

Contents

PART I. X-RAY PHYSICS

Chapter 1. Excitation and Nature of X-Rays; X-Ray Spectra

1.1. Historical	3
1.2. Definition of X-Rays	6
1.3. Properties of X-Rays	8
1.4. Units of X-Ray Measurement	8
1.4.1. Frequency	8
1.4.2. Wavelength	8
1.4.3. Energy	10
1.4.4. Intensity	11
1.5. The Continuous Spectrum	13
1.5.1. Nature	13
1.5.2. Generation	13
1.5.3. Short-Wavelength Limit	15
1.5.4. Origin of the Continuum	16
1.5.5. Effect of X-Ray Tube Current, Potential, and Target	17
1.5.6. Significance	19
1.6. The Characteristic Line Spectrum	19
1.6.1. Atomic Structure	19
1.6.2. Nature and Origin	21
1.6.2.1. General	21
1.6.2.2. Band Spectra	24
1.6.2.3. Selection Rules	24
1.6.2.4. Notation	24

xiv CONTENTS

1.6.2.5. Wavelength	26
1.6.2.6. Intensity	30
1.6.3. Excitation—General	31
1.6.4. Primary Excitation	36
1.6.5. Secondary Excitation	38
1.6.5.1. X-Ray Absorption Edges	38
1.6.5.2. Principles	40
1.6.5.3. Relationship of Absorption Edges and Spectral-Line Series	41
1.6.5.4. Excitation with Polychromatic X-Rays	43
1.6.5.5. Other Contributions to the Specimen Emission	43
1.7. Comparison of Primary and Secondary Excitation	44
1.7.1. X-Ray Tube Potential	44
1.7.2. Features	45
1.8. Excitation by Ion Bombardment	47

Chapter 2. Properties of X-Rays

2.1. Absorption	51
2.1.1. X-Ray Absorption Coefficients	51
2.1.2. X-Ray Absorption Phenomena	55
2.1.3. Relationship of μ/ρ , λ , and Z	57
2.1.4. Absorption Edges	59
2.1.5. Comparison of X-Ray and Optical Absorption	61
2.1.6. Significance	64
2.1.7. Half-Thickness and Absorption Cross Section	65
2.1.8. Inverse-Square Law	67
2.2. Scatter	68
2.2.1. General	68
2.2.2. Modified (Compton) Scatter	68
2.2.3. Relationship of Unmodified and Modified Scatter	71
2.2.4. Significance	73
2.3. Diffraction by Crystals	73
2.4. Specular Reflection; Diffraction by Gratings	79
2.4.1. Specular Reflection	79
2.4.2. Diffraction by Gratings	80
2.5. Auger Effect; Fluorescent Yield	81
2.5.1. Auger Effect	81
2.5.2. Fluorescent Yield	82
2.5.3. Satellite Lines	84

**PART II. THE X-RAY SPECTROMETER,
ITS COMPONENTS, AND THEIR OPERATION****Chapter 3. X-Ray Secondary-Emission (Fluorescence) Spectrometry;
General Introduction**

3.1. Nomenclature	89
3.2. Principle and Instrument	92
3.2.1. Principle	93
3.2.2. The X-Ray Spectrogoniometer	93
3.2.3. Electronic Readout Components	96
3.2.4. Qualitative, Semiquantitative, and Quantitative Analysis	97
3.2.5. Phases of a Quantitative X-Ray Spectrometric Analysis	97
3.3. Appraisal	98
3.3.1. Advantages	98
3.3.1.1. X-Ray Spectra	98
3.3.1.2. Excitation and Absorption	100
3.3.1.3. Absorption-Enhancement Effects	100
3.3.1.4. Spectral-Line Interference	100
3.3.1.5. Nondestruction of Specimen	101
3.3.1.6. Specimen Versatility	101
3.3.1.7. Operational Versatility	102
3.3.1.8. Versatility of Analytical Strategy	102
3.3.1.9. Selected-Area Analysis	103
3.3.1.10. Semiquantitative Estimations	103
3.3.1.11. Concentration Range	103
3.3.1.12. Sensitivity	103
3.3.1.13. Precision and Accuracy	104
3.3.1.14. Excitation	104
3.3.1.15. Speed and Convenience	105
3.3.1.16. Operating Cost	105
3.3.1.17. Automation	105
3.3.1.18. Process Control	106
3.3.1.19. Use with Other Methods	106
3.3.2. Disadvantages	106
3.3.2.1. Light Elements	106
3.3.2.2. Penetration	106
3.3.2.3. Absorption-Enhancement Effects	107
3.3.2.4. Sensitivity	107
3.3.2.5. Qualitative Analysis	107

xvi CONTENTS

3.3.2.6. Standards	107
3.3.2.7. Instrument Preparation	108
3.3.2.8. Components	108
3.3.2.9. Instrument Settings	109
3.3.2.10. Error	109
3.3.2.11. Tedium	109
3.3.2.12. Cost	110
3.4. Trends in X-Ray Spectrochemical Analysis	110

Chapter 4. Excitation

4.1. Principles	113
4.1.1. General	113
4.1.2. Excitation by Monochromatic X-Rays	115
4.1.3. Excitation by Continuous Spectra	118
4.2. The X-Ray Tube	121
4.2.1. Function and Requirements	121
4.2.2. Construction	121
4.2.3. Design Considerations	122
4.2.4. Practical Considerations	124
4.2.4.1. Excitation Efficiency	124
4.2.4.2. Spectral-Line Interference	127
4.2.4.3. Temperature	128
4.2.4.4. Evaluation of the Condition of the X-Ray Tube	128
4.2.5. Special X-Ray Tubes	129
4.2.5.1. Dual-Target Tube	129
4.2.5.2. End-Window Tube	130
4.2.5.3. Demountable Tubes	130
4.2.5.4. Tubes for Ultralong Wavelength	131
4.2.5.5. Low-Power Tubes	132
4.2.5.6. Field-Emission Tubes	136
4.3. X-Ray Power Supply	138
4.3.1. Function and Requirements	138
4.3.2. Components and Operation	138
4.3.2.1. High-Potential Supply	140
4.3.2.2. X-Ray Tube Filament Supply	142
4.3.2.3. Operation	143
4.3.2.4. Stabilization	145
4.3.2.5. Safety and Protective Devices	146

4.3.3. Practical Considerations	147
4.3.3.1. Constant Potential	147
4.3.3.2. Maximum Target Potential	149
4.3.3.3. Operating Conditions	149
4.4. Filters in Secondary Excitation	156
4.4.1. Attenuation Filters	156
4.4.2. Enhancement Filters	156
4.4.3. Enhancement Radiators	158
4.5. Specimen Presentation	158

Chapter 5. Dispersion

5.1. Introduction	161
5.2. Collimators	163
5.2.1. Function	163
5.2.2. Features and Considerations	165
5.3. Radiation Path	169
5.4. Analyzer Crystals	171
5.4.1. Introduction	171
5.4.2. Features	172
5.4.2.1. Wavelength Range	172
5.4.2.2. Diffracted Intensity	174
5.4.2.3. Resolution	176
5.4.2.4. Peak-to-Background Ratio; Crystal Emission . .	178
5.4.2.5. Thermal Expansion	180
5.4.2.6. Miscellaneous Features	181
5.4.2.7. Aligning and Peaking the Goniometer	183
5.4.3. Other Dispersion Devices	186
5.4.3.1. Gratings and Specular Reflectors	186
5.4.3.2. Multilayer Metal Films	187
5.4.3.3. Metal Disulfide–Organic Intercalation Complexes	187
5.4.3.4. Multilayer Soap Films	188
5.4.3.5. Pyrolytic Graphite	191
5.5. Basic Crystal-Dispersion Arrangements	191
5.5.1. Multichannel Spectrometers	192
5.5.2. Flat-Crystal Dispersion Arrangements	193
5.5.2.1. Bragg and Soller	193
5.5.2.2. Edge-Crystal	194
5.5.2.3. Laue	195
5.5.2.4. Other Flat-Crystal Arrangements	197

5.5.3. Curved-Crystal Dispersion Arrangements	200
5.5.3.1. General	200
5.5.3.2. Transmission	202
5.5.3.3. Reflection	203
5.5.3.4. Von Hamos Image Spectrograph	205
5.6. Curved-Crystal Spectrometers	207
5.6.1. Semifocusing Spectrometer	207
5.6.2. Continuously Variable Crystal Radius	209
5.6.3. Naval Research Laboratory Design	209
5.6.4. Applied Research Laboratories Design	211
5.6.5. Cauchois Spectrometer	212
5.6.6. Spherically Curved-Crystal Spectrometers	213
5.7. Photographic X-Ray Spectrographs	214

Chapter 6. Detection

6.1. Introduction	219
6.2. Gas-Filled Detectors	220
6.2.1. Structure	220
6.2.1.1. Components, Classifications	220
6.2.1.2. Windows	221
6.2.1.3. Gas Fillings	226
6.2.2. Operation	228
6.2.2.1. Phenomena in the Detector Gas Volume	228
6.2.2.2. Proportionality in Gas Detectors	230
6.2.2.3. Gas Amplification; Types of Gas Detectors	232
6.2.2.4. Quenching	235
6.2.3. Proportional Counters	236
6.2.3.1. Phenomena in the Detector Gas Volume	236
6.2.3.2. Detector Output; Escape Peaks	240
6.3. Scintillation Counters	241
6.3.1. Structure	241
6.3.1.1. Scintillation Crystal	241
6.3.1.2. Multiplier Phototube	243
6.3.2. Operation	245
6.3.2.1. Proportionality in Scintillation Counters	245
6.3.2.2. Phenomena in the Scintillation Counter	245
6.4. Lithium-Drifted Silicon and Germanium Detectors	247
6.4.1. Structure	247
6.4.2. Operation	249

6.4.3. Advantages	251
6.4.4. Limitations	255
6.4.5. Avalanche Detectors	257
6.5. Evaluation of X-Ray Detectors	257
6.5.1. Detector Characteristics	257
6.5.1.1. Rise Time	257
6.5.1.2. Dead Time	258
6.5.1.3. Resolving Time	259
6.5.1.4. Recovery Time	259
6.5.1.5. Linear Counting Range	259
6.5.1.6. Coincidence Loss	259
6.5.1.7. Choking	264
6.5.1.8. Plateau	264
6.5.1.9. Slope	267
6.5.1.10. Inherent Noise and Background	267
6.5.1.11. Quantum Efficiency	267
6.5.1.12. Resolution	267
6.5.2. Comparison of Conventional Detectors	271
6.5.3. Modified Gas-Filled and Scintillation Detectors	271
6.6. Other X-Ray Detectors	279
6.6.1. Photographic Film	279
6.6.2. Photoelectric Detectors	281
6.6.2.1. The Phosphor-Phototube Detector	281
6.6.2.2. Photoelectric Detectors for the Ultralong-Wave- length Region	282
6.6.3. Crystal Counters	284

Chapter 7. Measurement

7.1. Instrumentation	285
7.1.1. Introduction	285
7.1.2. Preamplifier	288
7.1.3. Amplifier	288
7.1.4. Pulse-Height Selectors	289
7.1.4.1. Pulse-Height Selector; Discriminator	289
7.1.4.2. Pulse Reverter	291
7.1.4.3. Pulse-Shape Selector	293
7.1.5. Ratemeter and Recorder	293
7.1.6. Scaler and Timer	294
7.1.7. Computers	296

xx CONTENTS

7.2. Measurement of Intensity	297
7.2.1. Ratemeter Methods	297
7.2.2. Scaler-Timer Methods	298
7.2.2.1. Preset-Time Method	298
7.2.2.2. Preset-Count Method	299
7.2.2.3. Integrated-Count Method	299
7.2.2.4. Monitor and Ratio Methods	299
7.2.3. X-Ray Dose and Dose Rate	301
7.3. Background	303
7.3.1. Definition and Significance	303
7.3.2. Origin and Nature	303
7.3.3. Measurement	305
7.3.4. Reduction	308
7.3.5. Considerations	313

**Chapter 8. Pulse-Height Selection; Energy-Dispersive Analysis;
Nondispersive Analysis**

8.1. Pulse-Height Selection	315
8.1.1. Principle of Pulse-Height Selection	316
8.1.2. Pulse-Height Distribution Curves	320
8.1.2.1. Introduction	320
8.1.2.2. Single-Channel Pulse-Height Selector	322
8.1.2.3. Multichannel Pulse-Height Analyzer	323
8.1.3. Pulse-Height Selector Displays	326
8.1.4. Pulse-Height Selector Operating Controls	330
8.1.5. Use of the Pulse-Height Selector	331
8.1.5.1. Evaluation of Detector and Amplifier Char- acteristics	331
8.1.5.2. Establishment of Pulse-Height Selector Settings	333
8.1.6. Applications and Limitations	337
8.1.7. Automatic Pulse-Height Selection	338
8.1.8. Problems with Pulse-Height Selection	342
8.1.8.1. General	342
8.1.8.2. Shift of Pulse-Height Distribution	342
8.1.8.3. Distortion of Pulse-Height Distribution	346
8.1.8.4. Additional Pulse-Height Distributions Arising from the Measured Wavelength	347
8.1.9. Unfolding of Overlapping Pulse-Height Distributions . .	350
8.1.9.1. Principle	350

8.1.9.2. Application	352
8.1.9.3. Simplified Variations	353
8.2. Energy-Dispersive Analysis	356
8.2.1. Introduction	356
8.2.1.1. Principles	356
8.2.1.2. Advantages	357
8.2.1.3. Limitations	358
8.2.2. Instrumentation	361
8.2.2.1. General	361
8.2.2.2. Excitation by X-Rays	361
8.2.2.3. Excitation by Radioisotopes	366
8.2.2.4. Energy-Dispersive Multichannel X-Ray Spectrometer Systems	373
8.2.3. Energy-Dispersive Diffractometry-Spectrometry	389
8.3. Nondispersive Analysis	394
8.3.1. Selective Excitation	394
8.3.2. Selective Filtration	397
8.3.2.1. Methods	397
8.3.2.2. X-Ray Transmission Filters	400
8.3.3. Selective Detection	401
8.3.4. Modulated Excitation	401

Chapter 9. Laboratory, Automated, and Special X-Ray Spectrometers

9.1. Introduction	405
9.2. Laboratory X-Ray Spectrometers	408
9.2.1. General	408
9.2.2. Instrument Arrangements	409
9.2.3. Accessories	411
9.3. Automated X-Ray Spectrometers	413
9.3.1. General	413
9.3.2. Sequential Automatic Spectrometers	416
9.3.3. Simultaneous Automatic Spectrometers	421
9.3.4. “Slewing” Goniometers	424
9.4. Special X-Ray Spectrometers	425
9.4.1. Portable Spectrometer	425
9.4.2. Primary Excitation	426
9.4.3. Ultralong-Wavelength Spectrometry	427
9.5. X-Ray Safety and Protection	430

PART III. QUALITATIVE AND SEMIQUANTITATIVE ANALYSIS

Chapter 10. Qualitative and Semiquantitative Analysis

10.1. General	435
10.2. Recording the Spectrum	436
10.3. Instrument Conditions	438
10.4. Identification of the Peaks	441
10.4.1. Spectral-Line Tables	441
10.4.2. Identification of Peaks	447
10.5. General Procedures for Qualitative and Semiquantitative Analysis	450
10.5.1. Normalization Factor Method	451
10.5.2. Method of Salmon	452

PART IV. PERFORMANCE CRITERIA AND OTHER FEATURES

Chapter 11. Precision and Error; Counting Statistics

11.1. Error in X-Ray Spectrometric Analysis	459
11.1.1. Nature of Error	459
11.1.2. Elementary Statistics	462
11.1.3. Sources of Error	465
11.1.3.1. General	465
11.1.3.2. Instrumental and Operational Error	467
11.1.3.3. Specimen Error	469
11.1.3.4. Chemical Effects	471
11.2. Counting Statistics	472
11.2.1. Nature of the Counting Error	472
11.2.2. Calculation of Counting Error	474
11.2.2.1. Counting Error for Accumulated Counts . .	474
11.2.2.2. Counting Error for Intensities	476
11.2.3. Counting Strategy	480
11.2.3.1. Measurement of Net Intensity	480
11.2.3.2. The Ratio Method	488
11.2.4. Figure of Merit	490
11.3. Analytical Precision	491
11.3.1. Nature of Analytical Precision	491

11.3.2. Evaluation of Precision	494
11.3.2.1. General Considerations	494
11.3.2.2. Instrumental Instability	495
11.3.2.3. Operational Error	495
11.3.2.4. Specimen Error	496
11.3.2.5. Evaluation of Internal Consistency of Data	498

Chapter 12. Matrix Effects

12.1. Introduction	501
12.2. Absorption-Enhancement Effects	502
12.2.1. General; Definitions	502
12.2.2. Effects on Calibration Curves	505
12.2.3. Prediction of Absorption-Enhancement Effects	507
12.2.3.1. K Lines	507
12.2.3.2. L Lines	509
12.2.4. Nonspecific Absorption Effects	510
12.2.5. Specific Absorption-Enhancement Effects	514
12.2.6. Secondary Absorption-Enhancement Effects	517
12.2.6.1. General	517
12.2.6.2. Secondary Absorption Effects	518
12.2.6.3. Secondary Enhancement Effects	520
12.2.7. Unusual Absorption-Enhancement Effects	521
12.3. Particle-Size, Heterogeneity, and Surface-Texture Effects	524

Chapter 13. Sensitivity and Resolution; Spectral-Line Interference

13.1. Sensitivity	529
13.1.1. Definitions	529
13.1.2. Factors Affecting Sensitivity	532
13.1.2.1. Excitation Conditions	532
13.1.2.2. Specimen Conditions	533
13.1.2.3. Optical System	534
13.1.2.4. Detector and Readout Conditions	535
13.1.3. Photon Losses in the X-Ray Spectrometer	535
13.1.4. Sensitivity Performance	540
13.2. Resolution	546
13.2.1. Definitions	546
13.2.1.1. Resolution	546

xxiv CONTENTS

13.2.1.2. Dispersion	546
13.2.1.3. Divergence	547
13.2.2. Factors Affecting Resolution	548
13.3. Spectral-Line Interference	552
13.3.1. Definition	552
13.3.2. Origin of Interfering Spectral Lines	553
13.3.2.1. Wavelength Interference	553
13.3.2.2. Energy Interference	557
13.3.2.3. Common Sources of Spectral Interference	559
13.3.3. Reduction of Spectral Interference	560
13.3.3.1. General Methods	560
13.3.3.2. Excitation of Analyte and Interferant Lines	561
13.3.3.3. Transmission and Detection of Analyte and Interferant Lines	563
13.3.3.4. Experimental and Mathematical Correction of Spectral Interference	564

PART V. QUANTITATIVE ANALYSIS

Chapter 14. Methods of Quantitative Analysis

14.1. Introduction	571
14.2. Standard Addition and Dilution Methods	575
14.2.1. Principles and Considerations	575
14.2.2. Methods	576
14.2.2.1. Standard Addition	576
14.2.2.2. Standard Dilution	578
14.2.2.3. Multiple Standard Addition	578
14.2.2.4. Slope-Ratio Addition	578
14.2.2.5. Double Dilution	581
14.3. Calibration Standardization	583
14.3.1. Principles	583
14.3.2. Special Calibration Methods	588
14.3.2.1. Single-Standard Method	588
14.3.2.2. Two-Standard Method	589
14.3.2.3. Binary-Ratio Method	590
14.3.2.4. Mutual Standards Method	592
14.3.2.5. Sets of Calibration Curves	592
14.4. Internal Standardization	594
14.4.1. Principles	594

14.4.2. Selection of Internal-Standard Element	596
14.4.3. Advantages and Limitations	599
14.4.4. Considerations	600
14.4.5. Special Internal-Standardization Methods	602
14.4.5.1. Single-Standard Internal-Standard Method .	602
14.4.5.2. Variable Internal-Standard Method	602
14.4.6. Other Standardization Methods	603
14.4.6.1. Internal Control-Standard Method	603
14.4.6.2. Internal Intensity-Reference Standard Method	603
14.4.6.3. External-Standard Method	604
14.5. Standardization with Scattered X-Rays	604
14.5.1. Background-Ratio Method	605
14.5.2. Graphic Method	610
14.5.3. Scattered Target-Line Ratio Method	610
14.5.4. Scattered Internal-Standard Line Method	612
14.5.5. Ratio of Coherent to Incoherent Scattered Intensities	613
14.5.6. Slurry-Density Method	615
14.6. Matrix-Dilution Methods	617
14.6.1. Principles	617
14.6.2. Discussion	619
14.7. Thin-Film Methods	621
14.7.1. Principles	621
14.7.2. Infinite (Critical) Thickness	624
14.7.3. Discussion	625
14.8. Special Experimental Methods	627
14.8.1. Emission-Absorption Methods	627
14.8.2. Method of Variable Takeoff Angle	631
14.8.2.1. Basic Excitation Equations	631
14.8.2.2. Evaluation of Mean Wavelength and Excita- tion Integral	634
14.8.2.3. Mass per Unit Area of an Element Film from Its Own Line	635
14.8.2.4. Mass per Unit Area of an Element Film from a Substrate Line	636
14.8.2.5. Mass per Unit Area and Composition of Multi- element Films	636
14.8.2.6. Composition of Bulk Multielement Specimens	637
14.8.3. Indirect (Association) Methods	638
14.8.4. Combinations of X-Ray Spectrometry and Other Methods	639

Chapter 15. Mathematical Correction of Absorption-Enhancement Effects

15.1. Introduction	643
15.2. Geometric Methods	644
15.3. Absorption Correction	648
15.4. Empirical Correction Factors	651
15.5. Influence Coefficients	658
15.5.1. Introduction	658
15.5.2. Derivation of the Basic Equations	661
15.5.2.1. Birks' Derivation	661
15.5.2.2. Müller's Derivation; Regression Coefficients	665
15.5.2.3. Influence Coefficient Symbols	667
15.5.3. Solution of the Basic Equations	668
15.5.3.1. Simplified Solutions	668
15.5.3.2. Evaluation of a_{ij} Coefficients to a First Approximation	670
15.5.3.3. Evaluation of a_{ij} Coefficients to a Second Approximation	674
15.5.3.4. Simultaneous Evaluation of All a_{ij} Coefficients	675
15.5.3.5. Other Methods for Evaluation of a_{ij} Coefficients	676
15.5.4. Variations of the Influence-Coefficient Method	678
15.5.4.1. Method of Sherman	678
15.5.4.2. Method of Burnham, Hower, and Jones . .	679
15.5.4.3. Method of Marti	682
15.5.4.4. Method of Traill and Lachance	683
15.5.4.5. Method of Lucas-Tooth and Pyne	685
15.5.4.6. Method of Rasberry and Heinrich	689
15.6. Fundamental-Parameters Method	690
15.7. Multiple-Regression Method	696

**PART VI. SPECIMEN PREPARATION
AND PRESENTATION**

Chapter 16. Specimen Preparation and Presentation—General; Solids, Powders, Briquets, Fusion Products

16.1. General Considerations	701
16.1.1. Introduction	701
16.1.2. Classification of Applications	706

16.1.3. Problems Specific to the Light Elements	708
16.1.4. Standards	711
16.1.4.1. General	711
16.1.4.2. Permanence of Standards	711
16.1.4.3. Sources of Standards	712
16.1.5. Effective Layer Thickness	717
16.1.6. The Specimen-Preparation Laboratory	720
16.2. Solids	722
16.2.1. Scope, Advantages, Limitations	722
16.2.2. Presentation	723
16.2.2.1. Flat Specimens	723
16.2.2.2. Fabricated Forms and Parts	724
16.2.3. Preparation	727
16.2.4. Precautions and Considerations	728
16.3. Powders and Briquets	732
16.3.1. Scope, Advantages, Limitations	732
16.3.2. Powder and Briquet Standards	734
16.3.3. Preparation of Powders	736
16.3.4. Presentation	739
16.3.4.1. Loose Powders	739
16.3.4.2. Briquets	741
16.3.4.3. Thin Layers	743
16.3.5. Precautions and Considerations	747
16.3.5.1. Particle-Size Effects	747
16.3.5.2. Additives	750
16.3.5.3. Briquetting	751
16.3.5.4. Other Considerations	751
16.4. Fusion Products	751
16.4.1. Scope, Advantages, Limitations	751
16.4.2. Materials	752
16.4.3. Specific Fusion Procedures	754
16.4.4. Considerations	758

Chapter 17. Specimen Preparation and Presentation—Liquids; Supported Specimens

17.1. Liquid Specimens	763
17.1.1. Introduction	763
17.1.2. Advantages	765
17.1.3. Disadvantages	767

xxviii CONTENTS

17.1.4. Liquid-Specimen Cells	769
17.1.4.1. Forms and Materials	769
17.1.4.2. General-Purpose Cell	772
17.1.4.3. Somar "Spectro-Cup"	773
17.1.4.4. Cells for Use in Vacuum	774
17.1.4.5. Uncovered Cell	777
17.1.4.6. Frozen-Specimen Cell	778
17.1.4.7. Cell for Slurries	780
17.1.4.8. High-Temperature Liquid-Specimen Cell	780
17.1.4.9. Other Liquid-Specimen Cells	781
17.1.5. Precautions and Considerations	784
17.1.5.1. Interaction of the Primary Beam with Liquid Specimens	784
17.1.5.2. Composition	786
17.1.5.3. Miscellany	787
17.2. Supported Specimens	788
17.2.1. General	788
17.2.2. Specimens Derived from Solutions	791
17.2.3. Specimens Derived from Solids	795
17.2.4. Ion-Exchange Techniques	797
17.2.4.1. Principles	797
17.2.4.2. Techniques	798
17.2.5. Ashing Techniques	800
17.2.6. Bomb Techniques	801
17.3. Trace and Microanalysis	802
17.4. Radioactive Specimens	806

**PART VII. UNCONVENTIONAL MODES
OF OPERATION; RELATED X-RAY METHODS
OF ANALYSIS**

Chapter 18. Measurement of Thickness of Films and Platings	811
18.1. Principles and Basic Methods	811
18.2. Multiple-Layer and Alloy Platings	816
18.2.1. Multiple-Layer Platings	816
18.2.2. Alloy Platings—Composition and Thickness	817
18.3. Special Techniques	821
18.3.1. Special Specimen Forms	821

18.3.2. Selected-Area Analysis	823
18.3.3. Selective Excitation	824
18.3.4. Enhancement	824
18.3.5. Excitation by Radioactive Sources	824
18.3.6. Energy-Dispersive Operation	825
18.3.7. Decoration	825
18.3.8. Dynamic Studies	826
18.4. Considerations	826
 Chapter 19. Selected-Area Analysis	829
19.1. Principle and Scope	829
19.1.1. Principle	829
19.1.2. Applications	830
19.1.3. Advantages and Limitations	832
19.2. Selected-Area Analysis on Standard Commercial X-Ray Spectrometers	834
19.2.1. Specimen Irradiation	834
19.2.2. Selected-Area Apertures	837
19.2.2.1. General	837
19.2.2.2. Pinholes	837
19.2.2.3. Slits	840
19.2.2.4. Resolution	843
19.2.3. Dispersion	844
19.3. Instruments for Selected-Area X-Ray Spectrometric Analysis	846
19.4. Specimen Techniques	848
19.4.1. Preparation	848
19.4.2. Alignment of Selected Area and Aperture	848
19.5. Analytical Techniques	849
19.6. Performance	852
 Chapter 20. Other Analytical Methods Based on Emission, Absorption, and Scatter of X-Rays; Other Spectrometric Methods Involving X-Rays	859
20.1. X-Ray Absorption Methods	859
20.1.1. Polychromatic X-Ray Absorptiometry	860
20.1.1.1. Principles and Instrumentation	860
20.1.1.2. Advantages and Limitations	861

xxx CONTENTS

20.1.2. Monochromatic X-Ray Absorptiometry	862
20.1.2.1. Principles and Instrumentation	862
20.1.2.2. Advantages and Limitations	864
20.1.3. Applications of X-Ray Absorptiometry	864
20.1.4. X-Ray Absorption-Edge Spectrometry (Differential X-Ray Absorptiometry)	866
20.1.4.1. Principles and Instrumentation	866
20.1.4.2. Advantages and Limitations	871
20.1.4.3. Applications	873
20.1.5. X-Ray Contact Microradiography	878
20.1.6. X-Ray Absorption-Edge Fine Structure	879
20.1.7. Specimen Preparation for X-Ray Absorption	881
20.2. X-Ray Scatter Methods	882
20.2.1. Coherent Scatter	883
20.2.2. Coherent/Incoherent Scatter Ratio	883
20.2.3. Determination of Dry Mass	884
20.3. Scanning X-Ray Microscopy	885
20.3.1. Introduction	885
20.3.2. Scanning X-Ray Emission Microscopy	886
20.3.3. Scanning X-Ray Absorption Microscopy	887
20.4. X-Ray Photoelectron and Auger-Electron Spectrometry	888
20.4.1. Introduction	888
20.4.2. X-Ray Photoelectron Spectrometry	889
20.4.3. Auger-Electron Spectrometry	890
20.4.4. Photo- and Auger-Electron Spectrometer	893
20.5. X-Ray-Excited Optical-Fluorescence Spectrometry	895
20.6. X-Ray Lasers	897
20.7. X-Ray Appearance-Potential Spectrometry	899

Chapter 21. Electron-Probe Microanalysis

21.1. Introduction	903
21.2. Instrumentation	904
21.2.1. General	904
21.2.2. Electron-Optical Systems	905
21.2.3. Other Instrument Systems	908
21.3. Interaction of the Electron Beam and Specimen	909
21.3.1. Interaction Phenomena	909
21.3.1.1. Electron Phenomena	910
21.3.1.2. X-Ray Phenomena	911

21.3.1.3. Cathodoluminescence	912
21.3.1.4. Potential Distribution Pattern	912
21.3.2. Detection	913
21.3.2.1. Electron Detection	913
21.3.2.2. X-Ray, Luminescence, and Potential Detection	914
21.4. Modes of Measurement and Display	914
21.4.1. General	914
21.4.2. Measurement at a Point	915
21.4.3. Measurement along a Line (One-Dimensional Analysis)	915
21.4.4. Measurement over a Raster (Two-Dimensional Analysis)	918
21.4.5. Measurement Perpendicular to the Specimen Surface (Three-Dimensional Analysis)	927
21.4.6. Other Methods of Readout and Display	927
21.4.7. Color Displays	928
21.4.8. Considerations	930
21.5. Specimen Considerations	931
21.6. Quantitative Analysis	933
21.6.1. Principles	933
21.6.2. Intensity Corrections	934
21.7. Performance	938
21.8. Applications	942
21.9. Comparison with X-Ray Fluorescence Spectrometry	942

PART VIII. APPENDIXES, BIBLIOGRAPHY

Appendixes

Appendix 1. Wavelengths of the Principal X-Ray Spectral Lines of the Chemical Elements— <i>K</i> Series	951
Appendix 2. Wavelengths of the Principal X-Ray Spectral Lines of the Chemical Elements— <i>L</i> Series	954
Appendix 3. Wavelengths of the Principal X-Ray Spectral Lines of the Chemical Elements— <i>M</i> Series	958
Appendix 4. Photon Energies of the Principal <i>K</i> and <i>L</i> X-Ray Spectral Lines of the Chemical Elements	960
Appendix 5. Wavelengths of the <i>K</i> , <i>L</i> , and <i>M</i> X-Ray Absorption Edges of the Chemical Elements	964
Appendix 6. <i>K</i> , <i>L</i> , and <i>M</i> X-Ray Excitation Potentials of the Chemical Elements	968

xxxii CONTENTS

Appendix 7A. X-Ray Mass-Absorption Coefficients of the Chemical Elements at 0.1–30 Å	972
Appendix 7B. X-Ray Mass-Absorption Coefficients of Elements 2–11 (He–Na) at 40–100 Å	976
Appendix 8. Values of the <i>K</i> and LIII Absorption-Edge Jump Ratios <i>r</i> and $(r - 1)/r$ of the Chemical Elements	977
Appendix 9. Average Values of the <i>K</i> , <i>L</i> , and <i>M</i> Fluorescent Yields of the Chemical Elements	980
Appendix 10. X-Ray Spectrometer Analyzer Crystals and Multi-layer Films	981
Appendix 11A. Glossary of Frequently Used Notation	1003
Appendix 11B. Prefixes for Physical Units	1008
Appendix 12. Periodic Table of the Chemical Elements	1009

Bibliography

Books	1011
Periodicals	1014
General Reviews	1014
Bibliographies	1015
Tables of Wavelengths, 2θ Angles, and Mass-Absorption Coefficients	1016
Papers and Reports	1018

Index 1061