

**ELECTRON MICROPROBE
ANALYSIS**

S. J. B. REED

ELECTRON MICROPROBE ANALYSIS

S. J. B. REED

*Department of Mineralogy and Petrology
University of Cambridge*



5506397

CAMBRIDGE UNIVERSITY PRESS

CAMBRIDGE

LONDON • NEW YORK • MELBOURNE

5506397

Published by the Syndics of the Cambridge University Press
The Pitt Building, Trumpington Street, Cambridge CB2 1RP
Bentley House, 200 Euston Road, London NW1 2DB
32 East 57th Street, New York, NY10022, USA
296 Beaconsfield Parade, Middle Park, Melbourne 3206, Australia

© Cambridge University Press 1975

Library of Congress catalogue card number: 73-94356

ISBN: 0 521 20466 6

First published 1975

Printed in Great Britain
at the University Printing House, Cambridge
(Euan Phillips, University Printer)

EDTA/01

7086026

ACKNOWLEDGEMENTS

I am greatly indebted to Dr V. E. Cosslett and Mr N. G. Ware for reading the manuscript and offering a number of helpful suggestions, and to Dr T. Mulvey for reading chapter 4. I am also most grateful to Mrs N. Blundell for doing the typing, and Mr P. J. Statham for proof reading.

I acknowledge with thanks permission from the following to reproduce published material: American Society for Testing and Materials (tables A.3-5); Applied Research Laboratories Inc. (plate 5); Cambridge Scientific Instruments Ltd (plates 1, 3, (6); EDAX Inc. (plate 8); Geological Society of America (fig. 20.4); Hermann et Cie (figs. 18.1, 18.3); Institute of Electrical and Electronic Engineers (fig. 9.10); Institute of Physics (figs. 12.4, 18.2, 19.3); Japan Electron Optics Ltd (plate 2); Metallurgical Society of the American Institute of Mechanical Engineers (fig. 20.3); MIT Press (fig. 20.7); Ortec Inc. (plate 7); Pergamon Press Inc. (fig. 20.8); Schweitzerbartsche Verlagsbuchhandlung (fig. 15.6, table 15.6); Tube Investments Ltd (figs. 13.9, 14.7); John Wiley and Sons Inc. (table 14.3).

Finally I wish to express appreciation of the excellent facilities and pleasant surroundings provided by the Australian National University, Canberra, where this book was written during my tenure of a senior research fellowship in the Research School of Earth Sciences.

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 $1\text{ }\mu\text{m}$ 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.

Canberra

August 1973

S.J.B.R.

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 $1\text{ }\mu\text{m}$ 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.

CONTENTS

Acknowledgements page xiv

Preface xv

CHAPTER 1

Introduction

1.1	Principles of microprobe analysis	1
1.2	Characteristic X-ray spectra	2
1.3	Inner shell ionisation	3
1.4	The fluorescence yield	5
1.5	The continuous X-ray spectrum	6
1.6	X-ray absorption	8
1.7	Matrix corrections	9
1.8	Historical notes	10

CHAPTER 2

Essential features of the electron microprobe

2.1	The probe forming system	12
2.2	X-ray spectrometers	12
2.3	The specimen stage	13
2.4	The optical microscope	15
2.5	Scanning	16
2.6	The vacuum system	18
2.7	Specimen preparation	19
2.8	Related techniques	19
2.8.1	Scanning electron microscopy	19
2.8.2	Transmission electron microscopy and analysis	20

CHAPTER 3

The electron gun

3.1	The conventional triode gun	22
3.2	Alignment	22

3.3	Electrical supplies for the gun	<i>page</i> 23
3.4	Bias	24
3.5	Brightness	27
3.6	Stability	29
3.7	High brightness cathodes	31
3.8	The lanthanum hexaboride cathode	32
3.9	Field emission guns	34

CHAPTER 4

The probe forming system

4.1	Demagnification of the electron source	36
4.2	Magnetic lenses	37
4.3	Lens current stability	41
4.4	Spherical aberration	42
4.5	Astigmatism	42
4.6	Apertures	43
4.7	Alignment	45
4.8	Probe diameter and current	46
4.9	Probe current monitoring and stabilisation	49
4.10	Design of the final lens	51
4.11	Unconventional lenses	53

CHAPTER 5

Scanning

5.1	Deflection systems	55
5.2	Scanning electronics	56
5.3	X-ray scanning images	58
5.4	Electron images	60
5.5	Contrast and resolution in electron images	62
5.6	Electron detectors	64
5.7	Colour scanning pictures	66
5.8	Mechanical scanning	67
5.9	Phase analysis	68
5.10	Channelling patterns	69

CHAPTER 6

X-ray diffraction spectrometers

6.1	Bragg's law	<i>page</i> 72
6.2	Reflection by a perfect crystal	73
6.3	Reflection by imperfect crystals	75
6.4	Focusing geometry	76
6.5	Semi-focusing geometry	78
6.6	Fully focusing spectrometers	80
6.7	Diffracting crystals	82
6.8	Soap film pseudo-crystals	86
6.9	Efficiency and resolution	88
6.10	Grating spectrometers	90

CHAPTER 7

Proportional counters

7.1	Principles of operation	94
7.2	Entrance windows	95
7.3	Counter gas	97
7.4	Gas multiplication	100
7.5	Pulse height depression	101
7.6	The output pulse	102
7.7	Ionisation statistics	105
7.8	The anode wire	107
7.9	Escape peaks	108
7.10	Unorthodox proportional counters	110
7.11	Gas proportional scintillation counters	112

CHAPTER 8

Counting electronics

8.1	Counting systems for crystal spectrometers	113
8.2	The preamplifier	114
8.3	The main amplifier	116
8.4	Operation at high count rates	120
8.5	The discriminator and pulse height analyser	120
8.6	Automatic pulse height analysis	122

8.7	The ratemeter	page 124
8.8	The scaler and timer	127
8.9	Dead time	128
8.10	Measurement of dead time	130

CHAPTER 9

Lithium drifted silicon detectors

9.1	Principles of operation	132
9.2	Construction	134
9.3	The cryostat	135
9.4	Energy resolution	138
9.5	Trapping, recombination, and charge collection	140
9.6	Linearity	141
9.7	Efficiency	142
9.8	Peak to background ratio	144
9.9	The silicon escape peak	147
9.10	Ultra-soft X-ray detection	149
9.11	Applications	151

CHAPTER 10

Electronics for lithium drifted silicon detectors

10.1	The FET preamplifier	153
10.2	Preamplifier noise	155
10.3	Preamplifier feedback	156
10.4	Pulse shaping	157
10.5	Pole-zero cancellation	159
10.6	Baseline restoration	160
10.7	Multichannel pulse height analysis	163
10.8	Pulse pile-up	166
10.9	Dead time	170
10.10	Beam switching	172
10.11	The Kandiah system	173

CHAPTER 11

Experimental aspects of quantitative analysis

11.1	Mounting and polishing the specimen	175
11.1.1	Metals	175
11.1.2	Rocks and minerals	177
11.1.3	Biological samples	177

CONTENTS

ix

11.2	The conducting coating	<i>page</i> 178
11.3	Control of the conducting film thickness	180
11.4	Specimen damage under electron bombardment	182
11.5	Carbon contamination	185
11.6	Standards: pure elements and compounds	186
11.7	Metal, mineral and glass standards	188
11.8	Choice of accelerating voltage	189
11.9	Locating points for analysis	191
11.10	Background corrections	192
11.11	Counting strategy	195
11.12	Probe current monitoring	196
11.13	Limits of detection	197

CHAPTER 12

X-ray generation, stopping power, and electron range

12.1	Ionisation cross-section	198
12.2	Characteristic X-ray intensity	199
12.3	Stopping power corrections	202
12.4	The Bethe expression for stopping power	203
12.5	The mean excitation energy	204
12.6	Shell effects	208
12.7	Application of the logarithmic integral function	209
12.8	Electron penetration	211
12.9	Spatial resolution	214

CHAPTER 13

Backscattering

13.1	Elastic scattering	219
13.2	The electron backscattering coefficient	220
13.3	The energy distribution of backscattered electrons	225
13.4	Calculation of X-ray intensity loss	227
13.5	The Monte Carlo technique	228
13.6	Solution of the electron transport equation	232
13.7	Backscattering from compounds	234
13.8	Backscattering correction data	235
13.9	Non-normal electron incidence	237

CHAPTER 14

X-ray absorption

14.1	Theory of the absorption correction	<i>page</i> 240
14.2	Experimental determination of $\phi(\rho x)$ and $f(\chi)$	241
14.3	The Philibert absorption correction	244
14.3.1	The effect of the critical excitation energy	247
14.4	Reuter's version of Philibert's formula	247
14.5	The Andersen-Wittry absorption correction	249
14.6	Other methods of calculating absorption corrections	251
14.7	The Monte Carlo and transport equation methods applied to calculating $\phi(\rho x)$	252
14.8	Non-normal electron incidence	254
14.9	Mass attenuation coefficients	255
14.10	Measuring the incident electron energy	258
14.11	Bishop's 'square model' for $\phi(\rho x)$	260

CHAPTER 15

Fluorescence

15.1	Fluorescence excited by K lines	261
15.2	The absorption term	263
15.3	Data for K-K fluorescence corrections	267
15.4	Correction procedure for K-K fluorescence	268
15.5	Fluorescence excited by K_β radiation	270
15.6	Fluorescence involving L lines	271
15.7	Relative K and L intensities	275
15.8	Fluorescence excited by the continuous spectrum	278
15.9	Absorption of continuum fluorescence	282
15.10	Fluorescence near phase boundaries	284

CHAPTER 16

Practical correction procedures

16.1	Introduction	288
16.2	Example of a correction calculation	289
16.2.1	Absorption	289
16.2.2	Characteristic fluorescence	290
16.2.3	Continuum fluorescence	290

CONTENTS

xi

	16.2.4 Backscattering	<i>page</i> 291
	16.2.5 Stopping power	292
	16.2.6 Total correction factors	292
16.3	Simple iteration	292
16.4	Wegstein's method	293
16.5	Hyperbolic iteration	294
16.6	Alpha coefficients	295
16.7	Data handling	296
16.8	Correction programs	297

CHAPTER 17

Quantitative analysis with a nondispersive detector

17.1	Analytical procedure	299
17.2	Least squares fitting	300
17.3	Procedures applicable to complex spectra	302
17.4	Integration of peaks	304
17.5	Peak shift and broadening	306
17.6	Background: theory	308
17.7	Background corrections	310
17.8	K_{α} overlap	311
17.9	K_{β} overlap	312
17.10	Escape peaks	313
17.11	Iteration	314
17.12	Spectrum stripping	315
17.13	Collimation	315
17.14	Nondispersive analysis with a proportional counter	316

CHAPTER 18

Light element analysis

18.1	Introduction	318
18.2	Problems peculiar to light element analysis	318
18.3	Absorption corrections	320
18.4	The thin film model	322
18.5	The surface intensity ϕ_0	322
18.6	Mass attenuation coefficients	323

CHAPTER 19

Analysis of thin films

19.1	Introduction	<i>page</i> 326
19.2	X-ray generation in thin specimens	327
19.3	Quantitative thin film analysis: Philibert-Tixier method	328
19.4	Quantitative thin film analysis: continuum method	330
19.5	Thickness determination of films on substrates	332
19.5.1	Hutchins' method	334
19.5.2	Bishop's method	335
19.5.3	Reuter's method	337
19.6	Analysis of thin films on substrates	338
19.7	The X-ray intensity loss caused by the conducting coat on nonconducting specimens	338

CHAPTER 20

Applications

20.1	Metallurgy	340
20.1.1	Phase diagrams	340
20.1.2	Intermetallic phases	342
20.1.3	Diffusion	342
20.1.4	Precipitates	345
20.1.5	Nonmetallic inclusions	346
20.1.6	Corrosion	346
20.1.7	Archaeology	347
20.2	Radioactive materials	347
20.3	Electronic materials	348
20.4	Mineralogy	349
20.5	Petrology	352
20.6	Iron meteorites	355
20.7	Stone meteorites	357
20.8	Lunar rocks	359
20.9	Biological and medical research	365
20.9.1	Hard tissues	365
20.9.2	Soft tissues	366
20.10	Bulk analysis with the electron microprobe	367

CONTENTS

xiii

APPENDIX

X-ray spectra

A.1	Atomic structure	<i>page</i>	369
A.2	Origin of characteristic X-rays		370
A.3	Properties of characteristic X-ray spectra		372
A.4	Relative intensities		375
A.5	Satellite lines		376
A.6	Auger effect		377
<i>References</i>			381
<i>Index</i>			396

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