ELECTRON MICROPROBE
ANALYSIS

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PREFACE

In 1951 Raymond Castaing, under the supervision of Professor Guinier of the University of Paris, wrote a doctoral thesis describing the successful development of a new instrument destined to have an impact in many fields of science and technology comparable with that of the electron microscope. The electron microprobe owed its existence to developments in electron optics making it possible to produce an electron beam (or probe) focused to less than 1μm diameter, which could be used to excite characteristic X-rays in solid specimens.

The simplicity of X-ray spectra and the regular dependence of the wavelength of the characteristic lines on atomic number make the identification of the elements present a straightforward matter. Quantitative analysis may be performed by comparing the line intensities with those from pure elements, or sometimes standard compounds of known composition. Castaing developed a theoretical basis for the 'matrix corrections' that are necessitated by the dependence of the efficiency of X-ray excitation on composition. The methods of calculating these corrections in use today are still largely based on Castaing's work.

During the 1960s matrix correction procedures were refined and tested on a wide variety of samples. At present the accuracy of quantitative analysis is usually better than ± 2 per cent (relative), which is adequate for most practical purposes. In routine analysis the limit of detection is typically 100 ppm, though in favourable circumstances it may approach 10 ppm. The volume analysed is usually a few cubic micrometres, and the absolute elemental sensitivity is of the order of 10^{-15} g.

This book is intended to provide a fairly complete coverage of electron microprobe analysis for users of the technique in metallurgy and materials science, geology, biology, etc. The treatment emphasises physical principles, in relation to the design and operation of the instrument and the interpretation of results, but every effort has been made to avoid superfluous theoretical detail.

Much of the material included is relevant not only to the conventional electron microprobe, but should also be of interest to users of scanning electron microscopes, which nowadays are frequently fitted with X-ray spectrometers for analytical purposes.

Chapter 1 contains an outline of the necessary X-ray physics, while a more detailed discussion of X-ray spectra is reserved for the appendix. The physical principles and practical details involved in the construction and operation of the instrument are treated in the first half of the book. Two whole chapters are devoted to the important subject of lithium drifted silicon detectors, which are now competitive in many respects with the traditional Bragg crystal spectrometer. Other recent developments, such as electron guns of high brightness and new kinds of electron lens, are also described.

Chapters 11–16 deal with quantitative analysis, starting with experimental aspects (chapter 11), followed by a full treatment of matrix corrections (chapters 12–15) and a discussion of practical correction procedures, including a worked example (chapter 16). Chapter 17 is concerned with the special considerations involved in carrying out quantitative analysis with a lithium drifted silicon detector. Chapter 18 is concerned with analytical techniques for 'light' elements (atomic number less than 10), and chapter 19 deals with the analysis of thin specimens as used in transmission electron microscopy, which is a topic of increasing importance because of the high spatial resolution obtainable by comparison with conventional analysis of thick specimens. Finally examples of applications of microprobe analysis in different fields are described in chapter 20.

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X-ray spectra

INTRODUCTION

1.1 Principles of microprobe analysis

In electron microprobe analysis electron bombardment is used to generate X-rays in the sample to be analysed. From the wavelength and intensity of the lines in the X-ray spectrum the elements present may be identified and their concentrations estimated. The use of a finely focused electron beam gives the technique its peculiar advantage of enabling chemical analyses to be obtained on very small selected areas.

Qualitative analysis (identifying the elements present) requires the spectrum to be recorded by means of an X-ray spectrometer over the range of wavelengths within which relevant lines may be present (1–12 Å). Lines may be identified by reference to tables of wavelengths (see appendix for a selective tabulation, or White and Johnson (1972) for complete tables).

In quantitative analysis the intensities of the X-ray lines from the specimen are compared with those from standard samples of known composition. The measured intensities require certain instrumental corrections dependent on the characteristics of the measuring system, as well as correction for background, the chief source of which is the continuous X-ray spectrum (§1.5). The composition at the analysed point is calculated from the corrected intensities by applying 'matrix corrections' which take account of the various factors governing the relationship between intensity and composition (§1.7).

The electrons typically have a kinetic energy of 10–30 keV, and penetrate the sample to a depth of the order of 1 μm, spreading out laterally to a similar distance. This imposes a lower limit to the analysed area. Improving the spatial resolution further by reducing the electron energy is generally impracticable because the electrons must have sufficient energy for efficient X-ray excitation. For most purposes the resolution is thus limited to about 1 μm.

An understanding of the physics of X-ray production is important for an appreciation of the calculations required for