Preface to the Second Edition

The purpose of this book is to discuss X-ray microanalysis and computer-aided imaging at a level that promotes an understanding beyond merely “how-to” texts, but without overwhelming the reader with volume or complexity. No attempt is made to replace a full textbook for either technique. Rather, this volume is meant to be an introduction for newcomers to the fields and a reference for experienced microscopists to be reviewed as needed. More in-depth texts and articles, which include derivations of the mathematical relationships, are given as references for those who desire such information. Several tables and diagrams of relevant information are provided for quick reference.

X-ray microanalysis is a mature technique, whose fundamentals are discussed in detail along with the latest developments in the field. Qualitative and quantitative elemental analysis can be done routinely, as long as reasonable care is taken in selecting the conditions. To guide the analyst, essential relationships among the variables are described. These relationships must be understood, at least qualitatively, to achieve meaningful results. The precision and accuracy of the technique depend on various factors, many of which are under operator control. Because these statistical concepts are often misunderstood, I have included a chapter specifically on this subject, with definitions of statistical terms. Another chapter covers those aspects of microscope operation that relate to X-ray and digital image collection only.

Computer-aided imaging, on the other hand, is a rapidly growing field that naturally complements X-ray microanalysis on an electron microscope. As PCs have become more powerful, more operations can be done with software alone, and application-specific software is available to perform many of the tasks common in microscopy. In this book, I have attempted to cover the essentials of image analysis and some image processing as it is performed on images of microstructures. The distinct imaging functions of gathering information and then displaying it, graphically and numerically, are specifically addressed and illustrated with examples.

In this edition, the section on X-ray detectors has been updated to include silicon, germanium, and silicon drift detectors. Microcalorimeters are mentioned but not discussed further, because of their limited availability. The chapters on computer-aided imaging and X-ray mapping have been expanded, particularly the section on full spectrum methods, such as spectrum imaging and position-tagged spectrometry. The editorial assistance of Pat Friel and Marie Brezina is very much appreciated.

John J. Friel
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I. INTRODUCTION

X-ray microanalysis and digital image analysis are powerful, yet easy to use, techniques for revealing information from a small area of a specimen. X-ray microanalysis in an electron beam instrument such as a scanning electron microscope is capable of analyzing elements heavier than or equal to beryllium with spatial resolution of a few cubic micrometers. Although there are other spectroscopic and microanalytical techniques each with its own specific advantages, none are better than X-ray microanalysis for routine chemical analysis of small volumes. When X-ray analysis is combined with digital image analysis, one has a potent tool for understanding the composition and structure of materials or biological specimens.

The technique consists of detecting the characteristic X-rays that are produced by bombarding a solid specimen with high-energy electrons. Detection of these X-rays can be accomplished by an energy dispersive spectrometer, which is a solid-state device that discriminates among X-ray energies. Or it can be done with a crystal spectrometer that uses a diffracting crystal to select the wavelength of interest. The former method is called energy-dispersive spectroscopy (EDS), and the latter is called wavelength-dispersive spectroscopy (WDS), referring to the manner in which X-rays are distinguished.

It is possible to use either technique on any electron beam instrument capable of forming a probe; however, WDS is used primarily on electron microprobes, while EDS is dominant on scanning and transmission electron microscopes, including analytical electron microscopes. Both spectroscopic methods are capable of performing analysis of elements beginning with beryllium or boron in the periodic table, provided a suitable light element X-ray window is used. The low-energy limit is determined by the entrance window material and interference from noise, and the high-energy limit is determined by the energy in the electron beam.

One feature of electron beam microanalysis that describes the power of the technique is its absolute mass sensitivity. For example, it is often possible to detect less than $10^{-19}$ grams of an element in a thin sample and less than $10^{-13}$ grams in a microvolume of a bulk sample. Suitable quantification routines are available to convert the raw X-ray counts into elemental concentration, by use of standards or standardless methods. Moreover, since it is performed on a microscope, the chemical analysis can be related to other imaging signals and thus is complementary to image analysis.

X-ray microanalysis is routinely used by materials scientists for both qualitative and quantitative analysis of microstructures. It is also used by biologists to localize elements such as calcium, potassium and phosphorus, and to measure their concentration. In the description of the fundamentals of X-ray microanalysis that follows, the energy-dispersive technique is emphasized because there are many more of this type of instrument in use. WDS is also described, and much of the information applies equally to both methods. This document provides a brief, simplified description of the technique, both for the many newcomers continually entering the field as well as those looking for a quick review. It also provides a description of the capabilities of digital imaging, emphasizing image analysis over image processing.

For experienced users, there are tables of information, such as image analysis formulas, as well as definitions and equations that can be useful as a quick reference in the nature of a handbook.
Other Microanalytical Techniques

To place X-ray microanalysis in its proper place among microanalytical techniques, Table 1.1 lists microanalytical techniques with their input beam and output signals. The performance values listed are intended to be the best that are reasonably achievable. Under some circumstances, some laboratories might be able to do better. A review of materials characterization techniques beyond microanalytical ones can be found in Wachtman (1993).

Table 1.1 List of Various Microanalytical Techniques

<table>
<thead>
<tr>
<th>Method Name*</th>
<th>Input Beam</th>
<th>Output Signal</th>
<th>Lateral Resolution</th>
<th>Depth Resolution</th>
<th>Detection Limit</th>
<th>Lightest Element/ Imaging</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEM/EDS</td>
<td>Electrons (0.5-30 keV)</td>
<td>X-rays (&gt;100eV)</td>
<td>~1 µm</td>
<td>~1 µm</td>
<td>1000 ppm</td>
<td>Be/yes</td>
</tr>
<tr>
<td>EPMA/WDS</td>
<td>Electrons (0.5-50 keV)</td>
<td>X-rays (&gt;100eV)</td>
<td>~1 µm</td>
<td>~1 µm</td>
<td>100 ppm</td>
<td>Be/yes</td>
</tr>
<tr>
<td>AEM/EDS</td>
<td>Electrons (100-400 keV)</td>
<td>X-rays (&gt;100eV)</td>
<td>~5-10 nm</td>
<td>10-100 nm</td>
<td>1000 ppm</td>
<td>B/yes</td>
</tr>
<tr>
<td>AEM/PEELS</td>
<td>Electrons (100-400 keV)</td>
<td>Electrons (50 eV - E₀)</td>
<td>~1 nm</td>
<td>1-20 nm</td>
<td>10-100 ppm</td>
<td>Li/yes</td>
</tr>
<tr>
<td>AES/SAM</td>
<td>Electrons (1-3 keV)</td>
<td>Electrons (&lt;200 eV)</td>
<td>~50 nm</td>
<td>~3 nm</td>
<td>0.1-1 at%</td>
<td>Li/yes</td>
</tr>
<tr>
<td>XPS</td>
<td>X-rays (1-1.5 keV)</td>
<td>e⁻(&gt;10 eV)</td>
<td>1000 µm</td>
<td>&lt;3 nm</td>
<td>1000 ppm</td>
<td>He/yes</td>
</tr>
<tr>
<td>SIMS</td>
<td>Ions (4-15 keV)</td>
<td>Ions</td>
<td>1 µm</td>
<td>0.1 nm</td>
<td>1 ppb</td>
<td>H/yes</td>
</tr>
<tr>
<td>PIXE</td>
<td>H⁺, H++ (2-15 meV)</td>
<td>X-rays</td>
<td>2 µm</td>
<td>10 µm</td>
<td>1-100 ppm</td>
<td>Na/yes</td>
</tr>
<tr>
<td>Atom Probe</td>
<td>Atom Extraction</td>
<td>Atoms</td>
<td>Atomic</td>
<td>Atomic</td>
<td>One atom</td>
<td>H/yes</td>
</tr>
<tr>
<td>RBS</td>
<td>H⁺, H++ (2-15 meV)</td>
<td>H⁺, H++</td>
<td>1 mm</td>
<td>10 nm</td>
<td>1-1000 ppm</td>
<td>Li/no</td>
</tr>
<tr>
<td>Micro IR</td>
<td>Infrared light</td>
<td>Infrared light</td>
<td>10 µm</td>
<td>N/A</td>
<td>N/A</td>
<td>yes</td>
</tr>
</tbody>
</table>
Table 1.2 Comments and Advantages of Microanalytical Techniques

<table>
<thead>
<tr>
<th>Method Name*</th>
<th>Comments/Advantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEM/EDS</td>
<td>Routine specimen preparation, rapid</td>
</tr>
<tr>
<td>EPMA/WDS</td>
<td>Quantitative analysis</td>
</tr>
<tr>
<td>AEM/EDS</td>
<td>Normal thickness TEM specimens, high spatial resolution</td>
</tr>
<tr>
<td>AEM/PEELS</td>
<td>Very thin specimens required, light element analysis</td>
</tr>
<tr>
<td>AES/SAM</td>
<td>Quantitative surface analysis, depth profiles</td>
</tr>
<tr>
<td>XPS</td>
<td>Chemical shift</td>
</tr>
<tr>
<td>SIMS</td>
<td>Depth profiles, best element sensitivity</td>
</tr>
<tr>
<td>PIXE</td>
<td>Analytical sensitivity, depth profiles</td>
</tr>
<tr>
<td>Atom Probe</td>
<td>Sharp needle specimen required, atomic resolution</td>
</tr>
<tr>
<td>RBS</td>
<td>Non-destructive depth profiles</td>
</tr>
<tr>
<td>Micro IR</td>
<td>Molecular spectroscopy</td>
</tr>
</tbody>
</table>

*SEM/EDS = scanning electron microscope/energy-dispersive spectrometer  
EPMA/WDS = electron probe microanalyzer/wavelength-dispersive spectrometer  
AEM/EDS = analytical transmission electron microscope/energy-dispersive spectrometer  
AEM/EELS = analytical transmission electron microscope/parallel collection energy loss spectrometer  
AES/SAM = Auger electron spectrometer/Scanning Auger microscope  
SIMS = Secondary ion mass spectrometer  
PIXE = proton induced X-ray emission  
RBS = Rutherford backscattering

**Brief History**

It has long been known that X-rays emitted from excited atoms have an energy characteristic of the elements that produced them (Moseley, 1913). With the development of transmission electron microscopes (TEMs) in the 1930s and 1940s, attempts were made to excite specimens with electrons and measure the X-rays produced. But it was not until Castaing (1951) described the first static beam electron microscope in his Ph.D. thesis that X-ray microanalysis really became a reality. He even conceived of the corrections that would be necessary to quantify elemental concentration from X-ray intensity. To measure the intensity, he used a crystal spectrometer to disperse the X-rays on the basis of their wavelength, the technique we now call wavelength dispersive spectroscopy (WDS). The first commercial electron probe microanalyzer (EPMA) was built by Cameca in 1956, and others soon followed.

At the same time, the scanning electron microscope (SEM) was being developed by Cosslett and Dun-cumb (1956) in Cambridge, England. But it was not until the early 1960s that the first commercial SEM was built. At about the same time, correction procedures were developed to implement the concepts necessary for quantitative microanalysis originally proposed by Castaing (e.g. Philibert, 1963). SEMs and EPMA's...
generally maintained separate places, with the electron probe microanalyzer used for X-ray analysis, and the SEM for high quality imaging. Nowadays there is less of a distinction between the two, and either can provide a high quality image or a quantitative analysis.

Concurrent with the development of microbeam instruments, solid-state X-ray detector technology was advancing. A diode of lithium-drifted silicon, Si(Li), was used to detect X-ray photons of different energies virtually simultaneously. Analytical systems were developed capable of performing simultaneous analysis of all elements, limited only by transmission through the beryllium entrance window (~1 keV). No diffracting crystal was required to tune the system to the element of interest, as in the case of WDS systems. This was a promising feature for qualitative analysis on microanalyzers, and Fitzgerald, Keil and Heinrich (1968) described the early use of one on an EPMA. Moreover, the high efficiency of these detectors and their rapidly improving resolution made them attractive for application on SEMs where small probe sizes, necessary for optimal image resolution, produced low X-ray count rates. The first installation of a silicon detector on an SEM was by Princeton Gamma-Tech in 1968.

During the 1970s, the number of SEMs with solid-state X-ray detectors grew rapidly, as those who bought the microscope for its imaging versatility learned the value of microanalysis. Elemental analysis using these detectors, initially called non-dispersive analysis, became more precisely known as Energy-Dispersive X-ray Spectroscopy (EDS). The improvement in resolution of the spectrometers progressed, and resolutions of <130 eV are now standard. It also became commonplace for electron probe microanalyzers to be equipped with EDS systems for routine rapid X-ray analysis. Transmission electron microscopes combined with EDS systems became powerful tools for analysis of small particles and biological specimens. Scanning transmission electron microscopes opened new frontiers in small volume, high sensitivity analysis. Those instruments optimized for microanalysis are referred to as analytical electron microscopes (AEMs).

As an alternative to lithium-drifted silicon, high-purity germanium (HPGe) has sometimes been used for X-ray detection, in addition to its use for high-energy gamma-ray detection. Germanium is more efficient than silicon at higher X-ray energies, and it has inherently higher resolution. Barbi and Lister (1981) compared the two detector materials, and concluded the HpGe was not suitable for analysis of elements lighter than sulfur. However, later development of germanium detectors has made them useful for all energies (Cox et al., 1988). Sareen (1995) reviewed the use of HpGe detectors in microanalysis, and Darken and Cox (1995) described ongoing work and compared HpGe with Si(Li) X-ray detectors.

The development of EDS systems has been strongly linked to advances in computer technology. Early systems used multi-channel analyzers (MCAs) to store and manipulate spectra. As mini- and microcomputers became more powerful and less expensive, progressively more computer power was incorporated into the EDS system. Spectra are no longer stored in an MCA, but in computer memory for rapid recall and processing. The EDS computer can control the electron beam for digital imaging or even control many of the microscope functions.

One of the more recent significant developments in the field of EDS was reported by Mott et al. (1995, 1999), and it involves the ability to store an entire spectrum at every pixel in the image. From the 3-dimensional data structure created by position-tagged spectrometry (PTS), it is possible to extract maps for any element and spectra from any region.
II. ELECTRON-SPECIMEN INTERACTION AND X-RAY GENERATION

Electron Scattering

Electrons in the primary beam can interact with atoms in the specimen in many ways, which can be used to gain information through spectroscopy. These interactions can be divided into elastic and inelastic scattering of the electrons. Elastic scattering refers to a change in trajectory without loss of energy. Back-scattering of electrons, for example, is such an event. Inelastic scattering refers to a loss of energy of the electron with little change of direction. The production of secondary electrons, X-rays (both characteristic and continuum), and Auger electrons, for example, are such events. Some of the signals produced by these processes and used for imaging are summarized in Chapter VIII, “COMPUTER-AIDED IMAGING” on page 63.

This section, however, is confined to those signals used for spectroscopy—mostly X-rays. When an electron of sufficient energy strikes an atom, an inner shell electron may be ejected. To return the atom to its lowest energy state, an outer shell electron (of greater energy) fills the vacancy in the lower energy shell. In so doing, energy equal to transitions that occur within the atom is released either as an X-ray or Auger electron. The rest of the energy is deposited by other inelastic interactions with the specimen such as continuum X-ray generation and phonon excitation resulting in specimen heating.

Ionization Cross Section

The probability that an energetic electron will ionize an atom depends on the atom, the line to be excited, and the overvoltage. For high overvoltages, the probability (ionization cross section) can be quite small; consequently, few atoms are ionized, thus few X-rays or Auger electrons are produced. The units of cross section are area, usually cm$^2$, but this concept should not be confused with atomic or ionic radius.

Figure 2.1 X-ray production using Bohr model of the atom.
Characteristic X-rays

Figure 2.1 illustrates characteristic X-ray generation using a simplified model of the atom. When an electron of sufficient energy, commonly a few kilovolts, strikes the atom and ejects a tightly bound K-shell electron, an electron from a higher shell may drop to fill the K-shell. When this happens, for example, an L-shell electron may drop to fill the K-shell, lowering the energy of the atom and emitting Kα X-radiation in the process. If an electron from the M-shell fills the K-shell vacancy, Kβ X-radiation will be emitted. Similarly, if an L-shell electron is ejected and an electron from the M-shell fills the vacancy, Lα radiation will be emitted. Within a given shell, there may be electrons in orbitals that do not possess exactly the same energy because of bonding effects. Accordingly, small variations in energy called chemical shifts occur within α or β radiation. The Kα peak actually comprises the Kα1 and Kα2 X-rays. These are very close together and unresolved in an EDS system so that a Kα1,2 doublet is seen as the Kα peak at an energy between the two individual components and an intensity corresponding to a weighted average as follows:

\[ \frac{2K\alpha_1 + 1K\alpha_2}{3} \]

(Equation 2.1)

The most probable transition when a K-shell vacancy is created is the L to K transition, because these are adjacent energy shells. Therefore Kα radiation will always be more intense than Kβ radiation. It also follows that Kβ radiation will be of higher energy than Kα radiation, inasmuch as the energy difference between the M and K shells (Kβ radiation) is greater than the energy difference between the L and K shells (Kα radiation).

To ionize an atom, the incoming electron or ionizing radiation must possess a minimum amount of energy. That energy is the binding energy of the particular inner shell electron, which is a specific, characteristic energy for each electron in the atom. The binding energy for a K-shell electron, for example, is greater than that of an L-shell electron, since the K-shell electron is closer to the nucleus and more tightly bound. Therefore, if sufficient energy exists in the incident beam to excite K X-rays, L and M X-rays will also be excited if these shells and the one above them are occupied. The discrete and specific energy requirement necessary to excite any given X-ray line is called the absorption edge energy, or critical excitation potential. It is always slightly greater in energy than the corresponding X-ray emission line. As a consequence, one must select an accelerating voltage on the microscope that is greater than the absorption edge energy of the line intended for analysis. In practice, one must exceed this minimum energy by a comfortable margin, preferably by a factor of 1.5 to 3, to efficiently excite the X-ray line with an electron beam.

The energy difference between adjacent electron shells becomes less, progressing outward from the nucleus. It follows that the energy released upon electron transitions between adjacent shells in the outer shells is less than that released for inner shell transitions. That is, for a given atom, Mα radiation will be of lower energy than Lα radiation, which in turn will be of lower energy than Kα radiation.

Moseley’s Law

The energy of the characteristic radiation within a given series of lines varies monotonically with atomic number. This is Moseley’s Law (Moseley, 1913), expressed by Equation 2.2:

\[ \sqrt{E} = C_1(Z - C_2) \]

(Equation 2.2)
where:

- $E$ = energy of the emission line for a given X-ray series (e.g. Kα)
- $Z$ = atomic number of the emitter
- $C_1$ and $C_2$ are constants

For qualitative chemical analysis, if the energy of a given K, L or M line is measured, then the atomic number of the element producing that line can be determined. The energies for K, L and M lines are plotted as a function of atomic number in Figure 2.2. A table of the most frequently encountered X-ray lines and absorption edges is located in the Appendix. A more complete listing of emission lines can be found in a tabulation published by ASTM (Johnson and White, 1970). The ASTM tables are particularly useful when heavy elements are being analyzed, since many unfamiliar M and L lines may be encountered with the high Z elements.

![Figure 2.2 Variation of energy of characteristic X-ray lines as a function of atomic number.](image)

Figure 2.2 Variation of energy of characteristic X-ray lines as a function of atomic number.

Figure 2.3 shows a series of K lines from Na to Zn in which the intensities are typical of what one would see in an EDS spectrum.

![Figure 2.3 Synthetic EDS spectrum showing the relative intensities of the Kα lines of elements from Na to Zn.](image)

Figure 2.3 Synthetic EDS spectrum showing the relative intensities of the Kα lines of elements from Na to Zn.
Fluorescence Yield

The fraction of ionizations that actually result in X-rays emitted from the atom is called the fluorescence yield ($\omega$). The fraction of ionizations that produce Auger electrons is called the Auger yield ($\alpha$), and the sum of these two yields is unity. Auger yields are higher for light elements and for L and M primary ionizations; whereas, fluorescent yield dominates for heavier atoms and most K ionizations. Although it would seem that Auger electron spectroscopy (AES) would be ideal for light elements, it turns out that because of their low energy, an ultra-high vacuum system is necessary to detect them. Moreover, even though many of them are produced, few escape the solid, and AES is largely a surface analytical technique sensitive to about the top 1 nm. In recent years, light element X-ray microanalysis has become much more common with thin entrance windows, improved spectral resolution, and lower noise detectors. The X-ray fluorescence yield, $\omega$, for K, L, and M X-ray lines is shown graphically in Figure 2.4. Note that, within a given series of lines, $\omega$ increases with atomic number and, for a given atomic number, is greatest for K lines and progressively less for L and M lines.

![Figure 2.4 Variation in fluorescence yield with atomic number.](image)

Continuum Generation

Besides characteristic X-rays, inelastic scattering of the beam electrons produces continuum X-rays. When electrons strike solids, they can undergo a deceleration in steps, with each deceleration causing the emission of an X-ray with an energy equal to that lost by the electron. The range of energies of these X-rays is from nearly zero to the maximum energy of the electron beam. This latter energy is called the short-wavelength limit (SWL), or the Duane-Hunt limit. This type of radiation is called continuous or white radiation. The white radiation spectrum is called the continuum or Bremsstrahlung, meaning “braking radiation.”

The continuum is the major source of background in the electron beam-excited X-ray spectrum. And this background under the characteristic peaks consists of real X-rays detected at the crystal, not electronic noise. Continuum X-rays are detected up to the beam energy, which in intermediate voltage electron microscopes can be 300 or 400 keV. Just because the microanalysis system is not calibrated beyond 20 or 30 keV, or the display shows 0 - 10 keV, does not mean that these X-rays are not being detected and processed by the pulse processing system, and contributing to dead time. Figure 2.5 shows a spectrum measured on pure molybdenum represented in black superimposed on the continuum shown in gray.
Note the presence of a sharp change in the continuum intensity at approximately 2.6 keV. This sudden change is due to the significant difference in ability of Mo atoms to absorb X-rays above and below the critical excitation potential (absorption edge) for the Mo L line. The intensity of the continuum generated at any energy is directly proportional to atomic number and beam energy. But the shape of the background seen in the spectrum includes the detector efficiency and detector-specimen geometrical effects. For quantitative analysis, the continuum must be removed, and the methods available for that will be described in Chapter V, “QUANTITATIVE ANALYSIS” on page 35.

Absorption

Thus far, this chapter has discussed the generation of X-rays. The next chapter will discuss methods of detecting and measuring them. However, it is of fundamental importance to understand the concept of X-ray absorption that occurs in the specimen between the time X-rays are generated and the time when they are detected. Equation 2.3 (Beer’s Law) describes the fractional transmitted intensity ($I/I_o$) that occurs when an X-ray of intensity $I_o$ is generated in a material at depth $x$:

\[
\frac{I}{I_o} = e^{-(\mu/\rho)\rho x}
\]

(Equation 2.3)

where:

- $\mu/\rho$ = the mass absorption coefficient
- $\rho$ = the density of the material

The mass absorption coefficient, $\mu/\rho$, is a function of the atomic number of the absorber ($Z$) and the energy ($E$) of the incident X-ray:

\[
\mu/\rho = kZ^3/E^3
\]

(Equation 2.4)
Equation 2.4 applies for the smooth portion of the $\mu/\rho$ versus $E$ curve shown in Figure 2.6 for iron.

![Figure 2.6 Mass absorption coefficient of Fe for X-rays of various energies.](image)

The sharp discontinuity in Figure 2.6 is the Fe K absorption edge ($K_{ab}$). The shape of the curve can be rationalized in the following manner. At high energies, absorption is low, because the X-ray can pass through the atom with low probability of interaction. As the energy decreases, the absorption increases (as $k/E^3$) until it reaches maximum at the K absorption edge. Absorption is now taking place with maximum ionizations of the Fe atoms occurring. There is a sharp drop in absorption as the energy of the incident X-ray drops below $K_{ab}$, because the X-ray no longer possesses sufficient energy to eject a K electron. As X-ray energy further decreases below the edge, absorption again increases (as $k/E^3$) until another absorption edge is reached.

Absorption occurs over the distance that the X-ray travels through a solid. The longer the distance, the more absorption takes place. The path length is related to the depth from which the X-rays were generated and the take-off angle to the detector as follows:

$$L = z \cdot \csc (\psi)$$

(Equation 2.5)

where:

- $L$ = absorption path length
- $z$ = depth
- $\psi$ = take-off angle

The take-off angle and its effect on quantitative analysis procedures are discussed more in Chapter V “QUANTITATIVE ANALYSIS” on page 35 and shown in Figure 5.5. The mass absorption coefficient for an X-ray of a given energy in a specific matrix (composition through which the X-ray travels) is simply the average of the individual mass absorption coefficients of the elements present in the matrix, weighted by their concentration. That is,

$$\left( \frac{\mu}{\rho} \right)_{\text{matrix}} = \sum W_i \left( \frac{\mu}{\rho} \right)_i$$

(Equation 2.6)
where:

\[ W_i = \text{the weight fraction of element } i \text{ in the matrix} \]
\[ (\mu/\rho)_i = \text{the mass absorption coefficient of element } i \text{ for the X-ray of interest} \]

In quantitative analysis, values of \( \mu/\rho \) must be known accurately. There is lack of agreement, however, among different compilations of mass absorption coefficients, and this can be a source of error in quantitative calculations. The mass absorption coefficients used in quantitative analysis programs are usually selected from various sources thought to be the best values for each emitter-absorber combination.

**Fluorescence**

Characteristic or continuum X-rays of sufficient energy can cause the emission of an X-ray of lower energy. This is called secondary emission or fluorescence when it is caused by X-rays that were generated by the primary incident electron beam. If an X-ray generated in the specimen has sufficient energy to eject an electron in an inner shell of another atom, it may be absorbed, causing an X-ray to be emitted from the absorbing atom. For example, in a Cu-Fe sample, Cu K\( \alpha \) radiation (8.04 keV) is of sufficient energy to excite Fe K radiation (K\( \alpha_b \) = 7.11 keV). As a consequence, the measured iron intensity would be enhanced due to fluorescence by copper, while the copper intensity would be suppressed due to strong absorption by iron. These interactions of absorption and fluorescence must be appropriately handled in any quantitative analysis scheme, and this subject will be covered in more detail in Chapter V “QUANTITATIVE ANALYSIS” on page 35.
III. X-RAY MEASUREMENT

Today, most SEMs have EDS systems and a few have a wavelength spectrometer. Electron probe microanalyzers all have WDS systems and most often an EDS system as well. It is, therefore, worth describing the two systems and comparing them in terms of their ability to perform X-ray microanalysis. Moreover, with the recent improvements in EDS detectors, it is useful to describe the essentials of X-ray detection.

Energy Dispersive Spectroscopy

**General Description**

In an energy dispersive spectrometer, X-rays of all energies are detected by a detecting material, most commonly a lithium-drifted silicon (Si(Li)) crystal. On their way to the detecting crystal, X-rays may be absorbed by a window, a metallic contact layer on the crystal and a silicon dead layer. The active area in the silicon crystal is typically 10 mm$^2$ or 30 mm$^2$, though it may be larger, such as 60 or 80 mm$^2$, and it is about 3-5 mm thick. The X-rays produce charge pulses in the crystal that are proportional to their energy, and X-rays of all energies are detected virtually simultaneously. In Si, an electron-hole pair is created for every 3.76 eV of incoming X radiation. For a germanium detector, the number is 2.96 eV. EDS detectors require no focusing of the X-rays, so all are detected if they are present within the solid angle subtended by the crystal. The electron-hole pairs created by the incoming X-rays are swept away by the bias voltage of several hundred volts and converted to a voltage pulse in the FET located within the X-ray detector. The pulse then enters the external stages of the preamplifier.

**Detectors**

Although Si(Li) and HpGe are the most common EDS detectors, others are used, though they are seen infrequently in X-ray microanalysis applications. A listing of some of these detectors is given in Table 3.1.

<table>
<thead>
<tr>
<th>Detector Type</th>
<th>Typical Application/ Operating Temperature</th>
<th>Mn Resolution</th>
<th>Advantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si(Li)</td>
<td>X-ray microanalysis/ 100K</td>
<td>129-145 eV</td>
<td>Routine quantitative analysis</td>
</tr>
<tr>
<td>HpGe</td>
<td>X-ray microanalysis/ 100K</td>
<td>115-130</td>
<td>Good resolution; high efficiency</td>
</tr>
<tr>
<td>Si Drift Chamber</td>
<td>X-ray microanalysis/ XRF/-15°C</td>
<td>127-170</td>
<td>High count-rate; near RT operation</td>
</tr>
<tr>
<td>µCalorimeter</td>
<td>Low-voltage microanalysis/70 mK</td>
<td>~10</td>
<td>High resolution</td>
</tr>
</tbody>
</table>
A photograph of a typical EDS spectrometer is shown in Figure 3.1, in which the most prominent feature is the liquid nitrogen dewar. A field-effect transistor (FET) is located directly behind the detecting crystal and provides the first stage of signal amplification. The actual charge induced in the detector is extremely small. Therefore, to minimize noise, the FET must be located as close to the detector as possible, and must be operated at liquid nitrogen temperature (except in the case of a silicon drift detector. To achieve the required temperature, the detector and FET are connected through an efficient heat conductor to a liquid nitrogen Dewar. The metal tube housing the detector assembly and cold finger is called the endcap, which must be evacuated to prevent heat loss through its walls.

![Figure 3.1 Energy-dispersive spectrometer](image)

A very thin window of low atomic number material is used to enclose the endcap to ensure its vacuum integrity while providing high X-ray transmission. This window may be 7.5 µm beryllium or <0.25 µm carbon- or boron-based material. Completely windowless detectors are also available, but these must have a window that can be closed for sample changes in the microscope.

**Silicon Drift Detector**

This type of detector uses a pattern on the back surface of silicon to create a field through which electrons drift toward a collecting anode. Holes are not collected. The detector can be operated at or near room temperature, and it has the ability to operate at high count rate. Its resolution is usually not quite as good as Si(Li), and it is not capable of detecting boron or beryllium. However, because of its potential performance and convenience of operation, work is ongoing on both the semiconductor device and the associated electronics to optimize it as a detector for X-ray microanalysis (Lechner, et al., 2001)

**Microcalorimeter**

The principle of operation in this detector is the measurement of the small temperature rise that occurs when an X-ray photon hits a suitable absorber. For this difference in temperature to be significant, the detector must be operated at a temperature of only a few milliKelvin. Its resolution is about as good as that of WDS, but its count rate is limited to < 1000 cps by the time necessary for the absorber's temperature to return to a steady state.
Detector Comparison

Si(Li) detectors comprise the overwhelming majority of EDS detectors in use, and much experience has been gained with them over the years. HpGe detectors are far less common, but they provide better resolution and high-energy efficiency. SDDs provide convenient near-room-temperature operation, and they are more sensitive to light elements, because they do not require an atmospheric thin window. However, they are not at all sensitive to boron or beryllium.

Table 3.2 Comparison of Advantages of Three Common EDS Detector Types

<table>
<thead>
<tr>
<th>Si(Li)</th>
<th>HpGe</th>
<th>SDD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Better light-element detection</td>
<td>Better resolution</td>
<td>Convenient liquid nitrogen-free operation</td>
</tr>
<tr>
<td>More robust</td>
<td>Better high-energy efficiency</td>
<td>Higher maximum count rate</td>
</tr>
<tr>
<td>Escape lines minor</td>
<td></td>
<td>Rapid cool down</td>
</tr>
<tr>
<td>Quantitative routines well established</td>
<td></td>
<td>Better light-element sensitivity down to carbon</td>
</tr>
</tbody>
</table>

Analog Processing

In the case of traditional analog signal processing, the preamplifier output signal is further processed in the main amplifier to obtain the proper pulse amplitude and shape. The height of the voltage pulse remains proportional to the charge initially incident on the FET and, therefore, to the energy of the X-ray quantum absorbed by the detector, i.e., the energy of the X-ray that produced it.

Also in the amplifier is a pulse pileup rejection circuit to prevent pulses closely spaced in time from being measured as one pulse of twice the energy. The total time the system is not available to accept pulses is called “dead time.” Time during which pulses are measured is called “live time,” and the elapsed time on a clock is called “real time.” The effect of dead time is compensated by extending the X-ray acquisition time. Live time is usually specified by the operator, and the system counts for whatever real time is necessary to achieve it. Live time correction is necessary for quantitative analysis or quantitative comparisons among spectra, and this time extension is automatically done in the electronics.

One way to increase the maximum count rate of an EDS system is to shorten the shaping time constant of the main amplifier. This is accomplished, however, at the sacrifice of resolution. Several discrete shaping times are usually available, such as 12µs, 6µs and 3µs, etc. The longer times produce the best resolution but limit the usable count rate. One should operate at the longest shaping time that will permit the desired count rate. In analog processing, the output of the amplifier is digitized with an analog-to-digital converter (ADC) and fed into a host computer for processing and display. Older systems use a multi-channel analyzer for spectrum storage and display.
There also exists a technology to digitize the output of the preamplifier and perform digital signal processing (DSP) on the resulting data stream. Pulses are resolved better in time and amplitude to give improved throughput, greater light element sensitivity, and lower limits of detectability (Friel and Mott, 1994).

A diagram of the essential components of a microscope/EDS system is shown in Figure 3.2 (above), and both analog and digital signal processing are illustrated. The analog amplifier, pulse pileup rejector, and ADC are shown. In the digital system, all processing is done within the digital module. Once the preamplifier signal is digitized, all further manipulation of the signal is linear and noise free. Digital filtering is precise and reproducible compared with the non-ideal behavior associated with analog components and finite tolerances. Moreover, digital filtering is not constrained to those filter shapes realizable with physical components (Mott and Friel, 1995).

One of the key elements of digital processing is adaptive shaping; i.e. the shaping time can change "on the fly." To do this it is necessary to know when the next pulse is coming, but that is easily accomplished by buffering the digital signal in memory. Knowing the arrival sequence of pulses before they are measured permits shaping times to be tailored to fit the data exactly. Widely spaced pulses are measured with great precision, yet closely spaced pulses are not lost. As a consequence, count rate and resolution are both improved.
Figure 3.3 Schematic representation of fixed vs. adaptive pulse shaping.

Figure 3.3 shows the situation schematically. Five separate pulses are depicted at various energies and times of arrival in the X-ray detector. Step height corresponds to energy, with small rises representing soft X-rays and large rises corresponding to more energetic X-rays. The top trace is the actual pulse stream (digital or analog), and the middle and bottom traces represent the response of an analog amplifier or digital pulse processor, respectively. Note the equally spaced tick marks on the analog trace compared with the variable widths on the digital trace. The time between these marks represents the pulse processing time. The analog system measures only one of the five pulses—the first, because the signal does not return to baseline by the time the next pulse arrives.

Because of the near ideal filter shapes available in a digital system, soft X-rays associated with light elements are better discriminated from noise. Thus, a digital detector is more sensitive to soft X-rays and collects more of them than do analog systems. Moreover, soft X-rays are not only hard to detect when widely separated in time, they are even harder to detect when they arrive closely spaced. It is possible, however, to distinguish two events from a single one by working directly with the digitized data stream rather than trying to infer them from a smoothed analog signal. The result is pulse pileup rejection to lower energies than is possible with analog processing.

**Detector Resolution**

The spectral resolution of an EDS spectrometer is only one measure of system performance. Moreover, it is not even a fixed number; it varies with X-ray energy, detector area, amplifier shaping time, and count rate. Resolution is typically quoted at manganese, because the radioactive source, $^{55}$Fe, emits the Mn Kα X-ray. It is specified as the full width at half the maximum peak (FWHM). Instead of sharp lines at specific energies, EDS peaks are near Gaussian in shape and of finite width. This width arises from statistical factors within the detecting crystal and is called the intrinsic resolution. The intrinsic resolution is characteristic of a particular detecting crystal and is determined as follows:

$$FWHM_{Intrinsic} = 2.35\sqrt{F \cdot E \cdot \epsilon}$$

*(Equation 3.1)*
where:

- $F$ = a statistical factor called the Fano factor (about 0.12)
- $\varepsilon$ = the energy required to produce an electron-hole pair in the crystal (3.76 eV for Si(Li) and 2.96 for Ge)
- $E$ = the energy of the X-ray in eV (5898 for Mn)

In addition to the intrinsic resolution, there is a contribution from extrinsic noise, and these factors add in quadrature as shown in Equation 3.2:

$$FWHM = \sqrt{Intrinsic^2 + Extrinsic^2}$$

*(Equation 3.2)*

The extrinsic component is constant for a particular system and is not dependent on energy. Therefore, knowing a manganese resolution, we can predict the resolution for other energies as follows:

$$FWHM(\text{el}) = \sqrt{FWHM_{Mn}^2 + 2.49E - 14696}$$

*(Equation 3.3)*

The term 2.49E comes from the intrinsic contribution at the energy of interest, and the constant, 14696, comes from the intrinsic contribution at manganese. Thus, if a particular system has a manganese resolution of 135 eV, we should expect 89 eV at Si, and 63 eV at B, etc.

Inasmuch as the energy to produce an electron-hole pair is less for a germanium detector, its intrinsic resolution is better than that of Si(Li); however, it is more susceptible to leakage currents and must be shielded from infrared radiation inside the detector. Consequently, the light element performance of germanium is not as good as that of Si(Li).

Despite the popular discussion of the importance of spectrometer resolution, it is generally not as important as the number of counts collected. The EDS technique is good enough to distinguish most X-ray lines, and severe overlaps can be separated by peak deconvolution software. Other aspects of EDS system performance are maximum count rate, analytical software, ease of use, and the degree of optimization of the mechanical interface to the particular electron column instrument.

**Count Rate vs. Resolution**

There is always a trade-off between maximum count rate and resolution. As the shaping time is decreased to get more counts per second, resolution is degraded—although less so in a digital system. The precision of quantitative analysis, defined in Chapter VI "PRECISION AND ACCURACY" on page 54, has been shown to improve markedly by operating at less than the best resolution, while accuracy remains constant (Fiori and Swyt, 1992). Throughput reaches a maximum at roughly 50% dead time.
Figure 3.4 Relationship between throughput and resolution, both analog and digital.

Figure 3.4 shows a plot of throughput, defined as counts into the spectrum per second of real time vs. resolution at manganese. This plot is at 50% dead time, and the near vertical lines represent the range of count rates possible at each of several discrete amplifier shaping times. The upper continuous curve applies to digital processing and is discussed below. The best resolutions at the left side of the plot were obtained at the longest shaping times and lowest count rates. For many SEM and TEM applications, count rates are inherently low, and a 10 µs shaping time or longer can be used for highest resolution. However, whenever high count rates are needed, such as in X-ray maps, it is often desirable or even mandatory to sacrifice resolution for improved count rate by selecting a short shaping time. Silicon drift detectors, with their high count-rate capability, are particularly appropriate for these applications.

At times it is desirable to work at lower dead times. For example, (1) to reduce beam damage and carbon contamination, (2) to work under high-resolution imaging conditions, (3) to minimize sum peaks discussed below, or (4) when the beam current is limited such as in some field emission SEMs. As dead time is lowered, the count rate of a digital system does not decrease as fast as that of an analog system, because of digital’s adaptive shaping. For example, if the dead time is 10% as illustrated in Figure 3.5, then 500,000 counts can be collected into a spectrum digitally in 55 seconds; whereas, it takes almost 3 minutes for the analog system to collect the same 500,000 counts at equal resolution.
A comparison of spectra collected under identical conditions is shown in Figure 3.6. The specimen was B4C, and only the pulse processing was changed from one spectrum to the next. One can see the improved resolution and greater throughput associated with the digital processor.

**Quantum Efficiency**

A typical 3.5 mm Si(Li) crystal with a 7.5 µm beryllium window has a quantum efficiency of 100% between about 2.5 and 15 keV. Below 2.5 keV, absorption in the beryllium window becomes significant, and above about 15 keV, some of the energetic X-rays pass through the crystal without being detected. For light element analysis, a windowless or ultra-thin window is indicated. In either of these cases, high efficiency is extended to lower energies; however, the contact layer and the dead layer still cause loss of efficiency at very low energies. Figure 3.7 shows efficiency vs. X-ray energy for Si and Ge detectors on a log-log plot. Note that the Ge detector is more efficient at higher energies because of its greater density. It is somewhat less efficient than Si(Li) at lower energies, because Ge is more sensitive to infrared radiation than is Si, and so a foil must be placed in front of the crystal at cryogenic temperatures to shield it.
Beryllium window detectors are good for routine analysis of elements as light as sodium. Ultra-thin window (UTW) detectors extend the detection range down to beryllium. Windowless detectors are also useful as low as beryllium, and they have increased efficiency throughout the range of light elements. Most analysts, however, prefer a detector with a UTW to protect the detecting crystal from the environment of the microscope. Silicon drift detectors can also be used for light element detection in a window or windowless mode, and they are less susceptible to contamination because of their higher operating temperature.

**Collection Efficiency**

Inasmuch as the quantum efficiency of any system is largely constant for a given energy, the efficiency of collection is controlled by the sample-to-detector geometry. The two factors that affect the number of X-ray photons that reach the detector are solid angle and take-off angle. Both of these are generally under control of the operator of an SEM, but usually are not for the operator of an EPMA. The concept of solid angle and its effect on count rate is discussed below, but we will defer the discussion of take-off angle to Chapter V, “QUANTITATIVE ANALYSIS” on page 35.
Solid Angle

The count rate incident on an X-ray detector is directly proportional to the size of the solid angle, which may be defined as follows:

\[ \Omega = \frac{A}{r^2} \]  

(Equation 3.4)

where:
- \( \Omega \) = solid angle
- \( A \) = active area of the detector
- \( r \) = sample-to-detector distance

The count rate on a 30 mm\(^2\) EDS detector is three times that of a 10 mm\(^2\) detector, although resolution is slightly degraded. Moving the detector closer to the specimen by a factor of 0.5 increases the count rate by a factor of four. This relationship is shown in Figure 3.8. The total geometrical efficiency in a well-designed EDS system is about 2%. WDS geometrical efficiency is variable as the spectrometers move, but generally <0.2%.

Figure 3.8 Diagram showing the solid angle subtended by the EDS detector.

Spectral Artifacts

There are a number of artifacts possible with EDS, but most of them are related to detector electronics and are rarely seen in a properly functioning system. Two artifacts that are commonly seen are pulse pileup peaks and escape peaks. Pileup peaks occur when X-ray photons reach the detector at nearly the same time, and the pulse processing electronics erroneously record the sum of their energies rather than each one individually. Lowering the beam current lowers the count rate and usually eliminates the problem. Alternatively, the amplifier shaping time can be decreased; this action will allow pulses to be processed faster, but at the expense of degraded spectral resolution. Digital pulse processing, with its adaptive shaping, is much better at reducing sum peaks and keeping the dead time low.

Escape peaks occur when the detecting crystal is ionized and emits an X-ray that escapes the crystal. The result is a peak at 1.74 keV below the parent peak for Si(Li) detectors. The effect is greatest just above the crystal absorption edge—about 2% of the parent peak for phosphorus with a Si(Li) crystal. The effect is not possible below the \( k_{ab} \), and its magnitude decreases rapidly with increasing energy. For Ge crystals, escape peaks from L lines are possible (Ge L\(\alpha\) = 1.19 keV), but escape peaks from K lines are significant (Ge K\(\alpha\) = 9.89 keV). The intensity of germanium escape peaks is commonly 10% - 15% of a parent peak.
(above 11.1 keV, K\textsubscript{αβ} of Ge) (Rossington, et al., 1992). Moreover, germanium K\textsubscript{α} and K\textsubscript{β} escape peaks can be seen from both the K\textsubscript{α} and K\textsubscript{β} of the parent, for a total of four escape peaks. An example of a spectrum illustrating sum peaks and Si escape peaks is shown in Figure 3.9.

![Figure 3.9 Spectrum of chromium acquired at a high count rate showing the Cr sum peak at twice the K\textsubscript{α} energy, and the Si escape peak at 1.74 keV below the Cr K\textsubscript{α} peak.](image)

**Wavelength Dispersive Spectroscopy**

**General Description**

In wavelength dispersive spectroscopy (WDS), an analyzing crystal is placed in front of the X-ray detector to screen out all but the desired wavelength. This is done by diffracting the X-rays through an analyzing crystal according to Bragg’s Law, as follows:

\[ n\lambda = 2d \sin \theta \]  

(Equation 3.5)

where:

- \(n\) = an integer number of wavelengths (order)
- \(\lambda\) = the wavelength
- \(d\) = the known spacing between atom planes in a crystal
- \(\theta\) = the diffraction angle

The relationship between energy and wavelength is:

\[ E (\text{keV}) = \frac{12.4}{\lambda (\text{Å})} \]  

(Equation 3.6)

To satisfy Bragg’s Law, the spectrometer must be moved throughout a range of angles, and it is necessary for the crystal to remain on the focusing circle throughout its range of motion. In like manner, the location on the specimen from which X-rays are produced must be in X-ray focus. One consequence of this requirement is that X-ray maps cannot be collected at magnifications less than about 2000X, because at lower magnifications, the beam is deflected to a point out of X-ray focus. This limitation is not nearly so
severe with an inclined spectrometer. Space limitations, however, usually limit the number of such spectrometers to one.

Some wavelength spectrometers scan over a large range of angles, but even these need several analyzing crystals to cover the entire range of X-ray wavelengths, and only one crystal can be used at a time. Other WDS spectrometers are fixed or have a narrow range of motion and are used to analyze specific elements. For example, one might select a crystal specifically to separate the S Kα, Mo Lα, and Pb Mα lines. An example of how the S Kα and Mo Lα overlap would look in EDS and WDS is shown in Figure 3.10.

![Figure 3.10](image)

**Figure 3.10** A) EDS spectrum showing the overlap of the Mo Lα line with that of the S Kα.  
B) The same pair of lines shown using a WDS spectrometer.

**Efficiency**

The quantum efficiency of wavelength spectrometers is usually significantly less than that of EDS detectors, and may be about 30% (Goldstein et al., 2003). This is a consequence of losses in the diffraction crystal, the counter window material, and the counter tube. Moreover, the specimen-to-spectrometer distance is variable and usually greater than that of the EDS detector, so the collection efficiency is reduced as well. WDS systems, however, can be operated at a much higher beam current than can EDS systems. Therefore, many X-ray counts can be collected in a short time if the specimen is not damaged by the electron beam. The high peak/background ratios associated with wavelength spectrometers result in a low minimum detectability limit, often about 0.01%.

**Spectrometer Resolution**

Detectors are typically proportional counters with a spectral resolution of only about 1000 eV, so resolution is achieved by using a crystal of known d-spacing and only admitting those X-rays that are diffracted according to Bragg’s Law (Equation 3.5). Analyzing crystals can be obtained that have both good reflectivity and resolution, and modern synthetic crystals are being used almost exclusively in light element analysis. A resolution of about 10 eV is common in WDS, but higher order lines may be present. These are lines that are multiples of the desired wavelength that get through the diffracting crystal and have to be removed by some form of pulse processing, such as a single-channel analyzer that discriminates X-rays on the basis of their energy.
Comparison of Detection Techniques

Some of the specific advantages and disadvantages of EDS and WDS are compared in Table 3.3.

Table 3.3 Comparison of EDS and WDS

<table>
<thead>
<tr>
<th></th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDS</td>
<td>Collect entire spectrum at once</td>
<td>Peak overlaps</td>
</tr>
<tr>
<td></td>
<td>No moving parts</td>
<td>Spectral artifacts</td>
</tr>
<tr>
<td></td>
<td>High quantum efficiency</td>
<td>Detectability limit</td>
</tr>
<tr>
<td></td>
<td>High collection efficiency</td>
<td></td>
</tr>
<tr>
<td>WDS</td>
<td>High spectral resolution</td>
<td>One element at a time</td>
</tr>
<tr>
<td></td>
<td>Detectability limit</td>
<td>Higher order lines</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Defocusing</td>
</tr>
</tbody>
</table>

From this comparison, we may conclude that the techniques are complementary, but EDS is the simplest for general-purpose analysis. WDS is particularly valuable for separating overlapped peaks and for trace element analysis. WDS is also useful for light element analysis, but windowless and sealed ultra-thin window detectors have now brought a light element capability to EDS. The following points in Table 3.4 summarize the applicability of the instrumentation currently available:

Table 3.4 Applicability of X-ray Microanalysis Instrumentation

<table>
<thead>
<tr>
<th>Instrumentation</th>
<th>Typical Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPMA with many WDS spectrometers</td>
<td>Routine quantitative analysis with standards</td>
</tr>
<tr>
<td>SEM with one WDS spectrometer</td>
<td>Analysis of specific elements (overlaps)/trace element analysis</td>
</tr>
<tr>
<td>SEM with ultra-thin window EDS</td>
<td>Routine qualitative analysis</td>
</tr>
<tr>
<td></td>
<td>Standardless or standards quantitative analysis</td>
</tr>
<tr>
<td></td>
<td>X-ray maps</td>
</tr>
<tr>
<td>SEM with windowless detector</td>
<td>High-efficiency light element analysis</td>
</tr>
<tr>
<td>SEM with microcalorimeter</td>
<td>Low-voltage L-line or light element analysis</td>
</tr>
<tr>
<td>SEM with silicon drift detector</td>
<td>Routine microanalysis of carbon and heavier elements</td>
</tr>
<tr>
<td></td>
<td>Fast collection of maps or spectrum images</td>
</tr>
</tbody>
</table>

Spatial Resolution

The minimum size of a specimen that can be analyzed with electron-generated X-rays is not nearly so small as the electron beam diameter. As the beam of a given energy enters the specimen, it undergoes scattering, and wherever the electrons are scattered, X-rays of equal or lower energy may be produced.
The linear term “X-ray range” is often used instead of “volume” because it is easier to visualize. The reason that image and X-ray resolutions are not the same is that secondary electrons that form the image have no more than 50 eV of energy. With so little energy, they can only escape from a very thin surface layer of less than 10 nm, where the beam has not yet spread significantly. Secondary electrons continue to be generated as the beam penetrates the specimen but do not escape and, consequently, do not contribute to the image. Higher energy backscattered electrons can escape from much greater depths in the specimen; thus, a backscattered electron image is of poorer resolution than a secondary electron image. Finally, X-rays can continue to be generated by the primary beam and, since photons can travel farther than electrons, they escape from still deeper within the specimen. Figure 3.11 illustrates the escape volumes for secondaries, backscattered electrons, and X-rays.

![Image](image.png)

*Figure 3.11 Escape depth for secondary electrons, backscattered electrons, and X-rays.*

It should be apparent from this figure than one cannot perform a microanalysis on features smaller than the X-ray escape volume, though these features may be clearly visible at high magnification. For example, submicrometer features are readily imaged but may be difficult to analyze without interference from neighboring features. One of the basic requirements for quantitative analysis is that the X-rays measured must come through the composition that is iteratively calculated. Neither scanning the beam nor defocusing it produces an average analysis. Furthermore, because X-rays come from a volume, the thickness of a particular feature is important. Thin coatings often have interferences from the substrate, and porous specimens may have misleading peak heights because of subsurface pores. Thus, one must constantly be aware of the difference between image and X-ray spatial resolution to properly interpret microanalysis results. Backscattered electrons originate from a volume more closely approximating that of X-rays, and therefore are a useful imaging signal to correlate with the X-ray analysis. In fact, the BSE signal is the signal of choice for correlation with X-ray maps.

X-ray spatial resolution depends on density and overvoltage (accelerating voltage divided by the critical excitation voltage). Figure 3.12 shows schematically the variation in X-ray volume with voltage and atomic number of the specimen (Duncumb and Shields, 1963). One must also be aware that in a specimen containing light and heavy elements, each one has its own escape volume.
Although several persons have published expressions for X-ray range or X-ray spatial resolution, the one given below (Anderson and Hasler, 1966) has been shown to give a good practical estimate of X-ray interaction with actual samples (Friel, 1986).

\[
R = \frac{0.064 \left( E^1.68 - E^1.68_c \right)}{\rho}
\]

(Equation 3.7)

where:
- \( R \) = spatial resolution in \( \mu \text{m} \)
- \( E_o \) = accelerating voltage in keV
- \( E_c \) = critical excitation energy in keV
- \( \rho \) = mean specimen density in g/cc

One can immediately see that the X-ray range depends only on the nature of the specimen and the overvoltage. Changing the spot size has no effect on X-ray resolution. However, it may be possible to use a different line and a lower accelerating voltage to achieve submicrometer resolution. For example, if one were to analyze the L\( \alpha \) line of Zn in brass at 5 kV, an X-ray spatial resolution of 0.12 \( \mu \text{m} \) could be achieved. This situation is illustrated in Figure 3.13. This is a Monte Carlo plot (Joy, 1991) of sites where X-rays would be produced by 10,000 electron trajectories, and it shows similar results to the range equation. The plot on the left side is the number of X-rays as a function of depth, in other words a phi-rho-z curve. The vertical line is the range (R) calculated by Equation 3.5.
Range in Other Instruments

The concepts discussed above apply to X-ray microanalysis of bulk specimens, that is, those that are thicker than the excitation volume. For thin sections in the analytical electron microscope (AEM), the excitation volume depends on the beam diameter, and smaller useful beams are now being developed on AEMs with field emission guns. Absorption and beam spreading are assumed to be insignificant. These benefits of AEM over SEM or EPMA microanalysis all come at the expense of limited specimen size and difficult specimen preparation. Figure 3.14 shows a schematic comparison of the excitation volumes of thin and bulk specimens.

Low-voltage analysis has reduced the size of the analytical volume, especially in FESEMs, but the lines available are not well separated. Although the spatial resolution of the microcalorimeter is constrained by the electron range as with other electron beam instruments, its superb spectral resolution permits the analysis of L-lines without the overlaps associated with semiconductor detectors. Auger electron spectroscopy can also provide submicrometer spatial resolution, but the analytical information comes only from within a few nanometers of the surface.

Inasmuch as the essence of microanalysis is chemical analysis of small volumes, I believe the foregoing discussion on spatial resolution is a necessary part of X-ray measurement, before proceeding with the process of turning data into information.
IV. QUALITATIVE ANALYSIS

For many purposes, the identification of elements in a specimen on the basis of peaks in the EDS spectrum is sufficient. But even if quantitative analysis is contemplated, prior qualitative analysis is required. Failure to find an element or misidentification of a peak can sometimes have serious consequences. For example, consider the analyst who missed the rare earth elements in a mineral sample causing his company to overlook an economically valuable ore deposit. Qualitative analysis by EDS is much easier than by WDS, so only EDS will be covered. For purposes of this discussion, we will use the following definition of concentration: major (>10 wt.%), minor (1-10 wt.%), and trace (<1 wt.%) (Goldstein, et al., 2003).

Calibration

Before peaks can be identified, calibration must be assured. This is accomplished by acquiring a spectrum of a known element(s). If the peaks do not line up with their respective markers, then calibration is required. Some systems require just one peak such as Fe Kα; some require two peaks of the same element such as Cu Kα and Lα; and still others require two elements such as Cu Kα and Al Kα. Many modern systems use a zero strobe peak to fix the offset. A zero strobe is an artificial peak centered on zero energy, and from which offset can be continuously monitored. The gain of the amplifier, or digital module, must be set manually so that the calibration is close. The computer then makes the final calibration to the required precision. The range over which the system is calibrated and the number of channels in the ADC determines the eV/channel. For example, 0 - 10 keV is about 5 eV/ch; whereas, 0 - 20 keV is about 10 eV/ch.

The calibration range determines the maximum energy that can be analyzed, but the display can be expanded to cover a lesser range. Most elements have identifiable lines in the 0 -10 keV range. Higher energies are required for a few elements and are also useful to display K lines when the L lines are overlapped with other elements. The voltage on the microscope must be well above the highest energy lines of interest. The accelerating voltage, calibration range, and display range are not the same; they are related, but they can be set independently. A suitable set of conditions might be 10 eV/ch, display 0 - 10 keV, and 20 kV accelerating voltage, less for light elements. Once the energy calibration has been performed, the operating conditions of the microscope (e.g. kV) can be changed without recalibration.

Automatic Identification

Before proceeding with a step-by-step method of peak identification, computer-based methods should be discussed. Virtually all systems have some form of “AutoID.” These vary from simplistic to sophisticated, but they never take the place of good judgement on the part of the analyst. In the simplest case, the computer reads out the energy at a cursor, and one looks up the line corresponding to that energy. Sometimes all possible lines within the vicinity of the cursor are displayed by the computer. The sophisticated AutoID programs do background subtraction and peak deconvolution, and then apply an intelligent method of identification within constraints set by the operator. On a modern computer, the most sophisticated methods run fast and are quite good, but the results must always be viewed with some skepticism.

An example of an automatic identification of a complex specimen is shown in Figure 4.1. This is a glass sample from N.I.S.T., though not a certified standard. It contains 14 elements, and the AutoID program found 13, 12 correct and one incorrect. The detector had a beryllium window, so oxygen was not detected, and tellurium was determined to be in error after manual identification.
It is always appropriate to use one’s knowledge of chemical principles and of the specimen, but it can be a mistake to disregard elements reported by the computer too quickly; the rubidium in this sample was a surprise. Quantitative analysis programs do not identify peaks; they only quantify those the analyst selects. If all elements present in more than trace concentrations are not correctly identified for the quantitative program, its answers will be wrong.

**Step-by-Step Identification**

The following procedure is similar to the one described by Lyman et al. (1990), and is sometimes referred to as the “Lehigh method.”

1. Begin with the most intense line towards the high-energy region of the spectrum where lines within a family are well separated. If it is above 3.5 keV, it must be either a K or L line.

2. Using the KLM markers, compare the location of the peak to that of the marker. If it is one channel or less off, the same should be true for all nearby lines. If the markers can be scaled, check the relative intensities. If you identified a Kα line, then the Kβ line should be about 10% of the Kα intensity. Kα and Kβ lines are typically resolved at sulfur and above. If a K line is identified, look for L lines, if they occur for that element. This will aid in identifying the lines at low energy later.

3. If the line chosen does not correspond to a K line, try an L series. If the line is identified as the Lα, several other lines both above and below the Lα should be present and correspond to the element. The EDS system should be able to display them at their correct relative intensities. M lines do not exist above 3.2 keV, so one would not look for them at this point.

4. While working with the most intense line, look for escape and sum peaks. If they are not found for this line, they are unlikely to cause interferences. If they are present, keep looking for them after other identifications.
5. If (1) a peak is displaced relative to its marker, (2) relative intensities are wrong, or (3) there is a distortion in the peak shape, then there is an overlapping element. All three conditions will be present in an overlap situation. If one condition is seen, look for the others, and identify the second element.

6. Continue to identify lines while working towards lower energies and consider the possibility of M lines. The lines of an M series are generally not all resolved but contribute to an asymmetrical peak. In fact, M lines can often be recognized by this distortion, but beware of overlaps that may look similar.

7. When all high-energy lines and low-energy L and M lines are identified, light elements can be attempted. These will be K lines and may be overlapped with L lines from heavier elements. If it is not possible to distinguish them, peak deconvolution software or peak stripping may be necessary.

8. After all major and minor peaks are located, trace elements can be attempted. In this case, the problem is to confidently find a peak above background. Only the major peak of a series will be visible, and that may be lost in the background. If a peak cannot be identified with some certainty, the first step is to collect more counts. If it still cannot be confirmed, it is either not present or present below the limits of detectability (see Chap. VI, “PRECISION AND ACCURACY” on page 54) and another technique such as WDS is warranted.

**Overlaps**

Peak overlaps occur much more frequently in EDS than in WDS because of the resolution difference, but software is available in most cases to perform the deconvolution. In the first transition metal series (Sc-Zn), Kα lines of one element often overlap Kβ lines of the element one atomic number less. If the Kα line is of an element present in low concentration, it may be missed. Interactive computer stripping methods work quite well in most of these cases, and a full computer deconvolution works well except on trace elements. There are some overlaps that are particularly severe, e.g. Si/W, and S/Mo/Pb. Deconvolution of these is still possible provided that the elements are present in major amounts. When looking for overlaps in the spectrum, one should always expand the energy scale and usually the vertical scale. Again, the three signs of peak overlap are 1) peaks shifted from their correct energy, 2) asymmetrical or distorted peaks, and 3) incorrect relative intensities within a line series.

**Summary of Qualitative Analysis**

1. Calibrate the energy scale of the system, if needed.
2. Select an appropriate accelerating voltage and take-off angle.
3. Count long enough to detect confidently all elements present.
4. Use AutoID, but check it manually and apply common sense.
5. Use a systematic method on complicated multi-element specimens.
6. Look for artifact peaks and possible overlaps.
7. Quantitative analysis is not AutoID. Quantitative programs must know all the elements present; they do not find them. Moreover, quantitative analysis is not possible if peaks are misidentified.
V. QUANTITATIVE ANALYSIS

Quantitative chemical analysis using X-rays is an established technique that, when properly performed, yields an accurate analysis of a small area. There are about a dozen common microanalytical techniques, and although some of them have specific advantages over X-ray analysis, none are better than X-rays for routine quantitative analysis. For a review of microanalytical techniques, see Wachtman (1993).

We know from Moseley’s Law (Moseley, 1913) discussed in Chapter II, “ELECTRON-SPECIMEN INTERACTION AND X-RAY GENERATION” on page 9, that the wavelength or energy of characteristic X-rays is proportional to the atomic number of the element producing the X-ray. It is intuitive that the intensity of X-rays of a given element should be proportional to the concentration of that element in the specimen. In his doctoral thesis, Castaing (1951) actually carried out a quantitative microanalysis using electron-generated X-rays; moreover, he conceived of the various corrections that are needed to convert X-ray intensity into weight percent. In the years that followed, others formulated and refined these corrections into the standard matrix correction procedures that we know of as the ZAF method. For a detailed review of the development of the method, see Heinrich (1981).

Throughout the period of the 1970s and early 1980s, there was little work in the area of quantitative analysis of bulk samples. But with the advent of so-called “phi-rho-z” methods (Packwood and Brown, 1981), there has been an increased interest in improving the accuracy of X-ray microanalysis. ASTM published a standard guide to quantitative analysis by EDS (ASTM E 1508, 1998), which showed the actual precision one can expect from the technique.

In the following sections, we will discuss the steps in quantitative analysis, including background subtraction, peak deconvolution, and matrix correction procedures. And we will examine the effect of some variables on our goal of achieving an accurate, reproducible analysis of a small area of the specimen. The precision and accuracy of the method will be examined in more detail in the next chapter.

Background Subtraction and Deconvolution

**Background Subtraction**

Before the proportionality between X-ray intensity and elemental concentration can be calculated, several steps are required to obtain the intensity ratio (k) between unknown and standard. Or if the standard-less analysis technique is used, then a pure net intensity is required. An X-ray spectrum generated by electrons contains a background consisting of continuum X-rays and electronic noise. In the case of WDS, it is usually adequate to measure the background on both sides of the peak and do a linear interpolation before subtraction. An alternative is to set the spectrometer on the peak of interest and measure the intensity with the beam on an element of similar atomic number, but not containing the analyte.

In the case of EDS, the background is not linear, and a simple interpolation is inadequate. Two approaches are used in commercial systems today. One method is to construct a background model on the basis of the known physics plus suitable corrections for the real world. This method of background modeling is fast and lets the user see and pass judgement on the quality of the model.

The other method is that of a digital filter. In the digital filter method, the background is treated as a low frequency component of the spectrum and is mathematically set to zero. This method is not based on any model, and therefore is more general. It is also more useful for the light element region of the spectrum.
where earlier models, such as used in Frame C were never intended to be used. Although it does not take into account absorption edges, practical experience has shown that no significant loss of accuracy occurs. In a modern computer, there is no discernible speed difference between the methods. Figure 5.1 shows an example of a spectrum after digital filtering.

![Figure 5.1 Spectrum of a ceramic superconductor after digital filtering.](image)

**Deconvolution**

The other situation that needs to be considered before an intensity ratio can be measured is EDS peak overlap, an example of which is shown in Figure 5.2. This figure shows Ti K\(\alpha\) overlapped with Ba L\(\alpha\). The compound BaTiO\(_3\) is a common electronic ceramic with commercial importance, and the composition often needs to be quantified. Although the peaks could be resolved by WDS, computer deconvolution methods permit analysis by EDS.

![Figure 5.2 EDS Spectrum of BaTiO\(_3\) showing the Ba L lines with the Ti K lines.](image)
Again, there are two methods in common use. One of these is that of overlap factors. In this method, the convoluted peak is treated as the sum of pure element peaks, each multiplied by a factor between 0 - 1 representing the degree of overlap. These overlap factors can be measured or calculated. The second common method is that of multiple least squares. In this method, the convoluted peak is compared to standard Gaussian peaks for each element of interest. The amount of each pure element spectrum that best accounts for the unknown spectrum by minimizing the value of chi-squared is the best set of intensity ratios. The method of multiple least squares is sensitive to peak shifts, if any drift occurs between the time the reference spectra and unknown spectrum are collected. However, even the most severe overlaps can be deconvoluted in this manner provided that the concentrations of the elements making up the overlap do not differ widely, e.g. 90%/10%. Once the background is subtracted and the peaks are stripped of interferences, their intensities can be divided by those of similarly background-subtracted, deconvoluted standards that were collected under the same geometrical conditions, at the same accelerating voltage and beam current, and for the same length of time.

The ratio calculated in this manner is called a k-ratio, and it is the starting point for all analytical techniques involving standards. K-ratios may come from EDS or WDS, or they may be calculated by a standardless routine. Even standardless analysis requires background subtraction and peak deconvolution, but the intensity is calculated from pure element intensity curves and the ratio of peak integrals in the unknown spectrum. An example of such a curve for K lines is shown in Figure 5.3.

![Figure 5.3 Pure element curve for K lines showing calculated intensities.](image)

Standardless analyses always total 100%, or some other value entered by the user. And whether one chooses a standards or a standardless technique, a correction is necessary to account for the effect of other elements present in the unknown.
**Take-off Angle**

The take-off angle is defined as the angle between the surface of the sample and a straight line to the detector. If the sample is not tilted, the surface-normal is the beam direction, and the take-off angle, $\Psi$, is defined as follows:

$$\Psi = \tan^{-1}\left(\frac{W-V}{S}\right)$$

*(Equation 5.1)*

where:
- $W$ = working distance
- $V$ = vertical distance
- $S$ = spectrometer distance

Working distance is measured on the microscope. Vertical distance is the distance from the bottom of the pole piece to the centerline of the spectrometer; it usually can be measured on the microscope with a ruler. Spectrometer distance is the horizontal distance from the spectrometer to the beam; it is measured using the scale on the spectrometer slide. This situation is shown in Figure 5.4.

![Figure 5.4 Drawing showing the geometrical configuration and take-off angle when the specimen is not tilted.](image)

If the sample is tilted an effective take-off angle is used, and a horizontal or azimuthal angle is needed. This is the angle between the X-ray detector and the direction of tilt, usually toward the secondary electron detector. One implementation of the effective take-off angle used by PGT is as follows:

$$\Psi_{eff} = \tan^{-1}\left[\frac{X}{\sqrt{W-V/D}}\right]$$

*(Equation 5.2)*

where:
- $X = \sin(T) \cdot \cos(H) \cdot S/D + \cos(T) \cdot [(W - V)/D]$

*(Equation 5.3)*
and:

D is the detector distance defined as:

\[ D = \sqrt{(W - V)^2 + S^2} \]  

(Equation 5.4)

T = tilt
H = horizontal angle

Although the derivation of this relationship is not straightforward, it seems to work under a wide range of geometric conditions. Take-off angle or effective take-off angle should be minimized not only to increase collection efficiency, but also to minimize the absorption path length, thus reducing the magnitude of the absorption factor, as shown in Figure 5.5.

*Figure 5.5 Difference in absorption path length for low and high take-off angle.*
Figure 5.6 illustrates another geometric variable, namely, “variable z.” On some detectors, it is possible to tilt the endcap in the vertical plane to a pivot point that changes the position of the crystal with respect to the specimen and to the final lens. The benefits to such an arrangement are threefold:

1. Position the detector under the polepiece
2. Adapt to selected working distance for optimum solid angle
3. Avoid accessories such as BSE detector

**Standardless Analysis**

If standards are used, then the k-ratio is the ratio of the background-subtracted deconvoluted peak intensity in the unknown vs. the standard. If standardless analysis is used, then the calculation of a k-ratio is more complicated. Standardless methods use pure element intensities calculated on the basis of the physics of X-ray generation and detector efficiency. Specifically the factors listed in Table 5.1 are used in the calculation.
There is a temptation to try to model these factors on the basis of known physics. However, empirical factors often work better for some of them. Take the case of spectrometer efficiency; one could calculate absorption of the window, crystal contact, and crystal dead layer. A method that works much better, though, is to measure the actual background every few eV and solve multiple simultaneous equations, and then iterate the whole procedure. It is also necessary to change the algorithm below 1 keV. This is done by using the efficiency calculated for higher energies as the starting point for iterating the efficiency at low energy. We have found that it is even possible to use a “self-efficiency,” in which the spectrometer efficiency calculation is iterated on an unknown specimen along with the matrix correction.

An empirical approach to M lines is also superior, because constants for M lines are not well known, and they only exist over a narrow range of energy from about 1-3 keV. For this latter reason, and because the intensity is not spread over a series of resolved lines as with the L lines, we have found the use of M lines, where possible, gives better results than L lines.

It is often assumed that standardless methods are inferior to standards methods, but the data do not always substantiate this assumption (ASTM E 1508, 1998). To be sure, if one is using an EPMA with a fixed take-off angle, insignificant beam drift, and high quality standards, the analytical results will be better than those from a standardless analysis. But in an SEM, these conditions do not necessarily apply. A list of advantages of each technique is given in Table 5.2.

<table>
<thead>
<tr>
<th>Factors Used in Calculating Pure Element Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionization cross section</td>
</tr>
<tr>
<td>Fluorescence yield</td>
</tr>
<tr>
<td>Atomic weight</td>
</tr>
<tr>
<td>Backscatter factor</td>
</tr>
<tr>
<td>Absorption factor</td>
</tr>
<tr>
<td>Relative line intensities</td>
</tr>
<tr>
<td>Coster-Kronig yields for L and M lines</td>
</tr>
<tr>
<td>Spectrometer efficiency</td>
</tr>
</tbody>
</table>

**Table 5.2 Comparison of Quantitative Analysis with Standards and Standardless**

<table>
<thead>
<tr>
<th>Standards Advantages</th>
<th>Standardless Advantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factors cancel, if standards/unknowns are similar</td>
<td>Beam current drift not a factor</td>
</tr>
<tr>
<td>Absolute magnitude of constants is less important</td>
<td>Constant geometric configuration not important</td>
</tr>
<tr>
<td>Wide range of kV and take-off angles</td>
<td>High quality standards unnecessary</td>
</tr>
<tr>
<td>Actual analytical total—not just 100%</td>
<td>Standards for every kV/TOA unnecessary</td>
</tr>
<tr>
<td></td>
<td>Specimen change unnecessary</td>
</tr>
<tr>
<td></td>
<td>Fast</td>
</tr>
</tbody>
</table>
From the above list, it is evident that the advantages of the standards-based method tend to be theoretical; whereas, those of standardless tend to be practical. It is not surprising, therefore, that standardless methods are often overlooked in textbooks while 90% of those doing microanalysis use only the standardless method. It might be assumed that because of uncertainties in the constants used, standardless analysis could never be as good as analysis with standards. But on the contrary, ASTM E 1508 (1998) found that in practice standardless often works better. Specifically, when elements are present in 10 wt.% concentrations or more, the average precision of standardless was the same as that of standards and the accuracy was better. It seems that the strongest advantage of standards (factors cancel) is outweighed by the practical advantages of the standardless method, such as insensitivity to beam current. For a more thorough discussion of precision and accuracy, see Chapter VI, “OPERATION OF THE ELECTRON MICROSCOPE” on page 59.

Before concluding that standardless programs are superior, it should be stated that there are circumstances when they do not work well at all. Extremes of overvoltage or take-off angle should be avoided, as they should with standards. And standardless programs should always be verified against standards for each class of materials analyzed. However, once verified, standardless analysis eliminates many practical problems associated with quantitative analysis in an SEM.

**Matrix Correction**

The concept of correcting the k-ratio for inter-element effects is called a matrix correction, and is often not well understood and sometimes misunderstood. Although it is not necessary to know the derivation of each factor, it is not good practice to ignore these effects either. Simply put, one needs to understand the matrix effects well enough to operate the instrument and select standards that cause each factor to be as close to unity as possible. If the correction for atomic number, absorption, or fluorescence deviates significantly from unity, then the analyst must rely on the algorithm in the computer to accurately correct the k-ratio. To the extent that constants in the computer are in error, such as mass absorption coefficients or mean ionization potentials, so will be the concentration calculated.

**Calibration Curves**

In binary systems it is possible to make a series of compositions that cover either 0 - 100 wt.%, or at least the range most commonly analyzed. If the composition is known, the k-ratio can be measured at some accelerating voltage and sample-to-detector geometry, and the resulting calibration curve can be used to convert from k-ratio to weight percent. This method may seem crude, but in fact, it is extremely accurate because the standards are so similar to the unknowns that most effects cancel. An example of calibration curves is shown in Figure 5.7
Another simple case is that of trace element analysis. In this situation, a matrix correction is seldom necessary because the error associated with counting statistics is greater than any possible matrix effects. Accordingly, the k-ratio is a good estimate of concentration.

**ZAF Method**

The method of ZAF has been used by most microanalysts over the last 30 years or so, and its implementation as FRAME C had become the standard in most small computers since 1979 (Myklebust, et al., 1979). Most manufacturers of EDS or WDS systems now use their own computer programs with tabulated values of constants. Standardless programs are also popular, but even these need to use a matrix correction. For a discussion of the development of the ZAF method, see Goldstein et al. (2003), or for an even more detailed treatment, see Heinrich (1981). The purpose here, however, is to understand the method well enough to optimize a quantitative analysis and to be aware of its limitations.

**Atomic Number Correction**

The atomic number factor, or Z factor, corrects for the difference between the X-rays that are generated in the specimen compared with those generated in the standard. It arises because of differences in the backscatter coefficient and the electron stopping power between unknown and standard. It can be eliminated by using a standard similar in composition to the unknown, and it can be minimized by using a high overvoltage; however, as we will see, a high overvoltage would increase the absorption effect.

The example below shows a hypothetical analysis of a lead glass. Lead is a heavy element in a light matrix, and its k-ratio is only 0.108 even though its weight fraction is 0.1856. In this case, the Z factor is 1.60, or 60%. Although increasing the voltage from 15 to 30 kV would decrease the effect of Z, it would unacceptably increase the effect of absorption. Consequently, the strategy for this analysis should be to
obtain another homogeneous lead glass of known composition as a standard. The formulation for the Z factor was proposed by Duncumb and Reed (1968) and is a function of the following parameters:

$$Z = f(E_0, E_c, Z, A, Q, J)$$

where:
- $E_0$ = accelerating voltage
- $E_c$ = critical excitation potential
- $Z$ = atomic number
- $A$ = atomic weight
- $Q$ = ionization cross section
- $J$ = mean ionization potential

### Absorption Correction

The absorption factor, or A factor, is usually the most important one. It corrects for those X-rays that were generated in the specimen but absorbed before they were able to escape and be detected. The A factor is a ratio of the absorption behavior between the standard and the unknown. At some depth within the specimen, the number of X-rays generated reaches a maximum, and as overvoltage increases, so do this depth and the volume producing X-rays. On the other hand, X-rays produced deep within the specimen are more likely to be absorbed than those produced near the surface. As a result, there is an optimum overvoltage that yields a maximum peak/background ratio. Besides overvoltage, absorption is also affected by the path length, which in turn is affected by the take-off angle. The higher the take-off angle, the shorter is the absorption path length (see Figure 5.5). Increasing the take-off angle above 40° does not greatly reduce absorption, but a take-off angle less than 20° significantly increases it.

An example of a situation where absorption is significant is aluminum in copper as shown in Table 5.4, below.

### Table 5.3 Example Showing a Significant Atomic Number Correction

<table>
<thead>
<tr>
<th></th>
<th>$k$</th>
<th>$Z$</th>
<th>$A$</th>
<th>$F$</th>
<th>ZAF</th>
<th>Conc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb-M</td>
<td>0.108</td>
<td>1.600</td>
<td>1.067</td>
<td>1.000</td>
<td>1.708</td>
<td>18.56%</td>
</tr>
<tr>
<td>Si-K</td>
<td>0.340</td>
<td>0.953</td>
<td>1.147</td>
<td>1.000</td>
<td>1.094</td>
<td>37.33%</td>
</tr>
<tr>
<td>O-K</td>
<td>0.145</td>
<td>0.941</td>
<td>3.217</td>
<td>0.999</td>
<td>3.029</td>
<td>44.11%</td>
</tr>
</tbody>
</table>

PbO = 20.00%
SiO$_2$ = 80.00%
Under these analytical conditions, the absorption factor for Cu absorbing Al X-rays is a huge 7.051, when Cu is the dominant element present at 98%. If the take-off angle were increased to 52.5°, A would only go down to 3.03. However, if the voltage were decreased to 15 kV, A would decrease to 2.5, and if the voltage were further decreased to 10 kV and the Cu L line analyzed, the Al absorption factor would be 1.8. The formulation of the A factor was proposed by Philibert (1963) and is a function of the following parameters:

\[
A = f(E_0, E_c, Z, A, \mu/\rho, \psi)
\]

where:
- \(E_0\) = accelerating voltage
- \(E_c\) = critical excitation potential
- \(Z\) = atomic number
- \(A\) = atomic weight
- \(\mu/\rho\) = mass absorption coefficient
- \(\psi\) = take-off angle

The take-off angle and overvoltage are both under the analyst's control and can be used to minimize the magnitude of the matrix correction. It should be noted that each of the factors is a function of composition. For example, if the alloy cited above were actually 2% Cu in 98% Al, the A factor would be only 1.02, because there would be so little copper to absorb aluminum X-rays.

**Fluorescence Correction**

The characteristic fluorescence factor, or F factor, is usually the least significant. It corrects for those X-rays that are detected by the detector but were not generated by the electron beam. These X-rays are the result of secondary fluorescence by characteristic lines of other elements in the specimen. Because of its nature, the F factor is always less than one. As a rule-of-thumb, for the transition metals, fluorescence becomes significant 2, 3 and 4 atomic numbers below the fluorescing element, e.g. Cu fluoresces Co, Fe and Mn. Fluorescence is not significant in most geological or biological samples. An example in which fluorescence is significant is Ni in Fe as shown in Table 5.5, below.

### Table 5.4 Example Showing a Significant Absorption Correction

<table>
<thead>
<tr>
<th></th>
<th>20 kV</th>
<th>(\psi = 15^\circ)</th>
<th></th>
<th>20 kV</th>
<th>(\psi = 52.5^\circ)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>k</td>
<td>Z</td>
<td>A</td>
<td>F</td>
<td>ZAF</td>
</tr>
<tr>
<td>Al-K</td>
<td>0.003</td>
<td>0.844</td>
<td>7.051</td>
<td>0.999</td>
<td>5.953</td>
</tr>
<tr>
<td>Cu-K</td>
<td>0.975</td>
<td>1.004</td>
<td>0.999</td>
<td>1.000</td>
<td>1.004</td>
</tr>
</tbody>
</table>

Under these analytical conditions, the absorption factor for Cu absorbing Al X-rays is a huge 7.051, when Cu is the dominant element present at 98%. If the take-off angle were increased to 52.5°, A would only go down to 3.03. However, if the voltage were decreased to 15 kV, A would decrease to 2.5, and if the voltage were further decreased to 10 kV and the Cu L line analyzed, the Al absorption factor would be 1.8. The formulation of the A factor was proposed by Philibert (1963) and is a function of the following parameters:

\[
A = f(E_0, E_c, Z, A, \mu/\rho, \psi)
\]

where:
- \(E_0\) = accelerating voltage
- \(E_c\) = critical excitation potential
- \(Z\) = atomic number
- \(A\) = atomic weight
- \(\mu/\rho\) = mass absorption coefficient
- \(\psi\) = take-off angle

The take-off angle and overvoltage are both under the analyst's control and can be used to minimize the magnitude of the matrix correction. It should be noted that each of the factors is a function of composition. For example, if the alloy cited above were actually 2% Cu in 98% Al, the A factor would be only 1.02, because there would be so little copper to absorb aluminum X-rays.

**Fluorescence Correction**

The characteristic fluorescence factor, or F factor, is usually the least significant. It corrects for those X-rays that are detected by the detector but were not generated by the electron beam. These X-rays are the result of secondary fluorescence by characteristic lines of other elements in the specimen. Because of its nature, the F factor is always less than one. As a rule-of-thumb, for the transition metals, fluorescence becomes significant 2, 3 and 4 atomic numbers below the fluorescing element, e.g. Cu fluoresces Co, Fe and Mn. Fluorescence is not significant in most geological or biological samples. An example in which fluorescence is significant is Ni in Fe as shown in Table 5.5, below.
There is little change in the F correction between 15 and 30 KV. However, if the concentrations of the fluorescing and fluoresced elements are widely different, then the magnitude of the F correction changes greatly. The F factor was proposed by Reed (1965) and is a function of the following parameters:

\[ F = f \left( E_0, E_C, A, \mu/\rho, \Psi, \omega, r, P \right) \]

where:
- \( E_0 \) = accelerating voltage
- \( E_C \) = critical excitation potential
- \( Z \) = atomic number
- \( A \) = atomic weight
- \( \mu/\rho \) = mass absorption coefficient
- \( \Psi \) = take-off angle
- \( \omega \) = fluorescence yield
- \( r \) = absorption jump ratio
- \( P \) = type of fluorescence, e.g. KL

Besides character fluorescence, there may be continuum fluorescence. The effect is negligible for elements lighter than titanium (Armstrong, 1998), but because of the complexity of the calculation, most computer programs do not correct for it at all.

<table>
<thead>
<tr>
<th></th>
<th>15 kV</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \Psi = 40° )</td>
<td>k</td>
<td>Z</td>
<td>A</td>
<td>F</td>
<td>ZAF</td>
</tr>
<tr>
<td>Fe-K</td>
<td></td>
<td>0.399</td>
<td>1.010</td>
<td>1.002</td>
<td>0.893</td>
<td>0.903</td>
</tr>
<tr>
<td>Ni-K</td>
<td></td>
<td>0.628</td>
<td>0.995</td>
<td>1.025</td>
<td>1.000</td>
<td>1.019</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>30 kV</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \Psi = 40° )</td>
<td>Fe-K</td>
<td>0.413</td>
<td>1.014</td>
<td>1.009</td>
<td>0.852</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ni-K</td>
<td>0.586</td>
<td>0.992</td>
<td>1.100</td>
<td>1.000</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>30 kV</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \Psi = 40° )</td>
<td>Fe-K</td>
<td>0.028</td>
<td>1.022</td>
<td>1.014</td>
<td>0.677</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ni-K</td>
<td>0.975</td>
<td>1.000</td>
<td>1.005</td>
<td>1.000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fe-K</td>
<td>0.982</td>
<td>1.000</td>
<td>1.000</td>
<td>0.997</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ni-K</td>
<td>0.016</td>
<td>0.980</td>
<td>1.287</td>
<td>1.000</td>
</tr>
</tbody>
</table>

Table 5.5  Example Showing a Significant Fluorescence Correction
Figure 5.8 k-ratio vs. intensity in an Fe-Cr binary.

Figure 5.8 is a plot of k-ratio vs. wt% for the system Cr-Fe and shows the effects of absorption and fluorescence. The curve for Fe exhibits a negative deviation from linearity because the Fe X-rays are strongly absorbed by the Cr atoms in the matrix. For example, for a mass fraction of 0.5 Fe, the k-ratio is only 0.45. The curve for Cr exhibits a positive deviation from linearity because Cr X-rays are enhanced by fluorescence from Fe X-rays. These absorption and fluorescence effects must be considered and a correction applied to account for the deviation from linearity, or in other words, to account for the error in the assumption that the k-ratio is equal to the concentration. There exists no significant atomic number effect in this system because Fe and Cr are so similar in atomic number.

Phi-rho-z Method

A phi-rho-z curve is actually an ionization distribution in which ionizations, $\phi = f(\rho z)$ are plotted against mass-depth ($\rho z$). These curves have been measured experimentally by various researchers ever since Castaing suggested the experiment in the early 1950s. However, Packwood and Brown (1981) suggested using such a distribution to calculate the Z- and A- factors for quantitative analysis. To do this, one must know the shape of the curve accurately, and this is where the various groups disagree. Throughout the 1980s, models for phi-rho-z curves were proposed by Packwood and Brown in Canada, Love and Scott in the UK, Pouchou and Pichoir in France, Bastin in the Netherlands and others. Inasmuch as development is still ongoing, no one reference suffices. However, the proceedings of the Microbeam Analysis Society each year is a good place to look for the latest work. While a phi-rho-z curve describes a physical process, the equations used to generate these curves are actually fit to experimental data. In fact, the equations, that each group proposes are optimized to give the best results for one particular set of data. An example of a phi-rho-z curve for zinc at 30 kV accelerating voltage is shown in Figure 5.9.
Conceptually, if a phi-rho-z curve is known accurately, one can compare the intensity after absorption with the intensity generated and compute an absorption factor. Moreover, the ratio of intensity between unknown and standard gives the atomic number factor. The fluorescence factor is computed separately using the approach of Reed (1965), the same way it is calculated in the ZAF method. The intensity mentioned above is actually the area under the phi-rho-z curve. The more accurate the equations used to describe the curve, the more accurate the integration. The goal of this approach is to achieve increased accuracy compared with the traditional ZAF method. If precision associated with counting statistics is not limiting, then it is possible to achieve a more accurate analysis, particularly when absorption is significant.

Comparison of ZAF vs. phi-rho-z Methods

The four groups mentioned above who are working on phi-rho-z methods often propose new models as they improve on them. But in addition to their models, Armstrong (1982) proposed averaging the constants between two Packwood-Brown models, and it is this approach that PGT adopted, along with the atomic number correction of Love et al. (1978). For comparison, a set of k-ratios for a complex alloy used to develop the ASTM E 1508 standard were subjected to two different matrix corrections—the conventional ZAF and Armstrong's phi-rho-z. The results are listed in Tables 5.6 and 5.7, below.

<table>
<thead>
<tr>
<th>Element</th>
<th>k</th>
<th>Z</th>
<th>A</th>
<th>F</th>
<th>ZAF</th>
<th>Conc.</th>
<th>Actual</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-K</td>
<td>0.0121</td>
<td>1.006</td>
<td>1.035</td>
<td>0.862</td>
<td>0.896</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>Ni-K</td>
<td>0.7030</td>
<td>0.988</td>
<td>1.018</td>
<td>0.997</td>
<td>1.003</td>
<td>70.51</td>
<td>68.12</td>
</tr>
<tr>
<td>Cr-K</td>
<td>0.1682</td>
<td>1.008</td>
<td>1.028</td>
<td>0.924</td>
<td>0.958</td>
<td>16.11</td>
<td>14.76</td>
</tr>
<tr>
<td>Ta-K</td>
<td>0.0076</td>
<td>1.201</td>
<td>1.446</td>
<td>0.998</td>
<td>1.732</td>
<td>1.32</td>
<td>1.91</td>
</tr>
<tr>
<td>Mo-L</td>
<td>0.0138</td>
<td>1.118</td>
<td>1.252</td>
<td>0.993</td>
<td>1.389</td>
<td>1.92</td>
<td>1.91</td>
</tr>
<tr>
<td>Ti-K</td>
<td>0.0255</td>
<td>1.007</td>
<td>1.052</td>
<td>0.941</td>
<td>0.997</td>
<td>2.54</td>
<td>2.26</td>
</tr>
<tr>
<td>W-L</td>
<td>0.0207</td>
<td>1.210</td>
<td>1.401</td>
<td>0.997</td>
<td>1.691</td>
<td>3.50</td>
<td>3.91</td>
</tr>
<tr>
<td>Al-K</td>
<td>0.0137</td>
<td>0.927</td>
<td>2.567</td>
<td>1.000</td>
<td>2.379</td>
<td>3.26</td>
<td>4.00</td>
</tr>
</tbody>
</table>

Total: 100.16
These two matrix corrections produce similar results for this complex sample, and a few absorption corrections are italicized to highlight differences. The phi-rho-z method is more accurate for the lightest element, aluminum, and it is in light element analysis that most claims are made for phi-rho-z superiority. However, it should be evident that in many cases the differences between matrix corrections are less than the uncertainty associated with counting statistics, as discussed in the next chapter. Armstrong claims that his equations produce good results for oxides and silicates and other non-conducting materials. The choice of model does not seem to make much difference for heavier elements. Conventional ZAF produces results consistent with earlier analyses, while phi-rho-z may yield improved results for light elements. If the field converges on one model, it can easily be adopted.

**Bence-Albee Method**

The method of Bence-Albee is the most famous implementation of what may be called the empirical method or hyperbolic method. The hyperbolic relationship between concentration and k-ratio was suggested by Castaing and formalized by Ziebold and Ogilvie (1964). But it was not until Bence and Albee (1968) measured a number of binary oxide systems and explained how the technique could be applied to ternary and higher systems that it came into common use. In those days, the method had the advantage of simplicity. So-called “alpha factors” could be measured between binary oxides, and “beta factors” could then be calculated for multi-component systems. In fact, empirical alpha factors were soon replaced with calculated factors from ZAF (Albee and Ray, 1970). When these alpha factors are used, one obtains an analysis identical to that of ZAF. The only remaining advantage to the hyperbolic method, therefore, is speed of computation. However, the difference has not been a factor for many years, so there is no longer a reason to use this type of matrix correction.

**Summary of Matrix Corrections**

Regardless of the matrix correction procedure chosen, there are certain experimental parameters under control of the analyst that reduce the role of the matrix correction and improve the quality of the analysis. If sufficient counts are collected for each element so that counting statistics do not limit precision, then accuracy can be increased as follows:

---

### Table 5.7 Results of a phi-rho-z Matrix Correction on 8-Element Alloy

<table>
<thead>
<tr>
<th></th>
<th>k</th>
<th>Z</th>
<th>A</th>
<th>F</th>
<th>ZAF</th>
<th>Conc.</th>
<th>Actual</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-K</td>
<td>0.0121</td>
<td>1.004</td>
<td>1.033</td>
<td>0.861</td>
<td>0.896</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>Ni-K</td>
<td>0.7030</td>
<td>0.987</td>
<td>1.018</td>
<td>0.997</td>
<td>1.002</td>
<td>70.41</td>
<td>68.12</td>
</tr>
<tr>
<td>Cr-K</td>
<td>0.1682</td>
<td>1.006</td>
<td>1.026</td>
<td>0.924</td>
<td>0.954</td>
<td>16.04</td>
<td>14.76</td>
</tr>
<tr>
<td>Ta-K</td>
<td>0.0076</td>
<td>1.206</td>
<td>1.363</td>
<td>0.998</td>
<td>1.639</td>
<td>1.25</td>
<td>1.91</td>
</tr>
<tr>
<td>Mo-L</td>
<td>0.0138</td>
<td>1.085</td>
<td>1.236</td>
<td>0.993</td>
<td>1.331</td>
<td>1.84</td>
<td>1.91</td>
</tr>
<tr>
<td>Ti-K</td>
<td>0.0255</td>
<td>1.006</td>
<td>1.049</td>
<td>0.941</td>
<td>0.992</td>
<td>2.53</td>
<td>2.26</td>
</tr>
<tr>
<td>W-L</td>
<td>0.0207</td>
<td>1.207</td>
<td>1.314</td>
<td>0.998</td>
<td>1.582</td>
<td>3.27</td>
<td>3.91</td>
</tr>
<tr>
<td>Al-K</td>
<td>0.0140</td>
<td>0.922</td>
<td>2.901</td>
<td>1.000</td>
<td>2.672</td>
<td>3.74</td>
<td>4.00</td>
</tr>
<tr>
<td><strong>Total:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>100.08</td>
<td></td>
</tr>
</tbody>
</table>

These two matrix corrections produce similar results for this complex sample, and a few absorption corrections are italicized to highlight differences. The phi-rho-z method is more accurate for the lightest element, aluminum, and it is in light element analysis that most claims are made for phi-rho-z superiority. However, it should be evident that in many cases the differences between matrix corrections are less than the uncertainty associated with counting statistics, as discussed in the next chapter. Armstrong claims that his equations produce good results for oxides and silicates and other non-conducting materials. The choice of model does not seem to make much difference for heavier elements. Conventional ZAF produces results consistent with earlier analyses, while phi-rho-z may yield improved results for light elements. If the field converges on one model, it can easily be adopted.
1. Use a standard similar to the unknown.
2. Use a high take-off angle.
3. Use a moderate overvoltage.
4. Determine the background carefully.

Under these conditions the ZAF method produces reliable results for X-ray lines >1.0 keV. For X-rays softer than this, the phi-rho-z method is probably more accurate. It may also be more accurate for non-conducting specimens such as oxides and silicates.

### Requirements for Quantitative Analysis

Having discussed the methods of quantitative analysis, it is relevant to ask if there are any specific requirements in terms of sample or procedure that must be met. The following considerations are just some of those that could be cited.

**Polished Specimen:** Because of the importance of having a similar geometric arrangement in the standard and the unknown, if the surface of either is rough, the analysis will be in error. The specimen need not have a flawless metallographic or petrographic polish, but it must be flat in the vicinity of the points to be analyzed.

**Phase Size Larger than the X-ray Range:** Quantitative analysis assumes that the X-rays are emanating from the composition that the matrix correction calculated. If the specimen is homogeneous over a range greater than the X-ray range, then the matrix correction will work. If this condition is not met, then one should not expect a truly quantitative analysis. A discussion of X-ray range and spatial resolution can be found in Chapter III, “X-RAY MEASUREMENT” on page 16.

If analysis of extremely fine phases must be attempted, then the beam should be scanned rather than defocused. A scanning beam causes the specimen to receive a constant dose of electrons over the scan. A defocused beam has an unknown distribution of electrons. However, neither procedure is a substitute for specimen homogeneity, and an “average” analysis is not obtained.

**Appropriate Standards are Available:** The more similar the standards are to the unknown, the more accurate will be the analysis. An appropriate standard is of known composition and is homogenous at the micrometer level. Materials that are standards for bulk analysis are probably not suitable for microanalysis. They should be analyzed by an independent method and checked for homogeneity with the microanalysis system. For the most accurate work, standards and unknowns should be coated, if necessary, at the same time. Standards may be purchased from electron microscopy supply houses, or the National Institute for Standards Technology. The best source, however, for materials commonly analyzed in an industrial laboratory, is the company itself. Quite often, a particular company has the best capability to prepare and analyze a standard for the product it produces.

**Specimen Properly Coated:** If the specimen is non-conducting, then a thin conductive coating is required. For X-ray analysis, this coating is usually carbon. Carbon can be easily evaporated; it is highly conductive, and it does not heavily absorb X-rays. Heavy metals such as gold or gold/palladium are sometimes used for imaging because of their secondary electron yield. But because of their density, they do not make good coatings for X-ray analysis. If carbon is to be analyzed, then aluminum is a good choice of coating material. The standard and unknown must be coated with the same material, and if the highest accuracy is necessary, they should be coated at the same time. A coating of a few tens of nanometers should be enough.
No Severe Peak Overlap: When EDS is used, the computer cannot separate overlapped peaks accurately if the concentrations of each element are very different. For example, if 90% of one element is present and only 10% of the other, the deconvolution routine is less accurate. When WDS is used, one must check for higher order lines. These are more common than most people think and are often overlooked.

**Light Element Analysis**

Quantification of the concentration of light elements presents problems over and above those for other elements. Elements whose atomic number is less than 11 are considered light for purposes of X-ray microanalysis. These elements produce soft X-rays that are hard to detect, easily absorbed, and subject to chemical shifts. Low count rates reduce the precision of light element analysis, and uncertainties in the matrix correction reduce the accuracy. A windowless or ultra-thin window (UTW) detector is necessary, and digital processing helps because it is inherently more sensitive to the small pulses from soft X-rays. Some of the considerations in light element analysis are discussed below, and calculated precisions and detectabilities for various light element detectors are tabulated in the next chapter.

**Absorption:** Soft X-rays characteristic of light elements are more easily absorbed than are hard X-rays. Consequently, any inaccuracy in tabulated mass absorption coefficients is magnified by the heavy absorption of these X-rays. The appropriate accelerating voltage must be selected to maximize the peak/background. The take-off angle must also be as high as possible. These soft X-rays are also absorbed in the window of WDS instruments or ultra-thin window EDS detectors.

**Contamination:** Carbon contamination deposited on the specimen is more of a problem when analyzing soft X-rays than when analyzing hard ones. The contamination comes from interaction of the electron beam with residual pump oil in the chamber. It can be reduced by use of a cold trap, but a better method of controlling it is with an air jet. This technique is merely a controlled leak of dry air into the vacuum chamber over the specimen. As contamination begins to form, the carbon is oxidized by the air and swept away. The way to check for contamination is to observe whether the count rate of soft X-rays is stable with time, and whether a carbon X-ray begins to rise.

**Peak Shifts and Interferences:** Light elements exhibit chemical shifts; that is, the X-ray line shifts with the nature of the chemical bond in the sample. For example, the boron line is in a different position depending on whether boron is in a metal, boride, or borate. It sometimes even varies between crystallographic forms of the same compound, and this shift can easily be measured by WDS. Accordingly, the standard must be carefully selected. In EDS, the peak shifts are imperceptible, and the entire window integral is used for intensity. Light element WDS peaks are also broad, thus increasing the chance of interference from higher order lines of other elements that are also more energetic. This peak broadening may also require the use of peak integrals that are hard to obtain on some wavelength systems. Peak overlaps with the L-lines of transition metals are also a concern with either EDS or WDS.

**Atomic Number Effects:** Samples requiring a quantitative analysis of light elements probably also have heavy elements. In simple oxides and geological samples, it is more accurate to analyze the light elements by stoichiometry. However, carbon in steel or oxygen in a defect structure may require quantitative analysis directly. The presence of heavy elements increases the likelihood that the standard has a different average atomic number than does the unknown. As a result, the continuum may be significantly different at the low end of the spectrum, and the matrix correction program must correct for the atomic number effect.

**Choice of Coating Material:** For most analyses, carbon makes a good choice of coating for conductivity. However, for light element analyses, heavy elements such as gold are even less desirable than usual. If carbon is being analyzed, then aluminum is a good choice.
Choice of Standards: All of the foregoing discussion leads us to the inescapable conclusion that use of similar standards is even more important in light element analysis than usual. Except for contamination, all the problems cited above are minimized or eliminated if the standards and unknowns are similar. There is also evidence that conductive and non-conductive specimens are fundamentally different with respect to electron-induced X-ray generation (Armstrong, 1988). Therefore, one should avoid using metallic standards for oxide/silicate analysis, if possible. Standardless analysis of light elements is now possible with some systems, but the pure element curves are less well known, and the detector efficiency must be measured under the identical analytical conditions. Before accepting the results of a standardless light element analysis, they should be compared against standards.

Thin Film Analysis

In a STEM, the concentration of elements in a thin foil can be quantified without the use of standards (Cliff and Lorimer, 1975). The thin film assumption is that X-ray absorption and fluorescence effects are negligible. Background subtraction and peak deconvolution still have to be performed to get net intensities, but these are related to concentrations through a so-called “K-factor” as follows:

\[
\frac{C_1}{C_2} = k_{12}\frac{I_1}{I_2}
\]

(Equation 5.6)

The Cliff-Lorimer K-factor (not to be confused with k-ratio) can be experimentally measured in a binary system in which the concentrations of both elements are known, or it can be calculated from first principles, including the detector efficiency. Most users let the computer calculate them. For a review of quantitative analysis of thin specimens and the Cliff-Lorimer method, see Joy et al. (1986). If the thin film assumption is not valid; i.e., absorption is significant, then specimen thickness must be known and a correction applied to the data.

Biological Microanalysis

In biological microanalysis, the problem is to quantify the concentration of a few elements such as Ca, P and K in a matrix of C, H, O and N. The most widely used method is that of Hall (1979), in which the continuum is used to correct for differences in mass thickness in thin sections. The peak (I) and background (B) intensities are measured on a standard of known composition, and then on the unknown specimen, assuming that the matrix is sufficiently similar. The concentration of each element of interest is obtained from Equation 5.7.

\[
C_x = \frac{I_x}{I_x/I_b}_0 \cdot C_{x0} \cdot \frac{(Z^2/A)_0}{Z^2/A}
\]

(Equation 5.7)

where:

- \( X \) = the element of interest
- \( I_x \) = the intensity of element \( X \)
- \( I_b \) = the intensity in a peak-free region of the background
- \( _0 \) = measurements on a standard
- \( Z \) = atomic number
- \( A \) = atomic weight
In actual use, $Z^2/A$ for biological tissue does not change appreciably. Generally a value of $\sim 3.3$ is reasonable for soft tissue, and values have been tabulated. For a review of quantitative methods in biological microanalysis, see Hall (1979) or Hall and Gupta (1986).

**Monte Carlo Calculations**

The Monte Carlo method simulates the trajectory of electrons and the generation of X-rays within either a bulk or thin sample. It does this by modeling the angular deflection resulting from elastic scattering and the energy loss from inelastic scattering. So-called single scattering models treat each scattering event separately; whereas multiple scattering models group elastic scattering events together in one deflection. The latter approach saves computer time.

If one knows the complete spatial and energy distribution of electrons and the positions from which X-rays are generated, many parameters can be derived. Some of these include the phi-rho-z curve, the backscatter coefficient, continuum fluorescence, and absorption effects. The method depends on simulating thousands of electron trajectories for it to have statistical validity. It has been used to test ZAF or phi-rho-z quantitative methods on bulk samples, but it has its greatest value with samples in other geometrical configurations. The interaction of electrons with particles and thin films can be modeled thus permitting analysis when bulk methods are not applicable. It is also useful for modeling non-normal beam incidence.

An example of simulated electron trajectories for aluminum and gold at 15 kV and 25 kV is shown in Figure 5.10. The scales on each of them are identical. These Monte Carlo simulations used the Electron Flight Simulator software (Brundle, et al., 1996).

![Monte Carlo plots showing the effects of accelerating voltage and density.](image)

Figure 5.10 Monte Carlo plots showing the effects of accelerating voltage and density.
VI. PRECISION AND ACCURACY

Some of the most frequently asked questions of microscopists and X-ray analysts are 1) “What is the precision of the analysis?” 2) “What is the minimum concentration that you can detect?” and 3) “What is the minimum area on the sample that you can analyze?” We often answer 1) ± 2% relative, 2) 0.1% with EDS and 0.01% with WDS, and 3) ~2 µm (see Equation 3.5). These are reasonable numbers under average conditions, but the real numbers can be easily calculated for any set of conditions. For a thorough description and derivation of the relevant equations, see Goldstein et. al. (2003). ASTM standard E 1508 (1998) on quantitative analysis by EDS also has a section on precision and bias, and reports the results of a round-robin study.

Definitions

Before discussing some of the specific measures of precision and accuracy, some definitions of terms may be useful. Some of these are adapted from ASTM E 456, “Standard Terminology for Statistical Methods” (1996).

**Precision**: The closeness of agreement between randomly selected individual measurements or test results.

**Accuracy**: The closeness of agreement between an observed value and an accepted reference value.

**Repeatability**: A measure of precision at some confidence level (usually 95%) applicable to the variability between test results obtained within a single laboratory in the shortest practical time by a single operator with a specific set of test equipment using specimens taken at random from a single sample of material. This is often called intralaboratory repeatability.

**Reproducibility**: A measure of precision applicable to the variability between single test results obtained in different laboratories using specimens taken at random from a single sample of material. This is often called interlaboratory reproducibility.

**Analytical Sensitivity**: The range of values (elemental concentration) within which values are statistically indistinguishable at the 95% confidence level, generally expressed as wt.% absolute.

**Accepted Reference Value (ARV)**: A value (elemental concentration) that serves as an agreed-upon reference for comparison. A suitable ARV might be competent wet chemical analysis of a homogeneous sample.

**Bias**: A systematic error that results in deviation, plus or minus, of a population mean from the accepted reference value.

**Coefficient of Variation% (CV%)**: The repeatability or reproducibility as a percent of the mean value.

**95% Confidence Interval (95%CI)**: The repeatability or reproducibility (at the 95% confidence level) divided by the square root of the number of replicate analyses.

**% Relative Accuracy(%RA)**: The 95% confidence interval as a percent of the mean value.

**Uncertainty**: Variability of a measured value arising from both random and systematic error (precision and bias).
Precision

The analytical sensitivity of a test method is a measure of the precision of the method. In X-ray microanalysis, it is the precision that may be expected from counting statistics, that is, the irreducible minimum error. This means that at the 95% confidence level, it is not possible to distinguish two analytical results if they differ by less than the number calculated from Equations 6.1 or 6.2.

### Absolute Precision

\[
\Delta C > \frac{2.33 \cdot C \cdot 2\sqrt{N_{p+b}}}{N_{p-b}}
\]

*(Equation 6.1)*

### Relative Precision

\[
\frac{\Delta C}{C} > \frac{2.33 \cdot 2 \cdot \sqrt{N_{p+b}}}{N_{p-b}}
\]

*(Equation 6.2)*

where:
- \( C \) = concentration as a fraction
- \( N \) = the number of counts in the peak, background subtracted or not, as indicated. For example, if:
  - \( N_{p+b} = 102000 \) counts, and
  - \( N_b = 2000 \) counts, then
  - \( \Delta C/C = 0.015 \), or 1.5% relative

The ASTM results showed that for major elements (>10 wt.%), intralaboratory repeatability for each element was always better than 7% relative and interlaboratory reproducibility was better than 10% (Friel, 1992). These results suggest that the actual precision, under real world conditions, is worse than the 2% or 5% that is often quoted. For minor or trace elements, it may not be possible statistically to distinguish between two analyses that differ by 100%. Precision can be improved by collecting more counts, by using a higher beam current, better geometric configuration, or longer counting.

### Minimum Detectability Limit

The minimum detectability limit is the limiting concentration of a trace element analysis. It depends on the counts in the peak above background. Therefore, some combination of time and beam current is necessary to achieve a peak that can be distinguished from background. Accordingly, the background must be accurately measured. A suitable equation for estimating the minimum detectability limit is given below. Notice that the number of counts is measured on a pure element. The number calculated by this equation is the minimum concentration of an element that may be confidently detected when the analysis is conducted such as to produce the given counts on a pure element. If there is any doubt about the presence of a peak, one should count longer.
For example, if:

\[
N_{p+b} = 102000 \\
N_b = 2000 \\
ZAF = 1 \\
C_{DL} > 0.0014 \text{ or } 0.14 \text{ wt.}%
\]

**Precision of Light Element Detectors**

Light element X-ray microanalysis can be performed with a wavelength dispersive spectrometer or with an EDS detector having either an ultra-thin window or no window at all. The precision of each of these detection methods depends heavily on the number of counts in the peak and not directly on the type of spectrometer. The minimum detectability limit, on the other hand, depends on the peak/background ratio and the ability to determine the background accurately. A general comparison of EDS with WDS detectors is given in Table 3.3.

Although WDS, if available, is the preferred method for light-element quantitative analysis, EDS can be used. Within the category of EDS, the user has the choice of sealed ultra-thin window or windowless detectors for light element analysis. Within the category of WDS, the user has the choice of a multi-spectrometer electron probe microanalyzer or adding a single wavelength spectrometer to the SEM. The following table lists some characteristics of each of these detection systems for oxygen in Fe$_2$O$_3$.

**Table 6.1 Comparison of Light Element Spectrometers for Oxygen in Fe$_2$O$_3$**

<table>
<thead>
<tr>
<th>Spectrometer Type</th>
<th>P/B</th>
<th>Counts</th>
<th>Relative % $C_{DL}$</th>
<th>Sensitivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WDS</td>
<td>50</td>
<td>100000</td>
<td>0.44</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1000</td>
<td>4.4</td>
<td>15.0</td>
</tr>
<tr>
<td>EDS Windowless</td>
<td>13</td>
<td>100000</td>
<td>0.87</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1000</td>
<td>8.7</td>
<td>16.0</td>
</tr>
<tr>
<td>EDS UTW</td>
<td>9</td>
<td>100000</td>
<td>1.04</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1000</td>
<td>10.4</td>
<td>17.0</td>
</tr>
</tbody>
</table>

The calculations in the table were made using Equations 6.2 for analytical sensitivity and 6.3 for minimum detectability, and using a ZAF factor of 3 for oxygen in Equation 6.3. The counts were fixed at 100000 to simulate a point analysis and 1000 to simulate a high-quality X-ray map. One can readily obtain these counts by some combination of time, beam current and voltage. The comparison unmistakably shows that precision is not much affected by peak-to-background ratio, but only by the number of counts obtained by whatever means. Minimum detectability, however, does depend on P/B ratio.
Accuracy

The foregoing discussion of statistical considerations relates to the various measures of precision—the irreducible minimum error. Uncertainties in the matrix correction contribute to inaccuracy. So do many other factors, some of which are listed in Table 6.2.

Table 6.2  Factors Affecting Precision and Accuracy

<table>
<thead>
<tr>
<th>Precision</th>
<th>Accuracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Counts in the peak</td>
<td>Geometric configuration, known and reproducible</td>
</tr>
<tr>
<td>P/B ratio</td>
<td>Standards known and homogenous</td>
</tr>
<tr>
<td>Beam stability</td>
<td></td>
</tr>
<tr>
<td>Matrix correction</td>
<td></td>
</tr>
<tr>
<td>Phase size &lt; X-ray range</td>
<td></td>
</tr>
<tr>
<td>Coating</td>
<td></td>
</tr>
</tbody>
</table>

There are surely other factors that contribute to inaccuracy, but the point is that the precision calculated using Equation 6.1 or reported by the analyzer is the minimum concentration difference that can be confidently distinguished. A variety of other factors cause the analysis to be less accurate, and they are not all under control of the analyst. The ASTM study found no systematic errors, and the repeatabilities matched Equation 6.1. Repeatability assumes that instrument, environment, operator and calibration remain the same. Reproducibility assumes that these factors are not constant.

The choice of matrix correction algorithm does not make much difference. When seven different matrix corrections were run on the same set of k-ratios for a stainless steel, the standard deviation was less than 1% of the mean (Friel, 1992). In other words, given the same k-ratios, the seven matrix corrections calculated nearly the same answer—all well within the range of precision. These results are plotted in Figure 6.1. Matrix correction schemes are not all equal, especially for EPMA light element analysis. But the differences among them are not statistically significant when compared with the measured precision of SEM/EDS.

Figure 6.1 Various matrix corrections plotted within the measured precision range.
Summary of Precision and Accuracy

The practice of quantitative microanalysis is neither trivial nor impossible. With reasonable care, the analyst can measure the concentration of elements that are present in about 0.1 wt.% and occupying a volume of less than $1 \mu m^3$ in some cases. Moreover, with an analytical electron microscope (AEM), it is possible under the most favorable conditions to analyze a mass of about $10^{-19}$ grams or about 5000 atoms. The reasonable care mentioned above includes factors such as geometric configuration, accelerating voltage, standards or standardless program, sample preparation, count rate, and time. If these factors are properly selected, one can achieve a high-quality quantitative analysis of a small volume on a routine basis.
VII. OPERATION OF THE ELECTRON MICROSCOPE

A detailed discussion of the operation of an electron microscope is beyond the scope of this book. However, the accelerating voltage and the beam current are two parameters that affect the X-ray microanalysis as well as image resolution and contrast—both analog and digital. Hence, this chapter deals only with the optimization of these in the context of microanalysis and imaging. Optimization of the geometric configuration within the microscope has already been discussed under quantitative analysis.

Accelerating Voltage

The accelerating voltage for a particular X-ray line should be about three times the critical excitation voltage for that line. For example, $\text{Mn}_{\text{ab}}$ is about 6.5 keV, and thus a voltage of 20 kV would be appropriate. Lower overvoltage ratios ($E_o/E_c$) are less efficient at exciting the X-rays, though they penetrate the specimen less. Higher overvoltages degrade X-ray spatial resolution in accordance with Equation 3.5 and Figure 5.10. Imaging resolution is usually improved at higher accelerating voltages.

Obviously, it is not possible to have the optimum overvoltage for every element in a multi-element specimen, so compromises must be made. In general, 20-30 kV is used for metals, 15 kV for oxides and silicates, and 5-10 kV for analysis of light elements. If the concentration of light elements can be computed from stoichiometry, it should be. If L or M lines are available, they can be used at a lower voltage than used for K lines, and in some cases it may even be necessary to conduct the analysis at two voltages.

Electron Beam Current

The current in the electron probe is an important parameter that affects both image resolution and contrast. It is most conveniently controlled by the condenser lens, or spot size control. The minimum diameter of the probe (spot size) is limited by the beam current. This relationship is thoroughly reviewed by Goldstein, et al. (2003, p. 57). As one increases the beam current, contrast increases at the expense of maximum resolution. If maximum resolution is not needed, this trade-off is a good one.

Contrast

The limit to contrast is often the specimen itself. If contrast is defined as the difference between the signals from two parts of the image divided by the greater of them, then for backscattered electrons (BSE) contrast can be quantitatively calculated from the backscatter coefficients. Backscatter coefficients are a function of atomic number and accelerating voltage. For example, Au on C at 30 kV produces about 90% contrast, which is why such a specimen is often used to prove resolution. Yet, in more typical specimens, contrasts of 10% or less are common, and adjacent elements in the periodic table such as Ag and Pd produce only 1% contrast.

The contrast carried by the secondary electron (SE) signal is not as easily calculated as in the BSE case. The SE signal does not usually change greatly with composition, but is highly sensitive to topography. Inasmuch as the mean escape depth for SEs is only about 1% of that of BSEs, intuitively one would expect to detect most secondaries from points, ridges and edges of features. Consequently, the resolution possible with the secondary electron signal is potentially far better than with backscattered electrons that may emerge from the specimen several micrometers from the position of the beam. However, these BSEs are also capable of generating secondary electrons themselves. When these SEs along with the BSEs
reach the Everhart-Thornley detector, fine detail is lost. For a list of imaging signals and the contrast they carry, see Table 8.2.

For a given amount of contrast inherent in the signal, there is a certain minimum beam current required to distinguish features from random background noise. This current is called the threshold current, and it can be calculated from the following equation:

\[
I_b > \frac{4 \times 10^{-18}}{C^2 \varepsilon t}
\]

(Equation 7.1)

where:
- \(C\) = contrast with a value between 0 and 1
- \(t\) = the dwell time per pixel
- \(\varepsilon\) = electron collection efficiency

Assuming a collection efficiency of 0.15, typical of silicates, a beam current of \(1.7 \times 10^{-11}\) A would be the minimum necessary to observe features differing by 10% contrast in a 512 x 512 digital image collected for 40 seconds or a 1024 x 1024 image collected for 160 seconds.

A plot of the threshold current as a function of contrast and collection time for a 1024 x 1024 image (about one million pixels) is given in Figure 7.1. For a 512 x 512 image, divide the collection time by four. This plot is applicable to both digital and analog images, though digital systems often achieve the required collection time by frame averaging.

![Figure 7.1 Relationship among contrast, acquisition time and beam current.](image)
Resolution

Once we find the minimum current required for contrast, we can turn our attention to the maximum current permitted for resolution. Clearly, features smaller than the beam spot size cannot be resolved. If the eye can resolve about 0.2 mm on the screen (analog pixel), then the spot size must be set at a value smaller than the true size of a 0.2 mm feature at the selected magnification. Table 7.1 lists the true size of a 0.2 mm feature at several magnifications. Also listed is the maximum beam current in a spot of this size produced by a tungsten filament at 20 kV.

Table 7.1 Smallest Visible Feature and Maximum Beam Current at Various Magnifications

<table>
<thead>
<tr>
<th>Magnification (X)</th>
<th>True Size of 0.2mm Feature (nm)</th>
<th>Maximum Beam Current in Spot at 20 kV (Amperes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50,000</td>
<td>4</td>
<td>2.0 x 10^{-13}</td>
</tr>
<tr>
<td>20,000</td>
<td>10</td>
<td>9.1 x 10^{-12}</td>
</tr>
<tr>
<td>10,000</td>
<td>20</td>
<td>5.9 x 10^{-11}</td>
</tr>
<tr>
<td>5,000</td>
<td>40</td>
<td>3.7 x 10^{-10}</td>
</tr>
<tr>
<td>2,000</td>
<td>100</td>
<td>4.3 x 10^{-9}</td>
</tr>
<tr>
<td>1,000</td>
<td>200</td>
<td>2.7 x 10^{-8}</td>
</tr>
<tr>
<td>500</td>
<td>400</td>
<td>1.7 x 10^{-7}</td>
</tr>
<tr>
<td>200</td>
<td>1000</td>
<td>2.0 x 10^{-6}</td>
</tr>
</tbody>
</table>

As an example, at 5000 X, only features larger than 40 nm can be resolved, and the beam current must not exceed 0.37 nA. At this current and a collection time of 160 s, Figure 7.1 shows that features differing by 2.5% contrast or more could be discriminated. If the contrast is more than this value, a lower beam current could be used, and smaller features could be resolved at higher magnification. For bulk specimens, the actual resolution will be poorer than the calculated spot size, partly because of aberrations in the column, but primarily because of the contribution of backscattered electrons to the signal.

Increasing accelerating voltage decreases the minimum spot size at constant current and may be an appropriate strategy for a specimen with sharp features whose detail is not degraded by backscattered electrons. For smoother specimens, especially those of lower atomic number, a lower voltage may be appropriate. In either case, a higher brightness source such as LaB₆ or field emission would deliver more current in a given spot size.

It is not straightforward to include data relevant to field emission SEMs in Table 7.1. The first two columns would be unchanged, but the maximum current in a given spot size varies with too many parameters. Although the brightness of FE guns is two or more orders of magnitude greater than that of tungsten, these microscopes sometimes have limited maximum beam current, particularly at the low voltage at which they are often operated. There are also several types of FE guns, each with distinct characteristics. However, one could replace the values in the right column of the table with those applicable to one’s own instrument as given by the manufacturer.

How can we maximize the resolution for a given specimen? Once we have an estimate of the contrast, it is necessary to calculate the required beam current from the threshold Equation 7.1. A current less than
this value cannot possibly distinguish features due to lack of contrast. A current greater than the threshold current will produce increased contrast at the expense of a larger spot size, decreasing ultimate resolution. If the spot size approaches the dimensions of the features to be imaged, then the current becomes the limit to resolution. However, if the magnification is such that the spot size is not limiting, then there exists a range of current that will produce a satisfactory image.

Accordingly, the key to the problem is to estimate the required contrast and resolution, then set the beam current to an optimum level for both. The operating conditions just described apply equally to digital as well as analog images, but the ability to zoom digital images may dictate the use of more pixels. In like manner, image analysis, discussed in Chapter VIII, “COMPUTER-AIDED IMAGING” on page 63 requires the use of enough pixels to adequately describe the shape of small features, if low magnification is used to accommodate large features in the same image. None of this discussion of resolution applies to X-ray maps, whose resolution is defined by the X-ray/specimen interaction volume Equation 3.5 and Figure 5.10.

**Summary of Operations**

In summary, the factor limiting image resolution and contrast in most instances is the specimen itself. Increasing beam current increases contrast, but also increases spot size for a given type of gun. Increased spot size only becomes limiting at high magnifications used to image features so small that they approach the beam diameter. Spot size does not affect X-ray spatial resolution, but overvoltage and density do. The requirement for image processing or image analysis often dictates the need for more pixels for use in determining gradients or measuring shape precisely. Optimum operating conditions can be achieved by proper choice of accelerating voltage and beam current. This assertion assumes proper beam alignment, column cleanliness, aperture selection and working distance.
VIII. COMPUTER-AIDED IMAGING

In materials science, the microstructure is often the link between process and properties. Moreover, the extent to which one can quantify the microstructure determines the strength of the link. To aid the microscopist in this task, digital imaging systems are available, and they are complementary to X-ray microanalysis. Such systems have been used by metallographers since about 1980 to quantify the size and shape of features or the amount of each phase in a microstructure. These data then can be related to properties such as strength or toughness, and also to process variables such as composition or heat treatment. Operations that turn images into data fall into the category of image analysis. Operations that turn one image into another image, for example, edge finding or sharpening, fall into the category of image processing. Still another aspect of computer-aided imaging is image comparison, in which two or more images are compared pixel by pixel to find similarities and/or differences. Table 8.1, below, summarizes the operations.

Table 8.1 Aspects of Computer-Aided Imaging

<table>
<thead>
<tr>
<th>Objective</th>
<th>Operation</th>
</tr>
</thead>
<tbody>
<tr>
<td>To quantify</td>
<td>Image analysis</td>
</tr>
<tr>
<td>To improve</td>
<td>Image processing</td>
</tr>
<tr>
<td>To compare</td>
<td>Image comparison</td>
</tr>
</tbody>
</table>

Each of these operations assists in either or both of the following general categories, namely, gathering information and displaying information. In many cases, the computer-aided imaging system permits the investigator to discover information in the sample that would not otherwise be found, and to display it in a way that is clear to others. These two functions use different aspects of the system, but they are both equally important.

Images require a substantial amount of computer memory, because the image is actually an array of numbers, i.e., intensity at every location, \( I = f(x,y) \). For a 512 x 512 grayscale digital image, over a quarter of a million numbers must be stored, and many times as many calculations must be performed if the entire image is to be processed. Consequently, early image processing for remote sensing applications was done on large computers or with dedicated image processing hardware. Although image processing is easily performed on a PC, it does require significantly more processor speed and memory than most routine computing tasks.

Digitization

An image of a microstructure can be digitized from a video camera attached to a light microscope, or it can be digitized directly from one of the contrast-bearing signals in an electron microscope. Moreover, a flatbed scanner can be used to digitize photomicrographs already recorded on film, and of course, digital cameras are a common source of images. Once digitized, images can then be stored on disk CD-ROM for later analysis and/or processing or just for archival purposes. The operations of analysis, processing and comparison do not have to alter the stored data; thus, the original image can be reanalyzed if more information becomes necessary at some time in the future.
Resolution

A digital image has a discrete number of pixels (picture elements), each one containing an intensity value, usually scaled over the range 0-255. The number of pixels determines the resolution, with 512 x 512 being the most common, although 1024 x 1024 is usually available. Theoretically, image resolution is limited only by computer memory; however, it is usually not possible to display much more than 1024 x 1024. The limiting factor for display on a color CRT is the red/green/blue dot triad spacing called pitch. A high-quality CRT has a horizontal dot pitch approaching 0.2 mm, the size of an analog pixel. If the monitor is large enough, one 1024 x 1024 image or four 512 x 512 images can be displayed. For most practical purposes 512 x 512 resolution is adequate, but higher resolution is useful for analyzing large and small features at the same time. If one chooses a magnification low enough to see many large features, then too few pixels may be available to describe adequately the shape of the smaller ones.

The actual pixel resolution can be calculated as follows:

\[ R(\mu m/pixel) = \frac{L(cm)/M}{N(pixels)} \times 10000 \]  

(Equation 8.1)

where:
- \( R \) = pixel resolution
- \( L \) = length of the SEM CRT digitized by the imaging system (usually measured with a ruler)
- \( M \) = microscope magnification
- \( N \) = number of pixels available

For example, if:
- \( L = 10 \) cm
- \( M = 1000X \)
- \( N = 512 \) pixels, then
- \( R = 0.2\mu m/pixel \)

On a light microscope, the resolution is limited by the numerical aperture of the objective lens. Digital resolutions greater than 512 x 512 do not provide greater resolving power and take more disk space to store. On an SEM, resolutions of up to 4096 pixels are sometimes provided.

In the case of X-ray images, if the X-ray range (\( R \)) of a particular element in the sample is known, as from Equation 3.5, the number of pixels required can be calculated from Equation 8.2. In this case, the pixel resolution should be chosen to correspond with the X-ray range. Operating in this manner will prevent undersampling and losing data or oversampling and wasting time. X-ray maps are discussed in more detail in Chapter IX, “X-RAY MAPPING” on page 82.

Gray Levels

The foregoing discussion relates to the spatial aspect of the image, \( I = f(x,y) \). The number of gray levels available to digitize the intensity at each pixel is referred to as the depth of digitization. The human eye has an enormous range of \( 10^{10} \) brightness levels, but we can only discriminate about 20 levels at the same time. There is a concept in perceptual psychology called the “Weber ratio,” which requires a brightness change of more than about 2% of the average background for us to perceive it. One part in 64 gray levels is about 1.5%; therefore, 64 levels should be adequate for viewing. However, 256 levels are commonly provided and are necessary for discriminating different phases on the basis of their brightness. This pro-
cess is called thresholding, and it forms the basis for image analysis. Some images are digitized to more levels, and some image processing operations and X-ray maps require 16-bit images (65536 levels).

All digital imaging systems provide the user with a gray level histogram. This is a plot of the number of pixels at each gray level, and it is particularly useful for setting thresholds around phases. It is also useful for image collection to make sure that all the available levels are used. Therefore, it is essential to adjust the contrast and brightness to fill the histogram, rather than to please the eye. The way the image looks can be changed later, but data that were not collected are lost and cannot be retrieved later by processing.

**Pseudocolor**

Although the human eye can only discriminate about 20 levels of intensity at the same time, it can distinguish many more colors. Specifically, we can discern 128 different hues and 20 saturations in addition to the 20 brightness levels. In fact, experiments have shown that we can actually discriminate 17,000 colors of equal luminance (MacAdam, 1947). With 20 simultaneous luminances, 350,000 different shades of color can be discriminated. The significance of this fact is that pseudocolor can be used in an image to convey details that would be lost in the grayscale image. Pseudocolor does not increase the size of the image file.

**True Color**

When we speak of color in everyday conversation, we mean true color. But to a computer it means an image that is acquired with sufficient information to render it faithfully as we would see it. Unlike pseudocolored images, these images are collected and stored with at least 24 bits of information—8 each for red, green and blue (RGB). Alternatively, they may be collected in a hue/saturation/intensity (HSI) format. Although true color is not meaningful in an electron microscope, it may be the ideal contrast mechanism in a light microscope.

**Image Analysis**

The first step in quantifying some aspect of a microstructure is to be certain that the signal used for imaging carries a contrast mechanism that really portrays the desired information. Some common contrast-bearing signals along with the contrast mechanism that they convey are listed in Table 8.2. For example, reflected light may be suitable for fibers in a composite or for minerals in an ore sample, but backscattered electrons may be required to discriminate all the phases in a refractory brick or a tool steel. Besides the mechanisms commonly used in materials science, there is an entire science of staining for biological material, many of them specific for some biological structure.
Area Fraction—Once the contrast mechanism has been chosen, the microstructure can be digitized, and gray levels are set such that all the phases can be distinguished from one another. It is a simple matter for the computer to count all the pixels that fall within a range of intensities. This number divided by the total number of pixels in the entire image is the area fraction of the phase represented by that range of gray levels. As long as the phases are distinct, the area fraction of each can be measured simultaneously. In an image analysis system, this calculation is virtually instantaneous.

True Color—Special mention should be made about phase separation in true color images for image analysis. On the basis of the operator’s color selection on the rendered image, the computer must find the corresponding ranges in RGB or HSI coordinates. On some systems, the investigator need only point to colors, and the imaging system automatically finds all similar regions and segments them automatically. It is possible to use one contrast mechanism to select parts of an image and display those parts in another contrast. For example, Friel and Prestridge (2002) used true color in a light-optical microscope tint-etched image of cast-iron to extract the X-ray signals for Fe, Si and C from regions of different tint color.

<table>
<thead>
<tr>
<th>Signal</th>
<th>Contrast Mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>Secondary electrons</td>
<td>Voltage</td>
</tr>
<tr>
<td></td>
<td>Magnetic type 1 &amp; 3</td>
</tr>
<tr>
<td>Backscattered electrons</td>
<td>Topographic (trajectory)</td>
</tr>
<tr>
<td></td>
<td>Crystallographic (ECP and EBSD)</td>
</tr>
<tr>
<td></td>
<td>Magnetic type 2</td>
</tr>
<tr>
<td></td>
<td>Biological structure (stained)</td>
</tr>
<tr>
<td>X-rays</td>
<td>Composition</td>
</tr>
<tr>
<td>Absorbed electrons (specimen current)</td>
<td>Atomic number</td>
</tr>
<tr>
<td></td>
<td>Charge (EBIC)</td>
</tr>
<tr>
<td></td>
<td>Crystallographic (ECP)</td>
</tr>
<tr>
<td></td>
<td>Magnetic type 2</td>
</tr>
<tr>
<td>Cathodoluminescence</td>
<td>Composition</td>
</tr>
<tr>
<td></td>
<td>Electron state</td>
</tr>
<tr>
<td>Transmitted light</td>
<td>Specimen color</td>
</tr>
<tr>
<td></td>
<td>Interference colors and figures</td>
</tr>
<tr>
<td></td>
<td>Biological structure</td>
</tr>
<tr>
<td>Reflected light</td>
<td>Topographic</td>
</tr>
<tr>
<td></td>
<td>Crystallographic</td>
</tr>
<tr>
<td></td>
<td>Specimen color</td>
</tr>
</tbody>
</table>
Feature Analysis

Beyond measuring the area fraction of microstructural components, it is often necessary to count particles or the number of specific features in a microstructure. Furthermore, various measurements of size and shape are frequently used to characterize features in an image. This kind of information is particularly useful for establishing the link between process and material properties, as mentioned in the beginning of this chapter. These measurements are generally referred to as “feature analysis,” and most image analysis systems provide a series of standard measurements from which the investigator can select. Some measurements apply to the field of view as a whole, and some apply to the features individually. Moreover, some of the feature descriptors are measured directly, such as area, perimeter, and various measures of length. Others, such as circularity and roughness, are calculated from the primitive measurements. For a review of image measurements, see Friel (2000). Tables 8.3 and 8.4 list some common field and feature measurements with explanations.

Table 8.3 Some Standard Field Measurements

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Explanation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of features</td>
<td>Feature count</td>
</tr>
<tr>
<td>Area of features</td>
<td>Total area covered by features</td>
</tr>
<tr>
<td>Area fraction (A_A)</td>
<td>Area of features/area of field</td>
</tr>
<tr>
<td>Intercepts per length (N_L)</td>
<td>Number of intercepts/length of test line</td>
</tr>
<tr>
<td>Features per area (N_A)</td>
<td>Number of features/area of field</td>
</tr>
<tr>
<td>ASTM grain size (G)</td>
<td>(G = (6.6438\log N_L) - 3.288) (G = (3.3219\log N_A) - 2.954)</td>
</tr>
</tbody>
</table>

Table 8.4 Some Standard Feature Descriptors

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Explanation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Area (A)</td>
<td>Calibrated pixel count</td>
</tr>
<tr>
<td>Perimeter (P)</td>
<td>Diagonal pixel center to center</td>
</tr>
<tr>
<td>Longest Dimension (L)</td>
<td>Maximum Directed Diameter</td>
</tr>
<tr>
<td>Breadth (B)</td>
<td>Minimum Directed Diameter</td>
</tr>
<tr>
<td>Average Diameter (D)</td>
<td>Average Directed Diameter</td>
</tr>
<tr>
<td>Aspect Ratio</td>
<td>Max. dd/perpendicular dd</td>
</tr>
<tr>
<td>Area Equivalent Diameter</td>
<td>(\sqrt{4A/\pi}) (diameter, if circular)</td>
</tr>
<tr>
<td>Form Factor</td>
<td>(4\pi A/P^2) (perimeter sensitive always ≤ 1)</td>
</tr>
<tr>
<td>Circularity</td>
<td>(\pi L^2/4A) (longest dimension sensitive, always ≥ 1)</td>
</tr>
</tbody>
</table>
An image analysis system is particularly flexible if it allows the user to set limits on these parameters or to define his own parameter. For example, one may wish to analyze the large-area, high-aspect ratio features such as fibers, or, alternatively, the small-area, circular features such as porosity, all in the same microstructure. This analysis would be accomplished by combining the descriptors with the Boolean <AND> operator.

The output of feature analysis usually includes 1) Summary data with descriptive statistics, 2) Histograms showing the distribution of feature descriptors, such as: area or aspect ratio, 3) Scatter plots of one descriptor vs. another. Both field and feature-specific measurements can be reported separately. Figure 8.1 shows a microstructure converted to a binary image, and two plots representative of what might be in a Feature Analysis report. Table 8.5 and 8.6 list the summary statistics of some field and feature measurements derived from the image in Figure 8.1.

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean Intercept Length</td>
<td>$A / \text{Projected length (x or y)}$</td>
</tr>
<tr>
<td>Roughness</td>
<td>$P / \pi D$ (perimeter/perimeter of circle)</td>
</tr>
<tr>
<td>Volume of a Sphere</td>
<td>$0.75225 \times \sqrt[3]{A^3}$ (sphere rotated about D)</td>
</tr>
<tr>
<td>Volume of a Prolate Spheroid</td>
<td>$8 / 3 \pi \times \frac{A^2}{L}$ (ellipse rotated about L)</td>
</tr>
<tr>
<td>Fiber Length</td>
<td>$0.25 \times (P + \sqrt{P^2 - 16A})$ (Length, if rectangular)</td>
</tr>
<tr>
<td>Fiber Width</td>
<td>$0.25 \times (P - \sqrt{P^2 - 16A})$ (Width, if rectangular)</td>
</tr>
</tbody>
</table>

Table 8.4 Some Standard Feature Descriptors
Figure 8.1 Feature analysis of the microstructure of a Ni-based alloy with large and small grains.
Table 8.5 Summary of Field Measurements from Figure 8.1

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of Features</td>
<td>915.00</td>
</tr>
<tr>
<td>Number of Intercepts</td>
<td>14485.00</td>
</tr>
<tr>
<td>Average Area</td>
<td>165.14</td>
</tr>
<tr>
<td>$N_L$</td>
<td>6.637e-02</td>
</tr>
<tr>
<td>$N_A$</td>
<td>4.258e-03</td>
</tr>
<tr>
<td>Area Fraction</td>
<td>7.031e-01</td>
</tr>
<tr>
<td>Mean Free Path</td>
<td>4.47</td>
</tr>
<tr>
<td>Mean Intercept Path</td>
<td>10.59</td>
</tr>
</tbody>
</table>

Table 8.6 Summary of Feature Measurements from Figure 8.1

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Average</th>
<th>Median</th>
<th>Minimum</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>Length</td>
<td>17.05</td>
<td>14.20</td>
<td>5.39</td>
<td>122.10</td>
</tr>
<tr>
<td>Breadth</td>
<td>11.73</td>
<td>9.98</td>
<td>1.97</td>
<td>96.47</td>
</tr>
<tr>
<td>Area</td>
<td>165.14</td>
<td>81.47</td>
<td>11.64</td>
<td>6660.78</td>
</tr>
<tr>
<td>Average Diameter</td>
<td>14.28</td>
<td>12.07</td>
<td>4.48</td>
<td>105.98</td>
</tr>
<tr>
<td>Mean X-Intercept</td>
<td>7.96</td>
<td>6.89</td>
<td>1.75</td>
<td>56.36</td>
</tr>
<tr>
<td>Mean Y-Intercept</td>
<td>8.81</td>
<td>7.39</td>
<td>1.72</td>
<td>86.71</td>
</tr>
<tr>
<td>Form Factor</td>
<td>0.6833</td>
<td>0.6916</td>
<td>0.2946</td>
<td>0.9942</td>
</tr>
<tr>
<td>Circularity</td>
<td>2.0159</td>
<td>1.9158</td>
<td>1.2238</td>
<td>4.4364</td>
</tr>
<tr>
<td>Roughness</td>
<td>1.0353</td>
<td>1.0279</td>
<td>0.9138</td>
<td>1.4190</td>
</tr>
<tr>
<td>Fiber Length</td>
<td>15.15</td>
<td>12.26</td>
<td>0.00</td>
<td>166.25</td>
</tr>
<tr>
<td>Fiber Width</td>
<td>5.86</td>
<td>5.75</td>
<td>0.00</td>
<td>43.26</td>
</tr>
</tbody>
</table>

**Advanced Feature Analysis**

**Multi-Phase Feature Analysis**

Feature analysis in most systems is performed on a binary image; i.e., one in which every pixel is either on or off. In some image analysis systems, however, it is possible to perform multi-phase feature analysis.
analysis; i.e., analysis of more than one type of feature (phase) at the same time while keeping the data separate. In this type of system, the report would consist of separate data and plots from each phase.

**Feature Analysis with Adjacencies**

In a multi-phase analysis system, a further enhancement makes it possible to keep track of which kind of features border other kinds. That is, a "Table of Adjacencies" is constructed, consisting of a listing of each feature in the image with the percentage of the feature’s perimeter in contact with other features. Inasmuch as feature analysis measures the size and shape of all features, when information about neighboring features is added, a more complete characterization of the image results, and the analysis may be said to be “Universal.” Figure 8.2 shows an SEM image of a few inclusions in steel. EDS identified most of the large inclusions as MnS, but there are also four aluminate areas within the sulfide. Universal Feature Analysis reported that the perimeter of the aluminates was bordered 29% by steel, and 71% by sulfide. This type of position-sensitive analysis provides information not just about each phase, but also about the relationships among them.

![SEM image of duplex inclusions in steel](image1)

**Figure 8.2 Results of Multi-phase Feature Analysis including percent adjacency.**

**Standard Methods**

Besides general size and shape measurement, there are a number of standard methods for specific microstructural measurements. There are also procedures that standardize various aspects of the practice of microscopy. Tables 8.7 and 8.8 list some standards promulgated by the ASTM in their annual book of standards. The standards organizations of other countries, such as BSA, DIN, JIS, etc., plus ISO often adopt these or similar standard practices, so that data can be compared internationally.
Quantitative Stereoscopy

The height of any point of the surface of a specimen can be calculated from measurements on a pair of stereo images if the parallax angle is known. Stereo pairs of images are conveniently obtained using an SEM and recording images at two different tilt angles. The difference between the tilt angles is the parallax angle. Any displacement in the X direction between the two images is the result of differences in Z, the height above or below the reference plane. The geometric configuration is shown in Figure 8.3. Displacement in the X direction is perpendicular to the tilt axis and refers to the linear distance between corresponding features in the same units as the microstructure. The plane of reference (Z = 0) is the point or locus of points on the image where there is no shift in X. The equation that relates these measurements is as follows:

$$Z = \frac{P}{2 \sin(\alpha/2)}$$

(Equation 8.2)
where:

\[
Z = \text{height above the reference surface}
\]

\[
\alpha = \text{parallax angle}
\]

\[
P = \text{displacement in the X direction between images (\(\Delta x\)).}
\]

The greater the parallax angle, the more precise is the calculation of height. Six to ten degrees is common, but beyond about 12°, it is difficult to see the stereo effect. The displacement distance can be measured in calibrated units directly on the image analyzer. And if the analyzer can locate correlative points automatically, it can solve Equation 8.2, knowing position and the parallax angle. In this manner, one can click the mouse anywhere in the image and obtain a readout of the height. For a review of stereoscopy in the SEM, see Wells (1974).

If the height at many points in the microstructure is known, the true surface area can be approximated, limited only by the density of points chosen and the microscopic resolution. Figure 8.4 shows a mesh of points calculated from a fracture surface and tilted for better viewing. Each rectangular cell defined by four points is bisected into two triangles, and the sum of the area of these triangles is an approximation of the true surface area. Taken a step further, the surface area at different magnifications can be used to construct a plot of log(area) vs. log(magnification), from which a fractal dimension of the surface can be computed (Friel and Pande, 1993).

Figure 8.3 Schematic representation of stereoscopy at two tilt angles.

Figure 8.4 Computer reconstruction of a fracture surface.
Coatings Measurements

Using microscopy to measure coating thickness is a destructive method, but it has the advantage of revealing the structure of the coating and of making numerous precise thickness measurements. Except for specimen preparation, it does not matter whether the coating is metallic, organic, or other—the measurement is the same. When using an image analyzer, it is possible to make thousands of measurements along a coating. It is also possible to determine the thickness and variability of all layers within the coating.

A sophisticated coatings program automatically finds the coating layers in a grayscale image. It also lets the user select the method by which the computer defines the top and the bottom of the coating. For example, maximum or minimum brightness, maximum change, or percent slope are all valid definitions of coating edge in certain cases. An example of 100 thickness measurements on a layered electroplate is shown in Figure 8.5. The computer not only finds the mean thickness and its variance but also the minimum/maximum and lets the user set a pass/fail criterion.

![Figure 8.5 Coating thickness measurement by image analysis.](image)

Besides thickness measurement, image analysis of coatings can be used to measure the size and shape of splats in thermal spray coatings for the purpose of finding oxides or unmelted particles. Furthermore, when combined with X-ray microanalysis, image analysis can characterize the size, shape and composition of discrete phases in a multi-phase coating.

Tessellations

Although feature analysis easily measures the distribution of various size and shape parameters, one property of discrete features that is difficult to quantify is their spatial distribution. Such a distribution may be random, ordered or clustered. Or the features may be clustered but superimposed on a random background. Although the eye can often discern these patterns, they are difficult to quantify. Methods of quantifying clustering have been reviewed by Vander Voort (1990), but no single method has proven entirely successful.

One sophisticated computer method makes use of Dirichlet tessellations. Tessellation just means mosaic, and Dirichlet (1850) did not even use the term. But in this context, they are cells constructed by a computer by expanding regions outward from features until they meet those of their nearest neighbors. Figure 8.6 shows random, ordered and clustered features with their corresponding tessellation cells below. Every point within each cell is closer to the feature that generated it than it is to any other feature—a point...
Dirichlet was first to prove mathematically. The area of the cells is proportional to the nearest neighbor distance. Another name sometimes given to these cells is Voronoi tessellations or Voronoi polygons (Voronoi, 1908). Neither Dirichlet nor Voronoi were interested in images, but rather mathematics, but they gave rise to a concept that is used in widely diverse fields, such as geography, psychology, ecology, physics and even marketing.

Once an image of cells is constructed as in Figure 8.6, the entire power of feature analysis is available to characterize the cells. For example, their breadth is a measure of the first nearest-neighbor distance, and their longest dimension is a measure of the second nearest-neighbor distance. Horizontal and vertical Feret diameters give information about orientation. It should be evident that it is not only possible to make measurements on each field, but on every cell in the field and report distributions.

In the simplest case, the computer constructs a perpendicular bisector between the centroid of each feature and its neighbors. These lines are terminated when they meet another, and the result is a series of polygons around each feature. Using this simple approach, it is conceivable that a large feature close to another small one would actually extend beyond its cell. This is because the midpoint of the centroid-to-centroid line may be within the large particle. A more sophisticated approach suitable for image analysis is to grow the regions outward from the edge of features, not their centroid, using a “regions of influence” operator. The latter approach needs a more powerful computer, but it gives more meaningful results.

A method for distinguishing the different types of distributions was proposed by Schwarz and Exner (1983). They used actual nearest-neighbor distances not tessellation cells, but tessellations work also. They define a parameter “Q” as the ratio of the actual mean nearest-neighbor distance to the expected mean distance, as defined by Equation 8.3.
\[ E(r) = \frac{1}{2\sqrt{N_A}} \]  

(Equation 8.3)

where:

- \( E(r) \) = the expected mean
- \( N_A \) = the number of features per area

A parameter “\( R \)” is defined as the ratio of the actual variance of the nearest-neighbor distances to the expected variance (\( E(s^2) \)) as defined by Equation 8.4, below.

\[ E(s^2) = \frac{4 - \frac{\pi}{4\pi}}{\frac{1}{4\pi N_A}} \]  

(Equation 8.4)

The authors cited above then go on to distinguish between distributions on the basis of Q and R as follows:

<table>
<thead>
<tr>
<th>Distribution</th>
<th>Values (Q, R)</th>
</tr>
</thead>
<tbody>
<tr>
<td>random</td>
<td>(Q ~ 1, R ~ 1)</td>
</tr>
<tr>
<td>ordered</td>
<td>(Q &gt; 1, R &lt; 1)</td>
</tr>
<tr>
<td>clustered</td>
<td>(Q &lt; 1, R &lt; 1)</td>
</tr>
<tr>
<td>clustered on random background</td>
<td>(Q &lt; 1, R &gt; 1)</td>
</tr>
</tbody>
</table>

Spitzig et al. (1985) applied these measures to Dirichlet tessellations derived from actual materials. They also introduced the concept of local-area fraction, defined as the area of the feature divided by the area of its cell. This measurement is made on an image containing both the features and the tessellation cells. It is easily defined for the computer as “(area filled - area) / area filled,” if the features are treated as holes.

**Image Processing**

Image processing is the name for operations that alter an image or produce a new one, usually with the goal of improving the image. The only thing certain, however, is that the image is changed. No information can be extracted that was not present in the original image, and artifacts can be introduced. If the investigator’s ultimate goal is image analysis, image processing must sometimes be done first to enhance the features to be analyzed. Some image processing operations operate on grayscale images while others operate on binary images. Gray scale operations include: contrast transforms, sharpening, blurring, edge finding, background equalization, enhancement, and others. Binary image operations include: erosion/dilation, grain boundary reconstruction, particle cutting, hole filling, and others.

**Contrast Transforms**

One of the simplest image processing operations is brightness and contrast transformation. In this case, all pixels at a certain brightness level are transformed to some other level. For example, if one were looking at porosity, a photonegative of the image might be useful to make the pores bright and the other phases dark. A photonegative is just one example of a transformation; and in fact, each gray level could be transformed into any other. An example of a transform curve is given in Figure 8.6. Each gray level from 0-255 on the x-axis is transformed to some other value on the y-axis, in accordance with the curve. The out-
put of this particular curve is similar to a gamma function on an SEM—dark areas of the image are made more intense without affecting the light areas.

Figure 8.7 Original SEM image before (left) and after (right) contrast.

**Kernel Processing**

A higher level of sophistication involves using information from the neighboring pixels to process a grayscale image. In the simplest case, the intensity values of the eight nearest neighbors of every pixel are examined and used as a basis for changing the intensity of the center pixel. The number of neighboring pixels used is called a “kernel” and may be 3x3 or some other number. The kernel is passed through the image and each pixel is replaced by a value determined by its neighbors. The weights in each part of the kernel determine the operation performed by the process. For example, if the value of each pixel is replaced with the equally weighted average of all the neighbors according to the following kernel,

\[
\begin{bmatrix}
1 & 1 & 1 \\
1 & 1 & 1 \\
1 & 1 & 1 \\
\end{bmatrix}
\]

a smoothing operation results. Kernels that average are called low-pass filters and are useful for removing noise.

The weights in the kernel do not have to be positive; they can be anything that accomplishes the desired effect. High-pass filters find areas in the image where intensity varies greatly, and are often used for edge detection. An example of one of these is the Laplacian filter:

\[
\begin{bmatrix}
0 & -1 & 0 \\
-1 & 4 & -1 \\
0 & -1 & 0 \\
\end{bmatrix}
\]

This filter finds parts of the image that have intensity gradients, such as the edges of features. However, it is necessary to understand that in areas of no intensity variation, this and other derivative filters
return a value of zero. Zero is then rescaled to some value such as 128, producing a spike in the histogram at that value. All the useful information resides in the tails of the histogram because these positive and negative values represent the areas of change. But when the output of this filter is added back into the original image, one observes a marked crispening effect.

In addition to filters that replace pixels with some arithmetic function of their neighbors, logical filters are also possible. The maximum and/or minimum of the neighborhood can be found, and the center pixel can be replaced or not on the basis of what the neighborhood contains. An example of the use of such a filter is shown in Figure 8.8.

![Figure 8.8 Example of image processing to reveal subtleties not visible in the original image.](image)

This is a reflected light photomicrograph of an alumina refractory brick corroded by molten glass. The image on the left does not display much detail, but after using a so-called topographic filter, more information is revealed. A topographic filter is a logical filter that finds the maximum monotonic intensity gradient around each pixel and replaces that pixel with the absolute value of the gradient. The effect is to produce a “topographic” effect in the image. A description of some of the common filters is given in Table 8.9.
Table 8.9 Some Common Image Filters

<table>
<thead>
<tr>
<th>Filter Name</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Low-pass Arithmetic</strong></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>1 1 1 1</td>
</tr>
<tr>
<td></td>
<td>Smoothing filter</td>
</tr>
<tr>
<td></td>
<td>Removes noise</td>
</tr>
<tr>
<td></td>
<td>Causes blurring</td>
</tr>
<tr>
<td>Triangular</td>
<td>1 2 1</td>
</tr>
<tr>
<td></td>
<td>Removes noise by weighting the first nearest neighbor more heavily than the second.</td>
</tr>
<tr>
<td></td>
<td>2 4 2</td>
</tr>
<tr>
<td></td>
<td>1 2 1</td>
</tr>
<tr>
<td><strong>High-pass Arithmetic</strong></td>
<td></td>
</tr>
<tr>
<td>Differential</td>
<td>1 -8 1</td>
</tr>
<tr>
<td></td>
<td>Edge-finding filter sensitive to vertical gradients</td>
</tr>
<tr>
<td></td>
<td>1 1 1</td>
</tr>
<tr>
<td>Robert's Cross</td>
<td>1 0 1</td>
</tr>
<tr>
<td></td>
<td>Edge-finding filter sensitive to vertical gradients</td>
</tr>
<tr>
<td></td>
<td>0 0 0</td>
</tr>
<tr>
<td></td>
<td>1 0 0</td>
</tr>
<tr>
<td></td>
<td>0 1 0</td>
</tr>
<tr>
<td>Laplacian</td>
<td>0 1 0</td>
</tr>
<tr>
<td></td>
<td>Crispening filter</td>
</tr>
<tr>
<td></td>
<td>1 -4 1</td>
</tr>
<tr>
<td></td>
<td>0 1 0</td>
</tr>
<tr>
<td><strong>Low-pass Logical Filters</strong></td>
<td></td>
</tr>
<tr>
<td>Median</td>
<td>Puts all neighboring pixels in order and replaces the center pixel value with the median. Removes noise while preserving edges.</td>
</tr>
<tr>
<td>Replacement</td>
<td>Finds maximum and minimum of the neighborhood. If the maximum&gt;center&gt;minimum, leave unchanged, else set to close of maximum/minimum.</td>
</tr>
<tr>
<td><strong>High-Pass Logical Filters</strong></td>
<td></td>
</tr>
<tr>
<td>Topographic</td>
<td>Finds gradients in four directions: /, ,</td>
</tr>
<tr>
<td>Inverse Replacement</td>
<td>Finds maximum and minimum of the neighborhood. If maximum&lt;center&lt;minimum, leave unchanged or else set to the closer of max/min. Accentuates high rates of change, useful for finding boundaries.</td>
</tr>
</tbody>
</table>
When doing image processing, there are two rules that should be considered: one is to always store the image on disk before doing any processing, and the other is to record the order in which the operations are performed. These rules are a consequence of the following: 1) the first series of processing operations rarely achieve the desired result and must be redone on the original image, 2) the operations are not commutative, and 3) the last step is always wrong! Performing a mean filter followed by a derivative is not the same as a derivative followed by a mean. When processing does achieve its goal, it is crucial to have a record showing how it was achieved. Displaying images from each stage of processing simultaneously on the screen is helpful.

**Binary Image Processing**

Once the grayscale image has been optimized, it needs to be segmented or thresholded for image analysis. The segmenting operation is most commonly done by selecting a range of gray levels and displaying them in pseudocolor. Some systems convert the image to a true binary mask containing only pixels that are on or off. Others place a pseudocolor overlay on top of the original 8-bit image, while still others construct a multi-pseudocolor mask for simultaneous multi-phase operations. Whichever method is used, the image is reduced to something less than 8-bit, and other image processes are available to highlight the features of interest. The simplest of these binary operations is erosion/dilation.

**Erosion and Dilation**

Erosion and dilation operations are sometimes called etching and plating. They either strip pixels off the edge of features (erosion), or they add pixels to grow the features (dilation). The simplest approach to particle cutting is erosion followed by dilation with the constraint that the particles are not allowed to reconnect. These operations can be repeated numerous times and in different orders.

Erosion and dilation usually use a 3x3 square region around each pixel, but the size could be larger and the shape could be circular or hexagonal. Severe erosion followed by dilation may cause the original shape of the particles to change. For example, when circles are eroded and subsequently dilated they return as squares. Alternatively, using 3x3 and 5x5 matrices tends to preserve the original shape. Erosion and dilation are binary image editing operators useful to prepare images for feature analysis.

**Special Purpose Image Processing**

In addition to general-purpose methods, more sophisticated processing techniques have been developed to achieve specific results. In microscopy, some of these application-specific methods include: particle separation, grain boundary reconstruction, background equalization, twin identification and removal, crossed fibers, and others. The goal of most of these techniques is to prepare for automatic image analysis, thus their effectiveness can be measured by comparing results achieved by AIA with those measured manually. The example shown in Figure 8.9 compares a light microscope image of a ferritic steel before and after image processing. The processing steps included: background equalization, inclusion removal, grain boundary reconstruction and region cleaning.
Figure 8.9 Effect of several image processing steps on LOM image of ferrite in steel.

Image Comparison

One thing that computers are particularly good at is finding similarities or differences among data. Inasmuch as images are merely large arrays of intensity data, a digital imaging system can screen images for patterns quickly. As previously discussed, the investigator must choose a suitable imaging signal to start with—one that carries the desired contrast mechanism. Images can be compared directly based on pixel intensities or the position of features, or they can be compared indirectly based on image analysis results. Image comparison is particularly effective on X-ray compositional images (maps), as will be discussed in the next chapter.

Summary of Digital Imaging

Most digital imaging systems in use today on microscopes are a combination of image analyzer and image processor. Most imaging software, however, is designed for storage, retrieval, and making images look good. Although image analysis can be done manually, it is automatic image analysis that is commonly used to establish structure/property relationships. Some of the factors affecting the accuracy of image analysis are: choice of contrast mechanism, processing steps and their effect on the original data, choice of measurements, and data interpretation. Of the three generic uses of computer-aided imaging systems, the one of most use to materials scientists is image analysis. Whether one is doing research, quality assurance, failure analysis or other applications in microscopy, digital image analysis is a powerful method for:

1. Gathering information not available without a computerized system.
2. Obtaining enough information to be statistically valid.
3. Displaying such information.
IX. X-RAY MAPPING

X-ray mapping with full spectrum imaging is the ultimate combination of X-ray microanalysis with computer-aided imaging. Because knowing the distribution of elements in a sample is so important, X-ray maps have been collected since the early days of electron probe microanalysis (Duncumb and Cosslett, 1956). Maps can be used to see which elements associate with each other, and even discern concentration gradients. For a number of years, maps were primarily used to display the spatial distribution of concentration that was confirmed by quantitative point analysis. Modern maps, however, do far more than display information; they can be used to obtain information that would not otherwise be available without a computer to screen the large amount of data. Analog maps are briefly discussed below in the interest of giving some historical background, but digital maps are vastly more capable of providing information, and thus will be described more extensively. A review of X-ray mapping can be found in Friel and Lyman (2003).

Analog Maps

Analog maps are the result of setting EDS regions-of-interest or wavelength spectrometers on peaks of interest and displaying a dot on the photo-CRT everywhere the spectrometers detect an X-ray. Inasmuch as there is no way of knowing whether a characteristic X-ray or a continuum X-ray was collected, only a clustering of dots on a photograph is considered an indication of the distribution of elemental concentration. A total of 250,000 counts collected over many scans of the sample and taking several minutes usually provides a good representation of the distribution of that element. A step-by-step procedure for acquiring dot maps is given in Goldstein et. al (2003). While simple to acquire, dot maps have several disadvantages: they must be recorded (photographed) one element at a time upon acquisition, they lack discrete intensity levels, they lack a suitable method for background subtraction, and they are inherently qualitative (Newbury, et al., 1990). All of these difficulties are resolved by collecting the X-ray map digitally.

There are some artifacts associated with the high count rates commonly used for maps. When the beam scans over areas of high concentration of an element, it is possible to get a contrast reversal as the dead time goes beyond the point of maximum throughput, and fewer X-rays get through the pulse processor. Live-time correction solves this. Another artifact arises from continuum variation with average atomic number. As the beam scans from a low- to a high- Z phase, the concentration of trace or minor elements will appear to increase.

Digital Maps

Digital X-ray maps are merely digital images that use the X-ray signal to carry compositional information. Each pixel contains the number of X-ray counts instead of a brightness value as in a secondary or backscattered electron image. It is interesting that analog maps can only have a digital display, i.e., dot on or dot off. Digital maps, however, can produce a continuous display; that is, areas of high concentration can be portrayed in brighter colors. Even though digital maps are a superb way of displaying the spatial distribution of elements, it is the availability of computer-aided imaging that really provides the way to gain new information about the sample.

Collection

Insofar as X-ray maps are really X-ray images, they have a discrete number of pixels. A size of 128 x 128 often matches the X-ray range at intermediate magnifications, but it is a simple matter to calculate the
most appropriate resolution, if more than one is available. This is done by first calculating the X-ray range (R) according to Equation 3.5. Then the required number of pixels is calculated according to Equation 9.1 repeated below.

\[
R(\mu m/pixel) = \frac{L(cm)/M}{N(pixels)} \times 10000
\]

*(Equation 9.1)*

where:
- \(N\) = number of pixels
- \(M\) = magnification
- \(L\) = length of the SEM CRT digitized

The map size should be selected so that there are about as many pixels in one direction, e.g., 128, 256, 512, etc. as called for by the calculation of \(N\).

For example, if one were analyzing a Cu/Zn alloy at an average density of 8 g/cc using the \(K_{\alpha}\) lines at 20 kV accelerating voltage, Equation 3.5 predicts an X-ray range of about 1 \(\mu m\). If \(L = 10 \text{ cm}\), and \(M = 1000X\), then \(N > 100\). Accordingly, 128 x 128 pixels would be appropriate. If a magnification of 100X were indicated, \(N > 1000\), and 1024 x 1024 pixels would be required. Obviously, if the pixel resolution is too coarse, undersampling occurs and detail is lost. If resolution is too fine, oversampling occurs; the X-ray acquisition takes much longer but gives no more useful information. A better strategy would be to count fewer points at a longer dwell time.

The effect on X-ray maps of increased beam current is to improve the counting statistics. High beam current does not degrade X-ray spatial resolution, as it can in secondary electron images. It may also be desirable to decrease the time constant (shaping time) on an analog EDS amplifier. Such a decrease allows the system to process more X-rays in the same amount of live time without increasing the dead time. This increase in throughput is achieved at a loss in spectral resolution, which is usually not a problem when mapping. In a digital EDS system, adaptive shaping automatically adjusts to high count rate.

This “fast mapping” technique is often used to obtain the highest quality maps in the least time. Decreasing the shaping time from 10 \(\mu s\) to 3 \(\mu s\) permits an increase in beam current so that a factor of five increase in count rate is possible. Maximum throughput usually occurs around 50% dead time. Inasmuch as the presence of sum peaks or degraded spectral resolution are usually subordinate to accumulating many counts at each pixel, most operators choose a short time constant and 40-50% dead time. Time constants less than 3 \(\mu s\) permit even greater count rates, but be sure to calibrate the energy scale for each time constant. Selection of a specific time constant is not necessary with a digital pulse processor, because it adapts “on the fly.” Nor is calibration necessary, because the system automatically senses any shift and corrects for it.

**Image Math**

The real power of digital maps lies in the ability to extract and compare information not readily perceived visually. Software, often called Image Math, can screen the large datasets for elemental or spatial associations. Logical comparisons can be made among elements and regions of interest can be identified based on X-ray intensities. For example, a metallurgist may ask the digital mapping system to screen for those areas high in sulfur and also high in manganese, when looking for sulfide inclusions.

The capability to play “what if” by screening a multi-element map allows a researcher to understand his specimen in a way that would not be possible by manual methods. By quantifying the microstructure in this way, relationships with other material properties can be established. For example, the area fraction of a
precisely defined chemical phase can be compared with mechanical properties to better characterize a material. Or in mineralogy, elemental distributions can provide information on petrogenesis.

An example of the kind of information that can be extracted from digital maps is illustrated in Figure 9.1. This figure shows X-ray images of Fe, Mn, Cr, Si and C in a carbon steel that was annealed for several weeks to grow Fe$_3$C.

![Figure 9.1 Large carbides in steel.](image)

Having the actual X-ray counts allows us to precisely screen phases. The images in the bottom row were all produced by having the computer find areas in which the carbon intensity was greater than 270 counts; this setting effectively selected carbides. At the same time, the computer was instructed to display intensity of Fe, Mn, Cr and Si everywhere that carbon intensity was greater than 270. The resulting images show that Fe, Mn and Cr are all present in the same areas; we can infer from this observation that Mn and Cr are substituting for Fe in Fe$_3$C. Silicon, on the other hand, is not present in the same regions as Fe, Mn and Cr. The regions rich in Si and C are distinct, and from this association, we may infer the presence of SiC as a separate phase.

Unraveling the chemistry of the carbides in this specimen could have been done by numerous quantitative point analyses, but image analysis of X-ray maps is faster and more powerful. There is no limit to the number of selection rules that can be imposed to define regions, but two or three rules are usually sufficient. Moreover, operations need not be Boolean; simple arithmetic such as subtraction of one image from another is often useful, as in background subtraction.

**Chemical Classification**

Another example of the combination of image analysis with X-ray microanalysis is called chemical classification. In this method, an image of the entire field is collected, and image analysis is used to measure the sizes and shapes of features. Filters based on size or shape are applied, and the electron beam is driven to those features that pass the filter criteria and collects a specimen for a few seconds. The particles or grains thus selected are then classified by a set of rules based on chemistry.

In the following example, Chemical Classification was used to find those sulfide grains that contained silver in an ore sample. The sulfide grains in one field of view are shown as the bright areas in Figure 9.2 in
SE/BSE contrast. The grains were found by Feature Analysis, and those that were selected for Chemical Classification are shown in the image in the right of the figure and numbered.

Electron contrast (SE/BSE) is chosen for its speed of acquisition, and then the beam is driven back to the features selected for X-ray analysis. The minerals, selection rules and Chemical Classification results for 10 fields of view are given in Table 9.1.

![Figure 9.2 Chemical Classification of a Ag-bearing sulfide ore.](image)

Table 9.1 Chemical Classification of Minerals in a Silver Ore

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<th>Mineral Phase</th>
<th>Classification Rules</th>
<th>No. of Features</th>
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Full Spectrum Methods

Position-tagged Spectrometry

The ability to collect an entire EDS spectrum at each pixel has been desired for many years, but until recently, it would have taxed computer resources beyond their limit. In 1979, Legge and Hammond built a system on a proton microprobe that spooled a stream of position-tagged energies to magnetic tape in arrival-time order. These data were later sorted into a three-dimensional "spectrum image." The method of position-tagged spectrometry (PTS) as defined by Mott (1995, 1999) was invented independently and...
employs the same principle but performs the functions in real time. In this method, the beam is scanned at several frames per second (dwell time of a few microseconds), and the X-rays of every energy are tagged with the beam coordinates and sent to the computer for display in real time. The display can be a position-tagged spectrum of the scanned area or digital elemental maps or both—all developing with time. Spatial resolutions of the electron image, displayed maps and stored maps can all be different, but the position tags carry the full resolution of the electron image.

PTS collects and stores a spectrum image, but it differs from the method generally called “spectrum imaging” in that it collects the data in an essentially parallel fashion. Rather than have the beam step to a position and dwell while collecting a short spectrum, in PTS, the beam continuously scans, building the entire 3-D file at once. In so doing, it averages out any effect of beam current drift, and maps appear in seconds. Moreover, the PTS file is initially fully deflated, and planes are only promoted as necessary to hold the incoming data. The result is smaller file sizes than with spectrum imaging.

Post-processing operations consist of extraction of maps for any element, spectra for any region, and automatic segmentation into phases. Regions from which spectra can be extracted can be defined by a geometric shape such as a box or circle. More complex definitions might include: grain boundaries, coating/substrate interfaces, or the surfaces of fibers (Friel and Greenhut, 1999).

Autophasing can be automatic (Friel and Batchelor, 2002), in which the computer uses a method called recursive pixel allocation to look for associations among X-ray intensities, or it can be user-constrained phrasing. In this latter form of the method, the user marks points in the image that represent known phases or minerals, and the computer forces all of the pixels into one of these predetermined classes. A completely different method uses multivariate statistics like principal component analysis to reveal chemically defined components (phases) (Kotula, 2003). The two methods now being used to extract phases from spectrum images differ in the amount of judgment that is allowed to constrain the operation and in their speed of operation. Recursive pixel allocation is performed virtually instantaneously and always produces a result.

With WDS, maps can be quantified without collecting a spectrum. However, the creation of a quantitative EDS map requires a full spectrum for the purposes of background subtraction and peak deconvolution. The traditional approach to quantification of pixel data is to do the necessary spectral processing, generate a k-ratio, and perform a matrix correction on every pixel. These processes are not instantaneous and may take several minutes for a 128x128 map. The advantage to this approach is that each pixel can be queried for the concentration of each element.

A faster method involves exploiting the spectrum image by performing an AutoPhase calculation followed by quantitative analysis of each phase. If the phases are homogeneous, the results are the same as with quantitative pixels, but the time is only a few seconds. A full spectrum at every pixel does not imply displaying or analyzing single pixel spectra. If spectra are needed at selected pixels, it is more efficient to collect traditional spot analyses in an automated mode using digital beam control. The power of full spectrum methods lies in identifying and summing similar pixels. These can be chemically similar as revealed by AutoPhase or Principal Component Analysis, or they can be microstructurally similar, such as grain boundaries, coatings, interfaces, fibers, etc. By operating on regions rather than pixels, the full statistical power of spectrum imaging can be applied to mine the data and display it as high-quality maps and spectra.

**Summary of X-ray Mapping**

X-ray maps provide a rich source of data on the micrometer scale, from which to extract compositional information. That information can then be correlated with process or properties. Digital imaging systems have the power to perform complex arithmetic and logical operations on large arrays of numbers, such as
multiple X-ray maps or spectrum images and do it rapidly. The information available from such datasets is limited only by the questions that are asked, and of course, the information in the original image.
X. SUMMARY OF THE TECHNIQUES

The combination of X-ray microanalysis and image analysis is one of the most powerful techniques of materials characterization in common use. They provide a direct means of gathering data about the structure and composition of a specimen on a scale that often determines its properties. The techniques are complementary, because chemical and structural information form a basis for the specifications on which a material is selected. Localized chemical analysis, combined with a suitable measure of the amount and size of each phase, provides a good description of metallographic, petrographic or ceramographic samples.

In some instances, the techniques are supplementary. That is, one technique is sufficient to characterize the sample, but the other provides information over and above it. For example, the size distribution of a powder is usually sufficient to characterize it; nevertheless, X-ray microanalysis may reveal foreign materials in the product. Another example might be minerals in a rock. In this case, X-ray microanalysis is sufficient to establish the rock's history from an equilibrium phase diagram, but image analysis can provide information about the ability to liberate ore minerals.

In each of these examples, the commonality is the availability of information about a specimen on a scale of micrometers, and this scale is getting smaller, as some perform nanoanalysis in the AEM. Whether one is attempting to relate process and properties in materials science, or structure and function in the biosciences, microanalysis and image analysis provides the crucial link.

It is indeed fortuitous that not only can these two techniques be installed together on the same electron microscope, but also they can be found in one analytical system. The use of the same computer to collect and process many signals including X-rays, backscattered electrons, secondary electrons, absorbed electrons, transmitted electrons or light provides a wealth of data that can be turned into information by appropriate manipulation. Moreover, the speed of PCs is no longer a limitation. Hence, investigators can try several approaches to data analysis in order to extract the most meaningful information from the sample, and to display it in a way that is clear to others.

X-ray microanalysis and computer-aided imaging are both well-established techniques, and application-specific software makes previously time-consuming tasks routine. Together these analytical techniques make the electron microscope laboratory one of the most powerful and valuable assets in a research facility.
REFERENCES

Moseley, H. G. J. (1913) Phil. Mag., 26, 1024.
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