

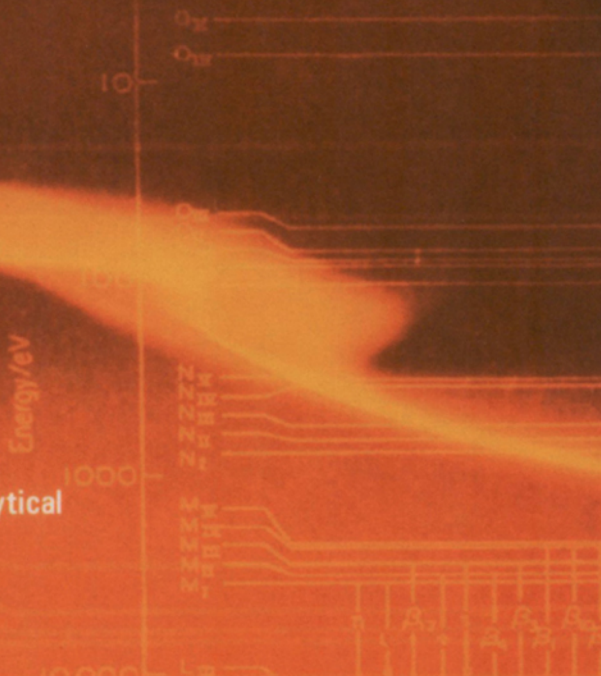
# X-RAY

## FLUORESCENCE SPECTROMETRY

SECOND EDITION

Volume 152 in Chemical Analysis:  
A Series of Monographs on Analytical  
Chemistry and Its Applications

J. D. Winefordner, Series Editor



The background of the cover features a faint X-ray fluorescence spectrum plot. The vertical axis is labeled 'Energy/eV' and has a logarithmic scale with major ticks at 10, 100, and 1000. The horizontal axis represents wavelength or energy. The plot shows a broad, low-intensity background with several sharp, high-intensity peaks. Labels for various elements and their characteristic lines are visible, including O<sub>K</sub>, O<sub>L</sub>, C<sub>K</sub>, C<sub>L</sub>, N<sub>K</sub>, N<sub>L</sub>, Si<sub>K</sub>, Si<sub>L</sub>, S<sub>K</sub>, S<sub>L</sub>, Ca<sub>K</sub>, Ca<sub>L</sub>, Ti<sub>K</sub>, Ti<sub>L</sub>, Fe<sub>K</sub>, Fe<sub>L</sub>, Ni<sub>K</sub>, Ni<sub>L</sub>, Cu<sub>K</sub>, Cu<sub>L</sub>, Zn<sub>K</sub>, Zn<sub>L</sub>, Ga<sub>K</sub>, Ga<sub>L</sub>, Ge<sub>K</sub>, Ge<sub>L</sub>, As<sub>K</sub>, As<sub>L</sub>, Se<sub>K</sub>, Se<sub>L</sub>, Br<sub>K</sub>, Br<sub>L</sub>, Kr<sub>K</sub>, Kr<sub>L</sub>, Rb<sub>K</sub>, Rb<sub>L</sub>, Sr<sub>K</sub>, Sr<sub>L</sub>, Y<sub>K</sub>, Y<sub>L</sub>, Zr<sub>K</sub>, Zr<sub>L</sub>, Nb<sub>K</sub>, Nb<sub>L</sub>, Mo<sub>K</sub>, Mo<sub>L</sub>, Tc<sub>K</sub>, Tc<sub>L</sub>, Ru<sub>K</sub>, Ru<sub>L</sub>, Rh<sub>K</sub>, Rh<sub>L</sub>, Pd<sub>K</sub>, Pd<sub>L</sub>, Ag<sub>K</sub>, Ag<sub>L</sub>, Cd<sub>K</sub>, Cd<sub>L</sub>, In<sub>K</sub>, In<sub>L</sub>, Sn<sub>K</sub>, Sn<sub>L</sub>, Sb<sub>K</sub>, Sb<sub>L</sub>, Te<sub>K</sub>, Te<sub>L</sub>, I<sub>K</sub>, I<sub>L</sub>, Xe<sub>K</sub>, Xe<sub>L</sub>, Ba<sub>K</sub>, Ba<sub>L</sub>, La<sub>K</sub>, La<sub>L</sub>, Ce<sub>K</sub>, Ce<sub>L</sub>, Pr<sub>K</sub>, Pr<sub>L</sub>, Nd<sub>K</sub>, Nd<sub>L</sub>, Pm<sub>K</sub>, Pm<sub>L</sub>, Sm<sub>K</sub>, Sm<sub>L</sub>, Eu<sub>K</sub>, Eu<sub>L</sub>, Gd<sub>K</sub>, Gd<sub>L</sub>, Tb<sub>K</sub>, Tb<sub>L</sub>, Dy<sub>K</sub>, Dy<sub>L</sub>, Ho<sub>K</sub>, Ho<sub>L</sub>, Er<sub>K</sub>, Er<sub>L</sub>, Tm<sub>K</sub>, Tm<sub>L</sub>, Yb<sub>K</sub>, Yb<sub>L</sub>, Lu<sub>K</sub>, Lu<sub>L</sub>.

Ron Jenkins



# X-Ray Fluorescence Spectrometry

# CHEMICAL ANALYSIS

A SERIES OF MONOGRAPHS ON ANALYTICAL CHEMISTRY  
AND ITS APPLICATIONS

*Editor*

**J. D. WINEFORDNER**

VOLUME 152



A WILEY-INTERSCIENCE PUBLICATION

**JOHN WILEY & SONS, INC.**

**New York / Chichester / Weinheim / Brisbane / Singapore / Toronto**

# X-Ray Fluorescence Spectrometry

Second Edition

**RON JENKINS**

International Centre for Diffraction Data,  
Newtown Square, PA



**A WILEY-INTERSCIENCE PUBLICATION**

**JOHN WILEY & SONS, INC.**

**New York / Chichester / Weinheim / Brisbane / Singapore / Toronto**

This book is printed on acid-free paper.

Copyright © 1999 by John Wiley & Sons, Inc.

All rights reserved.

Published simultaneously in Canada.

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, scanning or otherwise, except as permitted under Sections 107 or 108 of the 1976 United States Copyright Act, without either the prior written permission of the Publisher, or authorization through payment of the appropriate per-copy fee to the Copyright Clearance Center, 222 Rosewood Drive, Danvers, MA 01923, (978) 750-8400, fax (978) 750-4744. Requests to the Publisher for permission should be addressed to the Permissions Department, John Wiley & Sons, Inc., 605 Third Avenue, New York, NY 10158-0012, (212) 850-6011, fax (212) 850-6008, E-Mail: PERMREQ@WILEY.COM.

***Library of Congress Cataloging-in-Publication Data:***

Jenkins, Ron, 1932–

X-ray fluorescence spectrometry / Ron Jenkins. — 2nd ed.

p. cm. — (Chemical analysis ; v. 152)

“A Wiley-Interscience publication.”

Includes bibliographical references and index.

ISBN 0-471-29942-1 (cloth : alk. paper)

1. X-ray spectroscopy. 2. Fluorescence spectroscopy. I. Title.

II. series.

QD96.X2J47 1999

543'.08586—dc21

98-39008

10 9 8 7 6 5 4 3 2 1

## CONTENTS

<b>PREFACE TO THE FIRST EDITION</b>	<b>ix</b>
<b>PREFACE TO THE SECOND EDITION</b>	<b>xi</b>
<b>CUMULATIVE LISTING OF VOLUMES IN SERIES</b>	<b>xiii</b>
<b>CHAPTER 1 PRODUCTION AND PROPERTIES X-RAYS</b>	<b>1</b>
1.1 Introduction	1
1.2 Continuous Radiation	3
1.3 Characteristic Radiation	5
1.4 Absorption of X-Rays	7
1.5 Coherent and Incoherent Scattering	12
1.6 Interference and Diffraction	13
Bibliography	15
<b>CHAPTER 2 INDUSTRIAL APPLICATIONS OF X-RAYS</b>	<b>17</b>
2.1 Introduction	17
2.2 Diagnostic Uses of X-Rays	19
2.3 Tomography	21
2.4 Level and Thickness Gauging	23
2.5 X-Ray Thickness Gauging	24
2.6 Nondestructive Testing	26
2.7 Security Screening Systems	28
2.8 X-Ray Lithography	30
2.9 X-Ray Astronomy	32
Bibliography	35
<b>CHAPTER 3 X-RAY DIFFRACTION</b>	<b>37</b>
3.1 Use of X-Ray Diffraction to Study the Crystalline State	37
3.2 The Powder Method	38
3.3 Use of X-Ray Powder Cameras	39

3.4	The Powder Diffractometer	42
3.5	Qualitative Applications of the X-Ray Powder Method	43
3.6	Quantitative Methods in X-Ray Powder Diffraction	46
3.7	Other Applications of X-Ray Diffraction	48
	Bibliography	50
<b>CHAPTER 4</b>	<b>X-RAY SPECTRA</b>	<b>53</b>
4.1	Introduction	53
4.2	Electron Configuration of the Elements	53
4.3	Fluorescent Yield	55
4.4	Relationship Between Wavelength and Atomic Number	56
4.5	Normal Transitions (Diagram Lines)	60
4.6	Satellite Lines	62
4.7	Characteristic Line Spectra	62
4.8	<i>K</i> Spectra	62
4.9	<i>L</i> Spectra	69
4.10	<i>M</i> Spectra	72
	Bibliography	73
<b>CHAPTER 5</b>	<b>HISTORY AND DEVELOPMENT OF X-RAY FLUORESCENCE SPECTROMETRY</b>	<b>75</b>
5.1	Historical Development of X-Ray Spectrometry	75
5.2	Early Ideas About X-Ray Fluorescence	77
5.3	Rebirth of X-Ray Fluorescence	78
5.4	Evolution of Hardware Control Methods	80
5.5	The Growing Role of X-Ray Fluorescence Analysis in Industry and Research	81
5.6	The Arrival of Energy Dispersive Spectrometry	82
5.7	Evolution of Mathematical Correction Procedures	83
5.8	X-Ray Analysis in the 1970s	84
5.9	More Recent Development of X-Ray Fluorescence	85
	Bibliography	86



<b>CHAPTER 6</b>	<b>INSTRUMENTATION FOR X-RAY SPECTROMETRY</b>	<b>89</b>
	6.1 Introduction	89
	6.2 Excitation of X-Rays	89
	6.3 Detection of X-Rays	94
	6.4 Wavelength Dispersive Spectrometers	101
	6.5 Energy Dispersive Spectrometers	107
	Bibliography	108
<b>CHAPTER 7</b>	<b>COMPARISON OF WAVELENGTH AND ENERGY DISPERSIVE SPECTROMETERS</b>	<b>111</b>
	7.1 Introduction	111
	7.2 The Measurable Atomic Number Range	114
	7.3 The Resolution of Lines	116
	7.4 Measurement of Low Concentrations	117
	7.5 Qualitative Analysis	120
	7.6 Geometric Constraints of Wavelength and Energy Dispersive Spectrometers	121
	Bibliography	121
<b>CHAPTER 8</b>	<b>MORE RECENT TRENDS IN X-RAY FLUORESCENCE INSTRUMENTATION</b>	<b>123</b>
	8.1 The Role of X-Ray Fluorescence in Industry and Research	123
	8.2 Scope of the X-Ray Fluorescence Method	123
	8.3 The Determination of Low Atomic Number Elements	126
	8.4 Total Reflection X-Ray Fluorescence	130
	8.5 Synchrotron Source X-Ray Fluorescence—SSXRF	132
	8.6 Proton Induced X-Ray Fluorescence	136
	Bibliography	137
<b>CHAPTER 9</b>	<b>SPECIMEN PREPARATION AND PRESENTATION</b>	<b>141</b>
	9.1 Form of the Sample for X-Ray Analysis	141
	9.2 Direct Analysis of Solid Samples	144
	9.3 Preparation of Powder Samples	146
	9.4 Direct Analysis of Solutions	147

	9.5 Analysis of Small Amounts of Sample	148
	9.6 Preconcentration Techniques	148
	Bibliography	150
<b>CHAPTER 10</b>	<b>USE OF X-RAY SPECTROMETRY FOR QUALITATIVE ANALYSIS</b>	<b>153</b>
	10.1 Introduction to Qualitative Analysis	153
	10.2 Relative Intensities of X-Ray Lines	153
	10.3 Qualitative Interpretation of X-Ray Spectrograms	157
	10.4 Semiquantitative Analysis	159
	Bibliography	159
<b>CHAPTER 11</b>	<b>CONSIDERATIONS IN QUANTITATIVE X-RAY FLUORESCENCE ANALYSIS</b>	<b>161</b>
	11.1 Conversion of Characteristic Line Intensity to Analyte Concentration	161
	11.2 Influence of the Background	163
	11.3 Statistical Counting Errors	165
	11.4 Matrix Effects	167
	11.5 Analysis of Low Concentrations	172
	Bibliography	174
<b>CHAPTER 12</b>	<b>QUANTITATIVE PROCEDURES IN X-RAY FLUORESCENCE ANALYSIS</b>	<b>175</b>
	12.1 Overview of Quantitative Methods	175
	12.2 Measurements of Pure Intensities	178
	12.3 Single Element Methods	179
	12.4 Multiple Element Methods	182
	Bibliography	186
<b>CHAPTER 13</b>	<b>APPLICATIONS OF X-RAY METHODS</b>	<b>189</b>
	13.1 Comparison of X-Ray Fluorescence with Other Instrumental Methods	189
	13.2 Application of X-Ray Spectrometry	192
	13.3 Combined Diffraction and Fluorescence Techniques	193
	13.4 Portable XRF Equipment	195
	13.5 On-Stream Analysis	196
	Bibliography	198
<b>INDEX</b>		<b>201</b>

## PREFACE TO THE FIRST EDITION

It is now nearly 30 years since the publication, in 1959, of the Wiley/Interscience monograph *X-ray Spectrochemical Analysis* by Verne Birks. In the intervening years the X-ray fluorescence method has come through the birth pains of innovation, has survived the early frustrations of application, and has achieved the status of a reliable, fast, accurate and versatile analytical method. The analytical chemist of today has a vast array of different techniques available for the analysis and characterization of materials, and most would agree that among the more powerful and flexible of these methods are those based on the use of X-ray fluorescence spectrometry. The X-ray fluorescence method is a means of qualitatively and quantitatively determining elements by measurement of the wavelengths and intensities of characteristic emissions. The technique is applicable to all but the very low atomic number elements, with sensitivities down to the low part per million level. In the late 1950s the elements covered by the X-ray fluorescence method ranged from the higher atomic numbers down to titanium ( $Z = 22$ ). By the mid 1960s the advent of first the ethylene diamine d-tartrate (EDDT) crystal and then the penta-erythritol (PE) crystal, along with the chromium and rhodium anode X-ray tubes, increased the coverable atomic number range to include all elements down to and including aluminum ( $Z = 13$ ). Under certain circumstances even magnesium and sodium were measurable albeit with rather poor sensitivity. As we entered the mid 1980s the advent of layered synthetic microstructures (LSM's) has allowed measurements down to carbon ( $Z = 6$ ) with fair sensitivity, and even boron at concentration levels of several percent. The sensitivity of the X-ray fluorescence method for the determination of small quantities of material has also improved significantly. A "small" sample in the late 1950s and early 1960s was typically of the order of milligrams. Today, use of synchrotron or proton source excitation, along with total reflectance geometry, allows measurements at the picogram level. For some, it is difficult to imagine development at the same exciting level over the next two decades. Many believe that X-ray fluorescence has come as far as it will. I personally do not subscribe to this view. I believe that the problems of rapid and efficient sample homogenization will soon be solved. The development of room temperature solid state detectors has much still to yield. Use of the synchrotron is beginning to reveal areas of

application of X-ray spectrometry hitherto not even considered. The use of the personal computer has yet to find its full exploitation in automating both quantitative and qualitative analysis. The development of combination X-ray diffractometer/spectrometers is at last beginning to show fruit. Present indications are that X-ray fluorescence spectrometry will continue to be an exciting and dynamic discipline.

## PREFACE TO THE SECOND EDITION

I was gratified to learn that the first edition of this book found a place in the teaching of X-Ray Fluorescence Spectrometry. Both the American Chemical Society, and the International Centre for Diffraction Data, have, for a number of years, used the book as a course text in their X-ray fluorescence schools.

In preparing a second edition, I have taken the advantage in expanding the text to give more extensive coverage. In addition to a complete review and update of each chapter, new chapters have been added on "X-Ray Spectra" and "History and Development." The text is now about 30% larger than the first edition. I am grateful to those who have contributed to this work and am especially indebted to Dr. Sue Quick and Don Desrosiers for their painstaking work in proofing the manuscript.

*Newtown Square, PA*

RON JENKINS



# CHEMICAL ANALYSIS

## A SERIES OF MONOGRAPHS ON ANALYTICAL CHEMISTRY AND ITS APPLICATIONS

J. D. Winefordner, *Series Editor*

- Vol. 1. **The Analytical Chemistry of Industrial Poisons, Hazards, and Solvents.** *Second Edition.* By the late Morris B. Jacobs
- Vol. 2. **Chromatographic Adsorption Analysis.** By Harold H. Strain (*out of print*)
- Vol. 3. **Photometric Determination of Traces of Metals.** *Fourth Edition*  
Part I: General Aspects. By E. B. Sandell and Hiroshi Onishi  
Part IIA: Individual Metals, Aluminum to Lithium. By Hiroshi Onishi  
Part IIB: Individual Metals, Magnesium to Zirconium. By Hiroshi Onishi
- Vol. 4. **Organic Reagents Used in Gravimetric and Volumetric Analysis.** By John F. Flagg (*out of print*)
- Vol. 5. **Aquametry: A Treatise on Methods for the Determination of Water.** *Second Edition (in three parts).* By John Mitchell, Jr. and Donald Milton Smith
- Vol. 6. **Analysis of Insecticides and Acaricides.** By Francis A. Gunther and Roger C. Blinn (*out of print*)
- Vol. 7. **Chemical Analysis of Industrial Solvents.** By the late Morris B. Jacobs and Leopold Schetlan
- Vol. 8. **Colorimetric Determination of Nonmetals.** *Second Edition.* Edited by the late David F. Boltz and James A. Howell
- Vol. 9. **Analytical Chemistry of Titanium Metals and Compounds.** By Maurice Codell
- Vol. 10. **The Chemical Analysis of Air Pollutants.** By the late Morris B. Jacobs
- Vol. 11. **X-Ray Spectrochemical Analysis.** *Second Edition.* By L. S. Birks
- Vol. 12. **Systematic Analysis of Surface-Active Agents.** *Second Edition.* By Milton J. Rosen and Henry A. Goldsmith
- Vol. 13. **Alternating Current Polarography and Tensammetry.** By B. Breyer and H. H. Bauer
- Vol. 14. **Flame Photometry.** By R. Herrmann and J. Alkemade
- Vol. 15. **The Titration of Organic Compounds** (*in two parts*). By M. R. F. Ashworth
- Vol. 16. **Complexation in Analytical Chemistry: A Guide for the Critical Selection of Analytical Methods Based on Complexation Reactions.** By the late Anders Ringbom

- Vol. 17. **Electron Probe Microanalysis. Second Edition.** By L. S. Birks
- Vol. 18. **Organic Complexing Reagents: Structure, Behavior, and Application to Inorganic Analysis.** By D. D. Perrin
- Vol. 19. **Thermal Analysis. Third Edition.** By Wesley Wm. Wendlandt
- Vol. 20. **Amperometric Titrations.** By John T. Stock
- Vol. 21. **Reflectance Spectroscopy.** By Wesley Wm. Wendlandt and Harry G. Hecht
- Vol. 22. **The Analytical Toxicology of Industrial Inorganic Poisons.** By the late Morris B. Jacobs
- Vol. 23. **The Formation and Properties of Precipitates.** By Alan G. Walton
- Vol. 24. **Kinetics in Analytical Chemistry.** By Harry B. Mark, Jr. and Garry A. Rechnitz
- Vol. 25. **Atomic Absorption Spectroscopy. Second Edition.** By Morris Slavin
- Vol. 26. **Characterization of Organometallic Compounds (in two parts).** Edited by Minoru Tsutsui
- Vol. 27. **Rock and Mineral Analysis. Second Edition.** By Wesley M. Johnson and John A. Maxwell
- Vol. 28. **The Analytical Chemistry of Nitrogen and Its Compounds (in two parts).** Edited by C. A. Streuli and Philip R. Averell
- Vol. 29. **The Analytical Chemistry of Sulfur and Its Compounds (in three parts).** By J. H. Karchmer
- Vol. 30. **Ultramicro Elemental Analysis.** By Günther Tölg
- Vol. 31. **Photometric Organic Analysis (in two parts).** By Eugene Sawicki
- Vol. 32. **Determination of Organic Compounds: Methods and Procedures.** By Frederick T. Weiss
- Vol. 33. **Masking and Demasking of Chemical Reactions.** By D. D. Perrin
- Vol. 34. **Neutron Activation Analysis.** By D. De Soete, R. Gijbels, and J. Hoste
- Vol. 35. **Laser Raman Spectroscopy.** By Marvins C. Tobin
- Vol. 36. **Emission Spectrochemical Analysis.** By Morris Slavin
- Vol. 37. **Analytical Chemistry of Phosphorus Compounds.** Edited by M. Halmann
- Vol. 38. **Luminescence Spectroscopy in Analytical Chemistry.** By J. D. Winefordner, S. G. Schulman, and T. C. O'Haver
- Vol. 39. **Activation Analysis with Neutron Generators.** By Sam S. Nargolwalla and Edwin P. Przybylowicz
- Vol. 40. **Determination of Gaseous Elements in Metals.** Edited by Lynn L. Lewis, Laben M. Melnick, and Ben D. Holt
- Vol. 41. **Analysis of Silicones.** Edited by A. Lee Smith
- Vol. 42. **Foundations of Ultracentrifugal Analysis.** By H. Fujita
- Vol. 43. **Chemical Infrared Fourier Transform Spectroscopy.** By Peter R. Griffiths
- Vol. 44. **Microscale Manipulations in Chemistry.** By T. S. Ma and V. Horak
- Vol. 45. **Thermometric Titrations.** By J. Barthel
- Vol. 46. **Trace Analysis: Spectroscopic Methods for Elements.** Edited by J. D. Winefordner
- Vol. 47. **Contamination Control in Trace Element Analysis.** By Morris Zief and James W. Mitchell
- Vol. 48. **Analytical Applications of NMR.** By D. E. Leyden and R. H. Cox



- Vol. 49. **Measurement of Dissolved Oxygen.** By Michael L. Hitchman
- Vol. 50. **Analytical Laser Spectroscopy.** Edited by Nicolo Omenetto
- Vol. 51. **Trace Element Analysis of Geological Materials.** By Roger D. Reeves and Robert R. Brooks
- Vol. 52. **Chemical Analysis by Microwave Rotational Spectroscopy.** By Ravi Varma and Lawrence W. Hrubesh
- Vol. 53. **Information Theory as Applied to Chemical Analysis.** By Karl Eckschlager and Vladimir Štěpánek
- Vol. 54. **Applied Infrared Spectroscopy: Fundamentals, Techniques, and Analytical Problem-Solving.** By A. Lee Smith
- Vol. 55. **Archaeological Chemistry.** By Zvi Goffer
- Vol. 56. **Immobilized Enzymes in Analytical and Clinical Chemistry.** By P. W. Carr and L. D. Bowers
- Vol. 57. **Photoacoustics and Photoacoustic Spectroscopy.** By Allan Rosencwaig
- Vol. 58. **Analysis of Pesticide Residues.** Edited by H. Anson Moye
- Vol. 59. **Affinity Chromatography.** By William H. Scouten
- Vol. 60. **Quality Control in Analytical Chemistry. Second Edition.** By G. Kateman and L. Buydens
- Vol. 61. **Direct Characterization of Fineparticles.** By Brian H. Kaye
- Vol. 62. **Flow Injection Analysis.** By J. Ruzicka and E. H. Hansen
- Vol. 63. **Applied Electron Spectroscopy for Chemical Analysis.** Edited by Hassan Windawi and Floyd Ho
- Vol. 64. **Analytical Aspects of Environmental Chemistry.** Edited by David F. S. Natusch and Philip K. Hopke
- Vol. 65. **The Interpretation of Analytical Chemical Data by the Use of Cluster Analysis.** By D. Luc Massart and Leonard Kaufman
- Vol. 66. **Solid Phase Biochemistry: Analytical and Synthetic Aspects.** Edited by William H. Scouten
- Vol. 67. **An Introduction to Photoelectron Spectroscopy.** By Pradip K. Ghosh
- Vol. 68. **Room Temperature Phosphorimetry for Chemical Analysis.** By Tuan Vo-Dinh
- Vol. 69. **Potentiometry and Potentiometric Titrations.** By E. P. Serjeant
- Vol. 70. **Design and Application of Process Analyzer Systems.** By Paul E. Mix
- Vol. 71. **Analysis of Organic and Biological Surfaces.** Edited by Patrick Echlin
- Vol. 72. **Small Bore Liquid Chromatography Columns: Their Properties and Uses.** Edited by Raymond P. W. Scott
- Vol. 73. **Modern Methods of Particle Size Analysis.** Edited by Howard G. Barth
- Vol. 74. **Auger Electron Spectroscopy.** By Michael Thompson, M. D. Baker, Alec Christie, and J. F. Tyson
- Vol. 75. **Spot Test Analysis: Clinical, Environmental, Forensic and Geochemical Applications.** By Ervin Jungreis
- Vol. 76. **Receptor Modeling in Environmental Chemistry.** By Philip K. Hopke
- Vol. 77. **Molecular Luminescence Spectroscopy: Methods and Applications (in three parts).** Edited by Stephen G. Schulman
- Vol. 78. **Inorganic Chromatographic Analysis.** By John C. MacDonald

- Vol. 79. **Analytical Solution Calorimetry.** Edited by J. K. Grime
- Vol. 80. **Selected Methods of Trace Metal Analysis: Biological and Environmental Samples.** By Jon C. VanLoon
- Vol. 81. **The Analysis of Extraterrestrial Materials.** By Isidore Adler
- Vol. 82. **Chemometrics.** By Muhammad A. Sharaf, Deborah L. Illman, and Bruce R. Kowalski
- Vol. 83. **Fourier Transform Infrared Spectrometry.** By Peter R. Griffiths and James A. de Haseth
- Vol. 84. **Trace Analysis: Spectroscopic Methods for Molecules.** Edited by Gary Christian and James B. Callis
- Vol. 85. **Ultratrace Analysis of Pharmaceuticals and Other Compounds of Interest.** Edited by S. Ahuja
- Vol. 86. **Secondary Ion Mass Spectrometry: Basic Concepts, Instrumental Aspects, Applications and Trends.** By A. Benninghoven, F. G. Rüdener, and H. W. Werner
- Vol. 87. **Analytical Applications of Lasers.** Edited by Edward H. Piepmeier
- Vol. 88. **Applied Geochemical Analysis** By C. O. Ingamells and F. F. Pitard
- Vol. 89. **Detectors for Liquid Chromatography.** Edited by Edward S. Yeung
- Vol. 90. **Inductively Coupled Plasma Emission Spectroscopy: Part I: Methodology, Instrumentation, and Performance; Part II: Applications and Fundamentals.** Edited by J. M. Boumans
- Vol. 91. **Applications of New Mass Spectrometry Techniques in Pesticide Chemistry.** Edited by Joseph Rosen
- Vol. 92. **X-Ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS, and XANES.** Edited by D. C. Konigsberger
- Vol. 93. **Quantitative Structure-Chromatographic Retention Relationships.** By Roman Kaliszan
- Vol. 94. **Laser Remote Chemical Analysis.** Edited by Raymond M. Measures
- Vol. 95. **Inorganic Mass Spectrometry.** Edited by F. Adams, R. Gijbels, and R. Van Grieken
- Vol. 96. **Kinetic Aspects of Analytical Chemistry.** By Horacio A. Mottola
- Vol. 97. **Two-Dimensional NMR Spectroscopy.** By Jan Schraml and Jon M. Bellama
- Vol. 98. **High Performance Liquid Chromatography.** Edited by Phyllis R. Brown and Richard A. Hartwick
- Vol. 99. **X-Ray Fluorescence Spectrometry.** By Ron Jenkins
- Vol. 100. **Analytical Aspects of Drug Testing.** Edited by Dale G. Deustch
- Vol. 101. **Chemical Analysis of Polycyclic Aromatic Compounds.** Edited by Tuan Vo-Dinh
- Vol. 102. **Quadrupole Storage Mass Spectrometry.** By Raymond E. March and Richard J. Hughes
- Vol. 103. **Determination of Molecular Weight.** Edited by Anthony R. Cooper
- Vol. 104. **Selectivity and Detectability Optimization in HPLC.** By Satinder Ahuja
- Vol. 105. **Laser Microanalysis.** By Lieselotte Moenke-Blankenburg
- Vol. 106. **Clinical Chemistry.** Edited by E. Howard Taylor

- Vol. 107. **Multielement Detection Systems for Spectrochemical Analysis.** By Kenneth W. Busch and Marianna A. Busch
- Vol. 108. **Planar Chromatography in the Life Sciences.** Edited by Joseph C. Touchstone
- Vol. 109. **Fluorometric Analysis in Biomedical Chemistry: Trends and Techniques Including HPLC Applications.** By Norio Ichinose, George Schwedt, Frank Michael Schnepel, and Kyoko Adochi
- Vol. 110. **An Introduction to Laboratory Automation.** By Victor Cerdá and Guillermo Ramis
- Vol. 111. **Gas Chromatography: Biochemical, Biomedical, and Clinical Applications.** Edited by Ray E. Clement
- Vol. 112. **The Analytical Chemistry of Silicones.** Edited by A. Lee Smith
- Vol. 113. **Modern Methods of Polymer Characterization.** Edited by Howard G. Barth and Jimmy W. Mays
- Vol. 114. **Analytical Raman Spectroscopy.** Edited by Jeanette Graselli and Bernard J. Bulkin
- Vol. 115. **Trace and Ultratrace Analysis by HPLC.** By Satinder Ahuja
- Vol. 116. **Radiochemistry and Nuclear Methods of Analysis.** By William D. Ehmann and Diane E. Vance
- Vol. 117. **Applications of Fluorescence in Immunoassays.** By Ilkka Hemmila
- Vol. 118. **Principles and Practice of Spectroscopic Calibration.** By Howard Mark
- Vol. 119. **Activation Spectrometry in Chemical Analysis.** By S. J. Parry
- Vol. 120. **Remote Sensing by Fourier Transform Spectrometry.** By Reinhard Beer
- Vol. 121. **Detectors for Capillary Chromatography.** Edited by Herbert H. Hill and Dennis McMinn
- Vol. 122. **Photochemical Vapor Deposition.** By J. G. Eden
- Vol. 123. **Statistical Methods in Analytical Chemistry.** By Peter C. Meier and Richard Zund
- Vol. 124. **Laser Ionization Mass Analysis.** Edited by Akos Vertes, Renaat Gijbels, and Fred Adams
- Vol. 125. **Physics and Chemistry of Solid State Sensor Devices.** By Andreas Mandelis and Constantinos Christofides
- Vol. 126. **Electroanalytical Stripping Methods.** By Khjena Z. Brainina and E. Neyman
- Vol. 127. **Air Monitoring by Spectroscopic Techniques.** Edited by Markus W. Sigrist
- Vol. 128. **Information Theory in Analytical Chemistry.** By Karel Eckschlager and Klaus Danzer
- Vol. 129. **Flame Chemiluminescence Analysis by Molecular Emission Cavity Detection.** Edited by David Stiles, Anthony Calokerinos, and Alan Townshend
- Vol. 130. **Hydride Generation Atomic Absorption Spectrometry.** Edited by Jiri Dedina and Dimiter L. Tsalev
- Vol. 131. **Selective Detectors: Environmental, Industrial, and Biomedical Applications.** Edited by Robert E. Sievers
- Vol. 132. **High-Speed Countercurrent Chromatography.** Edited by Yoichiro Ito and Walter D. Conway
- Vol. 133. **Particle-Induced X-Ray Emission Spectrometry.** By Sven A. E. Johansson, John L. Campbell, and Klas G. Malmqvist

- Vol. 134. **Photothermal Spectroscopy Methods for Chemical Analysis.** By Stephen E. Bialkowski
- Vol. 135. **Element Speciation in Bioinorganic Chemistry.** Edited by Sergio Caroli
- Vol. 136. **Laser-Enhanced Ionization Spectrometry.** Edited by John C. Travis and Gregory C. Turk
- Vol. 137. **Fluorescence Imaging Spectroscopy and Microscopy.** Edited by Xue Feng Wang and Brian Herman
- Vol. 138. **Introduction to X-Ray Powder Diffractometry.** By Ron Jenkins and Robert L. Snyder
- Vol. 139. **Modern Techniques in Electroanalysis.** Edited by Petr Vanýsek
- Vol. 140. **Total-Reflection X-Ray Fluorescence Analysis.** By Reinhold Klockenkamper
- Vol. 141. **Spot Test Analysis: Clinical, Environmental, Forensic, and Geochemical Applications, Second Edition.** By Ervin Jungreis
- Vol. 142. **The Impact of Stereochemistry on Drug Development and Use.** Edited by Hassan Y. Aboul-Enein and Irving W. Wainer
- Vol. 143. **Macrocyclic Compounds in Analytical Chemistry.** Edited by Yury A. Zolotov
- Vol. 144. **Surface-Launched Acoustic Wave Sensors: Chemical Sensing and Thin-Film Characterization.** By Michael Thompson and David Stone
- Vol. 145. **Modern Isotope Ratio Mass Spectrometry.** Edited by T. J. Platzner
- Vol. 146. **High Performance Capillary Electrophoresis: Theory, Techniques, and Applications.** Edited by Morteza G. Khaledi
- Vol. 147. **Solid Phase Extraction: Principles and Practice.** By E. M. Thurman
- Vol. 148. **Commercial Biosensors: Applications to Clinical, Bioprocess, and Environmental Samples.** Edited by Graham Ramsay
- Vol. 149. **A Practical Guide to Graphite Furnace Atomic Absorption Spectrometry.** By David J. Butcher and Joseph Sneddon
- Vol. 150. **Principles of Chemical and Biological Sensors.** Edited by Dermot Diamond

# X-Ray Fluorescence Spectrometry



## CHAPTER

### 1

## PRODUCTION AND PROPERTIES X-RAYS

### 1.1. INTRODUCTION

X-rays are a short wavelength form of electromagnetic radiation discovered by Wilhelm Röntgen in 1895 [1]. X-ray based techniques provided important tools for theoretical physicists in the first half of this century and, since the early 1950s, they have found an increasing use in the field of materials characterization. Today, methods based on absorptiometry play a vital role in industrial and medical radiography. The simple X-ray field units employed in World War I were responsible for saving literally tens of thousands of lives, [2] and today the technology has advanced to a high degree of sophistication. Modern X-ray tomographic methods give an almost complete three-dimensional cross section of the human body, offering an incredibly powerful tool for the medical field. In addition, the analytical techniques based on X-ray diffraction and X-ray spectrometry, both of which were first conceived almost 70 years ago, have become indispensable in the analysis and study of inorganic and organic solids. Today, data obtained from X-ray spectrometers are being used to control steel mills, ore flotation processes, cement kilns, and a whole host of other vital industrial processes (see e.g., [3]). X-ray diffractometers are used for the study of ore and mineral deposits, in the production of drugs and pharmaceuticals, in the study of thin films, stressed and oriented materials, phase transformations, plus myriad other applications in pure and applied research.

X-ray photons are produced following the ejection of an inner orbital electron from an irradiated atom, and subsequent transition of atomic orbital electrons from states of high to low energy. When a monochromatic beam of X-ray photons falls onto a given specimen, three basic phenomena may result, namely, scatter, absorption or fluorescence. The coherently scattered photons may undergo subsequent interference leading in turn to the generation of diffraction maxima. The angles at which the diffraction maxima occur can be related to the spacings between planes of atoms in the crystal lattice and hence, X-ray generated diffraction patterns can be used to study the structure of solid materials. Following the discovery of the diffraction of X-rays by Max Von Laue in 1913 [4], the use of this method for materials analysis has become very important both in industry and research.