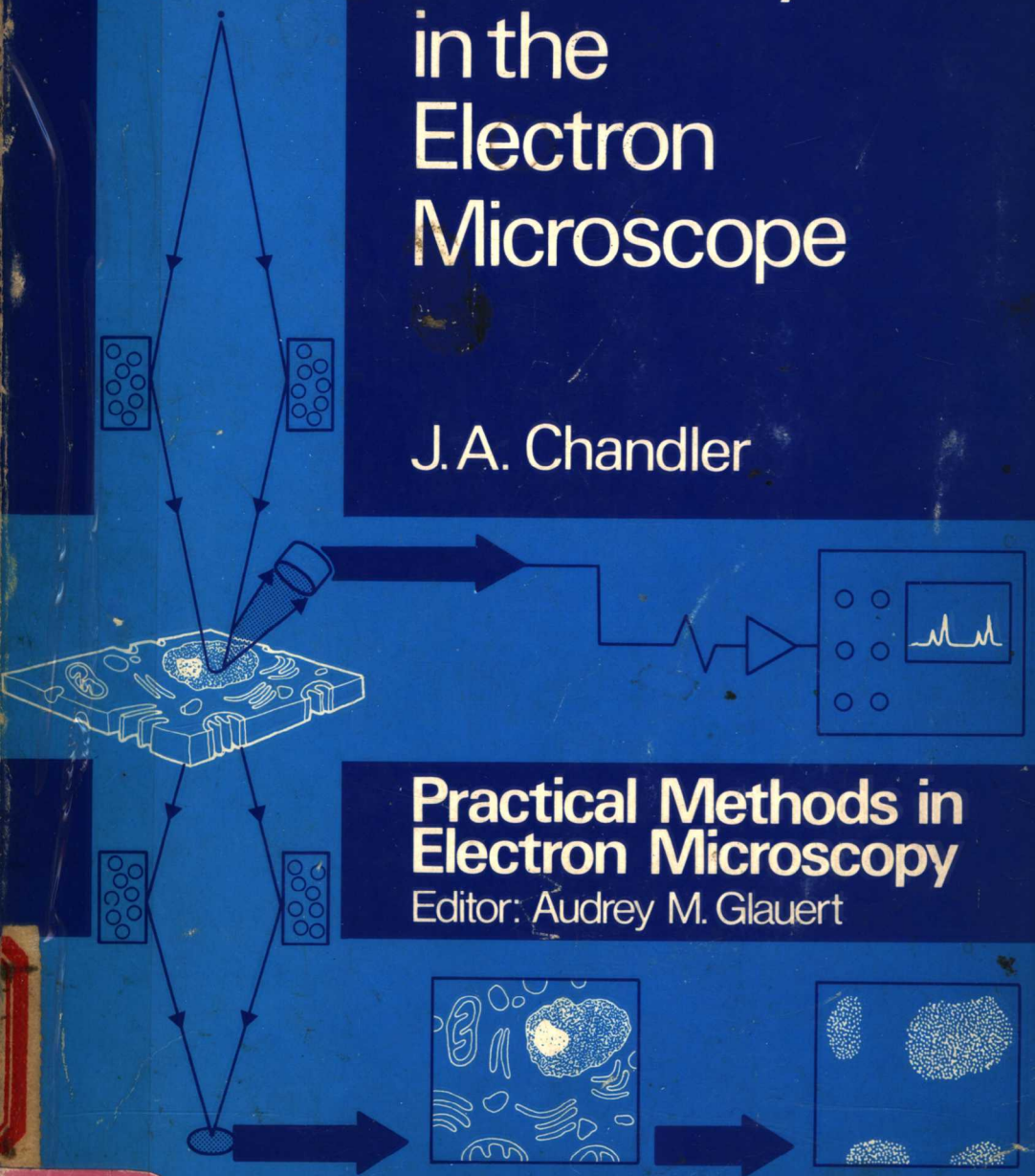
X-ray Microanalysis in the Electron Microscope

J. A. Chandler



Practical Methods in Electron Microscopy

Editor: Audrey M. Glauert

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Editor's preface

Electron microscopy is now a standard technique with wide applications in all branches of Science and Technology, and every year a large number of students and research workers start to use the electron microscope and require to be introduced to the instrument and to the techniques for the preparation of specimens. Many books are available describing the techniques of electron microscopy in general terms, but the authors of Practical Methods in Electron Microscopy consider that there is an urgent need for a comprehensive series of laboratory handbooks in which all the techniques of electron microscopy are described in sufficient detail to enable the isolated worker to carry them out successfully. The series of books will eventually cover the whole range of techniques for electron microscopy, including the instrument itself, methods of specimen preparation in biology and the materials sciences, and the analysis of electron micrographs. Only well-established techniques which have been used successfully outside their laboratory of origin will be included.

Great care has been taken in the selection of the authors since it is well known that it is not possible to describe a technique with sufficient practical detail for it to be followed accurately unless one is familiar with the technique oneself. This fact is only too obvious in certain 'one author' texts in which the information provided quickly ceases to be of any practical value once the author moves outside the field of his own experience.

Each book of the series will start from first principles, assuming no specialist knowledge, and will be complete in itself. Following the successful innovation, made by the same publishers in the parallel series Laboratory

Techniques in Biochemistry and Molecular Biology (edited by T. S. Work and E. Work), each book will be included, together with one or two others of the series, in a hardback edition suitable for libraries and will also be available in an inexpensive edition for individual use in the laboratory. Each book will be revised, independently of the others, at such times as the authors and editor consider necessary, thus keeping the series of books continuously up-to-date.

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AUDREY M. GLAUERT, SC.D.
General editor

To my family

Acknowledgements

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The manuscript could not have been completed without the continuous cooperation of, and discussion with, my colleagues in the Tenovus Institute. I am particularly indebted to Professor Keith Griffiths and to the Tenovus Organisation for providing facilities from which much of the information was obtained.

A number of the figures have been reproduced with the permission of John Wiley & Sons, Inc., New York. Photographs of some instruments were kindly provided by manufacturers as indicated.

My thanks go especially to Dr. Audrey Glauert who edited the manuscript with such care and provided constructive guidance throughout its preparation.

I am doubly grateful to Mr. Ron Alderson for both reviewing the manuscript and for first introducing me to the trials and rewards of X-ray analysis several years ago during my sojourn with AEI.

JOHN A. CHANDLER

Contents

Chapter 1

Introduction

1.1 *The nature of X-ray microanalysis*

When an electron beam strikes a solid specimen a number of interactions occur, the most important of these being illustrated in Fig. 1.1. Electrons may be back-scattered from the front face of the specimen with little or no energy loss, or they may interact with surface atoms to produce secondary (low energy) electrons. Some electrons may be absorbed by the specimen with transfer of energy to heat and sometimes to light. Transmitted electrons may be unchanged in direction or scattered at different angles. Scattered electrons may be elastic (no energy loss) or inelastic (having lost some energy). If energy is transmitted to the specimen it may also result in the production of Auger electrons or X-rays. Each of these events can provide information about the specimen. However the interaction which is the subject of this book is the generation of X-rays by high energy electrons passing through a thin specimen ($< 10\ \mu m$) in the electron microscope. These X-rays carry information about the atoms within the specimen in the region being irradiated, and thus provide a means of correlating the ultrastructural information in the electron microscope image with chemical analyses of very small regions of the specimen. X-ray microanalysis makes use of the fact that atoms, when struck by electrons from an external source, yield X-rays which are characteristic of those atoms. Consequently, the X-rays can be used to identify and quantify the elements present. Suitable detectors, placed close to the specimen, collect the X-rays and the information thus obtained is displayed for immediate interpretation of the specimen composition.

The two techniques of electron-optical imaging and X-ray analysis were

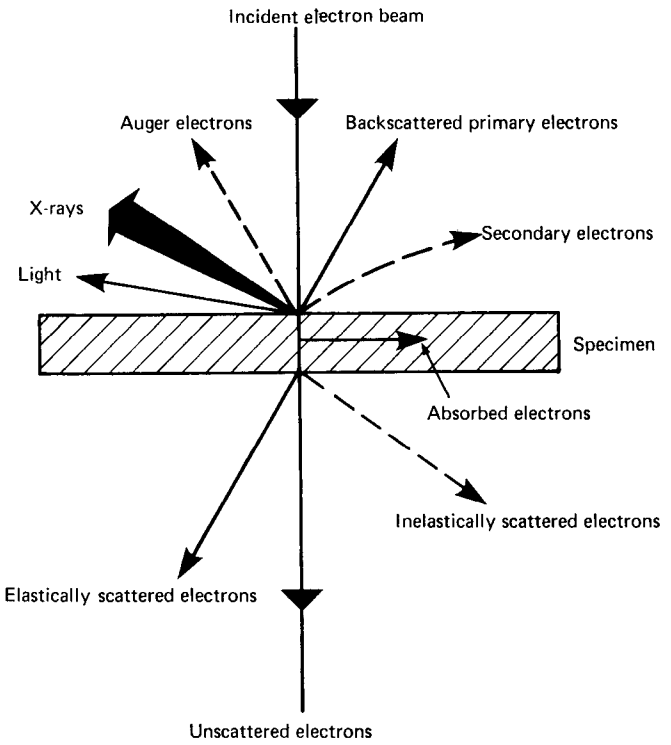

Fig. 1.1. The various effects of electron-specimen interaction. Light is emitted as visible fluorescence; elastically scattered electrons suffer no energy loss; inelastically scattered electrons lose some energy, and secondary electrons are of much lower energy than the primary electron beam.

first combined in the late 1940s by Castaing and Guinier (1949). Since then, and especially in the last 15 years, many hundreds of instruments with facilities for X-ray microanalysis have been produced and used in such diverse scientific areas as metallurgy, physics, electronics, mineralogy, environmental pollution and geology, and more recently in zoology, pathology, biochemistry and other biological fields.

This book describes the instruments and techniques involved in the analysis of relatively thin specimens, i.e. those specimens in which the full capabilities of electron microscopy are utilised. Application in both the transmission and scanning electron microscopes is discussed. The immensely large field of electron-probe microanalysis (mainly for bulk specimens) is not included except as an introduction to thin specimen analysis and the

reader is referred to other literature for a detailed treatment of these techniques (see end of Chapter for list of references).

Throughout this book the emphasis is placed on practical aspects of analysis and only the minimum discussion of theoretical considerations is included. More detailed descriptions of the theoretical basis of microanalysis will be found in the references listed in Chapter 6. The information contained within this book is provided for both the beginner, with little or no experience in analytical techniques but with some knowledge of electron microscopy, and the more experienced operator who wishes to more fully understand some of the practical aspects of analysis in the electron microscope. Only well established techniques which have been used successfully outside their laboratory of origin are included.

1.2 *The philosophy of X-ray microanalysis*

Modern electron-optical instruments are able to provide resolving powers of less than 0.5 nm and the limitations to obtaining ultrastructural detail lie not so much in instrumental factors as in methods of specimen preparation, and in the techniques of image analysis available. The need also frequently arises to complement the available morphological information with a chemical analysis of certain regions of the specimen in order to determine the relationship between ultrastructural changes and variations in chemical composition of the specimen components. Without local chemical analysis or cytochemical techniques the electron microscopist can only interpret the image in terms of fine structure. For example the biologist, observing dynamic effects in a tissue, will want to know the relationship between the observed changes in structure and variations in elemental distribution throughout the material. Conversely the metallurgist, knowing the elemental composition of particular areas of his material will have a greater understanding of the morphological information presented by the microscope.

Clearly then there is a need to combine a method of obtaining high resolution images of thin specimens with simultaneous elemental analysis of a non-destructive nature of the same regions of the specimen. X-ray microanalysis fulfils these needs by providing an *in situ* means of identifying elements within microvolumes of thin specimens to a very high degree of sensitivity and with very precise localisation of the regions being analysed. This requires a combination of a high performance electron microscope with X-ray detectors that can be incorporated into the electron-optical system without compromising other facilities for specimen examination.

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Chapter 2

Production of X-rays

Every element in the periodic table has a very well-defined distribution of electrons within the atom. X-ray microanalysis is dependent on the excitation of these electrons to produce an emitted X-ray spectrum characteristic of the element concerned.

2.1 Model of the atom

Figure 2.1 represents a simple schematic representation of the atom. The nucleus, composed of protons and neutrons, is surrounded by electrons circulating in orbits. Each orbit corresponds quantum mechanically to a certain energy level of the electrons. The number of these orbits and energy levels depends on the size and state of the atom, and the orbits are grouped together into major units called shells. Elements are thus characterised by their nuclear charge and the energy distribution of their orbital electrons. Heavy elements, having large atoms, contain large numbers of electron orbits and shell units. In this simple model the shells nearest the nucleus are taken to contain electrons with the least potential energy. The shells are given the notation K, L, M etc. (Fig. 2.1) and in each shell there are a number of energy levels.

2.2 Ionisation of atoms

If one of the orbital electrons is in some way removed from its normal energy level, and perhaps ejected from the atom altogether, the atom is then in an excited state and is said to be ionised. In order to stabilise the atom an electron from a higher energy orbit falls immediately into this gap and its