The Electron Microprobe as a Metallographic Tool


ABSTRACT: The electron microprobe (EMP) is an electron optical instrument in which compositional and topographic information are obtained from regions ≤1 μm in diameter on a specimen. Photographs of compositional and topographic changes in 1-mm² to 20-μm² areas on various types of specimens can also be obtained which are strikingly similar to optical photomicrographs. This paper discusses the various signals that are measured in the EMP (X-rays, secondary electrons, backscattered electrons, etc.), their resolution, and the types of information that can be obtained. In addition to elemental analysis, the solid state detector and scanning techniques will be discussed. The last sections will cover characterization of phases-homogeneity-trace element analysis-quantitative metallography and various techniques which extend the instrument capabilities such as deconvolution and soft X-ray analysis. Various applications will be discussed and illustrated.

KEY WORDS: metallography X-ray spectra, quantitative analysis, electron probe, spectroscopy, resolution, background, microanalysis, X-ray spectrometers, solid state counters, trace element analysis, homogeneity

The electron microprobe (EMP) is one of the most powerful techniques for the examination of the microstructure of materials. The instrument employs a high voltage electron beam (1 to 30 kV) focused to ≤1 μm in diameter, and information such as composition and topography are obtained from the bombarded region. The characteristic X-ray spectra emitted by the specimen allows its elemental composition to be determined. By combining electron beam scanning and X-ray detection, the EMP becomes a logical extension of the optical microscope. The spatial distribution of one or several elements in a fixed area of a specimen can be obtained by this technique. In addition, topographic information is obtained when other signals, specimen current, backscattered electrons (BSE), cathodoluminescence, and secondary electrons (SE) are collected in the scanning mode. General descriptions of the electron probe technique can be found in various references [1-3].

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2 The italic numbers in brackets refer to the list of references appended to this paper.
Electron Microprobe

Electron Probe Diameter and Current

In the EMP a two- or three-lens system is used to demagnify the crossover image formed in the electron gun. The submicron electron beam which is produced bombards the specimen surface. A schematic drawing of the electron optical column of the Applied Research Laboratory (ARL) electron optical system is shown in Fig. 1. The amount of current in the finely focused electron beam which impinges on the specimen determines the magnitude of the signals (X-ray, sample current, etc.) emitted, other things being equal. In addition, the size of the final probe spot determines the resolution of the instrument, although in many cases it does not determine the excitation volume from which the signal is produced. Therefore, the electron optical system in the EMP is designed such that the maximum possible current is obtained in the smallest possible electron probe.

It is possible to determine the maximum current \(i\) available in an electron probe of diameter \(d_p\) when the effects of aberrations in the electron optical system, chromatic, spherical, and diffraction are considered together. Pease and Nixon [4] calculated the theoretical limits to probe current and probe diameter.
by considering only spherical aberrations and diffraction. They obtained the following relation:

\[ i_{\text{max}} = 1.26 \frac{J_c}{T} \left( \frac{0.51 d_p^{8/3}}{C_s^{2/3} \lambda^2} \right) - 1 \times 10^{-10} \]  

(1)

where

- \( J_c \) = emission current density (A/cm\(^2\)) of the filament,
- \( T \) = temperature of the filament (K),
- \( C_s \) = spherical aberration coefficient (cm), and
- \( \lambda \) = wavelength of the electrons (cm).

It can be seen from Eq 1 that the incident beam current will vary with the \( 8/3 \) power of the probe diameter. Figure 2 illustrates the relationships between probe current and the size of the electron beam as given by Eq 1 at two operating voltages of 15 and 30 kV. The values of \( C_s \) (2 cm), \( J_c \) (2.0 to 4.0 A/cm\(^2\)), and \( T \) (2700 to 2820 K) that were chosen, are typical of operational instruments using a tungsten hairpin filament.

**FIG. 2—Relationship between probe current and electron beam diameter, \( d_p \).** The curves are given for two accelerating voltages, 15 and 30 kV.
It can be observed from Fig. 2, that the maximum current available in a 1-μm electron beam using a conventional tungsten filament is 0.5 to 1.0 \times 10^{-6} \text{ A} \text{ at } 15 \text{ kV and 1.0 to } 2.0 \times 10^{-6} \text{ A} \text{ at } 30 \text{ kV. This amount of current is well above the minimum (1.0 \times 10^{-8} \text{ A}) normally considered necessary to perform satisfactory quantitative X-ray analysis with X-ray, wavelength dispersive spectrometers. Successful X-ray analysis can, therefore, be obtained using a tungsten filament with minimum electron beam sizes \(d_p\) of the order of 0.25 μm. As will be discussed later, a spot size of 0.25 μm is usually well below the diameter of the region of X-ray emission from the specimen.

**Resolution of the Emitted Signals**

A large number of interactions occur when a focused electron beam impinges on the specimen surface. Among the signals produced are SE, BSE, characteristic and continuum X-rays, and photons of various energies (Fig. 3). Each of these signals are obtained from specific emission volumes within the specimen and these are strong functions of electron beam voltage and the atomic number of the specimen. In fact the resolution of the EMP, for a particular signal, is primarily determined by its excitation volume and not by the electron probe size.

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**FIG. 3—Signals produced when a focused high voltage electron beam bombards the specimen surface.**

Electrons having energies in the range 1 to 30 kV impinging on the solid specimen, undergo elastic scattering (change of direction with negligible energy loss) and inelastic scattering (energy loss with negligible change in direction). Elastic scattering is caused mainly by interactions with the nucleus and significant deviations from the incident direction occur. Inelastic scattering is caused by two mechanisms; inelastic interaction with the atomic nucleus and inelastic interaction with the bound electrons.
Inelastic scattering is primarily responsible for producing the signals that one attempts to utilize (Fig. 3). If inelastic scattering occurs through interaction with the nucleus of the atoms, the moving electrons lose energy in the coulomb field of the nucleus and emit white or continuum X-ray radiation. If inelastic collisions occur between the loosely bound outer electrons and the incoming beam, energy is lost and SE are produced. The SE which are no longer bound to the original atom have an energy typically less than or equal to ~ 50 eV. If the SE recombine with the holes formed during the scattering process, a photon of energy is produced which has a wavelength in the visible or near infrared range. This visible luminescence can be seen optically when one is analyzing transparent materials. In all of these inelastic collisions, the process is combined with the loss of some or all of the incoming energy of the electrons. Inelastic collisions can also occur between the incident electrons and the inner electrons of the atoms. In this case characteristic X-ray lines are obtained. The primary electron (PE) beam loses energy equivalent to the binding energies of the K, L, M, etc. shells, $V_K$, $V_L$, $V_M$, etc.

Elastic scattering results in a large change of direction of the impinging electron beam. At some depth within the target the original direction of the electron beam is lost and the electrons diffuse through the material at random. The position at which this occurs is called the depth of complete diffusion ($X_d$). The scattering cross section at constant energy varies with $Z^2$, and the probability of scattering through a given angle varies as $Z^2/V^2$. For low atomic number specimens, there is not much scattering near the surface of the specimen as the electrons enter. Only a few electrons are scattered through large angles and leave the specimen as BSE. In a high atomic number specimen, however, there is considerable scattering close to the surface and a large fraction of the incoming electrons are backscattered. In the case of a heavy element, such as gold, diffusion sets in much nearer the surface than for a light element. The shape of the electron distribution within the target as a function of voltage and atomic number can, therefore, be determined qualitatively as discussed by Duncumb and Shields [5], Fig. 4. This figure shows the electron distribution as a function of depth $z$ and the outside limits of the distribution represent zero voltage. At the same voltage, the electrons appear to penetrate more deeply into the low atomic number element and the electron distribution appears to be more pear-shaped. If the energy of the incident electrons is increased, the path length of each electron is lengthened, and the envelope is expanded but retains essentially the same shape.

**Electron Range and Spatial Resolution of the Primary Electron Beam**

The electron range ($R$) is defined as the distance (measured from the surface of the specimen) that the electron penetrates into the specimen. The spatial resolution is the spread of the electron beam laterally from the center of impact. For the incident electrons, the electron range and the spatial resolution are similar in value since they are both defined by the amount of elastic scattering.
FIG. 4—The shape of the electron scattering distribution within the target as a function of voltage and atomic number.

Kanaya and Okayama [6] have derived an expression for the maximum range \( R \) where the electron beam energy is reduced to zero using a total scattering cross section which takes into account both elastic and inelastic collisions. The range \( R \) is expressed as

\[
R = 0.0276V_o^{1.67} \left( \frac{A}{Z} \right)^{8/9} / \rho
\]  

(2)

where \( V_o \) is the high voltage given in kV, \( \rho \) is the density in g/cc, and \( R \) is in microns. Table 1 gives a comparison of experimental values of \( R_{\text{max}} \) [7] and the calculated ranges \( R \).

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The calculated maximum range \([6]\) appears to agree quite closely with the measured values of \(R_{\text{max}}\) and can be used in a practical sense to determine the electron range for analysis. Other expressions for electron range are also available \([3]\). It is obvious that the electron range varies greatly with atomic number at a given voltage and that the spatial resolution of the electron beam can be improved by selecting low voltages for analysis.

**Backscattered Electrons**

Backscattered electrons (BSE) are produced by elastic scattering of the primary electron beam. Because the amount of elastic scattering increases with atomic number \(Z\), the fraction \(\eta\) of electrons which are backscattered also increases \([8,9]\). If the specimen surface is rough, the BSE yield can be selectively absorbed or increased depending on the beam position. Therefore, the intensity of the BSE in the direction of the detector is also a function of the topography of the specimen. However, it should be noted that if the specimen is polished flat, as in the preparation of specimens for quantitative analysis, one can obtain the average atomic number of the analyzed area of the specimen.

The BSE have an electron range which is smaller than that of the electron beam \((R)\) and, therefore, the range and also the spatial resolution of the backscattered signal is improved over that of the primary electron beam. According to Cosslet and Thomas \([10]\) the backscattered fraction comes from a “mean” depth of about 0.3 \(R\) in copper to 0.2 \(R\) in gold at 25 kV. Shimizu and Murata \([11]\) have calculated that the vast majority of electrons are backscattered laterally with a small diameter, about \(R/2\).

**Low Energy Secondary Electrons**

The secondary electrons (SE) have an energy typically less than 50 eV. If these SE are produced within a few hundred angstroms of the surface, they have a high probability of escaping from the specimen. These electrons are absorbed, however, if they are produced much below (>500Å) the surface of the specimen. For metals and coated specimens this value is smaller (>250Å). Within this maximum depth the spread of the primary beam is small. Therefore, the area from which the SE are produced, by the incident electron beam, is primarily limited by the electron probe spot size \((d_p)\). It is these low energy SE which are used in the scanning electron microscope (SEM) to obtain surface topography.

**X-ray Range and Spatial Resolution**

When the electron beam strikes a specimen both continuum and characteristic X-rays are produced. The X-ray continuum varies in wavelength and can be excited as long as the electron beam voltage is greater than zero. The X-ray continuum forms the background X-ray radiation and determines the minimum detectability limit for the particular element that is measured, assuming
that instrumental factors are negligible. The range for continuum X-ray production will be similar to that of the primary electron beam since X-radiation can be produced even at low electron energies.

The characteristic radiation is produced by the interaction of incident electrons with the inner shell electrons of the atoms in the specimen and the wavelengths of the characteristic radiation are specific for each element. Detection of a characteristic X-ray line indicates that the element is present in the specimen and these characteristic lines may also be used to obtain the composition of the specimen. The range for characteristic X-ray radiation ($R(x)$) will usually be smaller than that of electrons, since characteristic X-rays can only be produced at energies above the critical excitation potential ($V_c$). Several equations for X-ray range ($R(x)$) have been developed [1,12-14]. The range equation obtained by Anderson and Hasler [13] where

$$R(x) = 0.064 \left( V_o^{1.68} - V_c^{1.68} \right)/\rho$$

was based on experimental data and is probably more correct.

Figure 5 shows the X-ray range, calculated from Eq 3, for various X-ray lines $\text{Al}_{K\alpha}$, $\text{Cu}_{K\alpha}$, $\text{Cu}_{L\alpha}$, $\text{Au}_{L\alpha}$ generated within the element targets aluminum, copper, and gold as a function of operating voltage $V_o$. The three matrix elements shown in Fig. 5 were chosen to represent the

![Figure 5 - X-ray range R(x) for various X-ray lines (Al_{K\alpha}, Cu_{K\alpha}, Cu_{L\alpha}, Au_{L\alpha}) in selected targets (aluminum, copper, gold).]
range of specimen densities which are likely to be analyzed, and the X-ray lines were chosen to represent the common X-ray wavelength ranges measured. The electron range \( (R) \) for aluminum [6] is shown for comparison purposes. The X-ray ranges depend not only on the density of the matrix (aluminum = 2.7 g/cm\(^3\), copper = 8.93 g/cm\(^3\), and gold = 19.3 g/cm\(^3\)) but, also, on the value of the energy of the X-ray line produced. One can see that, in general, to obtain an X-ray source size \(<1 \mu m\) the voltage of the electron beam may have to be adjusted depending on the matrix material and line measured.

To define the X-ray source size or spatial resolution one can assume that the lateral X-ray production range is the same as \( R(x) \), the X-ray range. This relation, however, assumes that the size of the electron beam impinging on the specimen is vanishingly small. The total X-ray spatial resolution \( R_x \) is, therefore, equal to the sum of the X-ray range \( R(x) \) and the size of the electron beam \( (d_p) \) hitting the specimen. As discussed previously, the electron beam size \( (d_p) \) can be as small as 0.25 \( \mu m \). Since the X-ray range \( (R(x)) \) is usually a micron or more, the total X-ray spatial resolution is essentially given by \( R(x) \). Generally, there is little advantage for the X-ray spatial resolution, in reducing \( d_p \) below 0.25 \( \mu m \).

**Summary—Range and Spatial Resolution**

The result of electron beam specimen interactions is to produce various complex interactions. These interactions are responsible for the signals which can be used to reveal the topography and local chemistry of the specimen. Figure 6 summarizes the range and spatial resolutions of the various signals (BSE, SE, and X-rays) available from the EMP for a pure element of low to medium atomic number. The spatial resolution for X-rays and BSE are approximately the same as their respective ranges \( R(x) \) and \( X_a \). On the other hand, the spatial resolution of the SE is independent of the range of these signals. The spatial resolution of SE is approximately the same as the probe diameter \( (d_p) \), whereas the spatial resolution of the BSE and X-ray signals are usually much larger than \( d_p \). As illustrated in Fig. 5, the X-ray spatial resolutions of several X-ray lines measured in the same material are different.

**Elemental Analysis**

**Element Detection**

In the EMP, the crystal spectrometer is the principal method of measuring X-ray spectra. Figure 1 shows the typical X-ray focusing optics in an EMP. The system includes a source, the bombarded area, a crystal for diffracting the X-ray spectra, and a counter for X-ray detection. The source, crystal, and detector are all maintained on the same circle, called the focusing circle. In addition, the angle between the specimen surface and the measured X-ray beam is the X-ray emergence angle or take-off angle. In most EMP's this angle is held constant as the diffraction angle at the crystal \( (2\theta) \) is varied.

Qualitative spectral scans of the type shown in Fig. 7 involve displaying the
FIG. 6—Schematic of the range and spatial resolution of the various signals produced in the EMP.

X-ray ratemeter output as a function of diffraction angle (2θ) or wavelength. Once the peaks are detected their identity can quickly be established. Figure 7 shows a spectral scan of the matrix and of inclusions in a stainless steel [15]. The carbide inclusion is rich in titanium, manganese, and chromium, while the matrix exhibits normal iron, chromium, and nickel, and small amounts of cobalt and manganese.

Usually one or more crystal spectrometers are available in the EMP. A broad selection of analyzing crystals is used to cover and optimize spectrometer performance in the range from 0.2 to 140 Å and elements from beryllium upward can be detected. Among the most useful crystals are lithium fluoride (LiF) for wavelength coverage 3.5 to 0.2 Å, ammonium dihydrogen phosphate (ADP) for 10 to 2 Å, potassium acid phthalate (KAP) for 25 to 5 Å, and lead stearate for 90 to 20 Å. For element detection, the spectrometers scan portions of the spectrum for periods of a few minutes to several hours depending on the desired level of sensitivity.

To obtain an optimum count rate of X-ray intensity with a wavelength dispersive detector, a probe current of $10^{-6}$ A is sufficient for most elements at concentration levels above 0.1 percent. However, a lower count rate of $10^{3}$/s can be used for scanning and point analysis. The typical efficiency of a dispersive detector allows count rates of $10^{3}$/s at 25 kV for most elements with atomic number 12 (Mg) at a beam current of $10^{-9}$ A [16]. Using Fig. 2, this beam current allows a probe diameter of < 1000 Å.
Recently, improved lithium-drifted silicon solid state detectors allow detection and energy dispersion of X-rays of ~ 1 to 30 kV energy in the EMP [17-19]. The energy resolution of such energy dispersive detectors is still significantly inferior to the standard focusing crystal spectrometer. As discussed by Lifshin [20], they have attracted widespread interest because (1) X-ray signals of all detectable energies from element 11 (sodium) and above are collected simultaneously, and a whole spectrum can be obtained in a few minutes, (2) higher counting rates at low beam currents greater than those obtained with a crystal spectrometer are possible, and (3) the detector responds to X-ray energy independent of specimen position, unlike the crystal spectrometer which requires the source of the X-ray spectra to be on the focusing circle.

The operating principles of the solid state detector system are shown schematically in Fig. 8. The X-ray signal passes through a thin window into

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**FIG. 7**—Spectral scan, intensity versus diffraction angle 20, of a stainless steel using a crystal spectrometer, carbide and inclusion (top), stainless steel matrix (bottom).
the lithium-drifted silicon crystal. Energy is lost both to the crystal and in the formation of electron-hole pairs. These electron-hole pairs are swept away by an applied bias and are eventually converted to a voltage pulse and amplified by the preamplifier and linear amplifier. These pulses are stored by a multichannel analyzer which sorts the incoming pulses by amplitude. The resulting spectrum can be displayed on a cathode ray tube, an X-Y recorder, a teletype, or transmitted to a computer.

Figure 9 shows the spectra obtained, with a solid state detector on an EMP, from a stainless steel specimen similar to that used for the data in Fig. 7. The difference in resolution can clearly be seen in a comparison between Figs. 7 and 9. In practice, the resolution of crystal spectrometers, which can be 5 eV for iron $K\alpha$, is limited to the mosaic spread of the analyzing crystal. The resolution of the solid state X-ray detector is about 160 eV for iron $K\alpha$ and is limited by both the statistical nature of electron-hole pair formation and electronic noise [20].

By far the most useful application of solid state detectors on EMP's is for qualitative analysis. The speed of obtaining useful spectra for identifying elements present in the specimen is a great advantage. Multichannel analyzers equipped with large enough memories also make it relatively easy to compare the spectra obtained from several different points on a specimen with each
FIG. 9—Spectra, intensity versus voltage (kV) of a stainless steel using a solid state detector.

other or with standards. What the detector lacks in resolution is partially compensated for in total collected counts. However, the need for optimum resolution is particularly important when one analyzes complex multielement specimens in which peak overlap occurs. It is unfortunate that as the X-ray counting rate increases the resolution of the solid state detector is degraded [21].

Crystal spectrometers are not being replaced for qualitative analyses. They provide the highest sensitivity in most wavelength ranges, and their superior energy resolution virtually eliminates peak overlap problems and ambiguities in spectral identification. Crystal spectrometers are, so far, still the only means of measuring in the light element range (beryllium, boron, carbon, nitrogen, oxygen, and fluorine) where large “d-“ spacing crystals make analyses down to beryllium possible. Programmable spectrometers now make qualitative scans more efficient by only scanning through specific wavelength ranges corresponding to suspected peak positions.

**Composition Measurement**

Since much of our understanding of how materials behave depends on knowing the composition of the various phases in a microstructure, the method of quantitative electron probe microanalysis has been highly developed. In his doctoral thesis, Castaing [22] laid out the basis for the theory of quantitative electron probe microanalysis. He pointed up that the intensity of characteristic radiation generated directly in complex multielement specimens is approximately proportional to the mass fraction of the
emitting element. He proposed that the corrections which need to be applied to each of the measured characteristic lines to obtain mass fractions are:

1. An atomic number correction \( Z \) to correlate the effects of energy dissipation and electron backscattering with the atomic number of the specimen.

2. An absorption correction \( A \) which takes into account the absorption of X-rays emerging from the specimen.

3. A fluorescent correction \( F \) which takes into account the effect of any indirect X-ray generation by other elements.

The proportionality constant between the measured intensity \( I_A \) and the concentration of a given element \( C_A \) is given by the above corrections.

Because of the difficulties involved in making absolute intensity measurements, the X-ray intensity from the unknown specimen \( I_A \) is always compared with that from a standard specimen \( I(A) \) under identical external conditions of excitation. In both cases the continuum background radiation is subtracted from the peak intensity. Where possible it is convenient to use the pure element \( A \) as the standard, but less of a correction is necessary if the standard of composition \( C(A) \) is close in composition to the unknown specimen.

The ratio \( I_A/I(A) \) can be measured and related to the ratio of the concentrations \( C_A/C(A) \) by the relation

\[
\frac{I_A}{I(A)} = \left[ \frac{ZAF_A}{ZAF(A)} \right] \frac{C_A}{C(A)}
\]

This "classical" ZAF scheme of data reduction has essentially remained the commonly used approach to quantitative analysis. It has been described along with potential sources of error in many publications \([3,23,25]\) and numerous examples of its use have been published \([3,26,27]\). The objective of this section is to point out some of the problems and newer developments in quantitative analysis.

For quantitative X-ray analysis it is necessary to have a flat polished specimen for analysis free from the effects of selective etching. In addition, the specimen should not be affected by the impinging electron beam. The use of the EMP for the examination of alkali-containing glasses, and to a lesser extent, minerals, presents specific difficulties not encountered in conducting materials. Under the action of the beam, the glass apparently undergoes a composition change as shown by the change in intensity of the characteristic X-ray emission of the alkali metal present \([28-30]\). It is clear that before glasses can be analyzed, their stability under the beam should be proved for the conditions of kilovolt and beam current to be used. For biological specimens, unbound water must be removed from the specimen to make it suitable for vacuum insertion. In addition, the specimen must be electrically and thermally conductive, and the surface must be smooth and flat for analysis. The critical requirement is that in preparing the specimen, the structural-chemical relationships existing at the level of spatial resolution of...
the microprobe should not be disturbed [30].

Although the methods for quantitative microprobe analysis have been worked out in great detail, there are surprisingly few standards available for microprobe analysis. In many cases pure elements can be used for standards. For geological specimens pure oxides have been used as standards when the Bence-Albee correction [31] is employed. Recently, the National Bureau of Standards (NBS) certified and issued alloys of nominal composition 80W, 20Mo, and 3Si in iron and a series of binary alloys in the gold-silver and gold-copper systems. The major uses of these NBS alloys are to give the analyst experience with specimens which are well characterized to check out their own measurement procedures, data reduction, and calculation procedures.

In any composition measurement with the EMP the continuum background which underlies the characteristic X-ray peak must be measured and subtracted from the peak intensity. Generally, two methods are available. One can measure continuum background at a wavelength or energy adjacent to the X-ray peak, or one can use a specimen which is of similar composition but does not contain the element of interest. It is, however, difficult to obtain specimens for the latter method. With the solid state detector the background measurements are complicated by spectral overlap of peaks (Fig. 9). To overcome this problem, deconvolution techniques (spectrum stripping) using digital analysis are very helpful [32]. Another technique is to calculate the size of one of the interfering peaks from another peak from the same element that has no interference and subtract it from the total count of the composite peak [33]. Quantitative analysis with the solid state detector has been demonstrated for certain applications [3]. However, under normal microprobe operating condition, with the beam current 10\(^{-8}\) A or above, the total X-ray intensity available and the system count rate can be much higher than that acceptable by a solid state X-ray detector, and, as discussed earlier, resolution is degraded. Along with the fact that the peak to background ratios of a tuned crystal spectrometer are higher, the crystal spectrometer has a decided edge in quantitative EMP work over that of the solid state detector.

There are several ways in which the computer is used to provide the microprobe user with more and better information. For quantitative microprobe analysis, the ZAF correction procedure as given in Eq 4 is calculated using a computer. For a given X-ray line, operating voltage, and a particular X-ray optics, the emergent intensities contained in Eq 4 can be calculated as a function of the composition of the specimen or standard. However, it is not possible to simply invert the equation in order to obtain the unknown mass-fraction of the emitting element corresponding to the intensity ratio \(I_A/I(A)\) since the values for the correction factors depend on the specimen composition. The calculation of the mass fraction, therefore, requires an iterative procedure in which a computer is necessary.

Several dozen computer programs now exist to accomplish the task of converting X-ray intensity ratios to chemical compositions, for example,
In the more widely used programs the constants are stored in matrix form within the program making input quite simple and printout fairly extensive. These programs have generally required fairly large storage requirements and must be run on fairly large machines. If extended output is not required, and, if one is willing to input the constants required for the various corrections at the necessary time, then the program for data reduction may be small enough to fit into a standard minicomputer.

Automation of the EMP with the computer can vary greatly from one laboratory to another depending on the degree of sophistication desired. Several parts of the EMP can be automated, for example (1) the stage: specimens and standards are moved under the electron beam, and (2) the spectromers: they are moved through their wavelength ranges and intensities are read out. For quantitative analysis, accurate peaking of spectrometers is also necessary. In addition, other components which can be automated are the pulse height analyzer, X-ray amplifier, and high voltage, or even the high voltage and current of the electron gun.

Software as well as hardware must be obtained in order to operate efficiently. The software consists of a peak seeking program, sequencing of data collection, statistical analysis of data, and ZAF quantitative calculations. Several different automation systems have been developed [37-40]. The design of the system is often dictated by the major type of specimen to be studied (geological, thin film, etc.) and the types of analyses desired.

Quantitative EMP analysis of the light elements is particularly difficult, since the correction models developed for quantitative analysis may not be applicable in the light element range. In addition, the attenuation of the primary radiation is large when these long wavelength, low energy X-rays are measured. A large absorption (A) correction is usually necessary and unfortunately, necessary parameters such as the mass absorption coefficient are not well known. One can minimize the absorption effect by working at low electron energies and using high X-ray emergence angles from the specimen. Nevertheless, reliable quantitative results are best obtained by comparison with standards of known composition close to that of the specimen.

Calculations of oxygen content on well characterized oxides have been made using oxygen intensities measured with the EMP [41]. The results do not agree well in all cases, and the disagreement is due mainly in the uncertainty of the mass absorption coefficient and the influences of chemical bonding. When the same measurements were repeated in a later study [42] and after more accurate mass absorption coefficients became available, the relative errors between the electron probe microanalysis and the wet chemical analysis at various operating potential 5, 10, 15, 20, 25, and 30 kV were less than a few percent.

Complications in light element analysis also arise because of the presence of the L-spectra from heavier metals. Duncumb and Melford [43] have shown that even if overlapping occurs, a qualitative analysis can be obtained. In steels, for example, titanium carbonitride (TiNC) inclusions which are prob-
ably solid solutions of titanium nitride (TiN) and titanium carbide (TiC) are found. Figure 10 shows a comparison of the titanium L-spectra obtained from TiN, TiC, and pure titanium. The TiNC phase gave a more intense peak at the titanium L₁-wavelength than that of pure titanium. This peak contains mainly titanium L₁ at 31.4 Å (18.3° θ) together with a small amount of nitrogen Kα emission indistinguishable from it at 31.6 Å (18.5° θ), Fig. 10. The titanium L₂-wavelength at 27.4 Å (16.0° θ) is heavily absorbed by nitrogen and is about one third as intense as that from pure titanium. The titanium L₁-emission, however, is only slightly absorbed by nitrogen.

![Graph showing comparison of titanium L-spectra](image)

**FIG. 10**—Comparison of the titanium L-spectra (intensity versus diffraction angle, θ) obtained from pure titanium (left), TiN (center), and TiC (right) at 10 kV operating potential.

The analysis of this type of inclusion may appear to be impossible, but Duncumb and Melford analyzed the titanium content by using the Kα radiation and analyzed the carbon content by use of the TiC standard, Fig. 10. The results indicate about 80Ti and 4C. The analysis for nitrogen was not possible for reasons already stated and was obtained by difference from 100 percent. In another study, Shiraiwa et al [44] also attempted to analyze TiNC inclusions in steel. They measured the nitrogen Kα directly, however, by setting the spectrometer slightly off the nitrogen Kα peak at 31.7 Å where the intensity of the titanium L₁ peak was negligible.

It is well known that a specimen subjected to electron bombardment in a diffusion pumped vacuum gradually becomes covered with a "contamination" layer due to polymerization, under the action of the beam, of organic matter absorbed on the surface [1]. The organic molecules come from the oil vapors from the vacuum pumps and the outgassing of any organic material present in the instrument. The effect is not very troublesome unless the deposited layer...
absorbs the emitted X-rays to a great extent. For the light element radiation, particularly beryllium, boron and carbon, the absorption of the long wavelength X-radiation can be severe. The problem in the case of carbon analysis is increased because the “contamination” layer is composed to a large extent with carbon. It is crucial, however, that the specimen should be free of contamination from polishing and storage before insertion in the EMP.

Two methods have been used to avoid the contamination layer. Castaing and Descamps [45], as early as 1954, showed that directing a low pressure jet of gas on the specimen at the region bombarded by the beam in the microanalyzer permits the practical suppression of contamination. Air jets have been installed on various EMP’s [46-48]. Not only is the contamination rate reduced to zero, but previously absorbed surface layers are removed. Although the vacuum system in the EMP is degraded by this process and the accompanying decrease in filament life is not severe.

The other generally used method is to provide a surface within the EMP which is cold relative to the surface of the specimen. Organic molecules will then tend to collect on the colder surface rather than on the specimen. The cold surface or cold finger must however be placed in very close proximity to the specimen. Cold fingers have been installed on various EMP’s [49-52] and have effectively reduced the contamination rate to close to zero. In one case [53] both an air jet and a liquid N₂ cold finger have been used.

In one example, for the determination of carbon in steels, calibration curves of counting rate versus percent carbon were constructed from a series of high purity iron-carbon alloys which had been transformed to martensite to ensure homogeneity. Figure 11 shows the linear calibration curve between count rate and carbon content for the iron-carbon alloys and Fig. 12 shows a plot of carbon content versus distance across a proeutectoid ferrite grain boundary allotriomorph in an Fe-0.11C-1.95Mo alloy [49].

Scanning Electron Probe

Cosslett and Duncumb [54] demonstrated that a beam deflecting or scanning system can be added to an EMP so that a magnified image of the scanned specimen area appears on the oscilloscope system. The image can be formed by the various signals that are obtained such as BSE, SE, target current, cathodoluminescent photons, and X-rays. The addition of scanning to the normal X-ray capability of the EMP allows one to obtain photographs of the composition distribution across a selected area on the surface of the specimen. Positive identification of phases can be made and compared directly to the optical micrographs. The resolution of the various images obtained depends on the range of the signal as discussed earlier in this paper. Since it is difficult to reduce the effective volume of X-ray emission below 1 μm, X-ray pictures are limited to about X3000. An excellent review of the various scanning techniques is presented by Heinrich [55].

Figure 13 shows a comparison of scanning X-ray pictures obtained from a solidified section of a M2 tool steel [56]. The eutectic interdendritic areas are
FIG. 11—Linear calibration curve between carbon \( K_{\alpha} \) count rate and carbon content for iron-carbon alloys. A more detailed view at carbon levels below 0.3 percent is given by the insert.

FIG. 12—Variation of carbon content with distance across a proeutectoid ferrite grain boundary allotriomorph in an Fe-0.11%-C-1.95% Mo alloy. The metallographic view of the analyzed area is also shown. The specimen was heated 15 min at 1300°C, isothermally reacted 50 s at 850°C, and quenched.
FIG. 13—Scanning pictures from a solidified section of a M2 tool steel. The scanned area is 90 x 80 μm in size. The various signals are tungsten Lα (upper left), molybdenum Lα (upper right), chromium Kα (center left), Vanadium Kα (center right), iron Kα (bottom left), and BSE (bottom right).

rich in chromium, molybdenum, and tungsten while the dendritic areas are iron-rich. In many cases the scanning X-ray analysis pictures may be much more important to the analyst than detailed quantitative analyses of specific areas. In most EMP laboratories scanning X-ray analysis represents a major portion of the analysis work. Various examples of scanning X-ray work can be found in review articles concerned with applications in geology [27], metallurgy [26,57], and biology [58,60].

X-ray images showing the distribution of a specific element are normally obtained by using the output of a crystal spectrometer to modulate the brightness of the scanning system cathode ray tube (Fig. 13). The same type of X-ray imaging is possible using a solid state detector. Figure 14 shows an example of a scanning X-ray distribution in a nickel matrix containing blocky tantalum carbide (TaC) particles [20]. If the discriminators on the multi-channel analyzer of the solid state detector are set to include only the portion of the energy spectra corresponding to a nickel or tantalum line, it is possible
FIG. 14—Scanning pictures from a nickel matrix containing blocky tantalum carbide particles. The X-ray scanning pictures are for tantalum Lα (left bottom) and nickel Kα (right bottom).

...to get an output much the same as with the crystal spectrometer. This output can be used to modulate the oscilloscope image as shown in Fig. 14.

Black and white photographs showing the topographic distribution of a single signal are widely used. It is difficult, however, to show the correlation of signals from two or more X-ray lines without the use of color. Composite color photographs using X-ray images from the EMP have been produced. One such method uses the black and white scanning images as color-separation-positives and with appropriate filters, color prints are made [61].

A more quantitative approach to X-ray scanning can be taken by using a device that produces abrupt changes of the oscilloscope beam brightness at predetermined signal levels. The contrast produced by a signal which is only slightly higher than the background can be enhanced so that only signal levels above background are obtained. Melford [62] demonstrated such an expanded contrast method in which brightness modulation by the ratemeter signal has been employed for image formation. This method can also be used to enhance differences at high concentration levels. Another technique developed by Heinrich [55] is called concentration mapping. In principle, this method shows the location of defined concentration ranges. To obtain this information, all concentration differences within each range are suppressed.

Since the backscattering fraction is a function of atomic number, a useful contrast between regions of differing atomic number can be obtained in the BSE images taken on flat specimens (Fig. 13).
also varies with the specimen topography, a contrast can be developed between regions of different height. Figure 14 shows the mixed effects of topographic and atomic number contrast in the BSE pictures taken of the TaC particles in a nickel matrix. The backscattering image can be improved however. If one only collects BSE at a relatively low angle to the specimen surface and only electrons that have lost less than a few hundred eV in the specimen, the BSE range can be as small as 100 Å below the specimen surface [63]. These BSE are assumed to travel in a straight line into the specimen until they are deflected by a single wide-angle scattering event.

The SE have spatial resolutions close to that of the primary electron beam. Most newer EMP’s have secondary electron detectors. Although resolutions below 500 to 1000 Å are not usually available in EMP’s, most instruments have secondary electron detectors in order to take advantage of the superior quality of the images they produce, Fig. 14, even at relatively low magnifications (X10 to 2500).

A simple way of obtaining a signal for image formation is to isolate the specimen from ground and observe the variations in the current flowing from the target to ground during the scanning process. This output is called the target or specimen current. The signal is complex because it is the current left over after the backscattered and low energy SE have been lost from the specimen. It is affected not only by the topography of the specimen but also by variations of the electron backscatter coefficient of the target. In conventional target current images the gray level is a function of both composition and topography. If a specimen contains areas of widely differing atomic numbers, topographic details are difficult to see. The images produced on the oscilloscope screen can also be mixed electronically with its first derivative [64]. The use of a mixed signal reduces the effects of composition variation so that topographic details appear more clearly.

Besides the signals already discussed, the emission of light in the visible and infrared ranges (cathodoluminescence) can also be used to obtain information concerning the region excited by the electron beam. The intensity and spectral distribution of the radiation is usually affected by trace amounts of some elements which activate the process.

Cathodoluminescence has found particular application in several fields. In geology studies, the EMP is a very suitable tool since the instrument has an optical microscope which allows viewing and photography of the specimen while under electron bombardment. In addition, the wide variation in beam size allows the examination of <1 to >300 µm². Long and Agrell [65] studied the visual luminescence of several minerals. They showed that identification of small grains can be accomplished because of a particular color. Variations in trace elements which behave as activators or as quench agents can also be observed. Since the concentrations involved are often small, their variation would not be easily observed except for detailed EMP measurements involving long counting times. The spatial resolution obtainable by using an optical microscope to observe cathodoluminescence is limited by diffraction to ~0.6 µm.
In insulators and semiconductors an appreciable fraction of the energy which is dissipated from the electron beam is used for the excitation of excess carriers and the excitation of optical energy levels. Radiation can result from the recombination of excess hole-electron pairs that are produced. In a study carried out by Kyser and Wittry [66], excess carriers were produced in gallium arsenide (GaAs) using an EMP with instrumentation for measuring infrared radiation. Local fluctuations in the intensity of recombination radiation over 10 to 50 µm regions were observed indicating a wide variation in the concentration of impurities or lattice defects. In a later study, Wittry [67] measured tellurium concentration by quantitative EMP analysis and found a correlation with the local variations in cathodoluminescence efficiency. Previous attempts to observe such a correlation failed because the practical limits of detectability using X-rays in the EMP are of the same order as the solubility limit of tellurium in GaAs.

Spectral analysis of cathodoluminescence was conducted by Kyser and Wittry [66] and others [68-71]. A typical emission spectrum may have a width of 500 Å, with a peak at 5000 Å, and different activators may not give distinguishable emission spectra. The effects of altering the accelerating potential and other parameters, and the effects of charging on the spectra were studied by Muir et al [68], also small single crystal cathodoluminescence characteristics of common phosphors were studied [72]. Analysis of rare earth materials have also been made using the cathodoluminescence spectra [69] in the ultraviolet and visible regions. Potentially, the cathodoluminescence method should be able to measure trace elements contents well below that of the X-ray EMP technique. However, it should be noted that the cathodoluminescence signal exhibits saturation effects and is not always proportional to beam current.

**Characterization of Phases**

**Specimen Preparation**

For quantitative X-ray analysis we need to have the flatest specimens possible. The effect of roughness of the specimen on the type or quality of data obtained increases as the take-off angle of the instrument (Fig. 1) decreases [73]. This relation exists because the relative errors in the calculation of the composition, due particularly to the absorption effect, increase with decreasing take-off angle. Although a high take-off angle probe may minimize the effect of surface roughness, a flat specimen is, nevertheless, desirable. Another reason for analyzing flat specimens is to obtain accurate composition measurements at phase boundaries and edges of the specimen. If flat specimens are not available, the total path length which the X-rays traverse on their way out of the specimen can be changed. The effects of corners and edges cannot be corrected for and must be minimized. Depending on the type of specimens to be analyzed, it may be necessary to try to maximize the flatness of the specimen at the expense of any other of the type of specimen preparation.
Limited qualitative microprobe analyses can be accomplished on rough fracture surfaces if several precautions are taken [74]. To make sure that scanning X-ray measurements of the elements present in the alloy are real and not just the effect of topography, the spectrometer can be set off-angle and a scanning image taken of the distribution of background intensity. In this way fluctuations in the X-ray signal caused by surface irregularity can be seen and spurious indications in the characteristic line image can be rejected to determine the distribution of elements of interest.

For organic materials, 1 to 4-μm-thick specimens are mounted on substrates. An ultramicrotome is used and tissues are usually dehydrated and embedded before they are cut. One can use dyes with tissues to highlight areas of interest as long as the materials which make up the dyes do not interfere with the concentrations to be measured within the specimen. It is also important to note that for biologic materials, all the standards should be of the same thickness as the specimens themselves. If the specimens and standards are prepared at different times this is very difficult to achieve.

Most geological and biological specimens are coated to ensure electrical and thermal conductivity. The most frequently employed coating is carbon. The coating should be as thin as possible, transparent to visible light for microscopy and also yield a stable sample current. Furthermore, the thinner the coating, the less is the X-ray absorption within it and the less is the energy loss of the primary electron beam entering the specimen. Usual coating thicknesses vary from 50 to 500 Å. It is desirable to have the same thickness of coating on both specimen and standards, but, for light element analyses it is a necessity.

Statistics—Homogeneity, Composition Differences, and Trace Analysis

It is important to note that X-ray production is statistical in nature. X-rays which are produced from a given specimen and interact with radiation detectors are completely random in time but have a fixed mean value. The distribution or histogram of the number of determinations of X-ray counts from one point on a specimen versus the number of X-ray counts for a fixed time interval may be closely approximated by the continuous normal (Gaussian) distribution. The individual X-ray "counts must lie upon the unique Gaussian curve for which the standard deviation is the square root of the mean ($\sigma_c = \sqrt{\bar{N}}$). Here, $\bar{N}$ is considered to be the most probable value of $N$, the total number of counts for a given time $i$. In as much as $\sigma_c$ results from fluctuations that cannot be eliminated as long as quanta are counted, this standard deviation is the irreducible minimum for X-ray emission spectrography. For example, to obtain a number with a minimum of a 1 percent deviation in $N$, at least 10 000 counts must be accumulated.

However, as Liebhański [75] pointed up, the actual standard deviation ($S_c$), given by

$$S_c = \sum_{i=1}^{n} (N_i - \bar{N})^2 / (n - 1)^{1/2}$$

(5)
where \( n \) is the number of determinations of \( i \) and \( S_c \) equals \( \sigma_c \) only when operating conditions are ideal. In most electron probes, instrument drift and specimen positioning create operating conditions which are not necessarily ideal. The high voltage-filament supply, the lens supplies, and other associated electron equipment may drift with time. After a specimen is repositioned under the electron beam, a change in measured X-ray intensity may occur if the effective "depth of focus" for the X-ray spectrometers is smaller than the "depth of focus" of the light optical system. In actual practice, for the usual counting time of 10 to 100 s/point, \( S_c \) is about twice \( \sigma_c \). If larger counting times are used, \( S_c/\sigma_c \) increases due to instrument drift. Only when counting times are short and the instrument has stabilized does \( S_c \) approach \( \sigma_c \). Besides the specimen signal, sources of variation may also occur if data from reference standards and background are required [76]. These, as well as faulty specimen preparation, may also affect the precision of an analysis. Therefore, both instrumental factors and signal variations must be considered when the precision of an analysis is given. Very rarely will the percent coefficient of variation (CV) of an analysis \( (S_c/\bar{N} \times 100) \) approach the theoretical limit \( (\sigma_c/\bar{N} \times 100) \).

Several studies have been made characterizing standard materials for use as electron probe standards [77,78]. The usual procedure for checking these standards is first to investigate inclusions and secondary phases if present. After this is done, a preliminary check on homogeneity of the matrix is made using a set of mechanical line scans. These line scans will point up any gross inhomogeneities (>10 percent of the amount present) on the 1 to 100-\( \mu \)-m level. The possibility of gross inhomogeneities on the 1-mm to 1-cm level should also be investigated by conventional means such as X-ray fluorescence. To check for inhomogeneities of less than 10 percent of the amount present, a static probe is used and X-ray quanta are accumulated at each point. The procedure normally used it to take data at many points, usually between 10 and 200 spread across the specimen. The criterion used for homogeneity is [77-79] that all points fall within the \( \bar{N} \pm 3\sqrt{\bar{N}} \) limits. If 100,000 counts are accumulated at each point, a variation of more than 1 percent of the amount present can be detected. Therefore, a homogeneity level of within ±1 percent of the amount present can be ensured.

A more exacting criterion for homogeneity would include (a) the use of the actual standard deviation \( S_c \) which accounts for instrument drifts and for focusing errors, and (b) the use of a confidence level for the determination of \( \bar{N} \). The confidence level, given as \( 1 - a \), is usually chosen as 95 or 99 percent. This means that we would expect on the average, only 5 (or 1 percent) of repeated random points to be outside the limits \( W_{95} \) or \( W_{99} \).

The width of a 99 percent confidence interval \( (W_{99}) \) is

\[
W_{99} = \pm C_i t_{n-1,0.99} \frac{CV}{\sqrt{n}} = \pm C_i t_{n-1,0.99} \frac{S_c}{\sqrt{n}} \frac{\bar{N}}{N}
\]
where
\[ C_i = \text{true chemical weight fraction of element } i, \]
\[ CV = \text{percent coefficient of variation}, \]
\[ t_{n-1}^{99} = \text{student's } t \text{ value for 99 percent confidence for } (n-1) \text{ degrees of freedom} \ [80]. \]

Other confidence intervals can be used by choosing other values of \( t \). Student's \( t \) values for \( t_{n-1}^{95} \) and \( t_{n-1}^{99} \) for various degrees of freedom \((n-1)\) are given in Table 2 [82].

<table>
<thead>
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<th>( n-1 )</th>
<th>( t_{n-1}^{95} )</th>
<th>( t_{n-1}^{99} )</th>
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<td>5.841</td>
</tr>
<tr>
<td>7</td>
<td>2.365</td>
<td>3.499</td>
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<tr>
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<tr>
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<tr>
<td>24</td>
<td>2.064</td>
<td>2.797</td>
</tr>
<tr>
<td>( \infty )</td>
<td>1.960</td>
<td>2.576</td>
</tr>
</tbody>
</table>

In a study of NBS Standard Reference Material 479, an austenitic iron-chromium-nickel alloy, the Eq 6 was applied for a criterion of homogeneity [80]. Using a 40-s counting interval on the specimen 900,000 iron counts, 340,000 chromium counts and 270,000 nickel counts were obtained at each point. In no case was \( CV > 1.5 \) percent for any element present. Therefore, if \( CV = 1.5 \) percent is used as a conservative value, and, if \( n \) is set equal to 16 in Eq 6

\[ W_{99} = \pm C_i \frac{2.947}{\sqrt{16}} (0.015) = \pm 0.0111 C_i \]

or \( C_i \pm 1.11 \) percent relative. The time to collect data for the 16 points was not prohibitive, being about 30 min. It is also possible to predict the degree of homogeneity as a function of \( N \), \( n \), and the desired confidence level that would be measured under typical operating conditions [26].

Several different methods have been devised for obtaining homogeneity data. The objective in all these cases is to obtain data from enough points to be representative, obtain a minimum number of counts per point for each element of interest and, yet, do this within a reasonable time interval so as not to run into stability problems due to instrument drift. Systems for automatic displacement of the electron beam [2,82] or the specimen stage by some sort of automation equipment are available. A matrix of a single string of points along a line or a square or rectangular area can be developed. The data must be handled efficiently (computer, multichannel analyzer, or tape) and a computation is needed to transform the mass of data into a format that permits easy interpretation. In most cases it is advantageous to obtain both
statistical output (standard deviations, frequency distributions, etc.) and topographical output (isoconcentration maps).

Normally the data are collected with crystal spectrometers. If the electron beam is displaced far enough from the electron optical axis of the EMP, the emitted X-rays will no longer be on the focusing circle of the X-ray spectrometer, and a loss of X-ray intensity will occur. Typically, electron beam displacements over 50 \mu m will cause defocusing effects. An interesting feature of the solid state detector, as compared to the crystal spectrometer system, is that the counting rates are not altered by displacement of the beam on the specimen. Therefore, the use of a solid state detector for the analysis of points in a raster as big as 1 mm$^2$, simplifies the operation and interpretation of data by eliminating a major source of error [2].

Analytical sensitivity usually indicates the ability to distinguish, for a given element $A$, between two compositions $C_A$ and $C'_A$ that are close together. X-ray signals for both compositions $\bar{N}$ and $\bar{N}'$ have a similar statistical variation. If one determines two compositions $C_A$ and $C'_A$ by $n$ repetitions of each measurement, taken for the same fixed time interval $\tau$, then these two values are significantly different at a certain confidence level $1-\alpha$ if

$$\bar{N} - \bar{N}' \geq 2 \sqrt{n} t_{n-1,\alpha} \sigma_c / \sqrt{n}$$ (7a)

and

$$\Delta C = C_A - C'_A \geq 2 \sqrt{n} t_{n-1,\alpha} \sigma_c / (\bar{N}_A - \bar{N}_B)$$ (7b)

where

- $C_A$ = element composition of one element in the specimen,
- $\bar{N}_A$ and $\bar{N}_B$ = average number of X-ray counts of element $A$ for the specimen and the element continuum background on the specimen,
- $t_{n-1,\alpha}$ = “student’s” factor dependent on the confidence level $1-\alpha$ (Table 2)

and,

- $n$ = number of repetitions.

Ziebold [83] has shown that the analytical sensitivity for a 95 percent confidence level can be approximated by

$$\Delta C = C_A - C'_A \geq 2.33 \frac{C_A}{\sqrt{n}} \frac{\sigma_c}{(\bar{N}_A - \bar{N}_B)}$$ (8)

Equation 8 represents an estimate of the maximum sensitivity that can be achieved when signals from both compositions have their own errors but instrumental errors are disregarded. Since the actual standard deviation ($\sigma_c$) is about two times larger than $\sigma_c$, $\Delta C$ is approximately twice that given in Eq 8.
If $N_A$ is much larger than $N_B$, Eq 9 can be rewritten as

$$\Delta C = C'_A - C_A \geq \frac{2.33 \, C_A}{\sqrt{nN_A}}$$

(9)

and the analytical sensitivity that can be achieved is given as

$$\frac{\Delta C}{C_A} \text{ (percent)} = \frac{2.33 \times 10^2}{\sqrt{nN_A}}$$

(10)

Shastry and Judd [84] investigated grain boundary solute segregation in an A1-6.86Zn-2.35Mg alloy which is susceptible to corrosion cracking. They found depletion or enrichment at the grain boundaries depending on the type of heat treatment and quench rates employed. They designed their experiments so values of $\Delta C/C_A$ (percent) for both zinc and magnesium were about 1 percent. In one case the relative change in concentration at the boundary was $\approx 5$ percent for both zinc and magnesium. To study olivine $$(FeMg)_2 SiO_4$$ compositional equilibration in large pallasite meteorites, olivine crystals from the opposite ends of several specimens $\sim 50$ cm apart were obtained [85]. Using Eq 7b at the 95 percent confidence limit, a sensitivity of $\Delta C/C_A$ (percent) was about 1 percent. In all three meteorites, differences between the olivine crystals were less than this limit.

As the elemental composition $C_A$ approaches 0.1 percent in EMP analysis, $N_A$ is no longer much larger than $N_B$. This composition range, below 0.1 percent is called the trace element analysis range. The analysis procedure now is to detect significant differences, between the specimen and the continuum background generated from the specimen. The detectability limit is governed by the minimum value of the difference $N_A - N_B$ which can be measured with statistical significance. Analogous to Eq 7a we have

$$N_A - N_B \geq \sqrt{2 \, t_{n-1} \, \alpha \, S_c}$$

(11)

where $S_c$ is essentially the same for both the specimen and background measurement.

For trace analysis, < 1000 ppm, the X-ray calibration curves (Eq 4) may be taken as a simple linear function. Therefore, $C_A$, the unknown composition, can be related to $N_A$ by the equation

$$C_A = \frac{(N_A - N_B)}{(N_S - N_{BS})} \cdot C(A)$$

(12)

where $N_S$ and $N_{BS}$ = mean counts for the standard and standard background for element $A$, and

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\[ C(A) = \text{percent of element } A \text{ in the standard.} \]

Using Eq 11 and 12, the detectability limit \( C_{DL} = C_A \) is \([86]\)

\[
C_{DL} = \frac{C(A)}{(\bar{N}_S - \bar{N}_{SB})} \frac{\sqrt{2} \left(t_{n.1}^{1-a}\right) S_c}{\sqrt{n}} \quad (13)
\]

The precision in a trace element analysis is equal to \( C_A/C_{DL} \) and approaches \( \pm 100 \) percent as \( C_A \) approaches \( C_{DL} \).

Ziebold \([83]\) has shown the trace element sensitivity to be

\[
C_{DL} \geq 3.29a/(n \tau I R)^{1/2} \quad (14)
\]

where

- \( \tau \) = time of each measurement taken,
- \( n \) = number of repetitions of each measurement,
- \( I \) = pure element counting rate,
- \( R \) = peak/background ratio of the pure element (it is the ratio of the counting rate of the pure element to the background counting rate of the pure element), and
- \( a \) = relation of composition and intensity of element \( A \) through the Ziebold and Ogilvie \([87]\) empirical relation.

To illustrate the use of this relation, the following values were used for calculating the detectability limit for germanium in iron meteorites \([88]\). The operating conditions were:

- high voltage, 35 kV
- specimen current, 0.2 \( \mu \)A
- \( I = 150,000 \) counts/s
- \( R = 200 \)
- \( \tau = 100 \) s
- \( n = 16 \)
- \( a = 1 \)

Using these numbers, \( C_{DL} \geq 15 \) ppm. The actual detectability limit after calculation of \( S_c \) and Eq 12 was 20 ppm. Equation 14 is very useful for determining the operating conditions for trace analysis before the actual data are taken.

Therefore, to do trace element analysis one needs to employ long counting times, high peak intensities, and a high peak to background ratio (\( R \)). Because of instrumental drift, and specimen contamination, a practical limit on the counting time is 15 to 30 min. The peak intensities can be raised by increasing the beam current. However, beam currents over 0.2 \( \mu \)A tend to heat the specimen locally and increase the size of the electron beam. Unfortunately, the peak to background ratio cannot be reduced below a certain limit since continuum X-ray radiation is always present and very small peaks from trace elements are difficult to separate statistically from the background continuum.

Trace element measurements have been made by various authors. Heidel
GOLDSTEIN ON THE ELECTRON MICROPROBE

[89] measured \( C_{DL} \) for metallic elements in a silicate glass. Using ±3 \( \sigma_e \) above background as \( \bar{N}_A - \bar{N}_B \), he found a detectability limit of 150 to 350 ppm for 20 kV, 2 x \( 10^{-8} \)A specimen current and 10-s counting times. If 2 x \( 10^{-7} \)A specimen current and 100-s counting times were used, a detectability limit of 15 to 35 ppm could have been achieved. Buseck and Goldstein [85] made trace element measurements of manganese, nickel, titanium, and calcium in olivine crystals. Operating at 30 kV, 2 x \( 10^{-7} \)A specimen current and taking four 100-s counts per crystal, the detectability limits according to Eq 13 were 40 ppm for manganese, 20 ppm for nickel, 10 ppm for titanium, and 15 ppm for calcium. In practice, therefore, it is very difficult to obtain measurements below a detectability limit of 10 ppm.

Trace element measurements are almost always made in the EMP using X-ray crystal spectrometers. The peak to background ratio (\( R \)) is quite high (> 100) and at the specimen currents typically used, the peak intensity is also quite high, >\( 10^4 \) to \( 10^5 \) counts/s from the pure elements. The background intensity (\( \bar{N}_B \)) must be obtained to determine (\( C_A \)) the unknown composition, Eq 12. As discussed the previous section of this paper, with careful usage, the background intensity can be obtained by going off the wavelength peak on the specimen itself.

It would be of great advantage to obtain trace analysis measurements at low beam currents, \( \leq 10^{-9} \) A, where it might be possible to have a smaller X-ray excitation area. The solid state detector might be a logical instrument to use in this case. The peak intensity (\( I \)) is high at these specimen currents although the peak to background ratio (\( R \)) is much poorer than that obtained with the crystal spectrometer. According to Eq 12, \( C_{DL} \) would approach 100 ppm in the best cases. However, detectability limits of <1000 ppm (0.1 percent) are difficult to achieve in practice since it is difficult to measure the background continuum intensity accurately.

EMP Analysis of Phases

The application of the EMP to phase analysis is practically unlimited. Several typical examples of applications will be given here. Phosphides and sulfides are common nonmetallic inclusions found in metallic and nonmetallic (stony) meteorites. Figure 15 shows the distribution of cobalt, iron, and nickel across a phosphide found in the kamacite (\( \alpha \)-FeNi) phase of the Breece iron meteorite [90]. The data are taken by attaching a motor to the X- or Y-drive of the specimen stage and recording the X-ray output for cobalt, iron, and nickel on a chart recorder. The data are taken in a matter of minutes. Even though it is qualitative in nature, it shows the relative homogeneity of the phosphide, the nickel gradients in the surrounding kamacite, and the effect of the cracks which were present in the phosphide. Calculations reveal that the phosphide is a complex (FeCoNi)\(_3\)P mineral.

Quantitative EMP analyses can be carried out by either moving the specimen automatically in micron-sized steps under the electron beam or moving the electron beam itself. In this way, the phase is covered by rows of analyses. An
FIG. 15—Distribution of cobalt, iron, and nickel across a phosphide inclusion in the kamacite (α) phase of the Breece iron meteorite.

example of such a concentration-distance plot for a sinoite (Si₂N₂O) grain in the Jajh deh Kot Lalu enstatite chondrite is given in Fig. 16 [97]. The matrix surrounding sinoite is enstatite. The data were obtained by moving the section after every analysis in steps of 3 μm. Quantitative analyses were obtained using appropriate standards and the ZAF corrections, Eq 4.

Many phases have chemical gradients caused by various phenomenon. Figure 13 showed the C concentration which developed in the austenite phase of a steel due to the growth of ferrite. Figure 17 shows the effects of solidification on the phase compositions of the dendrites in a M2-tool steel (Fig. 13) [92]. The concentration profile of tungsten, molybdenum, chromium, and vanadium across the primary dendrite axis is given. These results indicate a slight alloy enrichment at the dendrite core and a relatively uniform distribution of chromium in comparison with more pronounced segregation of tungsten, molybdenum, and vanadium. Figure 18 shows the diffusion profile developed
FIG. 16—Concentration distance plot for silicon, nickel, and oxygen across a sinoite (Si$_2$N$_2$O) grain in the Jajh deh kot Lalu enstatite chondrite. The analyses are point-by-point measurements obtained by moving the section after every analysis in steps of 3 μm under the fixed electron beam.

FIG. 17—Concentration profiles of tungsten, molybdenum, chromium, and vanadium across a primary dendrite axis in a unidirectionally solidified M2 steel.
when a gold versus a Au-6.1Ni couple diffused for one week at 875°C. The couple was one phase face centered cubic (fcc), and the gradient was controlled by the diffusivity at 875°C. The concentration profile was taken by moving the specimen under the electron beam and the concentration was determined by comparison with well characterized gold-nickel alloys [93]. Many other examples of electron beam X-ray phase analyses can be found in the literature.

In many investigations, it is of interest to know more than the chemical composition of the various phases present in the microstructure. The EMP can be used to obtain quantitative metallographic information such as volume fraction, mean particle size, surface area, and particle size distribution for the various phases. Many different systems have been developed for quantitative metallography with the EMP. Melford and Whittington [94] have developed a lineal scanning technique using a special purpose computer to handle the scanning probe data. For example, the aluminum $K_{\alpha}$, sulfur $K_{\alpha}$, and manganese $K_{\alpha}$ intensities are obtained from a line scan through inclusions of manganese sulfide (MnS), manganese oxide (MnO), and aluminum oxide (Al$_2$O$_3$). Using the two X-ray signals, logic circuitry compares them in such a way that the inclusions can be recognized. An oxide particle might be recognized by the fact that it contained either (a) aluminum, (b) manganese +

FIG. 18—Diffusion profile developed when a gold versus a Au-6.1Ni couple was heated for one week at 875°C.
aluminum, or (c) manganese but not sulfur. The size of the inclusion can also be determined from the line scan and the information stored. To avoid double counting due to the beam crossing the same inclusion on more than one successive line, the signal obtained along one line is stored for comparison with the signal obtained along the subsequent line. Signals are counted only if they are not inhibited by a similar signal in the previous line. The inclusion type, size range, and volume percent can be determined.

Dörfler and Plöckinger [95] have developed a lineal analysis technique for quantitative metallography of phases containing the same elements but in varying concentrations. The various phases are delineated by measuring the voltage output of the ratemeter as the beam is moved across the specimen. A voltage band (corresponding to a certain concentration range of a characteristic element for the one phase) is selected by two variable thresholds. One phase is identified by being within the voltage band, and the other phase is identified as located outside the band. The ratio of the measured time for one phase to that of the entire analysis gives the fraction of that particular phase. Further development of this basic system [96] has lead to a procedure where the various quantitative metallographic information can be calculated. An automatic lineal analysis is accomplished by the scanning system. Two or more signals are measured and the phase integrator, which is similar to the system previously described, determines which phase is present and stores this information. A small special purpose computer is responsible for calculating the stereometric (quantitative metallographic) analyses.

White et al [97] have developed techniques for computer processing of SEM images to yield quantitative metallographic parameters. The same method can be applied to EMP scanning images. The fundamental characteristic of the computer approach is that the entire image is recorded on digital magnetic tape and all data reduction are left to the computer. Two methods can be used to process the data in the computer. (1) The intensity of each data point, corresponding to the brightness level at a given coordinate position on the scanning image, is reduced to a simple binary code that indicates whether the intensity was above or below a preselected value. The program analyzed the resultant binary coded map to extract the quantitative metallographic parameters. (2) The computer generates contour maps at selected intensity levels and then calculates the characteristics of each closed contour to yield size, shape, and orientation information. McMillan et al [98] have discussed various methods of handling the data produced from the scanning instrument and Gortz et al [99] discusses the inclusion of X-ray analysis to the method.

Another method of attack [100] involves the use of special hardware to perform analysis within the scanning time. The approach allows a more rapid analysis because little data storage is involved. The data, however, must first be displayed as video signals. For X-ray signals this necessitates a very slow scan. Detection is accomplished by extracting information on preselected grey levels in the signal and converting it into a digital signal for computation. If the X-ray and specimen current signals are mixed [101], using the X-ray
signal as discrete pulses, the specimen current can be used to define the outline of the phases and the X-rays to identify the phases themselves. It is apparent that quantitative metallography can be accomplished using the EMP and commercial units are now becoming available.

**Extension of Instrument Capability**

*Inclusion-Particle Analysis*

Accurate analyses of inclusions are subject to several subtle sources of error. When an inclusion is analyzed, one takes great pains to analyze particles larger than the excitation volume produced by the electron beam. However, because the electron beam penetrates beneath the specimen surface, it is possible for part of the beam to penetrate to the matrix (Fig. 19a). It is also possible that inclusion particles lying just below the specimen surface may contribute to the analysis of the matrix (Fig. 19b). Consequently, it is necessary to repeat measurements on several inclusions to be assured that these effects are minimized. Another subtle source of error can be caused by X-ray fluorescence. Even if the inclusion is larger than the X-ray excitation volume, the characteristic and continuous spectrum produced in the inclusion may penetrate into the matrix. In certain cases fluorescence of the matrix by characteristic or continuum radiation may then occur. This radiation will be measured, in addition to the X-ray intensity from the inclusion, if specimen absorption is low and the area fluoresced is still on the X-ray focusing circle. A practical consequence of such an effect was discussed by Duke and Brett [102] in their study of metallic copper inclusions in meteorites.

![Diagram of Inclusion Analysis](Authors Copy)

There are several ways to overcome the problems associated with the fact that the X-ray excitation volume under normal operating conditions may be the same size or larger than the particle of interest. One method is to isolate the particles and treat them essentially as thin films rather than as bulk samples. In this situation, the amount of elastic scattering in the thin specimen is minimized and X-ray resolution approaches that of the electron beam.
Submicron precipitates and inclusions have been studied by a combination of electron microscopy and EMP analysis. Fleetwood [103] identified precipitates smaller than 0.1 μm in maraging steels, and carbon extraction replicas were stripped from specimens of heat treated steel. Electron diffraction patterns were taken first in the transmission electron microscope (TEM). Subsequently, electron probe analysis of the same precipitates for nickel, iron, molybdenum, titanium, and cobalt were made. Since the precipitates were essentially thin films, some of the electron beam passed completely through the specimen and the amount of X-ray intensities were only used as a measure of the relative proportions of the elements present in the precipitates. Absorption corrections were applied to the thin films to more accurately determine the iron/molybdenum ratio in the precipitates. Ancey et al have also analyzed precipitates on extraction replicas in the EMP [104]. If characteristic X-rays from two elements are measured simultaneously, the concentration ratios could be calculated accurately despite the fact that the precipitates themselves varied greatly in thickness.

A combined electron microscope-electron probe (EMMA) has been designed by Duncumb [105]. In this instrument, the specimen can be studied by electron microscopy, electron diffraction, and either point or scanning electron probe analysis without altering the field of view. The electron beam can be focused down to a spot of 0.1 μm, and the maximum magnification from the objective and projector lenses is about X12,000 at 60 kV. To obtain structural information, the intermediate lens is adjusted to image the diffraction pattern from the particle; for chemical information, the characteristic X-ray emission is analyzed by means of a crystal spectrometer and proportional counter. The chief requirement of the X-ray spectrometer is that it should have as high a collection efficiency as possible since the X-ray intensity emitted from the submicron particles is very weak. Because of the rapid decrease of counting rate with particle size and contamination difficulties, the smallest sized particle that can be analyzed using a focusing spectrometer appears to be a particle of about 0.1 μm in size. A similar type of instrument was also used by Ancey et al [104] to study inclusion particles extracted from a fracture surface.

A new combined instrument has been developed [106,107] which allows a TEM resolution of 3Au at 100 kV. A minilens is also used to achieve a 0.2 to 0.3-μm probe. In an instrument of this type, particles down to 0.1 μm can be analyzed; it is relatively easy to locate regions for analysis in a transmission image, and selected area diffraction (SAD) can be accomplished. It should be possible now to analyze even smaller particles by means of the solid state detector.

In solid specimens one can attempt to reduce the finite size of the X-ray excitation volume below the normal resolution of 1 to 2 μm. The method of reducing the X-ray range \( R(X) \) in Eq 3 has been discussed previously. Since the total X-ray spatial resolution \( R_x \) is equal to the sum of the X-ray range \( R(X) \) and the size of the electron beam \( d_p \), there is no advantage in reducing the beam diameter below 0.2 μm, (2000 Å) if the X-ray range \( R(X) \)
is greater than about 0.5 μm. For example, if one is analyzing MnS inclusions in a steel at the normal operating potential of 20 kV, the X-ray range is about 2 μ for both manganese K- and sulfur K-radiation. At 10 kV operating potential the X-ray range is improved, 0.4 μm for manganese K and 0.6 μm for sulfur K. However, in neither case is there any real point in reducing the beam current and, subsequently, decreasing X-ray intensity in order to produce a beam size below 0.2 μm.

In a study of (manganese-iron)sulfur inclusions in steel a matrix effect was observed [108]. The electron beam at 25 kV potential passed partially through the inclusion exciting the iron matrix even if the particles had a visible diameter greater than 5 μm. Obviously the thickness of the particles was not sufficient to contain the electron beam, see Fig. 21a. In this study an empirical technique was developed on the basis that the sulfur K-intensity was decreased in proportion to the additional iron K-intensity generated from the matrix effect.

Bolon and Lifshin [109] have attempted to study the effect of reducing the electron probe size in order to increase X-ray spatial resolution. Their test system was that of unidirectionally solidified alloy containing 1.5-μm tantalum carbide (TaC) rods in a nickel-chromium matrix. The calculation of X-ray source size was accomplished by using a modification of the Monte Carlo method proposed by Curgenven and Duncumb [110]. X-ray data were collected with both 0.25 and 1.0-μm-diameter beams at 20 kV voltage. The Monte Carlo plots of simulated electron trajectories are shown in Fig. 20. The calculations show that the direct X-ray excited volume should be contained within the TaC rods in the case of the 0.25-μm beam but not for a 1.0-μm beam. The data obtained showed that the Monte Carlo calculations correctly predicted the dimensions of the X-ray excited volume.

Calculations using Eq 3 show that R(3k') is 0.45 μm for tantalum L- and 0.65 μm for tantalum M-radiation. Therefore, for \( dp = 0.25 \) μm, the calculated spatial resolution is about 0.8 μm in agreement with this study [109]. If \( dp \) was 1 μm, the X-ray source would be slightly larger than the TaC rods. It is clear that Monte Carlo calculations will be valuable in predicting the X-ray excited volume and the intensity generated from that volume provided that the shapes of these structures and the diameter of the electron beam are accurately known. A treatment of a similar problem, for lamellar Al-CuAl₂ eutectic plates of varying sizes, was given by Jackson et al [111].

**Measurements Near Interfaces**

One of the major applications of quantitative EMP analysis is the determination of compositions at phase interfaces. These measurements may indicate the last temperature of equilibration of a given system, the composition of various phases in an equilibrium phase diagram, or the discontinuous change of the composition of a component near an interface. As discussed by Reed and Long [112] there are three major effects which must be considered when
FIG. 20—Monte Carlo calculations of electron trajectories in 1.5 μm tantalum carbide rods at 20 kV operating voltage. Electron trajectories are contained in the rods in the case where $d_p = 0.25 \mu m$ (upper) but not in the case where $d_p = 1.0 \mu m$ (bottom).
making measurements at or near interfaces:

1. **Electron Diffusion-X-ray Excitation Volume**—If there are variations in the concentration of the analyzed element within the volume excited by the electrons, the apparent concentration will be an average of the concentration within that volume. Therefore, measurements at phase boundaries where part of the beam is in both phases is quite difficult to make. If one knows the distribution of X-ray production within the analyzed volume, it should be possible to improve the effective resolution of the probe.

2. **X-ray Absorption**—The $\mu$ correction for absorption can only be calculated for homogeneous specimens. An error may be introduced when the region through which the generated X-rays pass is of a different composition from the analyzed area. Such errors can be minimized by having a high takeoff angle and by choosing the orientation of the specimen so that the X-rays leave parallel to the phase interface in material of similar composition.

3. **X-ray Fluorescence**—When measurements are made near interfaces, not only may part of the electron beam excite X-ray radiation, continuum and characteristic, in the major phase, but the X-ray radiation produced could cause secondary fluorescence of elements across the boundary in the second phase. The measured X-ray intensity may, therefore, be modified by such a fluorescent effect.

The most important of these three effects is fluorescence since the errors may be large. The effect is most serious when the analyzed element is present in a large concentration in the adjacent phase, as in Fig. 21. In this figure an

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**FIG. 21**—Effect of finite beam size in the Fe-Ni system. Nickel $K_{\alpha}$ and iron $K_{\alpha}$ intensity from an undiffused Fe-Ni couple.
undiffused couple of pure iron versus pure nickel was polished and a micro-
probe trace was taken at two takeoff angles 15.5 and 52.5 deg for iron K- and
nickel K-radiation across the interface [113]. The nickel Kα-radiation will
produce secondary fluorescence of iron Kα. Ideally, when the data are taken
across the interface, a sharp gradient influenced only by the excitation volume
should be observed. In this case when the electron beam is situated in pure
nickel (Fig. 21), both the continuum radiation and the nickel K-characteristic
radiation travel across the interface and produce, by secondary fluorescence,
iron Kα-radiation which is measured by the X-ray spectrometer. The effect
extends up to 30 μm from the interface into the nickel. In some systems,
zirconium-columbium (Zr-Cb), yttrium-molybdenum (Y-Mo), the apparent
concentration is as high as 10 percent [114,115]. Calculations have been
made [112,114] to account for the effect of secondary fluorescence by
characteristic radiation near phase boundaries and have met with good success.
When the electron beam is situated in the iron (Fig. 21), the continuum
radiation travels across the iron-nickel interface and produces some nickel
Kα-secondary fluorescent radiation which is also measured by the spectro-
meter. This effect is more difficult to calculate although a few attempts have
been made [112,115]. It is clear, however, that if one is to attempt measure-
ments of compositions near interfaces, calculations of the possible fluorescent
effect should be made. Since it is not difficult to make undiffused couples, in
some cases experimental measurements are justified.

When steep concentration profiles are encountered, the finite volume from
which X-rays are excited in a specimen causes the true concentration profile
to be smeared. A schematic representation of this process is shown in Fig. 22
as modified from Rapperport [116]. The X-ray excitation volume is described
by a triangular-shaped function (f(x)), while the true concentration profile is
in the form of a step function (g(x)). The curve (h(x)) represents the observed
profile as the beam passes over the concentration step. A mathematical
expression describes the relationship between these functions and is of the
form [116]

\[ h(x) = \int_{-\infty}^{\infty} g(x-x_o) f(x) \, dx \]  

(15)

The observed profile (h(x)) is, therefore, the mathematical convolution of the
probe function and true concentration profile function.

One way in which the probe function can be experimentally determined is
by passing the electron beam across a known concentration step and plotting
the observed profile. By assuming a probe function which is Gaussian [117],
the resulting probe trace should be an error function. Figure 23 shows the
results of a step scan for nickel Kα taken at 1/4-μm intervals across an α-
phosphide interface in the Tucson meteorite [118]. The Gaussian probe
function is described by [119]
FIG. 22—Convolution of the probe function $f(x)$ with the true concentration profile $g(x)$. The resultant curve $h(x)$ is the mathematical convolution of $f(x)$ and $g(x)$.

The parameter $d$ can be determined by drawing a tangent to the curve at the midpoint and measuring the intercept on the distance axis (Fig. 23). Once the probe function is known, it can be generated across a predicted true concentration profile to give an expected probe result, which can be compared with experimental data. The value of $d$ varies with the composition step, so the experiment must be done for each system. An estimate of the true profile is attained, when a set of experiment points lies on the observed profile resulting from the convolution of the true profile and probe function. Operating at 20 kV and 0.01 μA, an average $d$ value of 0.45 μm was measured for the $\alpha$-phosphide combination. The value of $2d$ (0.9 μm) is quite similar to the value of 1.0 μm for the X-ray spatial resolution ($R_x$) predicted when $R(X) = 0.8 \text{ μm}$ (Fig. 5) and $d_p \simeq 0.2 \text{ μm}$.

$$f(x) = \frac{1}{d} \exp \left[ -\frac{\pi}{4} \left( \frac{x}{d} \right)^2 \right]$$

(16)
Deconvolution techniques have been used to determine the peak nickel concentrations in the γ-taenite phase at the α-γ interface in the Tucson meteorite [118]. This meteorite was cooled rapidly and the large nickel gradients developed due to the lack of time for diffusion of nickel in the taenite phase. Using a computer program, the probe function was generated across a predicted true concentration profile such as that illustrated in Fig. 24. The resulting convoluted profile is also shown, and indicated whether the predicted profile had been correct. In the analysis shown in Fig. 24, a peak nickel concentration of 21.7 percent was calculated for a true nickel value of 24.6 percent at the interface. Since the actual measured data points across the γ-α interface correspond closely to the calculated profile, it is reasonable to conclude that the true composition of taenite in equilibrium with kamacite is ~25Ni. In this example the interface equilibrium composition can be accurately determined. Effectively then, the deconvolution technique increases the spatial resolution of the electron microprobe. Interface compositions as well as steep compositional gradients can now be more effectively measured with the EMP. However this method can only be directly applied if the effect of fluorescence is unimportant.

FIG. 23—Step scan for nickel Kα across a kamacite (α)-phosphide interface in the Tucson meteorite.
Chemical Bonding, Soft X-ray Spectra

For the very light elements, the X-ray emission spectra consists mainly of a single band produced by the transition of a valence electron to a vacancy in the K shell. As pointed out by Fischer and Baun [120], the valence electrons are the ones most affected by chemical combination and the emission band can and does reflect the often large effects of changes in chemical bonding between atoms. These changes are signified by wavelength shifts, increases or decreases in the relative intensities of various lines or bands, and in their shape. This allows one to obtain an indication of how a particular element is combined chemically. Practical uses of the soft X-ray spectra analysis involve studies of corrosion layers on fracture and oxidized surfaces, thin films, and the formation of compounds with beryllium, boron, carbon, and nitrogen.

The determination of band shapes, relative intensities, and wavelength shifts and the changes which occur in them is not always a straightforward process. Self-absorption may seriously distort the true emission spectrum and can result in a false interpretation of the apparent spectral changes. The EMP with large d-spacing xxtals such as KAP, lead stearate, and clinochlore has been used to obtain the emission spectra. Originally, data for spectral shape and peak
positions were taken using a ratemeter and strip chart recorder. Such a technique requires careful calibration of the recorder, and the final evaluation is somewhat subjective. Currently, data are being handled and processed with the use of the computer. Several computer systems have been reported [121-123], and all of these lead to a significant improvement in the quality of the data.

Figure 25 shows the carbon K-band from carbon deposited by the electron beam compared to that of electrode grade graphite [124]. The wavelengths of

![Image: Carbon K-spectra from carbon deposited by the electron beam, electrode grade graphite, and various carbides. The target voltage was 4 kV.](image)

the peaks \(a\), \(b\), and \(c\), as well as the general band shape, are the same for both forms of carbon. Possible reasons for the differences in intensity distribution of the carbon K-bands is that carbon deposited by the electron beam may be amorphous or impure resulting in somewhat different bonding than for graphite. The carbon K-spectra of various carbides are also shown in Fig. 25. The energy shift of the carbides relative to graphite is significant and can be used to identify, in some cases, the type of carbide present.

Krause et al [125] have shown that measurements of the shifts of the oxygen \(K\alpha\)-X-ray peak, with respect to the oxygen \(K\alpha\)-peak from \(\alpha\) quartz, could be used to characterize structurally and chemically the thin, often amorphous, oxide layers that form when a metal corrodes. Experiments were performed to characterize oxide films on transition metals. They found that the magnitude of the shifts in the oxygen X-ray emission bands is a continuous function of
the metal to oxygen ratio of the emitter. In the three series of transition metal oxides (titanium, manganese, and iron) studied, the peaks shift toward shorter wavelength with increasing oxidation. The cation valence of these transition metal oxides can be determined from measurements of the oxide $K_{\alpha}$-wavelength. As an example [125], the oxygen band shift technique was applied to a thin (0.5 $\mu$m) oxide layer prepared by heating an iron bar. The oxide was identified as Fe$_3$O$_4$ by X-ray diffraction and shows the wavelength of the oxide $K_{\alpha}$-band emitted in the oxide is essentially the same as that measured from iron oxide (Fe$_3$O$_4$). Oxide films thicker than 100 Å can be investigated by this technique free of interference from the metallic substrate. In addition, the oxide films need not be crystalline or of uniform thickness.

Another application to the study of oxides is the characterization of thin film and bulk silicon oxide (SiO). The silicon $K$-emission spectra in the 7 Å region can easily be measured. Figure 26 shows the silicon $K_{\beta}$-X-ray bands for elemental silicon dioxide (SiO$_2$), and SiO [126]. Significant changes in the spectrum are noted when going from silicon to SiO$_2$. Only a single asymmetrical band is obtained from elemental silicon in contrast to the spectrum from SiO$_2$ where two bands are recorded. In SiO, the main $K$-band is split and the energy of the three components corresponds to positions found for silicon and SiO$_2$. White and Roy [127] used this band splitting as evidence that SiO was a mixture of silicon and SiO$_2$. In addition, the silicon $K_{\alpha}$-satellites $K_{\alpha3}$ and $K_{\alpha4}$, and silicon $K_{\beta'}$ are very sensitive to chemical combination. Figure 26 shows the oxygen $K$-spectrum from SiO and SiO$_2$ [126]. The oxygen spec-

FIG. 26a—Silicon K-X-ray bands from elemental silicon, SiO$_2$ and SiO.
FIG. 26b—Oxygen K-band for SiO and SiO$_2$ (α-quartz).

Trums are virtually identical indicating again that the condensed phase SiO consists of a variable mixture of silicon and SiO$_2$. Other studies have characterized films containing nitrogen [128]. In addition, combined EMP and ellipsometric study of thin SiO$_2$ films on silicon enabled data to be obtained on contamination films as well as the mass thickness and uniformity of the thin film [129]. Other examples of soft X-ray application to materials characterization have been reported in the literature [130-132] and give support for the use of this technique to microprobe analysis.

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References


Lifshin, E. in *Summer Course Notes*, Electron Probe Microanalysis and Scanning Electron Microscopy, Lehigh University, June 1972.


METALLOGRAPHY

Institute, Chicago, Ill., p. 169.


