MICROPROBE ANALYSIS

C. A. ANDERSEN

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Edited by C. A. ANDERSEN

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Preface

The invention of the optical microscope greatly increased man's ability to investigate the workings of the world around him. Microscopic studies over the last one hundred years or more have amply demonstrated that most solid materials are complex assemblages of chemically differentiated microstructures. It is self-evident that a thorough understanding of such a material comes only from a thorough understanding of its component parts and their interrelationships. The structural details of these component parts can be studied directly in the sample with optical and electron microscopes. This type of *in situ* study is advantageous because physical relationships of the component parts can be investigated in their undisturbed natural positions and orientations. For the same reasons it is desirable to perform *in situ* chemical analyses. This provides chemical information on the microstructure under observation and thus permits discovery of its chemical identity and of possible compositional variations and/or concentration gradients that might exist between various different microstructures. Also it eliminates the laborious, and in some cases impossible, task of physically separating enough of the microscopic components of one type for analysis by the more conventional chemical methods and reduces the risk of experimentally contaminating these components and invalidating the analysis.

In 1951 Professor R. Castaing made an extremely important contribution in the area of *in situ* chemical analysis when, while studying under Professor A. Guinier at the University of Paris, he developed the electron probe

microanalyzer. This instrument operates by exciting the characteristic x-ray spectrum in a microvolume of sample as small as a few cubic microns by using a finely focused beam of electrons. Generally from this instrument and the fertile minds of many other investigators a new class of microanalytical instrumentation has developed. There is no doubt that this type of instrumentation is having a great impact on the various fields of solid materials science. This statement is confirmed by the large number of such instruments put into worldwide service in their brief commercial history: approximately 800 electron microprobes in about 15 years at a price in excess of $100,000 apiece, approximately 50 laser microprobes in about 10 years at a price in excess of $25,000 apiece, and approximately 25 ion microprobes in about 5 years at a price in excess of $200,000 apiece. The future impact will be even greater as the contribution direct microanalysis makes to our total comprehension of the behavior of all solid materials is appreciated.

The basic theme of this book is the analysis and characterization of the microstructures of heterogeneous materials using microprobe instrumentation. The characterization is by means of morphology, chemistry, and crystallography. The three main classes of such instrumentation in general use today, in other words, the electron, laser, and ion microprobes, are discussed in relationship to their various fields of application. Common to all these modes of analysis are the problems of sample handling, analytical approach, and interpretation of data. It is hoped that this book will help to delineate the special advantages and areas of application of each of the techniques and instruments. The chapters on instrumentation give general descriptions of the basic instruments and emphazise the areas of instrumentation that are of vital importance to producing a reliable analysis. A special chapter on the important topic of high resolution scanning electron microscopy has also been included. The chapters on basic principles and analytic methods describe the fundamental principles upon which the analysis is based and discuss the models for quantitative interpretation of the data. The chapters concerned with applications review the types of problems that have been investigated and the contributions that have been made in each field. The chapters on special topics and techniques review the particular contributions of these methods to microanalysis. Where required for reliable analysis, individual chapters include special discussions of instrumentation, principles of analysis, sample handling and/or standardization. A study of this book should allow an investigator to select the most appropriate method of analysis for his particular problem.

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Goleta, California
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Contents

CHAPTER

ELECTRON MICROPROBE

1. Electron Microprobe Instrumentation 1

R. Fitzgerald

2. Principles of X-Ray Generation and Quantitative Analysis with the Electron Microprobe 53

S. J. B. Reed

3. High-Resolution Scanning Electron Microscopy of Surfaces 83

A. N. Broers

4. Applications of the Electron Microprobe to Solid-State Electronics 123

D. B. Wittry

CHAPTER

5. Applications of the Electron Microprobe in Geology 189
K. Keil

6. Applications of the Electron Microprobe in Ceramics and Glass Technology 241
W. T. Kane

7. Applications of the Electron Microprobe to the Analysis of Biological Materials 271
W. L. Robison

8. Applications of the Electron Microprobe to the Analysis of Free Particulates 323
M. Bayard

9. Applications of Soft X-Ray Spectroscopy to Chemical Bonding Studies with the Electron Microprobe 349
E. W. White

10. Applications of Cathodoluminescence in Electron Microprobe Analysis 371
R. N. Kniseley and F. C. Laabs

11. A Practical Examination of the Kossel X-Ray Diffraction Technique 383
H. Yakowitz

LASER MICROPROBE

12. Laser Microprobe Instrumentation 423
I. Harding-Barlow, K. G. Snetsinger, and K. Keil

13. Applications of the Laser Microprobe to Geology 457
K. Keil and K. G. Snetsinger

CHAPTER

14. Application of the Laser Microprobe to the Analysis of Biological Materials 477

I. Harding-Barlow and R. C. Rosan

15. Application of the Laser Microprobe to the Analysis of Metals 489

M. Margoshes

ION MICROPROBE

16. Ion Microprobe Instrumentation 507

C. F. Robinson

17. Analytic Methods and Applications of the Ion Microprobe Mass Analyzer 531

C. A. Andersen

Index 555

CHAPTER ONE

Electron Microprobe Instrumentation

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BRIEF HISTORICAL BACKGROUND

Interest in using characteristic x-rays for chemical analysis arose as a result of Moseley's historical work in 1913 on the relationship between an element's characteristic wavelength and atomic number [1]. The most notable early work is that of Von Hevesy during the 1920s and, in particular, the discovery and identification of hafnium (72) by Coster and Von Hevesy in 1923 [2]. Instrumentation specifically designed to furnish localized chemical information was described by Hamos in 1938 [3]. His device incorporated a large-area primary x-ray beam for excitation and a special focusing x-ray spectrometer to produce an image of the specimen on a photographic plate. The image was formed by characteristic radiation with approximately 50 μm point-to-point resolution.

Focusing an electron beam to small diameters (<1 μm) to produce localized specimen excitation was first proposed by Hillier in a patent issued in 1943, but this idea was not actively pursued [4]. However, in 1949, Castaing and Guinier demonstrated the first instrument utilizing a focused electron beam and x-ray spectrometer designed specifically for localized

quantitative element analysis. Castaing subsequently formulated theory and described methods of using pure elements as a means of calibrating the instrument [5, 6].

Numerous detailed descriptions of focused electron beam instruments (microprobe and scanning microscope) appeared in the literature in the last decade. A literature survey* shows that there are as many design concepts as there are different commercial and "one-of-a-kind" instruments, brought about by attempts to design for all aspects of performance with maximum flexibility and least compromise. This becomes a formidable task!

In existing design proposals it is evident that most compromises occur in the space to be occupied by the specimen. This area is occupied by a physically bulky final electron lens with an aperture holder and scanning coils, a mechanically complex specimen stage and, in most instances, visual light optics [7]. This mechanical design must also include multiple ports through which different detectors can simultaneously view the electron impact point at various preferred angles above the specimen surface. Besides precision electron optics and power supplies needed for focusing the electron beam to small sizes, the design must also incorporate special electronics to generate scanning images by sweeping the electron beam across the specimen surface [8]. Electron excitation produces a number of useful signals such as secondary and backscattered electrons, specimen current, cathodoluminescence and x-rays, all of which are useful to the analyst in the investigation of unknown specimens. Multiple data channels and devices to record all of these signals comprise a large electronic system. Instrumentation becomes even more complex when used for special applications such as microdiffraction Kossel line (transmission and reflection) [9, 10], electron diffraction [11], transmission electron imaging [12], handling of highly radioactive specimens [13], x-ray projection microscopy [14, 15], particle and size determinations by electron beam scanning under computer control [16], and others.

Before proceeding, it is interesting to note the fundamental differences between the microprobe and the scanning electron microscope (SEM), the two most common instruments. Both modern instruments provide a scanning electron beam to produce high resolution secondary electron images and a stationary electron beam to produce a quantitative element analysis of a single point on the specimen by detection of characteristic x-rays.

Historically the microprobe has been engineered as an analytical x-ray instrument incorporating up to four or five wavelength spectrometers for the simultaneous chemical analysis of several elements. A prime design goal is to

*A bibliography compiled by K. F. J. Heinrich lists papers which are related either directly or indirectly to electron microanalysis.

have the x-ray spectrometers view the excited x-ray volume from a high angle ($>30°$) with respect to the specimen surface. This reduces one predominant x-ray data correction (x-ray absorption) and lessens the effects of surface topography [17]. A low depth of field light microscope ($\sim 500\times$) is incorporated so that the position of the specimen surface can be visually adjusted to the focal point of the wavelength spectrometers. Both considerations are extremely important in quantitative analysis and can become limiting factors with respect to accuracy and precision. The light microscope has a secondary function of aiding the analyst in locating areas of interest in complex specimens by providing a familiar light image.

Electron beam scanning was added to the microprobe to facilitate faster specimen surveying for element distributions and higher point-to-point resolution by detecting backscattered electrons [18]. Subsequent improvements in the electron probe size (~ 250 Å), and the addition of secondary electron detection, has added "SEM" capability to the microprobe.

In contrast, the SEM is designed primarily as a high magnification microscope (useful magnification up to $100{,}000\times$) for study of specimen surfaces [19]. Fortuitously, a recent improvement in x-ray energy spectrometers has added, with little modification to the instrument, simultaneous elemental analysis capabilities to the microscope [20]. Therefore, distinction between the two instruments is not easily defined in terms of possible end results or information received by the analyst. Each instrument then might be characterized by the mode of operation in which it excels.

CHAPTER PURPOSE AND CONTENT

This chapter is directed toward the prospective analyst whose field of interest may be far removed from instrumentation using an electron beam for microinvestigation, but who wishes to use the technique to obtain microchemical analytical data. The most arduous aspect of this type of microinvestigation is quantitative element analysis. This is due to the required high accuracy and long measurement times needed for each determination that is further complicated by errors generated within instrumentation and inherent in the method. Performance and method of operation of the instrument play a major role in obtaining accurate x-ray intensity ratios between specimen and standard.

Therefore the emphasis will be on areas which need special attention and on the basic description and operational procedures of the electron beam column and x-ray detection system. These two subjects will be developed in as general and simplified a form as possible, and will be directed towards the

practical situation of instrument operation. The description of these instrument sections will stress the parts which require the analyst's attention during operation. In some cases, these may pertain to adjustments that optimize the instrument, in others, to operational procedures that overcome or reduce instrumental errors. For extended study in the fields of electron optics and x-ray physics, the reader is directed to the reference list.

GENERAL DESCRIPTION

Both instruments (microprobe and SEM) can be logically subdivided into three parts, each with a distinct function: (1) electron beam forming, (2) specimen handling, and (3) signal detection and recording.

Electron Beam Forming Section

The function of the electron beam forming section is to generate an energetic small diameter electron beam that can be projected on and subsequently interacted with the specimen material. In doing so however, the design and operation must be such that for a given beam diameter, sufficient electron current is present upon the specimen to create useful signal levels.

Physically this part of the instrumentation consists of an electron source (electron gun) which emits accelerated electrons, and an electron optical system which demagnifies the electron source produced in the gun. Associated with these elements are electronic power supplies, electron beam scanning circuits, and a vacuum system.

A vacuum on the order of 10^{-5} torr is required in the instrument to minimize the probability of interaction between gas molecules and the beam electrons. This prevents drift in the beam current caused by vacuum fluctuations and enlargement of the electron beam due to scatter. The mean free path length of a gas molecule at 10^{-5} torr is approximately four times the length of a normal beam column ($\sim$1 meter). It is also important to have a good vacuum surrounding the specimen. A better or cleaner vacuum will lower the deposition rate of disassociated hydrocarbons which form as a layer at the electron impact point. The beam electrons lose energy as they pass through such a layer. In addition a false carbon x-ray signal is generated. Contamination rates vary on different materials, which could alter the effective incident electron energy between a standard and a specimen and thereby produce an error in their x-ray intensity ratio. The analyst can check the magnitude of this error by monitoring the x-ray intensities as a function of time. The rate of intensity loss depends on the energy of the

analytical line measured and therefore differs for each element. The difference between the rate of intensity loss of the standard and the specimen, if not large (<5%), can be satisfactorily corrected by extrapolating the intensity ratios to zero time. Cooled surfaces (−135°C) in the specimen chamber effectively reduce the contamination problem [21].

Basically the analyst operates the electron beam in two modes: stationary and scanning. The use of a stationary electron beam is primarily for quantitative elemental analysis of a single microvolume (1–10μm^3) in the specimen. Approximate element concentrations are derived by comparing the specimen's characteristic x-ray line intensities with those of standards of known composition. These uncorrected line intensity ratios (k) are generally within 25% of the true value for element concentrations above 10%. Correcting the k values for nonlinearities in characteristic x-ray generation and absorption produced by the specimen material will reduce these errors to ±2% [22].

Instrumental errors, however, that are inherent in the technique or due to instrumental instabilities and nonlinearities must be recognized and corrected before those associated with the specimen material can be accurately corrected. Precision and accuracy of the measured x-ray intensity ratio (k = specimen/standard) depend on: (1) proper specimen and standard preparation; (2) ability of the specimen to withstand heat and a vacuum environment; (3) incident electron current and position stability of the electron beam; (4) measurement of standard and specimen contamination rate; (5) accurate positioning of the specimen surface with respect to the focal circle of the wavelength spectrometers; (6) accurate measurement of the electron beam energy; (7) ability to correct for wavelength and intensity shifts between low energy characteristic x-ray lines; (8) stability and linearity of the x-ray detection system; (9) correct measurement of the x-ray line and background intensities; (10) statistical accuracy in the collected x-ray data; and (11) well characterized standards.

Exact electron beam operational parameters depend on the elements to be analyzed, spatial resolution required, and counting capabilities of the x-ray detection system. Nevertheless, the range of operating conditions can be generalized as: (1) accelerating potential E_0: 5–30 kV (the exact value depends on the critical excitation energy (E_c) of the highest energy line used in each measurement. For adequate x-ray production E_0 should be 1.5 to 2 times E_c); (2) incident specimen current: 10^{-9} to 10^{-7} amp (the exact value depends on the beam size, collection efficiency, linear count rate range of the x-ray spectrometers, and thermal properties of the specimen material); and (3) electron probe diameter: ≥ 0.5 μm.

The stationary electron beam mode is also used to obtain the complete

x-ray spectrum by scanning the wavelength spectrometers through their entire wavelength range. The x-ray intensity as a function of wavelength is usually recorded on multiple strip chart or *x-y* recorders.

The scanning electron beam mode generates the necessary continuous pattern of excited volumes on the specimen surface for production of scanning images. This is accomplished by electrically scanning the focused electron beam across the specimen surface in a series of lines similar to the way a reader's eyes scan a printed page (i.e., left to right from top to bottom). Quanta generated at each point on the specimen by the moving beam are detected and displayed as a contrast on a similarly scanned cathode ray tube. As latter discussed, this two-dimensional image on the cathode ray tube can graphically display the topography, the average atomic number, or the elemental distribution in the specimen, depending on the signal used.

Beside generating two-dimensional images for photographing, the scanning mode is extremely useful for guiding the stationary beam to an exact point on the specimen. The analyst first views an image (secondary, backscattered electron, or specimen current) and determines the point of analytical interest. Then switching to the stationary mode and moving the spot on the CRT by adjusting manual X and Y position controls, the analyst can cause the electron beam to coincide exactly with the desired point on the specimen. This method provides the advantage of viewing the specimen at higher magnifications (1000–3000×) than possible with the light microscope (~500×). In addition, electrically deflecting the electron beam in lieu of translating a mechanical specimen stage provides a more precise movement of the excited x-ray volume. However caution should be exercised as beam deflections that cause the x-ray source at the specimen to leave the focal point of the wavelength spectrometers may result in a loss in x-ray intensity.

Specimen Handling

The specimen handling section includes a specimen chamber vacuum interlock valve, a specimen stage, and in the case of instruments equipped with wavelength spectrometers, visual light optics. In some instances the stage is removed from the instrument for specimen loading; in others the specimen is introduced to the stage through a port in the specimen chamber. To facilitate rapid specimen exchange, the specimen chamber is ordinarily separated from the main vacuum system by a vacuum valve. This maintains the stability of the electron beam as it permits the column to be operational during specimen exchange and also eliminates the likelihood of introducing foreign particles into the electron optics.

The specimen stage incorporates a number of translation motions

which the analyst operates manually from outside the vacuum chamber. Commonly, two mutually perpendicular translations (X and Y) are used to direct and position the specimen under the electron beam. Also, depending on stage design, a fast rotation about the center of the specimen holder may be incorporated to facilitate rapid movement between specimen quadrants. This motion, in conjunction with the X and Y controls, allows any arbitrary axis on the specimen's surface to be aligned with either one of the X or Y translations, or with one of the electron beam scanning directions. A second rotation about the electron beam impact point is used for visual mineral identification by polarized light measurements, provided the instrument is equipped with an integral light microscope. Due to the stringent focusing requirements of wavelength spectrometers, the specimen must also translate parallel to the electron beam axis (focus or working distance). This degree of freedom, in conjunction with the low depth of field (<3 μm) light optics, assures the analyst that the excited x-ray volume is focused exactly on the focal circle of the wavelength spectrometers. In fact, it may be necessary to optically refocus the specimen for each new point of analysis for careful quantitative work. This motion (working distance) is also used to vary scanning magnification over a large range. Scanning microscope stages are generally more complicated than those normally used in microprobes. Specimen tilt about an axis perpendicular to the electron beam is incorporated to increase the secondary electron signal level by optimizing the electron beam–specimen–detector geometry.

Signal Detection and Recording

The third part of the instrument is the signal detection–recording section which contains five basic channels of information, that is, three electron and two photon signals. Each channel consists of a detector or a collector plus amplifying, display, and recording electronics. The display and recording of information from each channel is accomplished by oscilloscopes, chart recorders, and scalers with printer output. In addition, for rapid x-ray data correction, computer entry equipment such as a paper tape, cardpunch, magnetic tape, or on-line direct computer interface electronics may be employed. The choice of what type of readout to use lies partly with the analyst. The analyst should choose those forms of readout that supply him with the maximum amount of accurate information in the shortest period of time.

As pointed out, the microprobe x-ray detection system classically consists of multiple wavelength spectrometers and therefore requires duplication of x-ray channels; in some instruments there are as many as five. In addition to the above signals, an electron current channel that monitors