

**TREATISE
ON
ANALYTICAL
CHEMISTRY**

**PART I
THEORY AND PRACTICE
VOLUME 5**

TREATISE ON ANALYTICAL CHEMISTRY

Edited by I. M. KOLTHOFF

School of Chemistry, University of Minnesota

and PHILIP J. ELVING

Department of Chemistry, University of Michigan

with the assistance of ERNEST B. SANDELL

School of Chemistry, University of Minnesota

PART I **THEORY AND PRACTICE**

VOLUME ~~5~~

INTERSCIENCE PUBLISHERS

a division of John Wiley & Sons, New York-London-Sydney

Copyright © 1964 by
JOHN WILEY & SONS, INC.

ALL RIGHTS RESERVED

LIBRARY OF CONGRESS CATALOG CARD NUMBER 59-12439

PRINTED IN U. S. A. BY MACK PRINTING CO., EASTON, PA.

TREATISE ON ANALYTICAL CHEMISTRY

PART I **THEORY AND PRACTICE**

VOLUME 5: SECTION D-3 **Optical Methods of Analysis**

Chapters 53-63

With the cooperation of EDWARD J. MEEHAN,
University of Minnesota, as section adviser

AUTHORS OF VOLUME 5

FRED W. BILLMEYER, JR.
ANNE L. CONRAD
J. H. GOLDSTEIN
FRANK P. HOCHGESANG
BRUNO JASELSKIS
DEANE B. JUDD
H. A. LIEBHAFSKY

E. J. MEEHAN
I. NIMEROFF
H. G. PFEIFFER
ALFRED A. SCHILT
E. H. WINSLOW
DAVID B. WITTRY

Acknowledgment

In view of the comprehensive nature of the Treatise, the Editors have felt it desirable to consult with experts in specialized fields of analytical chemistry. For Section D-3, dealing with "Optical Methods of Analysis," they have been fortunate in securing the cooperation of Dr. Edward J. Meehan. The competence of the authors in this Section, combined with Dr. Meehan's broad knowledge of the area, have resulted in a most succinct and timely treatment of optical and photometric methods. The constructive help of the authors and of Dr. Meehan in the preparation of Volumes 5 and 6 is acknowledged with gratitude.

PART I. THEORY AND PRACTICE

CONTENTS—VOLUME 5

SECTION D-3: Optical Methods of Analysis

53. Optical Methods. Emission and Absorption of Radiant Energy.	
By <i>E. J. Meehan</i>	2707
I. Classification of Optical Methods of Analysis.....	2708
A. Absorption Spectrophotometry.....	2709
1. Absorption in Various Spectral Regions.....	2709
2. Absorption Processes in Atoms and Molecules.....	2711
3. Survey of Applications of Absorption Spectrophotometry....	2713
a. Infrared.....	2713
b. Visible-Near-Ultraviolet Region.....	2715
c. Vacuum Ultraviolet.....	2716
d. Microwave.....	2716
e. X-Ray Absorption.....	2717
f. Neutron Absorption.....	2718
B. Photoluminescent Processes.....	2718
C. Emission by Sample: Spectrochemical Analysis.....	2723
D. Refractometry and Optical Rotation.....	2725
II. Characteristics of Radiant Energy.....	2726
A. Definitions.....	2726
B. Wave Motion.....	2727
C. Coherent and Incoherent Sources.....	2730
D. Refractive Index.....	2730
E. Units of Wavelength.....	2731
F. Energy of Electromagnetic Radiation.....	2731
G. Monochromatic Radiation.....	2732
H. Distribution of Energy in the Spectrum.....	2733
III. Processes Involved in Emission and Absorption of Radiant Energy	2734
A. Spectra of One-Electron Atoms and Ions.....	2734
B. Spectra of Alkalilike Atoms and Ions.....	2737
C. Fine Structure in Alkalilike Atoms and Ions.....	2738
D. Atoms with More Than One Valence Electron: Relative Stab-	
ility of Energy Levels.....	2740
E. Relative Intensities in Atomic Spectra.....	2743
F. Effect of Temperature. Boltzmann Distribution.....	2744
G. Internal Standards.....	2746
H. Self-Absorption.....	2748
I. Atomic Absorption Spectroscopy.....	2748
References.....	2749
 54. Fundamentals of Spectrophotometry. By <i>E. J. Meehan</i>.....	 2753
I. Absorption of Radiation.....	2754
A. General Aspects.....	2754

B. Lambert and Beer Laws	2755
C. Chemical Deviations from Beer's Law	2758
II. Nomenclature in Spectrophotometry	2761
III. Magnitudes of Concentrations and Amounts	2762
IV. Graphical Presentation of Data	2763
V. Sources of Error in Spectrophotometry	2765
A. Effect of Reflection	2765
B. Use of Nonmonochromatic Radiation	2767
C. Effect of Stray Radiation	2772
D. Cylindrical Absorption Cells	2773
E. Nonparallel Incident Radiation	2775
VI. Precision of Spectrophotometric Analysis	2777
A. General Aspects	2777
B. Visual Spectrophotometry	2777
C. Photographic Spectrophotometry	2779
D. Photoelectric Spectrophotometry	2780
VII. Improvement of Precision by Differential Measurements	2784
VIII. Analysis of Mixtures	2789
A. General	2789
B. Special Bases	2790
C. Choice of Wavelengths	2792
IX. Spectrophotometric Titrations	2795
References	2799

55. Spectroscopic Apparatus and Measurements. By *E. J. Meehan*. 2805

I. Introduction and Nomenclature	2805
II. Dispersion by Prism	2807
A. Reflection and Refraction	2807
B. Refraction through Plate with Parallel Sides	2809
C. Refraction by a Prism	2809
D. Transmission of Prism Materials	2811
E. Angular Dispersion	2811
F. Reflection Losses	2813
G. Diffraction and Resolving Power	2814
III. Types of Prisms and Prism Instruments	2818
A. Line Curvature	2818
B. Cornu Prism	2819
C. Prism Instruments	2820
1. Bunsen	2820
2. Littrow	2821
3. Féry	2821
4. van Cittert	2821
D. Special Prisms	2822
E. Summary of Numerical Values for Quartz Apparatus	2824
IV. Dispersion by Gratings	2826
A. Grating Equation	2826
B. Angular Dispersion	2828
C. Resolving Power	2829
V. Mountings of Concave and Plane Gratings	2831
A. Concave Gratings	2831
B. Plane Gratings	2831
C. Vacuum Ultraviolet	2833
VI. Comparison of Prism and Grating Instruments	2833
VII. Measurement of Wavelength	2833
VIII. Measurement of Intensity	2836
References	2837

56. Principles of Light Scattering. By Fred W. Billmeyer, Jr. 2839

I. Introduction	2840
A. General References	2841
II. Theory of Light Scattering	2841
A. Notation	2841
B. Light Scattering in Gases	2842
C. Light Scattering in Liquids	2844
D. Light Scattering from Solutions of Particles Small Compared with the Wavelength	2844
E. Particle-Size Determination from Light Scattering in Solutions of Larger Particles	2845
F. Molecular-Weight Determination from Light Scattering in Solutions of Larger Particles	2847
III. Determination of the Molecular Weights of High Polymers by Light Scattering	2849
A. Apparatus	2849
B. Sample Preparation	2854
C. Operating Techniques	2855
D. Treatment of Data	2856
IV. Applications of Light Scattering in Polymer Solutions	2857
A. Range of Applicability	2857
B. Absolute Molecular Weights	2857
C. Establishment of Viscosity-Molecular Weight Relations	2858
D. Determination of Chain Branching	2859
E. Special Cases	2859
1. Light Scattering in Mixed Solvents	2859
2. Effect of Polydispersity in Random Coil Polymers	2860
3. Critical Opalescence	2861
4. Light Scattering of Streaming Suspensions and Solutions	2861
5. Turbidimetric Titration	2861
F. Criteria for Unambiguous Determination of Weight-Average Molecular Weight	2861
V. Light Scattering by Colloidal Particles	2862
A. Scattering by Spheres of Arbitrary Size (Mie Theory)	2862
B. Classification of Scattering Systems	2862
C. Approximate Treatment for Angular-Dependence Light Scattering	2863
D. Instrumentation and Applications	2869
VI. Scattering and Absorption of Light in Pigmented Materials	2869
References	2870

**57. Specification and Designation of Color. By D. B. Judd and
I. Nimeroff 2873**

I. Introduction	2873
II. Nature of Color Vision and Color	2875
A. Physical Basis	2875
B. Psychological Basis	2876
C. Attributes of Color Perception	2882
III. The 1931 CIE Standard Observer System	2883
A. Standard Observer	2883
B. Spectrophotometric Colorimetry	2888
C. Direct Colorimetry	2893
IV. Colorimetry by Difference	2900
A. Perceptibility of Difference	2900

B. Visual Devices.....	2907
C. Photoelectric Devices.....	2909
D. Color Difference Units and Indexes.....	2911
V. Systems of Color Names and Material Standards.....	2914
A. ISCC-NBS Color Designation.....	2914
B. Transparent Media.....	2917
C. Opaque Media.....	2920
VII. One-Dimensional Color Scales.....	2926
A. Color Temperature.....	2927
B. Grading of Oils, Rosins, and Sugars.....	2929
VII. Limitations of the Methods.....	2930
A. Spectrophotometric Colorimetry.....	2931
B. Photoelectric Tristimulus Colorimeters.....	2935
1. Angular Conditions.....	2935
2. Spectral Character of Source.....	2936
3. Spectral Sensitivity of Filter-Photocell Combinations.....	2936
C. Material Standards of Color.....	2937
References.....	2938

58. Ultraviolet and Visible Spectrophotometry. By *Alfred A. Schilt* and *Bruno Jaselskis*..... 2943

Introduction.....	2945
Part I. Principles and Applications. By <i>Alfred A. Schilt</i>	
I. Principles and Theories of Radiant-Energy Absorption in the Ultra- violet and Visible Regions.....	2945
A. Processes Associated with Absorption.....	2945
1. Utilization of Radiant Energy.....	2945
2. Excited-State Transformations.....	2947
B. Characteristics of Electronic Spectra.....	2948
C. Types of Electronic Transitions.....	2950
1. Transitions Localized on Single Atoms.....	2951
2. Transitions Localized in a Group of Atoms.....	2952
3. Transitions Involving Nonlocalized Electrons.....	2953
4. Transitions Involving Intermolecular or Interionic Charge Transfer.....	2954
D. Environmental Effects on Absorption.....	2955
1. Intramolecular Effects.....	2956
2. Intermolecular Effects.....	2957
3. Extramolecular Effects.....	2959
II. Applications of Ultraviolet and Visible Spectrophotometry.....	2960
A. Qualitative Analysis.....	2960
1. Reliability of Electronic Spectra in Identification.....	2960
2. Means of Improving the Certainty of Spectrophotometric Identification.....	2961
3. Means of Expediting Comparisons of Spectra.....	2962
B. Quantitative Analysis.....	2962
1. Common Procedures in the Development of a Quantitative Spectrophotometric Method.....	2962
a. Selection of Appropriate Solvent and Solution Conditions.....	2963
b. Selection of Appropriate Wavelength or Wavelengths....	2967
c. Elimination of Interferences.....	2967
d. Evaluation of Reproducibility and Recognition of Vari- ables.....	2969
2. Some Representative Spectrophotometric Determinations....	2969
a. Inorganic Substances.....	2970
(1) Ultraviolet Absorber.....	2970

(2) Visible Absorber.....	2970
(3) Nonabsorber.....	2973
b. Organic Substances.....	2975
(1) Ultraviolet Absorber.....	2975
(2) Visible Absorber.....	2976
(3) Nonabsorber.....	2979
C. Applications Related to Qualitative and Quantitative Analysis.....	2979
1. Equilibrium Studies.....	2979
a. Determination of Empirical Formulas of Complexes.....	2980
b. Determination of Equilibrium Constants.....	2983
2. Kinetic Studies.....	2984
3. Miscellaneous.....	2985
Part 2: Instrumentation and Measurement By Bruno Jaselskis	
I. Components, Characteristics, and Comparisons of Instruments for Spectral Measurements.....	2985
A. Instrumental Components.....	2985
1. Source of Radiation.....	2986
2. Monochromators or Spectral-Band Selectors.....	2987
3. Detectors and Signal Amplification.....	2991
4. Presentation of the Output.....	3003
5. Cells, Cell Holders, and Accessories.....	3003
B. Principles in the Design of and Classes of Instruments.....	3005
1. Basic Considerations.....	3005
2. Design Patterns.....	3005
C. Some Commercially Available Instruments.....	3008
1. Visual Photometers.....	3008
2. Filter Photometers.....	3009
3. Nonrecording Spectrophotometers.....	3009
4. Automatic Recording Spectrophotometers.....	3012
II. Techniques and Evaluation of Spectral Measurements.....	3024
A. Methods for Checking Instrument Calibration.....	3024
1. Calibration of Wavelength Scale.....	3024
2. Calibration of Absorbance Scale.....	3026
B. Some Factors that Determine Measurement Procedure.....	3028
1. Physical State of the Sample and Amount Available.....	3028
2. Sample Stability.....	3029
3. Optical Properties of the Sample.....	3031
4. Multicomponent Colored Systems.....	3033
C. Methods of Improving Photometric Precision.....	3034
D. Real and Apparent Deviations from Beer's Law.....	3036
1. Instrumental Errors.....	3037
2. Deviations Due to the Nature of the Sample.....	3043
E. Treatment of Data.....	3045
1. Plotting of Spectral Data.....	3045
2. Calculation of Results.....	3046
3. Data Storage and Retrieval.....	3049
References.....	3052

59. Fluorimetry. By Anne L. Conrad..... 3057

I. Introduction.....	3057
A. Definitions.....	3057
B. Uses of the Method.....	3058
II. Historical Notes.....	3059
III. Theory.....	3061
A. Variables.....	3065
B. Instrumentation.....	3067
1. Filters.....	3068

2. Sample Cells.....	3069
3. Detectors.....	3070
4. Complete Instruments.....	3070
C. Standards.....	3073
IV. Applications.....	3074
References.....	3075

60. X-Ray Methods: Absorption, Diffraction, and Emission. By *H. A. Liebhafsky, H. G. Pfeiffer, and E. H. Winslow*..... 3079

I. Origin and Properties of X-Rays.....	3081
A. The Discovery and Generation of X-Rays.....	3081
B. Excitation of X-Rays.....	3082
C. The Interaction of X-Rays with Matter.....	3086
1. The Absorption of X-Rays.....	3086
2. The Scattering and Diffraction of X-Rays.....	3089
D. X-Rays and Atomic Structure.....	3091
E. Chemical Influences in X-Ray Absorption and Emission.....	3094
II. Schematic Summary of Instruments for Analysis.....	3094
III. The Measurement of X-Ray Intensity.....	3096
A. Introduction.....	3096
B. Functions of Electronic Circuitry.....	3098
C. Gas-Filled Detectors.....	3099
1. Ionization Chambers.....	3100
2. Geiger Counters.....	3101
3. Proportional Counters.....	3102
D. Photoelectric Detectors.....	3104
1. The Phosphor-Photoelectric Detector.....	3105
2. The Scintillation Counter.....	3105
E. Detector Reliability and Electronic Circuitry.....	3106
F. Pulse-Height Selection.....	3106
G. Guide to the Selection of the Detector.....	3108
IV. Analytical Methods Based on X-Ray Diffraction.....	3108
A. Introduction.....	3108
B. The Identification of Crystalline Powders.....	3109
1. Introduction.....	3109
2. The Crystal Lattice.....	3109
3. The Diffraction of X-Rays.....	3110
V. The Analysis of Crystalline Powders.....	3112
A. General Discussion.....	3112
B. Generation and Interpretation of the Diffraction Pattern.....	3113
1. Photographic Techniques.....	3113
2. Spectrometric Techniques.....	3115
3. The Interpretation of the Diffraction Pattern.....	3119
4. The X-Ray Powder Data File Card.....	3121
5. Identification of a Substance Containing Only One Crystalline Species.....	3122
6. Analysis of Mixtures.....	3122
7. Quantitative Analysis by Powder Diffraction.....	3123
VI. X-Ray-Diffraction Studies of Amorphous Materials and Small Crystals.....	3124
VII. X-Ray-Diffraction Studies of Linear Polymers and Fibers.....	3124
VIII. Absorptiometry with Polychromatic Beams.....	3126
A. Introduction.....	3126
B. Simple Photometer.....	3129
1. Direct Absorptiometry.....	3129
2. Comparative Absorptiometry.....	3133
3. Other Applications.....	3134

IX. Absorptiometry with Monochromatic Beams	3134
A. Introduction	3134
B. The Absorption-Edge Method	3135
C. Absorptiometric Determination of Film Thickness	3137
X. X-Ray-Emission Spectrography	3138
A. Variation of Line Intensity with Thickness and Determination of Film Thickness	3139
B. The Determination of Composition: Preliminary Discussion	3142
C. Sample Composition: Absorption and Enhancement Effects	3144
D. Deviations from Proportionality	3147
1. Comparison with a Standard	3147
2. Use of an Internal Standard	3147
3. Dilution	3147
4. Estimation of Class (I) Deviations	3148
5. Sample Preparation and Handling	3148
E. Methods of Excitation	3149
F. The Background Problem	3150
G. Crystals for X-Ray-Emission Spectrography	3151
H. Notes on Equipment	3155
XI. Applications of X-Ray-Emission Spectrography	3156
A. Trace Determinations	3156
B. Trace Determinations in Minerals on a Commercial Scale	3158
C. Major Constituents by Direct Comparison of Standard and Unknown Samples	3159
D. Major Constituents by Use of Internal Standards	3161
E. Determination of the Light Elements	3163
F. Quantitative Determinations in Complex Systems	3166
XII. Reliability of X-Ray-Emission Spectrography	3168
A. Simple Correction for Background	3170
B. Simple Ratio: the Comparative Method	3170
C. Ratio Corrected for Background: the Comparative Method	3171
References	3171

61. X-Ray Microanalysis by Means of Electron Probes. By *David*

B. Wittry..... 3173

I. Introduction	3174
II. Theory of X-Ray Microanalysis	3175
A. Physical Basis of the Method	3175
B. Basic Experiment Embodiment	3177
C. Qualitative Analysis	3178
D. Local Analysis	3179
E. Quantitative Analysis	3181
F. Derived and Related Techniques	3183
1. Point-Projection X-Ray Microscopy	3183
2. Scanning X-Ray Microscopy	3183
3. Scanning Electron Microscopy and Microanalysis Using Back-Scattered Electrons	3183
4. Selected-Area Electron Diffraction	3184
5. Local Crystallographic Analysis by Divergent-Beam X-Ray Diffraction	3184
III. Practice of X-Ray Microanalysis	3184
A. Instrumentation	3184
1. Formation of the Electron Probe	3184
2. Scanning of the Specimen	3187
3. Location of the Region Analyzed	3188
4. Detection and Analysis of the X-Radiation	3192

B. Commercial Instruments	3196
C. Operating Techniques	3200
1. Obtaining Optimum Spatial Resolution	3200
2. Specimen Preparation	3203
3. Control of Specimen Contamination	3205
4. Fixed-Charge <i>vs.</i> Fixed-Time Measurement	3206
5. Treatment of the Data	3207
IV. Uses of X-Ray Microanalysis	3214
A. Scope of the Method	3214
B. Applications of Electron Probe Microanalysis	3215
1. Physics of Solids and Physical Metallurgy	3215
a. Diffusion in Solids	3215
b. Identification of Precipitates, Segregates, and Inclusions	3220
c. Identification of Phases	3221
2. Process Metallurgy	3222
3. Process Control	3223
4. Ceramics	3225
5. Natural Science	3227
a. Geochemistry	3227
b. Biology	3228
c. Archeology and Cultural Anthropology	3228
References	3229

62. Microwave Spectrophotometry. By *J. H. Goldstein*..... 3233

I. Introduction	3234
A. Historical and Orientative Remarks	3234
B. General Features of Microwave Spectrographs and Spectra	3236
II. Theory of Microwave Spectra	3240
A. General	3240
B. The Spectra of Rigid Rotators	3242
1. Calculation of Moments of Inertia and Rotational Constants	3242
a. Linear Molecules	3242
b. Nonlinear Molecules	3243
c. Classification of Nonlinear Rotators (Tops)	3244
d. Asymmetry Parameters	3244
e. The Effect of Isotopic Substitution	3245
2. Equations for Transition Frequencies of Rigid Molecules	3245
a. Linear Molecules	3245
b. Symmetric-Top Molecules	3246
c. Spherical-Top Molecules	3247
d. Asymmetric-Top Molecules	3247
3. Intensities of Rigid-Rotor Transitions	3252
C. Effects Due to Internal Motion of Molecules	3255
1. Centrifugal Distortion	3255
2. Effects Due to Molecular Vibrations	3256
3. Internal Rotation	3257
D. Special Effects	3259
1. The Stark Effect	3259
2. The Nuclear Quadrupole Effect	3261
3. The Zeeman Effect	3263
III. The Techniques of Microwave Spectroscopy	3263
A. Introduction	3263
B. Microwave Spectrograph Components	3264
1. Waveguide	3264
2. Radiation Sources	3264
3. Accessory Microwave Components	3266
a. Attenuators	3266
b. Directional Couplers and Tees	3266

c. Cavity Wavemeters.....	3266
d. Crystal Detectors and Detector Mounts.....	3267
4. Cells.....	3268
5. Auxiliary Equipment.....	3270
C. Practical Spectrographs.....	3271
1. The Simple Absorption Spectrograph.....	3271
2. The Stark-Modulated Spectrograph.....	3273
D. Operation of the Stark-Modulated Spectrograph.....	3277
1. Sample Handling.....	3277
2. Searching for Spectra.....	3277
3. Precise Frequency Measurements.....	3280
4. Intensity Measurements.....	3281
IV. The Applications of Microwave Spectroscopy.....	3282
A. Applicability and Limitations.....	3282
B. Qualitative Analysis.....	3283
C. Quantitative Analysis.....	3285
V. Appendix: Sources of Supply.....	3286
References.....	3287

63. Nephelometry and Turbidimetry. By *Frank P. Hochgesang*.... 3289

I. Introduction.....	3290
A. What Are These Techniques?.....	3290
B. Historical Highlights.....	3291
C. Reasons for Use and Importance.....	3291
D. Summary of Literature References.....	3292
II. Theory of Nephelometry and Turbidimetry.....	3293
A. Absorption Law.....	3293
B. Effects of Particle Size Upon Intensity and Angular Distribution of Scattered Light.....	3295
C. Choice of Wavelength.....	3299
III. Particle Growth and Stabilization of Colloidal Systems.....	3301
IV. Practice of Nephelometry and Turbidimetry.....	3306
A. General Discussion of Instrumentation.....	3306
B. Instrumental Errors.....	3307
C. Description of Specific Instruments.....	3308
1. Turbidimeters.....	3308
2. Nephelometers.....	3311
3. Turbidimeters for Titration Techniques.....	3312
4. Turbidimeters for Continuous-Stream Analysis.....	3313
5. Turbidimeters for Classification of Particle Size by Sedimen- tation.....	3314
6. Instruments Specifically Designed for Measurement on Aero- sols.....	3314
D. Preparation of Sample and Operating Precautions.....	3315
E. Preparation of Principal Comparison Standards.....	3315
V. Uses of Nephelometry and Turbidimetry.....	3317
A. Scope.....	3317
B. Applications.....	3317
1. Inorganic Applications.....	3317
2. Organic Applications (Including Foods, Beverages, Etc.).....	3320
3. Biochemical Applications.....	3321
4. Titration Applications.....	3322
5. Continuous-Stream Applications.....	3323
6. Classification of Particle Size by Sedimentation.....	3323
References.....	3324

Subject Index for Volume 5	3329
---	-------------

VOLUME 6: SECTION D-3 (concluded)

64. **Emission Spectroscopy.** By *Bourdon F. Scribner* and *Marvin Margoshes*
65. **Flame Photometry.** By *Bert L. Vallee* and *Ralph E. Thiers*
66. **Infrared Spectrophotometry.** By *A. Lee Smith*
67. **Raman Spectroscopy.** By *E. J. Rosenbaum*
68. **Electron Diffraction and Scattering Techniques.** By *John H. Reisner*
69. **Neutron Absorption and Diffraction Spectroscopy.** By *George W. Leddicotte*
70. **Refractometry and Interferometry: Specific Dispersion.** By *S. Z. Lewin* and *N. Bauer*
71. **Optical Rotation: Polarimetry.** By *William A. Struck* and *Edward C. Olson*
72. **Chemical Microscopy.** By *Walter C. McCrone* and *Lucy B. McCrone*
73. **Electron Microscopy.** By *George C. Cocks*

