

# Contents

## Chapter 1

<b>Historical Introduction . . . . .</b>	<b>1</b>
1. Early Developments . . . . .	1
2. The Newtonian Era . . . . .	2
3. The Early 1800's (to Kirchhoff and Bunsen) . . . . .	3
4. The Later 1800's . . . . .	4
5. Arc and Spark Excitation . . . . .	6
6. Flame Emission Spectroscopy . . . . .	6
7. Atomic Absorption Spectroscopy . . . . .	7
8. Atomic Fluorescence Spectroscopy . . . . .	9
Selected Reading . . . . .	10

## Chapter 2

<b>The Origin of Atomic Spectra . . . . .</b>	<b>11</b>
1. The Nature of Electromagnetic Radiation . . . . .	11
2. Early Concepts . . . . .	13
3. The Balmer Equation . . . . .	14
4. From Balmer to Bohr . . . . .	16
4.1. Spectral Line Series for Hydrogen . . . . .	21
4.2. Energy Level Diagrams . . . . .	21
5. Modifications of the Bohr Theory. . . . .	21
5.1. Selection Rules for $n$ and $k(l)$ . . . . .	24
5.2. Atoms with Two Valence Electrons . . . . .	25
5.3. Selection Rules and the Schrödinger Equation . . . . .	26
6. Alkali Metal Atom Spectra . . . . .	28
6.1. Doublet Structure of Alkali Metal Spectra . . . . .	28
6.2. Electron Spin . . . . .	29
7. Alkaline Earth Atomic Spectra . . . . .	30

8.	Spectral Series and Spectroscopic Term Symbols . . . . .	31
9.	Zeeman and Stark Effects . . . . .	31
10.	Spectral Line Intensities . . . . .	33
10.1.	Statistical Weight . . . . .	33
10.2.	The Boltzmann Distribution Factor . . . . .	34
11.	Transition Probabilities—Oscillator Strengths . . . . .	35
12.	Spectral Linewidths . . . . .	37
13.	Atomic Fluorescence . . . . .	38
14.	Metastable States Laser Action . . . . .	39
14.1.	Laser Action . . . . .	39
15.	Molecular Spectra (Band Spectra) . . . . .	41
	Selected Reading . . . . .	45
 Chapter 3		
	<b>Filters, Prisms, Gratings, and Lenses . . . . .</b>	47
1.	Filters . . . . .	47
1.1.	Absorption Filters . . . . .	47
1.2.	Interference Filters . . . . .	49
1.3.	Circular Variable Filters . . . . .	51
2.	Prisms . . . . .	52
2.1.	Dispersion of a Prism . . . . .	53
2.2.	Resolving Power of a Prism . . . . .	55
2.3.	Prism Materials . . . . .	57
2.4.	Types of Prisms . . . . .	58
3.	Interferometers . . . . .	59
4.	Diffraction Gratings . . . . .	60
4.1.	Dispersion of a Grating . . . . .	63
4.2.	Resolving Power of a Grating . . . . .	63
4.3.	Production and Characteristics of Gratings . . . . .	65
4.4.	Grating Replicas . . . . .	66
4.5.	Concave Gratings . . . . .	66
4.6.	Holographic Gratings . . . . .	67
4.7.	Echelle Gratings . . . . .	67
5.	Lenses . . . . .	70
5.1.	Uses of Lenses . . . . .	70
5.2.	Lens Defects . . . . .	72
	Selected Reading . . . . .	74
 Chapter 4		
	<b>Spectrometers . . . . .</b>	75
1.	Prism Spectrometers . . . . .	75
1.1.	The Cornu Prism Spectrometer . . . . .	76

CONTENTS	xi
1.2. The Littrow Spectrometer . . . . .	76
2. Plane Grating Spectrometers . . . . .	78
2.1. The Ebert Spectrometer . . . . .	78
2.2. The Czerny-Turner Spectrometer . . . . .	81
2.3. The Two-Mirror, Crossed-Beam, Plane Grating Spectrometer . . . . .	82
2.4. The Double-Grating Spectrometer . . . . .	83
3. Concave Grating Spectrometers . . . . .	83
3.1. The Rowland Spectrometer . . . . .	84
3.2. The Paschen-Runge Spectrometer . . . . .	85
3.3. The Eagle Spectrometer . . . . .	86
3.4. The Wadsworth Spectrometer . . . . .	88
3.5. The Grazing Incidence Spectrometer . . . . .	89
3.6. The Seya-Namioka Spectrometer . . . . .	90
3.7. Vacuum Spectrometers . . . . .	90
4. Direct Reading Spectrometers . . . . .	92
5. Selection of a Spectrometer . . . . .	93
6. Adjustment and Care of Spectrometers . . . . .	94
6.1. Vertical Adjustment of the Entrance Slit . . . . .	94
6.2. Focusing the Entrance Slit . . . . .	95
6.2.1. Prism Instruments . . . . .	95
6.2.2. Grating Instruments . . . . .	95
6.3. Final Adjustments . . . . .	95
6.4. General Care of Spectrometers . . . . .	96
Selected Reading . . . . .	97
 Chapter 5 <b>Accessory Equipment for Arc and Spark Spectrochemical Analysis</b> . . . . .	 99
1. The Spectrometer Slit . . . . .	99
2. The Hartmann Diaphragm . . . . .	101
3. The Step Filter . . . . .	101
4. Rotating Sectors . . . . .	103
5. Excitation Sources . . . . .	103
5.1. The Direct Current Arc . . . . .	104
5.2. The Alternating Current Arc . . . . .	105
5.3. The Electric Spark . . . . .	106
5.4. The Plasma Arc . . . . .	108
5.5. The Laser Source . . . . .	112
5.6. Multiple Source Units . . . . .	113
6. Arc and Spark Stands . . . . .	114

6.1. Special Assemblies for the Arc-Spark Stand . . . . .	116
6.1.1. The Stallwood Jet . . . . .	116
6.1.2. The Petry Stand . . . . .	117
6.1.3. Rotating Disk Electrode Device . . . . .	117
7. Order Sorters . . . . .	118
8. Densitometers and Comparators . . . . .	118
9. Miscellaneous Accessory Equipment . . . . .	121
9.1. Electrodes . . . . .	122
Selected Reading . . . . .	123
Chapter 6	
<b>Recording and Reading Spectra . . . . .</b>	125
1. The Photographic Process . . . . .	125
1.1. Characteristics and Properties of the Photographic Emulsion . . . . .	126
1.2. The Characteristic Curve . . . . .	126
1.3. The Reciprocity Law . . . . .	129
1.4. The Intermittency Effect . . . . .	130
1.5. The Eberhard Effect . . . . .	130
1.6. Graininess and Granularity . . . . .	131
1.7. Resolving Power . . . . .	132
1.8. Spectral Sensitivity . . . . .	134
2. Processing of Spectroscopic Films and Plates . . . . .	135
2.1. The Developing Process . . . . .	135
3. Hadamard Transform and Fourier Transform Spectroscopy	139
4. Light-Sensitive Phototubes . . . . .	140
4.1. Spectral Response Designation . . . . .	140
4.2. General Characteristics of Multiplier Phototubes .	141
4.3. Solar Blind Phototubes . . . . .	143
5. Resonance Detectors . . . . .	144
6. Vidicon Detectors . . . . .	145
Selected Reading . . . . .	146
Chapter 7	
<b>Qualitative and Semiquantitative Arc-Spark Emission Spectrochemical Analysis . . . . .</b>	147
1. Sample Excitation . . . . .	148
2. Wavelength Measurements . . . . .	149
2.1. Line Identification by Wavelength Measurement . .	149
3. Comparison Spectra . . . . .	151

CONTENTS	xiii
4. Spectral Charts . . . . .	155
5. Wavelength Tables . . . . .	156
6. Some Special Problems and Techniques of Spectrochemical Qualitative Analysis . . . . .	157
6.1. Spectral Line Interferences . . . . .	157
6.2. Spectral Band Interferences . . . . .	157
6.3. Arc Continuum Interference . . . . .	158
7. Increasing Spectral Line Intensities . . . . .	158
8. Semiquantitative Spectrochemical Analysis . . . . .	159
8.1. Determination of a Concentration Level . . . . .	160
8.2. The Harvey Method of Semiquantitative Spectrochemical Analysis . . . . .	160
8.3. Matrix Effects . . . . .	164
8.4. The Wang Method of Semiquantitative Spectrochemical Analysis . . . . .	165
9. Some Special Spectrochemical Problems . . . . .	166
9.1. Microsamples . . . . .	166
9.2. Microarea Sampling . . . . .	166
Selected Reading . . . . .	167
 Chapter 8	
<b>Quantitative Spectrochemical Analysis . . . . .</b>	<b>169</b>
1. Some General Considerations . . . . .	169
2. The Internal Standard . . . . .	170
3. Spectroscopic Buffers . . . . .	172
4. Excitation of the Sample . . . . .	175
5. Selection of Spectral Lines . . . . .	177
6. Comparison Standards . . . . .	177
7. Sample Preparation . . . . .	179
8. Emulsion Calibration and Analytical Working Curves	180
8.1. Emulsion Calibration . . . . .	180
8.2. The Emulsion Calibration Curve . . . . .	185
9. The Working Curve . . . . .	188
9.1. Construction of a Typical Analytical Working Curve	188
10. The Calculating Board . . . . .	192
11. Background Correction . . . . .	193
12. Multielement Analysis with Direct Read-Out . . . . .	194
13. Types of Samples . . . . .	195
13.1. Liquid Samples . . . . .	195
13.2. Metallic Samples . . . . .	196
13.3. Powder Samples . . . . .	197

13.4. Organic Samples . . . . .	197
13.5. Special Samples . . . . .	198
14. Some Special Techniques . . . . .	198
14.1. Fractional Distillation . . . . .	198
14.2. Carrier Distillation . . . . .	199
14.3. Transfer Methods . . . . .	200
14.4. Laser Methods . . . . .	200
14.5. Controlled Atmospheres . . . . .	200
14.6. Cathode Layer Excitation . . . . .	201
14.7. Gases . . . . .	202
14.8. Radioactive Samples . . . . .	202
15. Time-Resolved Spectroscopy . . . . .	203
15.1. Time-Resolving Components . . . . .	203
15.2. Some Characteristics of Time-Resolved Spectra . . . . .	204
15.3. Analytical Applications . . . . .	205
16. Chemical Preparation of Samples . . . . .	205
17. Applications of Spectrochemical Analysis . . . . .	206
17.1. Metals and Alloys . . . . .	206
17.2. Geology . . . . .	207
17.3. Oils and Water . . . . .	207
17.4. Plants and Soils . . . . .	208
17.5. Men and Animals . . . . .	209
17.6. Environmental Studies . . . . .	209
17.7. Some Other Applications . . . . .	209
Selected Reading . . . . .	210

### Chapter 9

#### Flame Emission Spectroscopy . . . . .

1. Flame Emission Instrumentation Requirements . . . . .	212
2. The Analytical Flame . . . . .	212
2.1. Burners and Aspirators . . . . .	216
2.2. Fuel-Oxidant Control . . . . .	218
3. The Excitation Process in the Flame . . . . .	219
3.1. Flame Emission Spectra . . . . .	220
4. Flame Emission Interferences . . . . .	222
4.1. Spectral . . . . .	222
4.2. Ionization . . . . .	224
4.3. Cation-Anion Interferences . . . . .	227
4.4. Cation-Cation Interferences . . . . .	228
4.5. Oxide Formation . . . . .	228
4.6. Chemiluminescence . . . . .	228

4.7. Physical Interferences . . . . .	229
5. Control of Interferences . . . . .	231
5.1. Spectral . . . . .	231
5.2. Ionization Interference Control. . . . .	233
5.3. Cation–Anion Interference Control . . . . .	234
5.4. Control of Oxide Interference . . . . .	234
5.5. Control of Physical Interference . . . . .	235
6. Simultaneous Multielement Analysis . . . . .	235
7. Analytical Treatment of Data . . . . .	237
7.1. Establishment of a Working Curve. . . . .	237
7.2. Background Correction . . . . .	239
7.3. Sample Bracketing . . . . .	240
7.4. The Method of Standard Additions . . . . .	241
Selected Reading . . . . .	242

**Chapter 10**  
**Analytical Atomic Absorption Spectroscopy** . . . . . 243

1. The Atomic Absorption Process . . . . .	243
2. Instrumentation Requirements . . . . .	247
3. Radiation Sources . . . . .	248
3.1. Hollow Cathode Lamps . . . . .	249
3.1.1. High-Intensity Lamps . . . . .	251
3.1.2. Multiple-Element Lamps . . . . .	251
3.1.3. Demountable Lamps . . . . .	253
3.2. Gaseous Discharge Lamps . . . . .	253
3.3. Electrodeless Discharge Lamps . . . . .	254
3.4. Flame Emission Sources . . . . .	258
3.5. Continuous Sources . . . . .	258
4. Production of the Atomic Vapor . . . . .	259
4.1. Nebulization of the Sample . . . . .	259
4.1.1. Ultrasonic Nebulization . . . . .	261
4.2. Flame Systems . . . . .	262
5. Fuels and Oxidants . . . . .	264
5.1. Atomic Distribution in Flames . . . . .	264
6. Non-Flame Absorption Cells . . . . .	268
6.1. Hollow Cathodes. . . . .	268
6.2. L'vov Furnace . . . . .	269
6.3. Woodriff Furnace . . . . .	269
6.4. Delves Cup . . . . .	271
6.5. Carbon Rod Analyzers . . . . .	272
6.6. Tantalum Boat Analyzer . . . . .	273

6.7. Other Non-Flame Cells . . . . .	275
6.8. Special Systems . . . . .	278
7. Monochromators . . . . .	280
8. Detectors . . . . .	281
8.1. Resonance Detection . . . . .	282
9. Amplifiers . . . . .	283
10. Read-Out Devices . . . . .	284
11. Interferences in Atomic Absorption . . . . .	285
11.1. Spectral Interferences . . . . .	285
11.2. Ionization Interferences . . . . .	286
11.3. Chemical Interferences . . . . .	287
11.4. Interferences with Flameless Sampling . . . . .	288
12. Control of Interferences . . . . .	289
12.1. Spectral Interference Control . . . . .	289
12.2. Ionization Interference Control . . . . .	290
12.3. Chemical Interference Control . . . . .	290
12.3.1. Flame Temperature . . . . .	290
12.3.2. Fuel-to-Oxidant Ratio . . . . .	291
12.3.3. Flame Region . . . . .	291
12.3.4. Releasing and Chelating Agents . . . . .	291
12.3.5. Chemical Separations . . . . .	292
12.3.6. Background Correction . . . . .	292
13. Analytical Treatment of Data . . . . .	294
13.1. The Working Curve . . . . .	295
13.2. Analytical Procedures . . . . .	297
14. Simultaneous Multielement Analysis . . . . .	297
Selected Reading . . . . .	298

**Chapter 11****Atomic Fluorescence Spectroscopy . . . . .** 299

1. Theoretical Basis of Analytical Atomic Fluorescence Spectroscopy . . . . .	299
2. Advantages and Limitations of Atomic Fluorescence . . . . .	302
3. Instrumentation . . . . .	303
3.1. Excitation Sources . . . . .	304
3.1.1 Hollow Cathode Lamps . . . . .	304
3.1.2. Metal Vapor Lamps . . . . .	304
3.1.3. Electrodeless Discharge Lamps . . . . .	305
3.1.4. Continuous Sources . . . . .	305
3.1.5. Laser Sources . . . . .	306
4. The Sample Cell . . . . .	307

CONTENTS	xvii
4.1. Total-Consumption Aspirator Burners . . . . .	307
4.2. Laminar Flow Burners . . . . .	307
4.3. Non-Flame Sample Cells . . . . .	308
5. Monochromators . . . . .	308
6. Interferences in Atomic Fluorescence . . . . .	309
6.1. Spectral Interferences . . . . .	309
6.2. Chemical Interferences . . . . .	310
6.3. Physical Interferences . . . . .	310
7. Analytical Procedures . . . . .	312
7.1. The Analytical Working Curve . . . . .	313
7.2. Organic Solvents . . . . .	314
7.3. Detection Limits . . . . .	315
7.4. Sample Preparation . . . . .	315
8. Applications and Future Developments . . . . .	317
Selected Reading . . . . .	318
 Appendix I. Some Basic Definitions, Physical Constants, Units, and Conversion Factors . . . . .	319
Appendix II. Spectral Lines, Arranged by Wavelength, with <i>gf</i> and Intensity Values . . . . .	321
Appendix III. Spectral Lines, Arranged by Elements, with <i>gf</i> and Intensity Values . . . . .	337
Appendix IV. Spectral Charts . . . . .	347
Appendix V. Absorbance Values Calculated from Percentage Transmittances . . . . .	353
Appendix VI. Numerical Values of the Seidel Function . . . . .	355
Appendix VII. Four-Place Logarithm Table . . . . .	357
Appendix VIII. Detection Limits by Flame Emission and Atomic Absorption . . . . .	361
Appendix IX. Periodic Table of the Elements . . . . .	365
Appendix X. Relative Atomic Weights . . . . .	367
 Author Index . . . . .	369
Subject Index . . . . .	371