
14.5.1.2	The Silver–Silver Chloride Electrode.....	398
14.5.2	Indicator Electrodes .....	399
14.5.2.1	The pH Electrode.....	399
14.5.3	Combination Electrodes .....	400
14.5.3.1	The Combination pH Electrode .....	400
14.5.3.2	Ion-Selective Electrodes .....	401
14.5.4	Other Details of Electrode Design .....	403
14.5.5	Care and Maintenance of Electrodes .....	403
14.5.6	Potentiometric Titrations.....	404
14.6	Voltammetry and Amperometry .....	405
14.6.1	Voltammetry.....	405

14.6.2 Amperometry .....	406
14.7 Karl Fischer Titration .....	406
14.7.1 End Point Detection.....	406
14.7.2 Elimination of Extraneous Water.....	407
14.7.3 The Volumetric Method.....	407
14.7.4 The Coulometric Method .....	409
<b>Chapter 15 Miscellaneous Instrumental Techniques.....</b>	<b>417</b>
15.1 X-Ray Methods.....	417
15.1.1 Introduction .....	417
15.1.2 X-Ray Diffraction Spectroscopy .....	418
15.1.3 X-Ray Fluorescence Spectroscopy .....	421
15.1.4 Applications.....	421
15.1.5 Safety Issues Concerning X-Rays .....	422
15.2 Nuclear Magnetic Resonance Spectroscopy .....	422
15.2.1 Introduction .....	422
15.2.2 Instrumentation .....	423
15.2.3 The NMR Spectrum.....	425
15.2.3.1 Chemical Shifts .....	425
15.2.3.2 Peak Splitting and Integration .....	427
15.2.4 Solvents and Solution Concentration.....	428
15.2.5 Analytical Uses .....	428
15.3 Viscosity .....	428
15.3.1 Introduction .....	428
15.3.2 Definitions .....	429
15.3.3 Temperature Dependence.....	430
15.3.4 Capillary Viscometry .....	430
15.3.5 Rotational Viscometry .....	433
15.4 Thermal Analysis .....	434
15.4.1 Introduction .....	434
15.4.2 DTA and DSC .....	434
15.4.3 DSC Instrumentation.....	436
15.4.4 Applications of DSC.....	437
15.5 Optical Rotation .....	437
<b>Appendix 1: Formulas for Solution Concentration and Preparation Calculations .....</b>	<b>443</b>
<b>Appendix 2: The Language of Quality Assurance and Good Laboratory Practice (GLP) Laws: A Glossary .....</b>	<b>447</b>
<b>Appendix 3: Significant Figure Rules .....</b>	<b>451</b>
<b>Appendix 4: Answers to Questions and Problems.....</b>	<b>453</b>
<b>Index.....</b>	<b>501</b>