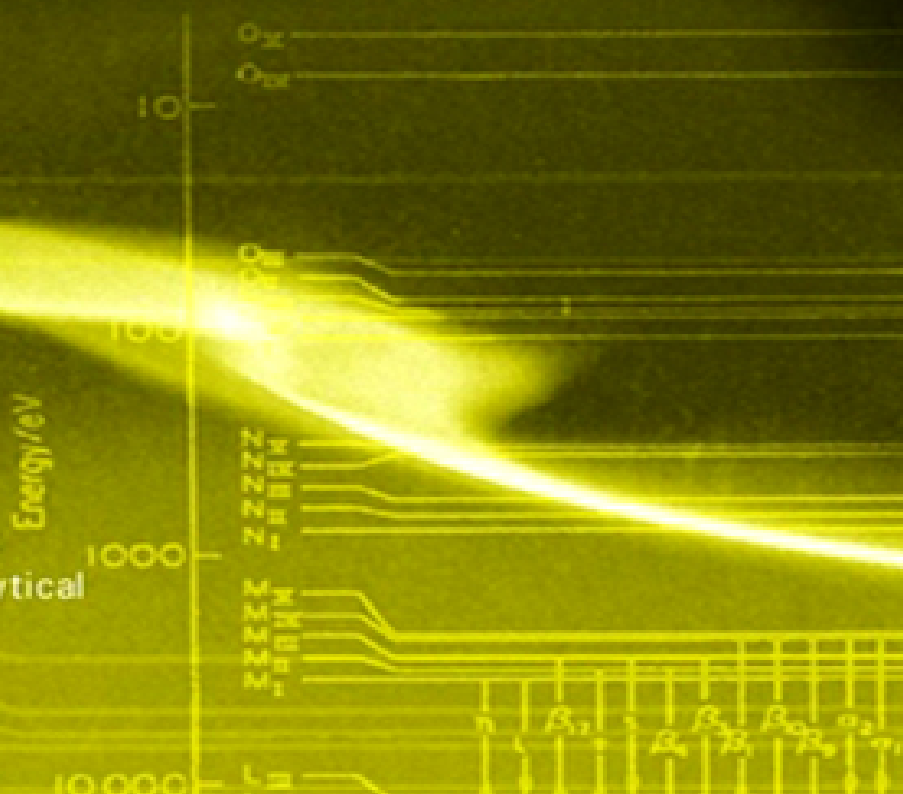


# X-RAY

## FLUORESCENCE SPECTROMETRY

SECOND EDITION

Volume 152 in Chemical Analysis:  
A Series of Monographs on Analytical  
Chemistry and Its Applications  
J. D. Winefordner, Series Editor



Ron Jenkins

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# 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

**RON JENKINS**

International Centre for Diffraction Data,  
Newtown Square, PA



A WILEY-INTERSCIENCE PUBLICATION

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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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# **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 absorptometry 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. Today, it is one of the most useful techniques available for the study of structure dependant properties of materials.

X-ray powder diffractometry involves characterization of materials by use of data dependant on the atomic arrangement in the crystal lattice (see e.g., [5]). The technique uses single or multiphase (i.e., multicomponent) specimens comprising a random orientation of small crystallites, each of the order of 1 to 50  $\mu\text{m}$  in diameter. Each crystallite in turn is made up of a regular, ordered array of atoms. An ordered arrangement of atoms (the crystal lattice) contains planes of high atomic density that in turn means planes of high electron density. A monochromatic beam of X-ray photons will be scattered by these atomic electrons and, if the scattered photons interfere with each other, diffraction maxima may occur. In general, one diffracted line will occur for each unique set of planes in the lattice. A diffraction pattern is typically in the

form of a graph of diffraction angle (or interplanar spacing) versus diffracted line intensity. The pattern is thus made up of a series of superimposed diffractograms, one for each unique phase in the specimen. Each of these unique patterns can act as an empirical “fingerprint” for the identification of the various phases, using pattern recognition techniques based on a file of standard single-phase patterns. Quantitative phase analysis is also possible, albeit with some difficulty, because of various experimental and other problems, not the least of which is the large number of diffraction lines occurring from multiphase materials.

A beam of X-rays passing through matter will be attenuated by two processes, scatter and photoelectric absorption. In the majority of cases the greater of these two effects is absorption and the magnitude of the absorption process, that is, the fraction of incident X-ray photons lost in passing through the absorber increases significantly with the average atomic number of the absorbing medium. To a first approximation, the mass attenuation coefficient varies as the third power of the atomic number of the absorber. Thus, when a polychromatic beam of X-rays is passed through a heterogeneous material, areas of higher average atomic number will attenuate the beam to a greater extent than areas of lower atomic number. Thus the beam of radiation emerging from the absorber has an intensity distribution across the irradiation area of the specimen, which is related to the average atomic number distribution across the same area. It is upon this principle that all methods of X-ray radiography are based. Study of materials by use of the X-ray absorption process is the oldest of all of the X-ray methods in use. Röntgen himself included a radiograph of his wife’s hand in his first published X-ray paper. Today, there are many different forms of X-ray absorptiometry in use, including industrial radiography,



diagnostic medical and dental radiography, and security screening.

Secondary radiation produced from the specimen is characteristic of the elements making up the specimen. The technique used to isolate and measure individual characteristic wavelengths is called X-ray spectrometry. X-ray spectrometry also has its roots in the early part of this century, stemming from Moseley's work in 1913 [6]. This technique uses either the diffracting power of a single crystal to isolate narrow wavelength bands, or a proportional detector to isolate narrow energy bands, from the polychromatic beam characteristic radiation excited in the sample. The first of these methods is called *Wavelength Dispersive Spectrometry* and the second, *Energy Dispersive Spectrometry*. Because the relationship between emission wavelength and atomic number is known, isolation of individual characteristic lines allows the unique identification of an element to be made and elemental concentrations can be estimated from characteristic line intensities. Thus this technique is a means of materials characterization in terms of chemical composition.

Although the major thrust of this monograph is to review X-ray spectroscopic techniques, these are by no means the only X-ray-based methods that are used for materials analysis and characterization. In addition to the many industrial and medical applications of diagnostic X-ray absorption methods already mentioned, X-rays are also used in areas such as structure determination based on single crystal techniques, space exploration and research, lithography for the production of microelectronic circuits, and so on. One of the major limitations leading to the further development of new X-ray methods is the inability to *focus* X-rays, as can be done with visible light rays. Although it is possible to partially reflect X-rays at low glancing angles, or diffract an X-ray beam with a single crystal, these

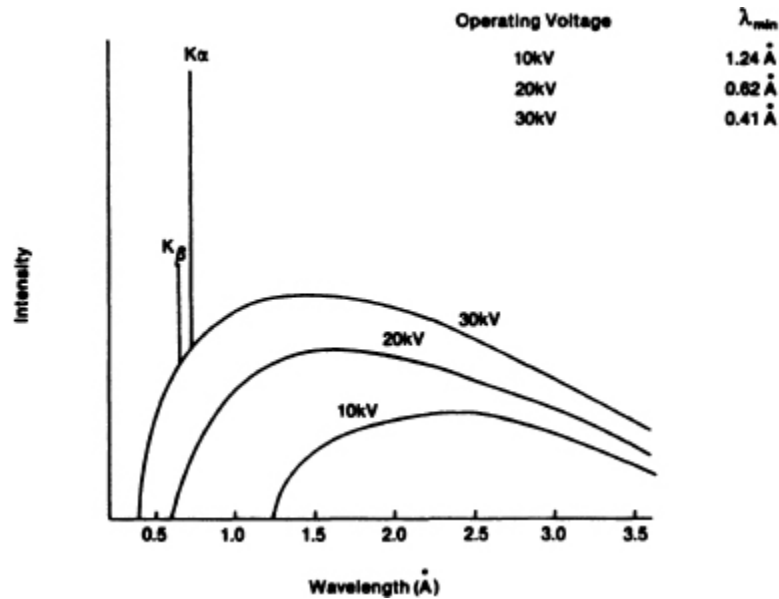
methods cause significant intensity loss, and fall far short of providing the high intensity, monochromatic beam that would be ideal for such uses as an X-ray microscope. Use of synchrotron radiation offers the potential of an intense, highly focused, coherent X-ray beam, but has practical limitations due to size and cost. The X-ray laser could, in principle, provide an attractive alternative, and since the discovery of the laser in 1960, the possibilities of such an X-ray laser have been discussed. Although major research efforts have been, and are still being, made to produce laser action in the far ultraviolet and soft X-ray regions, production of conditions to stimulate laser action in the X-ray region with a net positive gain is difficult. This is due mainly to the rapid decay rates and high absorption cross sections that are experienced in practice.

## 1.2. CONTINUOUS RADIATION

When a high energy electron beam is incident upon a specimen, one of the products of the interaction is an emission of a broad wavelength band of radiation called *continuum*. This continuum, which is also referred to as *white radiation* or *bremsstrahlung*, is produced as the impinging high energy electrons are decelerated by the atomic electrons of the elements making up the specimen. A typical intensity/wavelength distribution of this radiation is illustrated in [Figure 1.1](#) and is typified by a minimum wavelength  $\lambda_{\min}$ , which is roughly proportional to the maximum accelerating potential  $V$  of the electrons, that is,  $12.4/V$  keV. However, at higher potentials, an experimentally measured value of the minimum wavelength of the continuum may yield a somewhat longer wavelength than would be predicted due to the effect of Compton scatter.

The intensity distribution of the continuum reaches a maximum,  $I_{\max}$ , at a wavelength 1.5 to 2 times greater than  $\lambda_{\min}$ . Increasing the accelerating potential causes the intensity distribution of the continuum to shift towards shorter wavelengths. The curves given in [Figure 1.1](#) are for the element molybdenum ( $Z=42$ ). Note the appearance of characteristic lines of Mo  $K\alpha$  ( $\lambda = 0.71 \text{ \AA}$ ) and Mo  $K\beta$  ( $\lambda = 0.63 \text{ \AA}$ ), once the  $K$  shell excitation potential of 20 keV has been exceeded. Most commercially available spectrometers utilize a sealed X-ray tube as an excitation source, and these tubes typically employ a heated tungsten filament as a source of electrons, and a layer of pure metal such as chromium, rhodium, or tungsten, as the anode. The broad band of white radiation produced by this type of tube is ideal for the excitation of the characteristic lines from a wide range of atomic numbers. In general, the higher the atomic number of the anode material, the more intense the beam of radiation produced by the tube. Conversely, however, because the higher atomic number anode elements generally require thicker exit windows in the tube, the longer wavelength output from such a tube is rather poor and so these high atomic number anode tubes are less satisfactory for the excitation of longer wavelengths from low atomic number samples (see Section 6.2).

**[Figure 1.1](#)** Intensity output from a molybdenum target X-ray at 10, 20, and 30 kV.



## 1.3. CHARACTERISTIC RADIATION

If a high energy particle, such as an electron, strikes a bound atomic electron, and the energy  $E$  of the particle is greater than the binding energy  $\phi$  of the atomic electron, it is possible that the atomic electron will be ejected from its atomic position, departing from the atom with a kinetic energy  $(E-\phi)$ , equivalent to the difference between that of the initial particle and the binding energy of the atomic electron. The ejected electron is called a *photoelectron* and the interaction is referred to as the *photoelectric effect*. While the fate of the ejected photoelectron has little consequence as far as the production and use of characteristic X-radiation from an atom is concerned, it should be mentioned that study of the energy distribution of the emitted photoelectrons gives valuable information about bonding and atomic structure [7]. Study of such information forms the basis of the technique of *photoelectron spectroscopy* (see e.g., [8]). As long as the vacancy in the shell exists, the atom is in an unstable state and there are

two processes by which the atom can revert back to its original state. The first of these involves a rearrangement that does not result in the emission of X-ray photons, but in the emission of other photoelectrons from the atom. The effect is known as the *Auger effect*, and the emitted photoelectrons are called Auger electrons. The second process by which the excited atom can regain stability is by transference of an electron from one of the outer orbitals to fill the vacancy. The energy difference between the initial and final states of the transferred electron may be given off in the form of an X-ray photon. Since all emitted X-ray photons have energies proportional to the differences in the energy states of atomic electrons, the lines from a given element will be characteristic of that element. The relationship between the wavelength  $\lambda$  of a characteristic X-ray photon and the atomic number  $Z$  of the excited element was first established by Moseley (see Chapter 4). Moseley's law is written

$$(1.1) \quad \frac{1}{\lambda} = K[Z - \sigma]^2,$$

in which  $K$  is a constant that takes on different values for each spectral series.  $\sigma$  is the shielding constant that has a value of just less than unity. The wavelength of the X-ray photon is inversely related to the energy  $E$  of the photon according to the relationship

$$(1.2) \quad \lambda = \frac{12.4}{E}.$$

There are several different combinations of quantum numbers held by the electron in the initial and final states, hence several different X-ray wavelengths will be emitted from a given atom. For those vacancies giving rise to characteristic X-ray photons, a series of very simple selection rules can be used to define which electrons can be transferred. For a detailed explanation of these rules, refer to Section 4.4. Briefly, the principal quantum number  $n$  must change by 1, the angular quantum number  $\ell$  must

change by 1, and the vector sum of  $(\ell + s)$  must be a number changing by 1 or 0. In effect this means that for the  $K$  series only  $p \rightarrow s$  transitions are allowed, yielding two lines for each principle level change. Vacancies in the  $L$  level follow similar rules and give rise to  $L$  series lines. There are more of the  $L$  lines since  $p \rightarrow s$ ,  $s \rightarrow p$ , and  $d \rightarrow p$  transitions are all allowed within the selection rules. In general, electron transitions to the  $K$  shell give between two and six  $K$  lines, and transitions to the  $L$  shell give about twelve strong to moderately strong  $L$  lines.

Because there are two competing effects by which an atom may return to its initial state, and because only one of these processes will give rise to the production of a characteristic X-ray photon, the intensity of an emitted characteristic X-ray beam will be dependant upon the relative effectiveness of the two processes within a given atom. As an example, the number of quanta of  $K$  series radiation emitted per ionized atom, is a fixed ratio for a given atomic number. This ratio is called the fluorescent yield.

[Figure 1.2](#) shows fluorescent yield curves as a function of atomic number. It will be seen that, whereas the  $K$  fluorescent yield is close to unity for higher atomic numbers, it drops by several orders of magnitude for the very low atomic numbers. In practice, this means that if the intensities obtained from pure barium ( $Z = 56$ ) are compared to those of pure aluminum ( $Z = 13$ ), all other things being equal, pure barium would give about 50 times more counts than pure aluminum. Also note from the curve that the  $L$  fluorescent yield for a given atomic number is always less than the corresponding  $K$  fluorescent yield.

**[Figure 1.2](#)** Fluorescence yield as a function of atomic number.