

analytical emission spectroscopy

volume 1

part I

edited by
E. L. GROVE

VOLUME 1 (*In Three Parts*)

*ANALYTICAL EMISSION
SPECTROSCOPY*

PART I

Edited by E. L. GROVE

IIT RESEARCH INSTITUTE
CHICAGO, ILLINOIS

1971

MARCEL DEKKER, INC., New York

COPYRIGHT © 1971 by MARCEL DEKKER, INC.

ALL RIGHTS RESERVED

No part of this work may be reproduced or utilized in any form or by any means, electronic or mechanical, including xerography, photocopying, microfilm, and recording, or by any information storage and retrieval system, without permission in writing from the publisher.

MARCEL DEKKER, INC.
95 Madison Avenue, New York, New York 10016

LIBRARY OF CONGRESS CATALOG CARD NUMBER 79-134783
ISBN 0-8247-1254-4

PRINTED IN THE UNITED STATES OF AMERICA

VOLUME 1 (*In Three Parts*)

Analytical Emission Spectroscopy

PART I

ANALYTICAL SPECTROSCOPY SERIES

EDITED BY E. L. GROVE

VOLUME 1: Analytical Emission Spectroscopy (in three parts)

Other Volumes in Preparation

VOLUME 2: Applications of Emission and X-Ray Spectroscopy

VOLUME 3: Analytical X-Ray Spectroscopy

VOLUME 4: Mossbauer Spectroscopy

Preface

During the period that emission spectroscopy was rapidly developing into a widely used science and art, a number of excellent books were developed in several languages. Books in English included Brode, *Chemical Spectroscopy*, 1939, 1943; Twyman, *Metal Spectroscopy*, 1941, 1951; Sawyer, *Experimental Spectroscopy*, 1944, 1951; Harrison, Lord, and Loofbourow, *Practical Spectroscopy*, 1948; Nachtrieb, *Principles and Practice of Spectrochemical Analysis*, 1950, and Ahrens (Ahrens and Taylor), *Spectrochemical Analysis*, 1950, 1961. The first books were general in nature and treated the basic principles from the optics to methods. The latter emphasized the chemical and physical principles involved in spectrochemical analyses. These are valuable books and still are widely used. Other useful books, in addition to tables, include Harvey, *Semiquantitative Spectrochemistry*, 1947, 1950, and 1964; Kroonen and Vader, *Line Interference in Emission Spectrographic Analysis*, 1963; and the excellent work by Boumans, *Spectrochemical Excitation*, 1966.

Numerous new developments, changes, and consolidations of ideas have taken place in the last twenty years. Although the aurora of glamour has supposedly been transferred to other areas, it is estimated that 75% or more of the analyses in the metals industry are performed by emission spectroscopy. Although the number of large prism spectrographs being produced is decreasing, prism systems are widely used in the smaller spectrometers and new prism systems have been developed. Development of the replication process and improvements in materials and the arts of ruling have made excellent gratings available at reasonable prices. This and the development of recent plane grating mounts have contributed to the increasing popularity of grating spectrometers both in America and in Europe and the discontinuance of manufacture of some concave grating mounts. Other areas

of development and improvement include methods of excitation, the extension of spectrometers to the vacuum region accompanied by the widespread use for the analyses of nonmetals in metals, the use of controlled atmospheres, the increasing use of polychromators accompanied by improvements in readout, and the more recent interfacing with the computer. Much of the change that has and is taking place in industry, including the required quality control, would not have been possible had it not been for the developments in spectroscopy.

Much work on the evaluation and consolidation of procedure is being performed by the A.S.T.M. Committee E-2 on Emission Spectroscopy.

The need to consolidate this material from many sources of literature and the experience of authors, along with the proper perspective of the earlier basic materials, has been recognized by numerous spectroscopists for some time. However, the enormity of the project for one or two authors or even more has always been a major deterrent. After some prodding it was decided, with the help of other authors, to develop this program.

The objective was to develop a general but relatively comprehensive book, i. e., each chapters was to cover a particular area in a relatively comprehensive manner. For coherence and completeness, the material in each chapter coordinates the earlier basic developments with the more recent work. The chapters on principles and instrumentation include the basic physics of optics and the development of principles and instrumentation from the earlier instruments to those in use today. The chapter on excitation discusses the basic characteristics and electrical parameters of arcs and sparks, mechanisms of transport, spectral line intensities and source parameters, and special excitation sources. The chapters on analytical methods are not a conglomeration of referenced procedures but a systematic approach to the analyses of a multiplicity of materials. Flames, their structure and type, burners, and the theory of flame emission, flame absorption, and flame fluorescence, as well as atomization, solvent effects, and analytical methods, are thoroughly discussed. Other chapters include the theory of excitation, standards, basic statistics, and experimental design.

The completion of a project of this magnitude has necessarily required considerable time due to the fact that many of those with the required knowledge and experience were impeded by other unforeseen demands upon their time or by illness. Hence, there have been some unavoidable changes in authorship from time to time and some materials have been edited from very rough manuscripts and notes for the sake of expediency. The efforts of those authors who did complete their assignments are greatly appreciated.

We gratefully acknowledge the courtesy of John Wiley and Sons, Prentice Hall, Inc., Macmillan and Co., and other publishers and journals for permission to reproduce figures and tables, and the cooperation of manufacturers for illustrations of equipment. For help and suggestions on organization and reviews, and for advice on points of history and practice, Edwin S. Hodge, Fred Breck, A. C. Menzies, J. S. Ziomek, Alan Goldblatt, John Norris, Charlotte Moore Sitterly, N. H. Nachtrieb, Bill Henry, Art Mitteldorf, and others who are members of the Society of Applied Spectroscopy and/or the E-2 Committee of American Society for Testing Materials are recognized. And last, though not necessarily least, recognition is also given to Theresa Resce, Nick Resce, Frank Ribich, and Marjorie O'Dea for help on illustrations; to Karen Walters and Mrs. E. L. Grove for editing; and to Catherine Misheck for typing, editing, and keeping details in order.

E. L. GROVE

Contributors to This Volume

RAMON M. BARNES, Department of Chemistry, University of Massachusetts, Amherst, Massachusetts

HOWARD T. BETZ, IIT Research Institute, Chicago, Illinois

JAMES J. DEVLIN, S. J., Boston College, Chestnut Hill, Massachusetts

E. L. GROVE, IIT Research Institute, Chicago, Illinois

H. W. FAUST, Carl Zeiss, Oberkochen, West Germany

RICHARD F. JARRELL, Jarrell-Ash Company, Waltham, Massachusetts

GORDON L. JOHNSON, IIT Research Institute, Chicago, Illinois

Contents of Volume 1, Part II

Excitation of Spectra, P. W. J. M. BOUMANS,* *Laboratory for Analytical Chemistry, University of Amsterdam*

Flame Spectrometry, T. J. VICKERS, *Department of Chemistry, Florida State University, Tallahassee, Florida*, and J. D. WINEFORDNER, *Department of Chemistry, University of Florida, Gainesville, Florida*

Qualitative and Semiquantitative Analysis, M. S. WANG, W. T. CAVE, and W. S. COAKLEY, *Central Research Department, Monsanto Company, St. Louis, Missouri*

Quantitative Analysis, J. T. ROZSA, *Republic Steel Corporation, Research Center, Cleveland, Ohio*

* *Present address:* Philips Research Laboratories, Spectro-chemical Division, Eindhoven, Netherlands.

Partial Contents of Volume 1, Part III

The Measurement of an Effective Temperature Useful in Spectrochemistry,
CHARLES H. CORLISS, *National Bureau of Standards, Washington, D. C.*

The Preparation and Evaluation of Spectrochemical Standards, A. H.
GILLIESON, *Department of Energy, Mines and Resources, Mineral
Sciences Division, Ottawa, Ontario, Canada*

Contents

PREFACE	v
CONTRIBUTORS TO THIS VOLUME	ix
CONTENTS TO VOLUME 1, PART II	xiii
PARTIAL CONTENTS TO VOLUME 1, PART III	xv
 1. Historical Development, Some Uses and Definitions	 1
<i>E. L. Grove</i>	
1.1 Historical Development	2
1.2 Some Areas of Application	51
1.3 Some Basic Fundamentals	62
References	66
 2. Origins of Atomic Spectra	 73
<i>James J. Devlin, S. J.</i>	
2.1 Introduction	74
2.2 Early Studies with Series	75
2.3 The Bohr Atom	85
2.4 Energy Level Diagram of Hydrogen	91
2.5 Quantum Mechanical Theory of the Atom	93
2.6 Fine Structure of Spectral Lines	97
2.7 Multiplet Levels	107
2.8 Intensity of Spectral Lines	115
2.9 Zeeman Effect	118
2.10 Paschen-Back Effect	122
2.11 Stark Effect	125
2.12 Line Broadening	126
References	129
Bibliography	129

3. Prism Systems, Spectrographs, and Spectrometers	131
<i>H. W. Faust</i>	
3.1 Spectrometric Optics	132
3.2 Types of Prism Instruments	171
3.3 The Slit	184
3.4 Adjustment, Testing, and Working with Prism Instruments	191
3.5 Disturbances of Prism Instruments	202
References	205
 4. Gratings and Grating Instruments	 209
<i>Ramon M. Barnes and Richard F. Jarrell</i>	
4.1 Introduction	210
4.2 Theory and Production of Grating	216
4.3 Grating Instrument Mountings	263
4.4 Selection of Spectroscopic Instruments	315
References	317
 5. Spectroradiometric Principles	 323
<i>Howard T. Betz and Gordon L. Johnson</i>	
5.1 Introduction	323
5.2 Parameters Characterizing Spectrometers	324
5.3 Detectors and Detectivity	336
5.4 Sources and Entrance Optics	364
List of Symbols	376
References	381
 AUTHOR INDEX	 383
SUBJECT INDEX	391

CHAPTER

1

Historical Development, Some Uses and Definitions

E. L. GROVE
*IIT Research Institute
Chicago, Illinois*

1.1 Historical Development	2
1.1.1 The Newton Period.	2
1.1.2 Early 18th Century Developments	3
1.1.3 Characteristic Spectra	5
1.1.4 Related Developments	8
1.1.5 Spectrochemical Analyses	19
1.2 Some Areas of Application	51
1.2.1 Metallurgy	52
1.2.2 Agriculture.	54
1.2.3 Man and Medicine	55
1.2.4 Food and Beverage Processing	57
1.2.5 Geology and Prospecting	58
1.2.6 Forensic Spectroscopy.	58
1.2.7 The Petroleum Industry	59
1.2.8 Wear Metal Analysis	59
1.2.9 Astronomy	60
1.2.10 Spectroscopy in Chemistry and Physics	61
1.3 Some Basic Fundamentals	62
References	66

1.1 Historical Development

1.1.1 The Newton Period

Prior to the time of Sir Isaac Newton, 1642–1727, the accepted idea appears to have been that white light was changed into colors in the prism and that color was made up of light and darkness.

Newton observed that when red and blue strips of paper were placed side by side and viewed through a prism their apparent displacements were different. He (1) also observed that when sunlight from a small round hole in a shutter was passed through a prism it was dispersed to form a series of colored images of the hole (Fig. 1.1) which he called a spectrum. From ad-

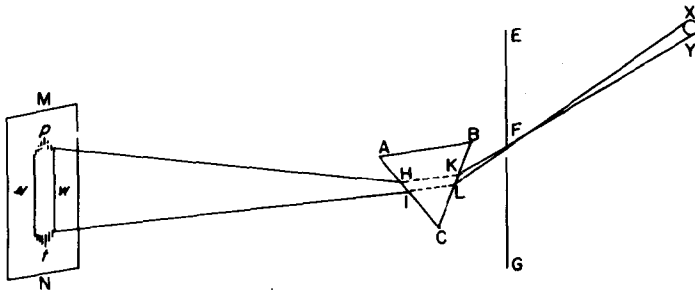


Fig. 1.1. Facsimile: Newton's early dispersion experiment. [From extracts from *Newton's Opticks*, 1675, Sir Henry E. Roscoe, *Spectrum Analysis*, Macmillan, London, 1885, p. 45.]

ditional experiments, he found that light dispersed by a prism was not further dispersed by a second prism, but only further refracted (Fig. 1.2). Since there was no color change when one color was isolated and passed through a second prism, he was satisfied that these colors were not produced by the prism. In another experiment, Newton found that by looking at the spectrum with a second prism in the proper positions he saw a spot of white light resulting from the converging light rays to form the original image (Fig. 1.3). Each color of light he called "homogeneous" because these rays had the same degree of "refrangibility." Thus, Newton showed that sunlight was heterogeneous light, i.e., consisted of rays with different refrangibilities, or that sunlight was a heterogeneous mixture of rays that are separated or sorted in the prism.

Newton improved the purity of the spectrum by the use of a lens between the hole and the prism to image the entrance hole on the screen. He formed fairly pure solar spectrum about 10 in. long. The only other contribution

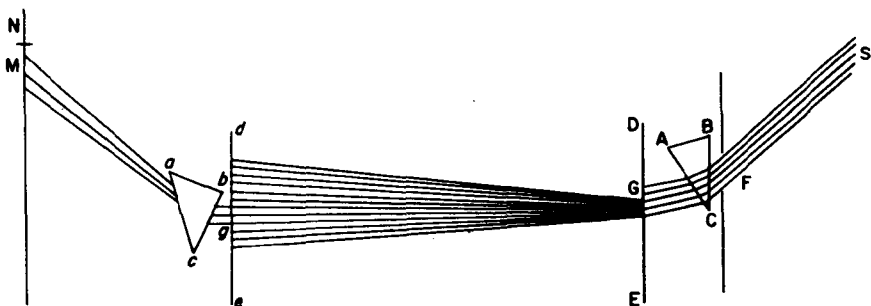


Fig. 1.2. Facsimile: Newton's experiment showing diffracted light is further diffracted. [From extracts from *Newton's Opticks*, 1675, Sir Henry Roscoe, *Spectrum Analysis*, Macmillan, London, 1885, p. 49.]

in the 18th century was Thomas Melvill's (2) first description of the emission spectrum of a sodium flame, which was published in his *Physical and Literary Essays* (Edinburgh, 1752).

1.1.2 Early 18th Century Developments

The next major step in spectroscopy did not occur until Wollaston (3), in 1802, and later Fraunhofer (4), in 1814, independently observed spectrum lines, i.e., images of a narrow slit each corresponding to a wavelength.

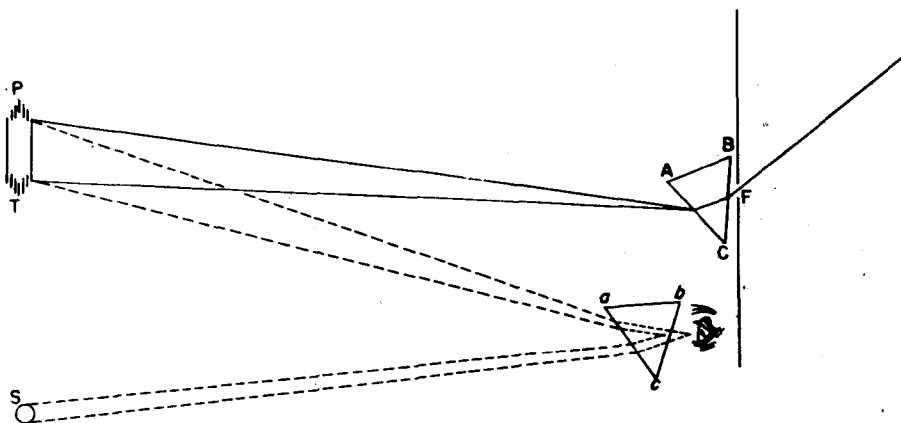


Fig. 1.3. Facsimile: Newton's experiment on reconverging of light. [From extracts from *Newton's Opticks*, 1675, Sir Henry E. Roscoe, *Spectrum Analysis*, Macmillan, London, 1885, p. 47.]

At this time Wollaston, as described in his article, admitted a beam of daylight into a dark room through a crevice $\frac{1}{20}$ in. broad to a flint glass prism 10 to 12 ft away. He observed a few of the stronger dark lines in the continuous spectrum of the sun and appears to have considered them as natural boundaries of the various pure colors. In the same paper he gave the first description of a flame spectrum. The blue light from the lower part of a flame, examined in the same manner, did not yield a continuous spectrum, but five images. One of these was bright yellow, which is now recognized as the yellow line of sodium. Wollaston appears to have attached no significance to the dark lines or to the discontinuous, i.e., bright line, spectrum. However, he was able to see these lines since he restricted the aperture to a narrow slit or crevice, the forerunner of the modern spectroscopic slit.

Fraunhofer (4) placed a 60° flint-glass prism 24 ft from a slit and viewed the sunlight entering the slit with a theodolite telescope. He observed many strong and weak dark lines and mapped about 700 of them, assigning the letters A through H to the eight most prominent lines. He also observed that line D consisted of two strong lines very close together.

When the slit was illuminated with a flame, the dark lines were absent, but a bright yellow line appeared to be in the position of the dark D line. At this time, and again later, Fraunhofer (5) observed the spectra from an electric spark.

Fraunhofer was the first stellar spectroscopist and laid the foundation for the science of astrophysics. He observed three broad bands in the spectrum of Sirius and lines in the spectra of some planets and other stars. Also, he noted that the spectra of Venus and the sun were similar but differed from those of the stars.

Fraunhofer's studies of the principle of interference with two, then with several, slits led to the discovery of the transmission grating. His first gratings were made by winding fine silver wire between two parallel screws with equal pitch, the finest of which had about 192 lines/cm. He later developed a ruling machine and, using a diamond point, ruled the first glass transmission gratings, (6) 1823. With two gratings, 3000 and 625 lines/cm, his measured values for the unresolved D lines were 0.0005886 and 0.0005890 mm. The present values for the doublet are 0.0005890 and 0.0005896 mm.

The infrared and ultraviolet regions were also discovered during this period. Herschel, 1800 (7), the well known British astronomer, while observing the sun through combinations of different colored glasses, noticed that with some combinations he had very little light but felt a sensation of heat. In his subsequent study of the distribution of heat in the sun's spec-