

065
W3
V:4

7863535

Wilson and Wilson's

COMPREHENSIVE ANALYTICAL CHEMISTRY

Edited by

G. SVEHLA, PH.D., D.SC., F.R.I.C.

*Reader in Analytical Chemistry
The Queen's University of Belfast*

VOLUME IV

Instrumentation for Spectroscopy
Analytical Atomic Absorption and Fluorescence Spectroscopy
Diffuse Reflectance Spectroscopy



ELSEVIER SCIENTIFIC PUBLISHING COMPANY
AMSTERDAM OXFORD NEW YORK
1975



E7863585

COMPREHENSIVE ANALYTICAL CHEMISTRY

ELSEVIER SCIENTIFIC PUBLISHING COMPANY
335 JAN VAN GALENSTRAAT
P.O. BOX 211, AMSTERDAM, THE NETHERLANDS

AMERICAN ELSEVIER PUBLISHING COMPANY, INC.
52 VANDERBILT AVENUE
NEW YORK, NEW YORK 10017

LIBRARY OF CONGRESS CARD NUMBER: 58-10158

ISBN 0-444-41163-1

WITH 134 ILLUSTRATIONS AND 16 TABLES

COPYRIGHT © 1975 BY ELSEVIER SCIENTIFIC PUBLISHING COMPANY,
AMSTERDAM

ALL RIGHTS RESERVED. NO PART OF THIS PUBLICATION MAY BE
REPRODUCED, STORED IN A RETRIEVAL SYSTEM, OR TRANSMITTED
IN ANY FORM OR BY ANY MEANS, ELECTRONIC, MECHANICAL,
PHOTOCOPYING, RECORDING, OR OTHERWISE, WITHOUT THE PRIOR
WRITTEN PERMISSION OF THE PUBLISHER,
ELSEVIER SCIENTIFIC PUBLISHING COMPANY, JAN VAN GALEN-
STRAAT 335, AMSTERDAM

PRINTED IN THE NETHERLANDS

COMPREHENSIVE ANALYTICAL CHEMISTRY

ADVISORY BOARD

R. Belcher, PH.D., D.SC., F.INST.F., F.R.I.C.

Professor of Analytical Chemistry, The University of Birmingham

The late F. Feigl, ENG., D.SC.

Laboratório da Produção Mineral, Ministério da Agricultura, Rio de Janeiro;
Professor at the University of Brazil

L.T. Hallett, PH.D.

Formerly Editor, *Analytical Chemistry*, Washington, D.C.

J. Haslam, D.SC., F.R.I.C.

Formerly Chief Analyst, Imperial Chemical Industries (Plastics Division),
Welwyn Garden City

H.M.N.H. Irving, M.A., D.PHIL., F.R.I.C.

Professor of Inorganic Chemistry, The University, Leeds

E.B. Sandell, PH.D.

Professor of Analytical Chemistry, The University of Minnesota, Minneapolis,
Minn.

A.A. Smales, O.B.E., D.SC., F.R.I.C.

Head of Analytical Chemistry Division, Atomic Energy Research Establishment,
Harwell

P.W. West, PH.D., D.SC.

Boyd Professor of Chemistry, Louisiana State University, Baton Rouge, La.



Contributors to Volume IV

R.W. Frei, Sandoz Ltd., CH-4002 Basle

M.M. Frodyma, National Science Foundation, Washington, D.C.

G.F. Kirkbright, Chemistry Department, Imperial College of Science & Technology, London

V.T. Lieu, Department of Chemistry, California State College, Long Beach, California

I.L. Marr, Department of Chemistry, The University, Aberdeen

M. Sargent, Chemistry Department, Imperial College of Science & Technology, London

WILSON & WILSON'S

COMPREHENSIVE ANALYTICAL CHEMISTRY

VOLUMES IN THE SERIES

- | | |
|----------|---|
| Vol. IA | Analytical Processes
Gas Analysis
Inorganic Qualitative Analysis
Organic Qualitative Analysis
Inorganic Gravimetric Analysis |
| Vol. IB | Inorganic Titrimetric Analysis
Organic Quantitative Analysis |
| Vol. IC | Analytical Chemistry of the Elements |
| Vol. IIA | Electrochemical Analysis
Electrodeposition
Potentiometric Titrations
Conductometric Titrations
High-frequency Titrations |
| Vol. IIB | Liquid Chromatography in Columns
Gas Chromatography
Ion Exchangers
Distillation |
| Vol. IIC | Paper and Thin-Layer Chromatography
Radiochemical Methods
Nuclear Magnetic Resonance and Electron Spin
Resonance Methods
X-Ray Spectrometry |
| Vol. IID | Coulometric Analysis |
| Vol. III | Elemental Analysis with Minute Samples
Standards and Standardization
Separations by Liquid Amalgams
Vacuum Fusion Analysis of Gases in Metals
Electroanalysis in Molten Salts |

Vol. IV

**Instrumentation for Spectroscopy
Atomic Absorption and Fluorescence Spectroscopy
Diffuse Reflectance Spectroscopy**

Preface

In *Comprehensive Analytical Chemistry* the aim is to provide a work which, in many instances, should be a self-sufficient reference work; but where this is not possible, it should at least be a starting point for any analytical investigation.

It is hoped to include the widest selection of analytical topics that is possible within the compass of the work, and to give material in sufficient detail to allow it to be utilised directly, not only by professional analytical chemists, but also by those workers whose use of analytical methods is incidental to their other work rather than continual. Where it is not possible to give details of methods, full reference to the pertinent original literature is made.

All the contributions to Volume IV are connected with spectroscopy. The aim of the chapter on instrumentation for spectroscopy (Chap. 1) is to assist the spectroscopist in selecting the proper instrument and/or the proper experimental conditions for his measurement. The contributions on atomic absorption and fluorescence spectroscopy (Chap. 2) and on diffuse reflectance spectroscopy (Chap. 3) cover modern techniques widely used nowadays in analytical laboratories. As usual, these contributions are written by outstanding internationally known experts in their fields. Contributions on other spectroscopic and optical methods will be published in further volumes.

Dr. C.L. Graham of the University of Birmingham assisted in the production of the present volume; his contribution is acknowledged with many thanks.

July, 1974.

G. Svehla

Contents

<i>Preface</i>	ix
--------------------------	----

<i>Chapter 1. INSTRUMENTATION FOR SPECTROSCOPY,</i> by I.L. Marr	1
---	---

1. Introduction	1
(A) Scope	1
(B) The nature of light — wavelength standards	2
(C) The spectrum	4
(D) Molecular and atomic spectra	5
(E) Observation of spectra	5
(F) Terminology	6
2. Sources	8
(A) Emission of electromagnetic radiation and its spectral energy distribution	8
(1) Band spectra, 11 — (2) Coherent radiation — lasers, 11 — (3) Requirements of sources for spectroscopy, 15	
(B) Atomic line sources	16
(1) Flames, 16 — (2) Arcs and sparks, 18 — (3) Gas discharge tubes, 19 — (4) Hollow-cathode lamps, 22 — (5) Electrode- less discharge tubes, 23	
(C) Thermal sources — black-body radiators	23
(1) The tungsten filament lamp, 23 — (2) Quartz-iodine lamp, 24 — (3) Nernst filament, 24 — (4) Globar, 25 — (5) Carbon rod, 25 — (6) Carbon arc, 25	
3. Spectrometers, spectrographs and monochromators	25
(A) The prism spectroscope	26
(1) Refraction, 27 — (2) The prism, 27 — (3) Resolving power of a prism spectrograph, 30 — (4) Transparency of optical materials, 31 — (5) Lenses in spectrographs, 33 — (6) The Littrow spectrometer (1863), 33 —	

	(7) The Wadsworth mounting (1894), 35 — (8) The Féry prism (1910), 35 — (9) The Pellin—Broca prism (1899), 36 — (10) The Rumsey “economical” prism (1962), 37 — (11) The Amici prism, 37 — (12) Van Cittert spectroscope, 37 — (13) Two interesting prism spectrometers, 38	
(B)	The diffraction grating	38
	(1) Dispersion of a grating, 40 — (2) Resolving power of a grating, 41 — (3) Reflection gratings, 42 — (4) Blazing, 42 — (5) Rotation of a grating in a scanning monochromator, 44 — (6) Development of the grating spectroscope, 45 — (7) The Abney mount (1886), 46 — (8) The Eagle mount (1910), 47 — (9) The Runge and Paschen mounting (1897), 47 — (10) The Wadsworth mounting (1896), 48 — (11) The Ebert spectrograph (1899), 48 — (12) The Czerny—Turner spectrograph (1930), 49 — (13) The Fastie—Ebert spectrograph (1952), 49 — (14) The Pfund—Hardy mount, 50 — (15) Grating or prism?, 50 — (16) Overlapping spectra, 51 — (17) Vacuum UV, 51	
(C)	The slits	52
	(1) Energy distribution about a given selected wavelength, 52 — (2) Line curvature, 54 — (3) Bilateral slits, 55 — (4) Constant energy and constant band-width, 55 — (5) Practical points affecting choice of slit width, 56 — (6) Care of slits, 57 — (7) Accessories for spectrograph slits, 57	
(D)	Fourier transform spectroscopy	58
	(1) Periodic scanning, 62 — (2) Aperiodic scanning with real-time computing, 63 — (3) A comparison with grating spectroscopy, 63 — (4) Applications, 64	
4.	Detectors	65
(A)	Introduction	65
	(1) Factors affecting the choice of a detector, 66	
(B)	Photo-emissive detectors	67
	(1) Vacuum photocells, 67 — (2) Photomultiplier tubes, 69 — (3) Gas-filled photocells, 73 — (4) Barrier-layer cells, 73	
(C)	Photo-conductive detectors	74
(D)	Thermal detectors	75
	(1) Thermocouples, 76 — (2) Bolometers, 76 — (3) Thermistors, 77 — (4) Superconducting bolometers, 77 — (5) Pneumatic heat detectors — The Golay cell, 78	

(E)	The photographic plate	79
	(1) Contrast, 80 — (2) Sensitivity and speed, 81 — (3) Reciprocity failure, 81 — (4) Spectral sensitivity, 82 — (5) Graininess and granularity, 82 — (6) The microdensitometer, 83	
(F)	The human eye	83
5.	Basic instruments	84
(A)	Photometers	84
	(1) Filters, 85	
(B)	Spectrophotometers	86
	(1) Manual instruments, single-beam, 86 — (2) High-precision, single-beam instruments, 86 — (3) Recording instruments, double-beam, 86	
	References	88

Chapter 2. ANALYTICAL ATOMIC ABSORPTION AND FLUORESCENCE SPECTROSCOPY, by G.F. Kirkbright and M. Sargent 95

1.	Introduction	95
2.	Theory	97
(A)	Essential spectroscopic theory	98
	(1) Einstein transition probability, 98	
(B)	The widths of spectral lines	100
	(1) Definition of line width, 101 — (2) Phenomena responsible for spectral line widths, 102 — (3) The total width of a spectral line, 107	
(C)	Atomic absorption spectroscopy	108
	(1) Introduction, 108 — (2) The absorption coefficient, k_ν , 109 — (3) The integrated absorption coefficient, K , 109 — (4) The Voigt expression for the absorption coefficient, k_ν , 110 — (5) The total absorption factor, A_T , 111 — (6) The total absorption factor where the absorption line half-width is narrow compared to the source line half-width, 113 — (7) The total absorption factor where the absorption line half-width is wide compared to the source line half-width, 115 — (8) The absorbance, A , with a sharp line source, 118	
(D)	Atomic fluorescence spectroscopy	119
	(1) Intensity of atomic fluorescence, 123 — (2) The ideal fluorescence intensity, 124 — (3) Ideal fluorescence intensity when the absorption line	

	half-width is narrow compared to the source line half-width, 126— (4) Ideal fluorescence intensity when the absorption line half-width is wide compared to the source line half-width, 126 — (5) The actual fluorescence intensity, 128	
(E)	Lambert—Beer Law	130
(F)	Effect of flame length on absorbance	131
(G)	Relationship between sample concentration, C , and the concentration, N_j , of atoms for absorption	132
3.	Instrumentation	134
(A)	Instrumental systems	134
	(1) Special requirements for AAS, 135 — (2) Special requirements for AFS, 136	
(B)	Radiation sources	137
	(1) Spectral classification, 137 — (2) Practical classification, 138	
(C)	Continuum sources	138
(D)	Hollow-cathode lamps	140
	(1) Construction and operation of hollow-cathode lamps, 141 — (2) Special types of hollow-cathode lamp, 146 — (3) Operation of hollow-cathode sources, 150	
(E)	Electrodeless discharge sources	150
(F)	Vapour discharge lamp sources	154
(G)	Other sources	155
(H)	Absorption and fluorescence cells	156
	(1) Flames, 156 — (2) Furnaces, 157 — (3) Hot filaments, 158 — (4) Hollow-cathode cells, 159 — (5) Other cells, 160	
(I)	Isolation of spectral lines	161
	(1) Introduction, 161 — (2) Filters, 162 — (3) Monochromators, 163 — (4) Resonance detectors, 165 — (5) Selective modulation, 166	
(J)	Detector and read-out systems	167
	(1) The detector, 167 — (2) Amplification and measuring system, 169 — (3) Modulation of the source, 170 — (4) Double-beam operation, 171 — (5) Noise, 172	
4.	Flames	173
(A)	Premixed flames	173
	(1) Primary reaction zone, 173 — (2) Interconal zone, 176 — (3) Secondary reaction zone, 178 — (4) Burners for premixed flames, 179	

(B)	Introduction of samples into premixed flames . . .	182
	(1) Pneumatic nebulisers and spray chambers, 183 —	
	(2) Non-pneumatic nebulisers, 186	
(C)	Unpremixed flames	187
	(1) Nebuliser-burners for unpremixed flames, 188	
(D)	Flames used in analytical flame spectroscopy . . .	190
	(1) Premixed nitrous oxide—acetylene flame, 191 — (2)	
	Premixed oxy-acetylene flames, 192 — (3) Premixed	
	nitrous oxide—hydrogen flame, 193 — (4) Hydrogen	
	flames, 193 — (5) Absorption tube devices, 194 —	
	(6) Separated flames, 195	
(E)	Formation of atoms in flames	196
	(1) Desolvation, 197 — (2) Vaporisation, 199 —	
	(3) Dissociation, 201 — (4) Ionisation, 206 —	
	(5) Distribution of atoms in flames, 209	
5.	Experimental techniques	211
(A)	Wavelength of measurement	212
	(1) Atomic absorption spectroscopy, 212 — (2) Atomic	
	fluorescence spectroscopy, 213	
(B)	Instrument operation	214
(C)	Preparation of sample and standard solutions . . .	215
(D)	Analytical sensitivity	217
(E)	Calibration graphs	221
	(1) AAS calibration graphs, 223 — (2) AFS calibration	
	graphs, 224	
(F)	Other calibration methods	224
	(1) Standard addition methods, 224 — (2) Dilution method,	
	225 — (3) Absolute analysis by AAS, 225	
(G)	Precision and accuracy	227
	(1) Precision, 227 — (2) Accuracy, 228	
6.	Interferences	229
(A)	Physical interferences	229
	(1) Aspiration, 229 — (2) Nebulisation, 231 — (3) Solvent	
	and solute vaporisation in flames, 233 — (4) High dissolved-	
	solid content samples and light scattering, 234	
(B)	Chemical interferences	236
	(1) Chemical interferences in the solid phase, 236 —	
	(2) Elimination of solid phase interferences, 240 —	
	(3) Use of releasing and protective agents, 241 —	
	(4) Chemical interferences in the vapour phase, 243	

(C)	Spectral interferences	247
	(1) Spectral interferences in AAS, 247 — (2) Spectral interferences in AFS, 251	
References	253
 <i>Chapter 3. DIFFUSE REFLECTANCE SPECTROSCOPY,</i>		
	by R.W. Frei, M.M. Frodyma and V.T. Lieu	263
 1. Introduction		
2.	Theory	264
(A)	Kubelka—Munk equation	264
(B)	Optimum concentration range for analysis	266
(C)	Differential reflectance spectrophotometry	270
	(1) Low-reflectance method, 270 — (2) High-reflectance method, 272	
(D)	Multicomponent systems	273
(E)	Diffuse reflectance spectra	275
	(1) Presentation of spectra, 275 — (2) Elimination of regular reflectance, 276 — (3) Effect of adsorbent, 277 — (4) Moisture effect, 278 — (5) Effect of particle size, 279 — (6) Qualitative analysis, 279	
3.	Instrumentation	280
(A)	The integrating sphere	280
(B)	Reference standards and sphere coating materials	283
(C)	Filter instruments	286
(D)	Monochromator instruments	288
(E)	Sample holders	296
	(1) Commercial and macro cells, 296 — (2) Semimicro cells, 297 — (3) Variable temperature cells, 298	
(F)	Instruments for in situ measurements of chromatograms	299
	(1) Commercial single-beam instruments, 300 — (2) Commercial double-beam instruments, 302	
4.	Applications	305
(A)	The measurement and comparison of color	306
	(1) Principles and methods of color measurement, 306 — (2) Pigments, 309 — (3) Biological materials, 311 — (4) Building materials, 311 — (5) Food analysis, 312 — (6) Geological materials, 313 — (7) Paper and pulp, 314 — (8) Pharmaceuticals, 315 — (9) Textiles, 316	

(B)	Theoretical applications	317
	(1) Surface phenomena, 317 — (2) The measurement of reflectance at other than ambient temperatures, 324 —	
	(3) Inorganic systems, 326 — (4) Chromatography, 329	
References	345
Index	355

Chapter 1

Instrumentation for spectroscopy

I.L. MARR

1. Introduction

(A) SCOPE

In these days of increasing specialisation it becomes increasingly difficult for a chemist to be fully conversant with the theory of optics, of electronics, of instrument design, and so on, yet more chemists, and analysts in particular, are using complex pieces of equipment routinely in the course of their work. The description by Julius [1] of the infrared spectrometer which he built and then used to investigate the absorption spectra of organic compounds (in 1888) makes fascinating reading, but very few chemists today have either the time or the “know-how” for such occupations and the majority rely on the wide range of excellent, commercially available equipment. This chapter will not attempt to reverse this situation; rather, it will try to help the chemist find his way through a sometimes difficult and confusing field. It is hoped that he can then appreciate the advantages and disadvantages of different pieces of equipment, the kind of things which can go wrong in, and the limitations of, the devices and instruments which he uses.

So many different topics are dealt with in the following pages that discussion has had to be restricted to the most important facts. An attempt has been made to give references to the more detailed and most readily available sources wherever possible. Interesting though original papers may be, they are not always the best starting point for the newcomer to a field who must rely on textbooks for a clearer exposition of the problem, the answer, and the reasons. The author has consulted many such books and the reader will be referred to

References pp. 88–93

1