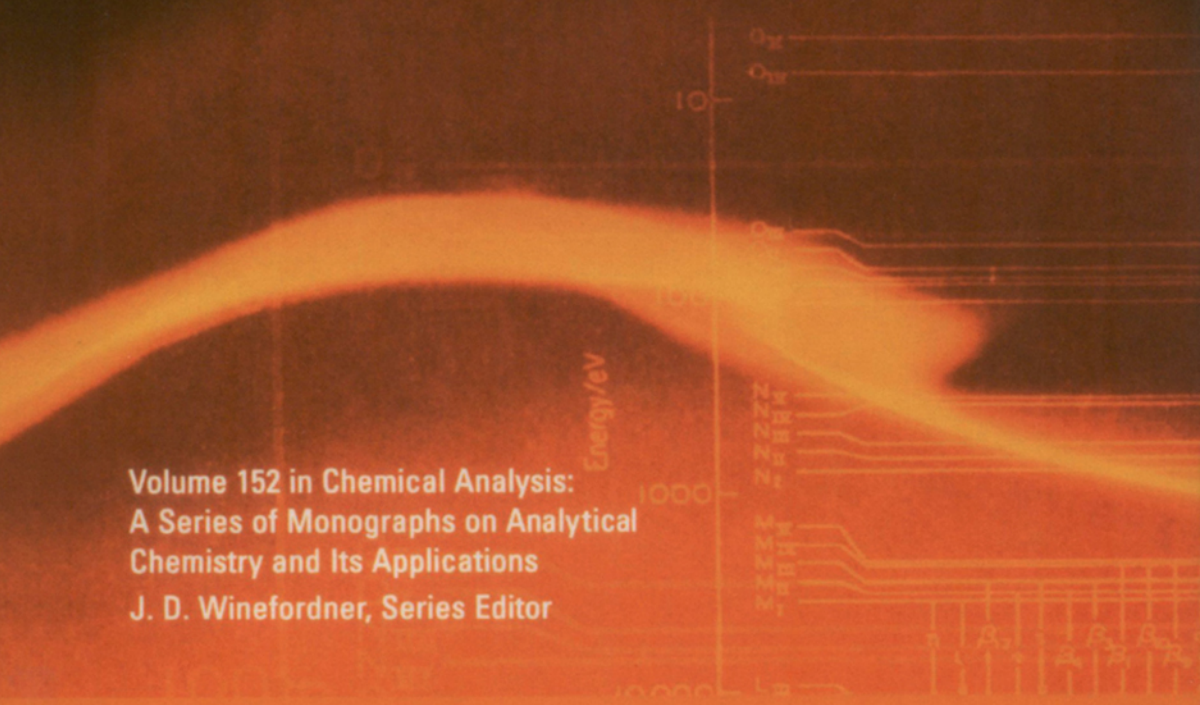
X-RAY FLUORESCENCE SPECTROMETRY

SECOND EDITION



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J. D. Winefordner, Series Editor

Ron Jenkins

X-Ray Fluorescence Spectrometry

CHEMICAL ANALYSIS

A SERIES OF MONOGRAPHS ON ANALYTICAL CHEMISTRY
AND ITS APPLICATIONS

Editor
J. D. WINEFORDNER

VOLUME 152

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X-Ray Fluorescence Spectrometry

Second Edition

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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

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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 absoptiometry 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.