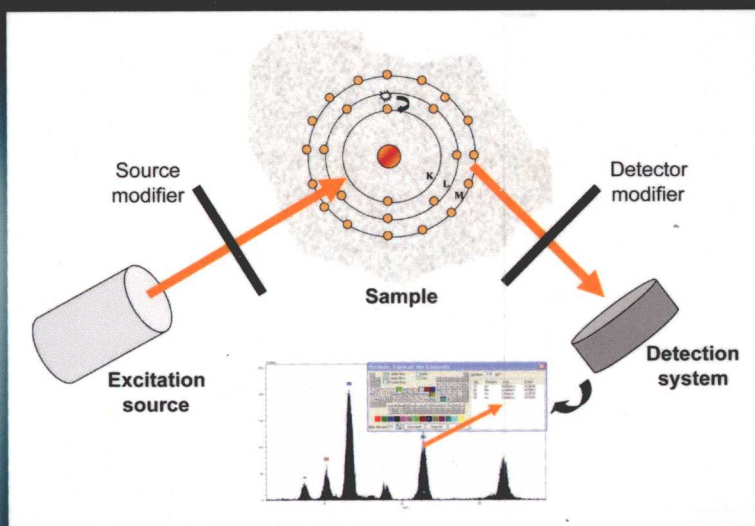


# X-RAY FLUORESCENCE SPECTROMETRY AND RELATED TECHNIQUES

AN INTRODUCTION



**Eva MarguÍ and René Van Grieken**



MOMENTUM PRESS

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**EVA MARGUÍ, RENÉ VAN GRIEKEN**



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**MOMENTUM PRESS, LLC, NEW YORK**

*X-Ray Fluorescence Spectrometry and Related Techniques: An Introduction*

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First published by Momentum Press®, LLC

222 East 46th Street, New York, NY 10017

[www.momentumpress.net](http://www.momentumpress.net)

ISBN-13: 978-1-60650-391-1 (hard back)

ISBN-10: 1-60650-391-X (hard back)

ISBN-13: 978-1-60650-393-5 (e-book)

ISBN-10: 1-60650-393-6 (e-book)

DOI: 10.5643/9781606503935

Cover design by Jonathan Pennell

Interior design by Exeter Premedia Services Private Ltd.,  
Chennai, India

10 9 8 7 6 5 4 3 2 1

Printed in the United States of America

**X-RAY  
FLUORESCENCE  
SPECTROMETRY  
AND RELATED  
TECHNIQUES**

# PREFACE

Nowadays, X-ray fluorescence spectrometry (XRF) is a well established analytical technique for qualitative and quantitative elemental analysis (usually covering elements of atomic number from Be to U) of a wide variety of samples. In particular, its truly multielement identification capability, acceptable speed, cost-effectiveness, and ease of automation, together with the possibility to directly analyze solid samples are among the most important features of the spectroscopic technique of the many that have made it a very mature analytical tool for routine quality controls in many industries, as well as for analytical support applications in many research laboratories. The recent technological advances, including the design of low-power microfocus tubes and novel X-ray optics and detectors have made it possible to extend XRF to the determination of low-Z elements and to obtain 2D or 3D information at a micrometer size scale. Furthermore, the recent development and commercialization of bench-top and portable instrumentation, which offer extreme simplicity of operation in a low-cost design, have promoted even more the approach of XRF for a wide range of analytical problems in many different and diverse fields.

This tutorial book provides an up-to-date account of the fundamentals of the XRF technique, instrumentation, sample preparation procedures, and applications. It is not focused on one specific type of spectrometer or one application area, but aims to give a broad overview of the main spectrometer types and applications. It is intended for people new to the field of XRF analysis or to help analytical chemistry technicians and researchers and other users of XRF to further expand their knowledge from a practical point of view. For this reason, difficult mathematical equations and X-ray physical postulates have been avoided and only a basic knowledge of these is required. We have tried to keep the language and explanations as straightforward and simple as possible. For more detailed information about XRF technique and applications readers can refer to books listed in the Bibliography of this work.

The first chapter provides a general introduction to the XRF technique including the origin of X-rays and the basic principles. Chapter 2 outlines the basic components of X-ray fluorescence spectrometers and the design of the different XRF systems. Following, in Chapter 3, some considerations for the qualitative and quantitative analysis by XRF are presented. For the latter case, a discussion of matrix effects is discussed and an overview of correction methods is given and commented upon. Information on the sample preparation procedures for various kinds of samples prior to X-ray measurements is reviewed in Chapter 4. Not only are commonly used methods covered, but also some specific techniques for specific kinds of materials are included, with emphasis on more recent applications and developments. Chapters 5, 6, and 7 are focused on the basic information on those XRF-based techniques that are now well

established and of recognized value to provide robust and fit-for-purpose analytical results; these include: wavelength dispersive XRF (WDXRF), energy dispersive XRF (EDXRF), and total reflection XRF (TXRF) spectrometry. At the end of each of these chapters a section of selected applications illustrating the possibilities and drawbacks of each particular technique is included. In addition, in Chapter 8, a brief description of special EDXRF configurations and XRF related techniques used in specific fields is presented. Finally, the current role of XRF in chemical analysis and comparison of the analytical capabilities of XRF systems with other elemental techniques such as atomic spectroscopy are discussed in Chapter 9. Trends and future perspectives of XRF are also included in this last chapter. A Buyer's Guide and Reference Section are also included in this book.

## KEY WORDS

X-ray fluorescence spectrometry (XRF); Energy dispersive X-ray fluorescence spectrometry (EDXRF); Wavelength dispersive X-ray fluorescence spectrometry (WDXRF); Total reflection X-ray fluorescence spectrometry (TXRF); Micro-XRF; Synchrotron radiation-induced X-ray emission (SRXRF); Metals; Sample preparation; XRF instrumentation; Industrial analysis; Environmental analysis; Geochemical analysis

# SERIES PREFACE

This *Spectroscopy* series of handbooks is intended to provide a library of books for the many widely used spectroscopic techniques used today in academia, industry, national laboratories, and museums. Each introduces, in a concise manner, the technique's concepts and basic theory and methodology, together with many application examples. Each volume of *Spectroscopy* will enable the reader to gain insight and understanding of the practical implementation of a particular technique, its attributes and limitations, and its current capabilities and developments.

*Spectroscopy* will cover both atomic and molecular spectroscopy techniques and their wide ranging applications and uses from within the laboratory to out in the field, covering a diverse range of applications, including materials and forensic sciences, security and bio-medical applications, uses within the pharmaceuticals industry, life sciences, and art/archaeological arenas.

Each volume in the series is authored by leading experts on a particular technique. All are individuals recognized for their state-of-the-art knowledge of current developments and practices. This exciting new series was launched by Momentum Press in 2012 with its first volume, *Solid-State NMR: Basic Principles & Practice* (co-authored by David C. Apperley, Robin K. Harris, and Paul Hodgkinson).

This book in the series, co-authored by Eva Margu  and Ren  Van Grieken, is devoted to *X-ray Fluorescence Spectroscopy and Related Techniques*. XRF spectroscopy, although a well-established key atomic spectroscopy technique, continues to evolve to greater sensitivities. This allows the subsequent development of new instruments, which has opened up many new, exciting, and challenging applications including portable instruments for field use.

As the Editor for this *Spectroscopy* series from Momentum Press, I am very pleased to add this excellent XRF spectroscopy book to the series library. Forthcoming volumes in this series include Atomic Absorption Spectrometry (AAS), Laser-Induced Breakdown Spectroscopy (LIBS), and THz spectroscopy.

John M. Chalmers (Series Editor),  
January 2013.

# SERIES EDITOR

John Chalmers, CChem FRSC, has been an independent consultant since 2000, following a distinguished career as a vibrational spectroscopist in the research department measurement science group of a division of a major UK chemical company, the then ICI plc. Mr. Chalmers is a past president of the Society for Applied Spectroscopy (SAS); he served for 9 years as chairman of the UK Infrared and Raman Discussion Group (IRDG); he has served for many years on the Royal Society of Chemistry Molecular Spectroscopy Interest Group. He has held part-time or honorary positions at the Universities of Nottingham, East Anglia and Lancaster. In 1994, Mr. Chalmers was the recipient of the Williams-Wright Award presented by The Coblenz Society for outstanding contributions in the '*Field of Industrial Infrared Spectroscopy*'. He is a co-editor (with Professor Peter Griffiths) of the highly acclaimed 5-volume reference work, *Handbook of Vibrational Spectroscopy*, published in 2002. Additionally, he has co-authored one book and edited or co-edited another 10 books/reference works, authored or co-authored 24 book chapters/reference works, and published over 50 peer-reviewed papers in scientific journals. Among other publishing-related activities, he is the Article Editor for *Spectroscopy Europe*.



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## CHAPTER 1

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# INTRODUCTION

### 1.1 BASIC PRINCIPLES OF X-RAY FLUORESCENCE

The principle of the X-ray fluorescence (XRF) technique is based on the use of some excitation radiation to produce ionization in the inner shells of the atoms present in the sample due to photoelectric absorption. The process of atom ionization and X-ray characteristic emission is illustrated in Figure 1.1.

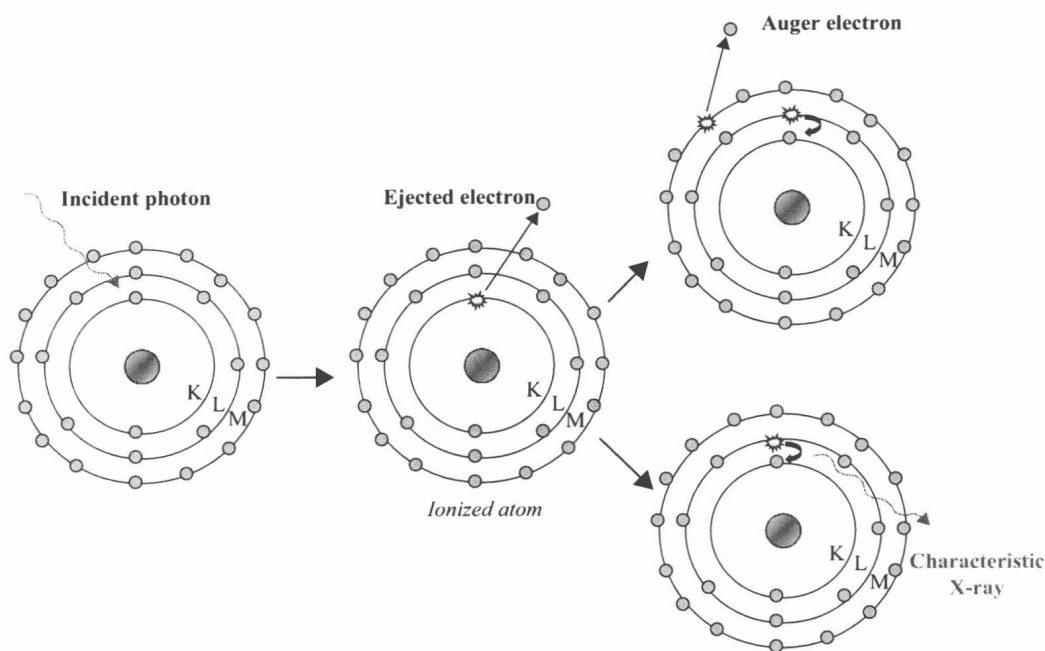
If a photon with energy larger than the binding energy of an inner electron orbital, impinges onto the atom, part of its energy can be absorbed with a certain probability (photoelectric absorption) and the atomic electron is ejected from its atomic position. As long as the vacancy created in the shell exists, the atom is in an unstable state (ionized atom) and there are two processes by which the atom can revert back to its original state. The first process involves a rearrangement that results in the emission of other photoelectrons (Auger effect). The second process, which is related with the origin of X-rays, is based on the transference of an electron from one of the outer orbitals to fill the vacancy. The energy difference between the initial and the final states of the transferred electron is given off in the form of an X-ray photon. Because there are two competing effects by which an atom may return to its initial state, the intensity of an emitted characteristic X-ray beam is dependent on the relative effectiveness of the two processes within a given atom, which is  $\omega$ , the probability of X-ray characteristic emission occurring (i.e., fluorescence yield).

It is important to note here that the fluorescent yield has a value of around unity for the higher atomic numbers to less than 0.01 for the low atomic number elements. It is mainly for this reason that the sensitivity of the X-ray spectrometric techniques is rather poor for light elements (see Figure 1.2).

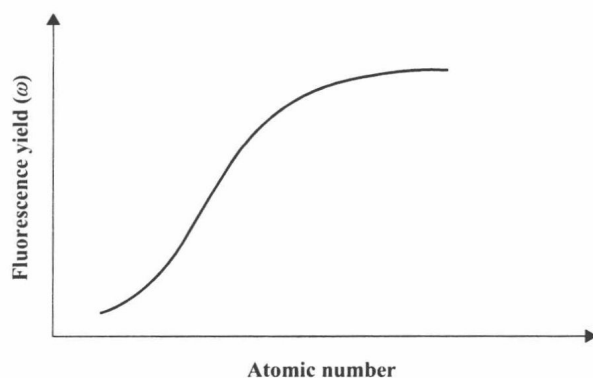
The law of Henry Moseley relates the wavelength,  $\lambda$ , of the characteristic emission to the atomic number,  $Z$ , as

$$1/\lambda = K(Z - \sigma)^2 \quad (1.1)$$

where  $K$  and  $\sigma$  are constants, the values of which are specific for the energy distribution levels and sublevels involved in a given transition. According to the quantum mechanics postulates,

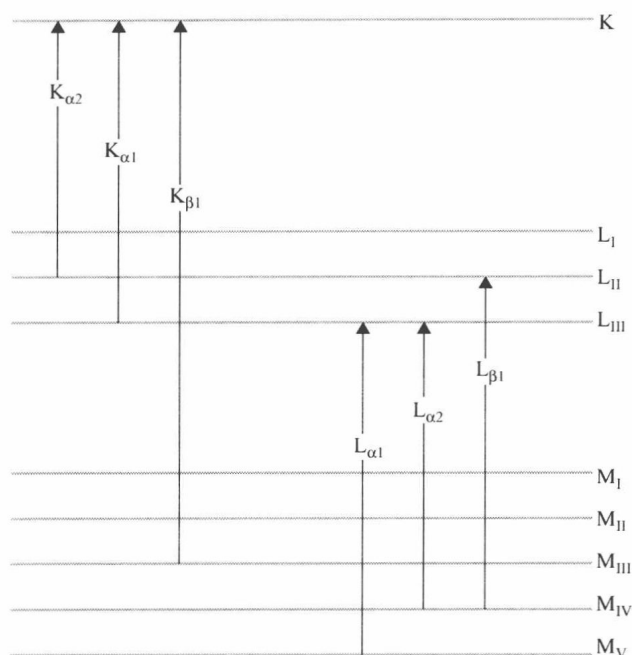


**Figure 1.1.** Processes of atom ionization and X-ray characteristic emission.

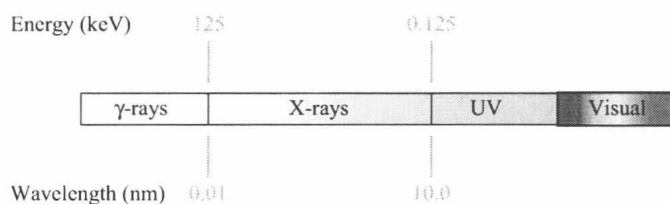


**Figure 1.2.** Fluorescence yield as a function of atomic number.

not all transitions are possible. In Figure 1.3, the principal allowed transitions yielding X-ray characteristic emission are shown. It should be mentioned that there are several conventions used to name the transitions that appear as lines in the resulting X-ray spectrum. The most commonly used are the Karl Manne Siegbahn (Siegbahn) and International Union of Pure and applied Chemistry (IUPAC) notations. In the first one, the line is named by the symbol of an element followed by the name of the shell in which the initial hole occurred plus a subscript Greek letter ( $\alpha$ ,  $\beta$ ,  $\gamma$ ) that indicates the relative intensity of the line. For instance, Zn  $K_{\alpha}$  is the strongest zinc line because of an expelled K electron. When using the IUPAC nomenclature, a line is indicated by the symbol of the element, the shell in which the initial hole occurred, and also by the shell from which the electron comes that fills this hole. For example, Zn  $KL_{III}$  is zinc radiation due to a hole produced in the K-shell filled by an electron in the  $L_{III}$ -shell.



**Figure 1.3.** Principal allowed transitions producing X-ray characteristic emissions.



**Figure 1.4.** Electromagnetic radiation and the X-ray region.

The wavelength,  $\lambda$ , and the energy of the emitted radiation,  $E$ , are related using the Planck's constant ( $h$ ) and the speed of light ( $c$ ):

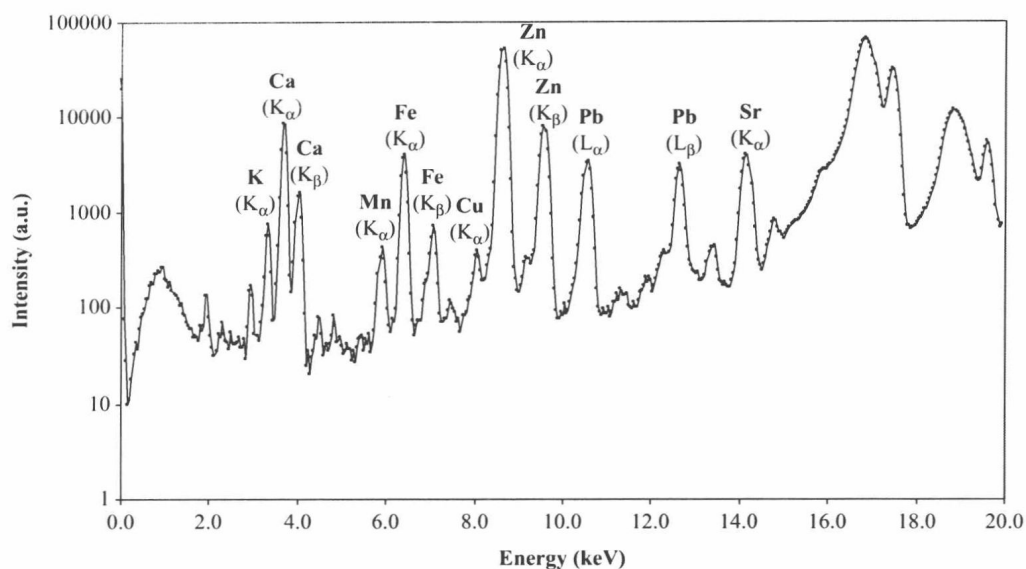
$$E = \frac{hc}{\lambda} \quad (1.2)$$

In the specific case of X-ray radiation, associated wavelengths are in the range of 0.01–10 nm, which corresponds to energies in the range from 0.125–125 keV (see Figure 1.4).

To achieve X-ray production from a given element, the only requirement is to use an excitation radiation with an energy larger than the absorption edge for the corresponding group of lines. Most commercially available X-ray spectrometers have a range of about 0.4–20 Å (40–0.6 keV), and this range allows measurement of the K series from F ( $Z = 9$ ) to Lu ( $Z = 71$ ), and the L lines from Mn ( $Z = 25$ ) to U ( $Z = 92$ ).

As characteristic emissions correspond to transitions ruled by quantum mechanics principles, the XRF method constitutes a unique technique for the identification of the atoms present





**Figure 1.5.** Typical spectrum of a vegetation sample measured with an XRF spectrometer.

in a sample (i.e., qualitative analysis). A straightforward identification of any element present in the sample is possible by detecting the presence of several of its characteristic emission energies (or wavelengths). As the X-ray production is (almost) independent of the chemical association of the elements (i.e., transitions arise from inner orbitals), the method also has a multielemental capability. As an example, in Figure 1.5, a typical X-ray spectrum for the analysis of a vegetation sample is shown. The positions of the characteristic X-ray emitted energies determine the elements present in the sample, while the heights of the peaks are related to the element concentrations.

## 1.2 INTERACTIONS OF X-RAYS WITH MATTER

In the previous section, we considered that the unique phenomenon resulting in the emission of electromagnetic radiation that takes place when a beam of X-ray photons falls onto a given specimen, was fluorescence. However, when the incident X-ray photon beam impinges on the sample, a fraction of this radiation can also be transmitted through the sample or scattered back from it, as is illustrated in Figure 1.6.

Scatter occurs when an X-ray photon interacts with the electrons of the target element. When this interaction is elastic (i.e., no energy is lost in the collision process), the scatter is named as *coherent* (Rayleigh) *scatter*. As no energy change is involved in this process, the Rayleigh radiation will retain exactly the same energy as the incident beam. However, the scattered photon can also transfer a part of its energy during the collision. In this case, it is referred to as *incoherent* (Compton) *scatter* and this radiation is characterized by a slightly lower energy compared to that from the incoming beam. Because of these phenomena, in addition to the characteristic radiation of the elements present in the irradiated sample, in an XRF spectrum one finds peaks that correspond to a Rayleigh and Compton scatter of the incident beam. In Figure 1.7, the appearance of Rayleigh and Compton peaks in an XRF spectrum