

Minimizing Errors in Electron Microprobe Analysis

Eric Lifshin^{1*} and Raynald Gauvin²

¹New York State Corporate Center for Advanced Thin Film Technology, State University of New York at Albany, Albany, NY

²Department of Mechanical Engineering, University de Sherbrooke, Quebec, Canada, J1K 2R1

Abstract: Errors in quantitative electron microprobe analysis arise from many sources including those associated with sampling, specimen preparation, instrument operation, data collection, and analysis. The relative magnitudes of some of these factors are assessed for a sample of NiAl used to demonstrate important concerns in the analysis of even a relatively simple system measured under standard operating conditions. The results presented are intended to serve more as a guideline for developing an analytical strategy than as a detailed error propagation model that includes all possible sources of variability and inaccuracy. The use of a variety of tools to assess errors is demonstrated. It is also shown that, as sample characteristics depart from those under which many of the quantitative methods were developed, errors can increase significantly.

Key words: precision, accuracy, quantitative analysis, energy-dispersive X-ray spectrometry, crystal diffraction spectrometry, Monte Carlo calculations, X-ray counting statistics

INTRODUCTION

Quantitative electron microprobe analysis is an analytical procedure in which the intensity of electron excited X-rays is measured for specific elements in a specimen, and that intensity data is then used to determine chemical composition. Castaing first described the basic principles of microprobe analysis 50 years ago in his PhD thesis (Castaing, 1951), and although his quantitative model has been improved upon since then, the basic concepts remain the same today. Detailed descriptions of how to collect and analyze data by a variety of approaches can be found in a number of texts (Goldstein et al., 1992; Reed, 1997). Selected compounds and alloys have been used to study the accuracy of different models for quantitative electron microprobe

analysis. Comparisons between these models and the results obtained by established classical analytical procedures show that, in some cases, accuracy of 2% relative or better is possible (Pouchou and Pichoir, 1991; Poole, 1968).

The precision of the measurements has been given far less scrutiny, however, and estimates are often based solely on X-ray counting statistics. Even those estimates rarely used propagation of error calculations to link the uncertainty of all of the X-ray measurements, including peaks and backgrounds with the uncertainty in the final composition. There are also a number of other factors that can effect the variability of quantitative analysis, and they are summarized in the process map given in Figure 1. The first step is sample selection. Sample selection is usually based on a desire to answer a specific question. For example:

- What have I made (as in the case of the discovery of a new material)?
- What changes have occurred in an established manufac-

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*Corresponding author, at University at Albany, State University of New York, CESTM, 251 Fuller Road, Albany, NY 12203.

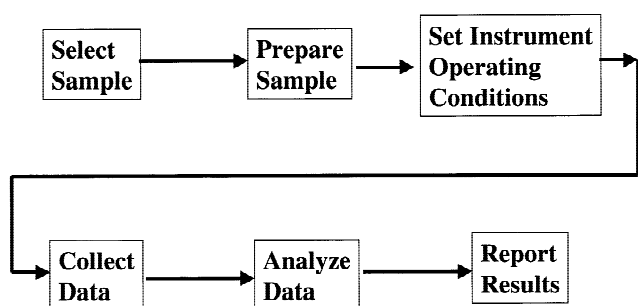


Figure 1. Microanalysis process map.

turing process leading to a change in the properties of a finished product (quality control)?

- Why has something failed?

When you are trying to explain the behavior of a critical component of a system, it is important to select a sample that tests some hypothesis. As an example, suppose you believe that a particle found in a pit in a fracture surface was suspected of being responsible for the initiation of that fracture. An analysis would be made of the particle to determine if it is some foreign material accidentally introduced into the casting operation that formed the finished component or the result of some departure from standard processing conditions. Also, knowing what to look for and why you are looking for it, at the beginning of an analysis, can save a lot of time, particularly since sometimes differences are found between samples, or between samples and material specifications, that may have no bearing on the problem to be solved.

Another important consideration is that of sample homogeneity. Electron microprobe analysis typically samples a volume of material of a few cubic microns. Since one cubic micron represents only 1 part in 10^{12} of a cubic centimeter, a single reading will not tell you whether the composition of a large region meets some average composition specification. Multiple measurements of a single point are necessary to establish the composition mean and variance of that point, and multiple point measurements are required to establish point-to-point differences (the degree of homogeneity). When an analyst is handed a sample with little information other than a request for the amounts of specific elements present, it is obvious that the final results will only be of value if a rigorous sample selection process was used.

What follows next is a description of how to look at the variability of the remaining steps in the process map given in Figure 1. The authors are not aware of any published studies that reflect an exhaustive set of measurements of the

type to be shown that lead to true confidence intervals in connection with any published microanalysis results. As you will see, there are just too many steps in the overall analytical process, and to determine all of the sources of variability would generally be too expensive and time consuming to ever become routine. Nevertheless, the approach given can help establish some guidelines so that the analyst can select experimental conditions that will minimize errors, although not always quantify them. In many of the examples given, data or calculations are for a standard of NiAl specially prepared to be very close to a one-to-one atomic ratio, as determined independently by wet chemical analysis, and determined to be homogeneous by microprobe analysis. This standard was selected because nickel-based superalloys are technologically very important, and also this system has significant atomic number and absorption corrections when doing quantitative analysis.

SAMPLE PREPARATION

Quantitative analysis has been traditionally performed on polished samples to eliminate the influence of topographic effects. These effects arise from the fact that X-ray emission varies with the electron beam incidence angle and the X-ray takeoff angle, not just composition. Since it is not always easy to determine if point-to-point variation in intensity is due to a change in composition or topography, most quantitative analysis models require measurements from flat specimens with a known orientation relative to the electron beam. Usually, normal incidence is selected because most quantitative models were derived under that assumption. Although it is frequently done in practice, use of these models for non-normal incidence has, in fact, never actually been rigorously justified.

Flat samples are most often prepared by metallographic mounting and polishing. Care must be exercised in polishing soft materials to avoid redistributing components over the surface of the sample. For example, when looking at cross-sections of layered structures containing soft phases, it may be necessary to only polish the sample parallel to the layers. If the sample has to be etched to delineate structure, the structure should be marked with a scribe or hardness indentations, and then the sample should be repolished since etching can also alter the composition. Edges in contact with the mounting material can also be tricky due to rounding problems associated with differences in hardness.

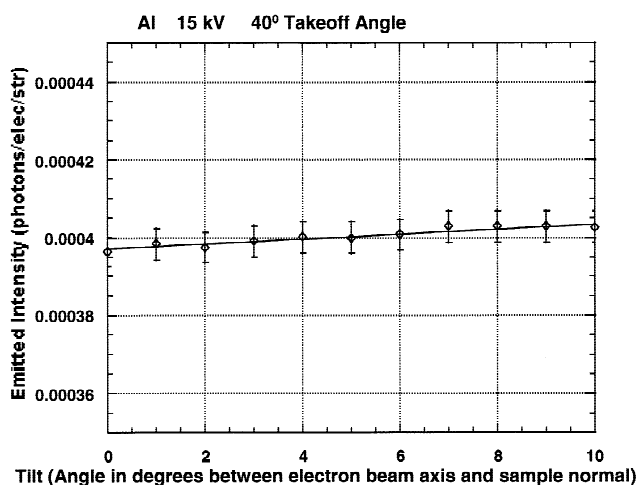


Figure 2. Variation of X-ray emission with sample tilt, based on Monte Carlo calculation using 10,000 electrons.

This is sometimes overcome by plating an additional layer of material over the surface of the sample for edge retention, and then mounting and polishing it. Another important potential source of error is the quality of standards. Even if pure elements are used, some polished samples oxidize over time leading to a change in surface composition. Therefore, standards should be periodically checked for surface finish and reprepared if necessary. If non-conducting samples are coated to avoid charging, then the standards also need to be coated at the same time or it must be established that the coating is not significantly affecting the measured signal.

Even if a sample is flat, how accurately does the orientation relative to the electron beam and the detector need to be known? While most specimen stages are machined to give accurate orientation information, it cannot always be assumed that the specimen orientation might not be shifted slightly from the stage reading, particularly if it is mounted on top of the specimen holder as is often done in scanning electron microscopes (SEMs). Figure 2 shows the results obtained with a relatively new Monte Carlo program (Lifshin and Gauvin, 1998) that has been applied to predict the variation of emitted X-ray intensity for pure aluminum as the sample is tilted toward the detector. The tilt angle is varied from normal incidence to 10°. The beam energy is 15 kV and the detector takeoff angle for normal incidence is 40°. It can be seen that the variation of intensity between 0° and 10° is less than 2%. Therefore, at least in this case, a modest error in tilt angle will not cause significant variation in the measured intensity.

The next question is what about an error in the takeoff angle? While this situation can also be modeled with Monte

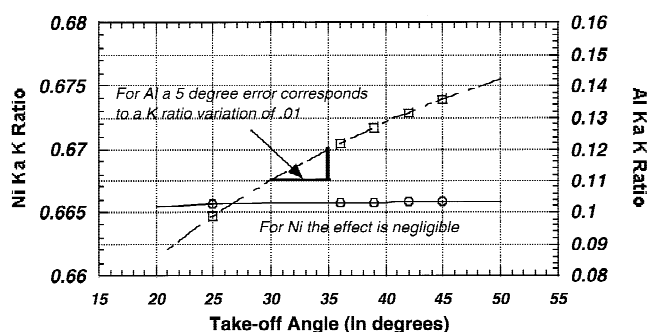


Figure 3. Effect of takeoff angle on k -ratios for NiAl, values calculated by ZAF at 20 kV. Squares, Al data; circles, Ni data.

Carlo calculations, an easier approach is to perform a conventional ZAF or $\phi(\rho z)$ calculation and see how much the measured k -ratio for a given element would change by assuming various takeoff angles. The k -ratio is the background and deadtime corrected intensity measured on a sample divided by the background and deadtime corrected intensity measured on a standard containing the element of interest. Both measurements must be made under identical operating conditions including beam voltage and current, electron beam incidence and X-ray takeoff angles, as well as all spectrometer settings. The k -ratios measured for each element in a sample along with the experimental settings are the critical inputs to all commonly used correction procedures. Even most so-called standardless analysis methods require an estimate of standard intensities and the use of k -ratios. Figure 3 shows the variation of NiK α and AlK α ratios with takeoff angles with normal electron beam incidence. In this case, it can be seen that a 5° variation has minimal effect on the NiK α , but a significant effect on the AlK α k -ratio, shifting it by 0.01 or about 8% relative. The difference between the elements is related to the high X-ray absorption of the lower energy AlK α in NiAl relative to the NiK α line.

Samples must sometimes be viewed “as is” because any attempt at further preparation might destroy or alter them. Even if that is not the case, metallographic preparation may be too expensive and time consuming, or the necessary facilities may not be readily available. Unprepared samples are often not flat, and the local orientation between the region analyzed and the electron beam as well as the X-ray takeoff angle can not be easily determined. An example of this type of situation would be the analysis of a vapor deposited film or a fracture surface.

Figure 4 shows the effect of surface roughness on the measured X-ray signal again simulating the interaction with

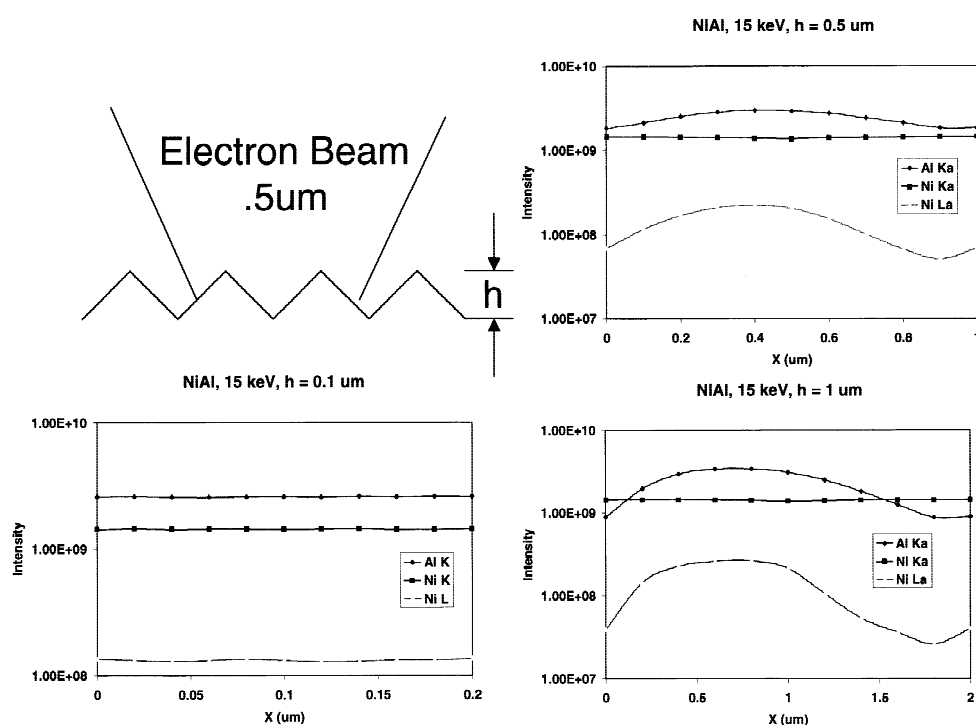


Figure 4. Monte Carlo simulation of surface roughness effects in NiAl.

Monte Carlo calculations. In the example shown, the surface is assumed to consist of a structure composed of repeated triangles in one direction, but with no variation in the perpendicular direction. This geometry is what might be expected with a sort of idealized polishing by a pyramid-shaped grit in just one direction. The depth of the grooves would correspond to the grit size used. Depending on the parameters for the electron beam size and groove height, h , selected in the model, the beam may be larger than, or smaller than, the repeat distance of the triangles. In this case, the emerging X-rays are assumed to travel in a direction perpendicular to the grooves. It can be readily seen that when h is 0.1 μm and the beam size is 0.5 μm , that neither the $\text{NiK}\alpha$ or $\text{AlK}\alpha$ show any noticeable variation with beam position as it is scanned across the surface. Even the relatively long wavelength $\text{NiL}\alpha$ shows no variation. However, when the groove height is increased to 0.5 μm and 1.0 μm , only the $\text{NiK}\alpha$ shows little or no variation with position across the structure. The reason again, as in the case of the tilted sample, is the high absorption of the $\text{AlK}\alpha$ X-rays relative to the $\text{NiK}\alpha$ X-rays. In practical terms, the conventional mirror polish obtainable with fine diamond, alumina, or chromium oxide would probably produce a flat enough structure such that it would not cause measurable error, while it could be significant for a roughly abraded surface, such as a fracture surface, or as a deposited surface.

INSTRUMENT OPERATING CONDITIONS

The beam voltage, beam current, element line, and counting time are the principal variables selected prior to an analysis. As stated previously, conventional microprobe analysis measurements are made on the specimen and reference standards under identical operating conditions. Therefore, when k -ratios are calculated, there is no need to know the beam current, solid angle of the emitted X-rays that are measured, or the detector efficiency, since they are constants that cancel when the k -ratio is formed. The beam voltage and takeoff angle, although constant, do enter in the equations for quantitative analysis and must be known. The latter has already been discussed. Figure 5 shows the effect of errors in the beam voltage on the k -ratios for $\text{NiK}\alpha$ and $\text{AlK}\alpha$. What can be seen is that an error of 1 kV produces an error of about 0.001 for $\text{NiK}\alpha$ or less than 1% relative, but one of about 0.01 for $\text{AlK}\alpha$ or about 8% relative. The issue again is the high absorption of $\text{AlK}\alpha$ in nickel. Changing the voltage has a noticeable effect on depth of excitation and therefore on absorption. Generally, the kV setting on modern instruments are sufficiently accurate so as to make this effect unimportant, however the examination of insulating samples can cause charging that effectively decreases the potential difference between electron source and the sample. Use of the X-ray high energy cutoff point as a

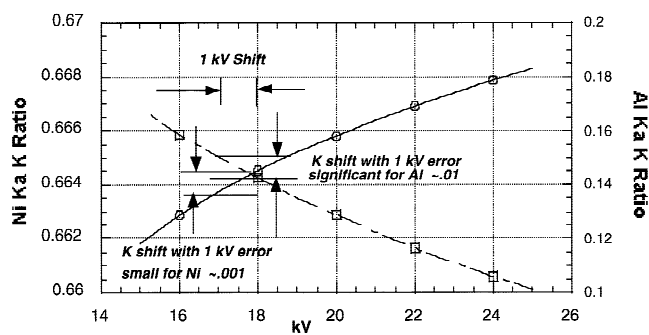


Figure 5. Effect of beam voltage on k -ratios for NiAl, values calculated by ZAF.

measure of beam voltage with an energy dispersive spectrometer is one way to measure the effective beam voltage. The high energy cutoff point is where the X-ray background goes to zero, since the highest energy X-rays produced by the electron beam can be no higher than the complete conversion of the incident electron energy to X-ray photons. This measurement is usually done by extrapolation of the linear portion of the high energy X-ray continuum to the cutoff point. Except at very low count rates, this is not the point in the spectrum where the continuum appears to go to zero because pulse pileup effects can give the appearance of higher energy photons beyond the real cutoff point.

Standardless analysis usually requires that the efficiency of the detector system must be known for all lines measured. This is because if a standard is not measured at the time of analysis, its value must be calculated either from theory or determined from previously stored standards. If calculated from theory, then some adjustment must be made to correct for any losses in the detector. The efficiency must also be determined if stored standard data is used from other elements. If standard data was obtained at different beam energies, electron beam incidence angles, X-ray takeoff angles, or electron beam currents, then corrections must be made to give the corresponding value for the conditions under which the sample was measured. If data has to be scaled to beam current, then there has to be some assurance that the beam current can be determined with high accuracy and precision.

In general, energy dispersive spectrometer (EDS) efficiency measurements have received little, if any, attention in the literature. Similarly, better publishable data is needed on the variation of X-ray yield with beam voltage and incident beam angle. Thus, all of these factors represent sources of error of generally unknown magnitude. The option of standardless analysis is limited to EDS since the efficiency of

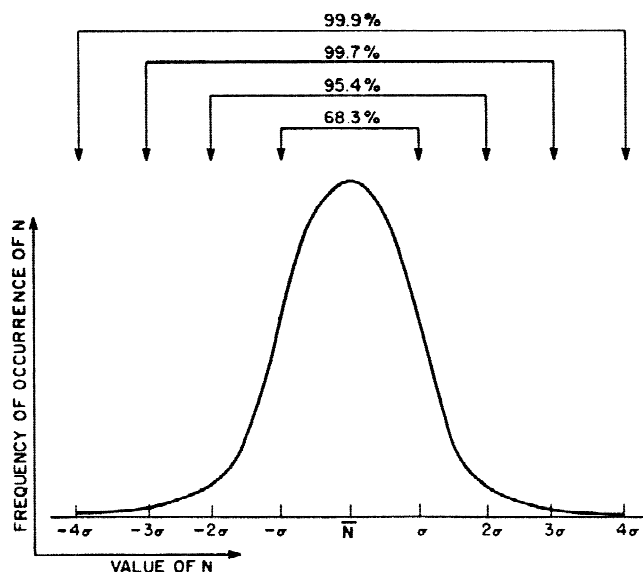


Figure 6. Precision: X-ray counting statistics.

wavelength dispersive spectrometers (WDS) is generally not known.

DATA COLLECTION

Data collection procedures are different for EDS and WDS measurements, however, in each case the goal is the same. It is to accurately and precisely determine the intensity of the characteristic X-rays of each element emitted from a specimen and corresponding standard at defined energy settings. This process requires both the determination of corresponding background levels and correction for any deadtime effects. Since X-ray emission is a random process over time, each measurement is a sample of a parent distribution consisting of all possible repeated measurements under identical operating conditions. The expected distribution can be described by Poisson statistics, but for large numbers of counts can be approximated with a normal distribution. If the distribution has a mean value of \bar{N} , then it will have a standard deviation equal to the square root of \bar{N} . Figure 6 shows such a distribution with a reminder that, if successive readings are made, 68.3% will be within $\pm 1\sigma$ and 95.4% will be within $\pm 2\sigma$, and so on. If \bar{N} only equals 100, then the relative standard deviation σ/\bar{N} would be 0.1, while if \bar{N} equals 10,000, then the relative standard deviation is 0.01. The smaller the relative standard deviation is, the higher the precision. Clearly, the more counts the better, and it is not uncommon to select operating conditions that

will ensure greater than 50,000 counts in any peak measurement of importance. While larger numbers of counts are sometimes possible by increasing the beam current or counting time, it may not always be practical to do so.

In electron microprobe analysis, what is ultimately of importance is the precision of the composition rather than just that of an individual intensity measurement. This point has been discussed in detail by a few authors (Ziebold, 1967; Lifshin et al., 1999). Note first that a K ratio consists actually of four measurements: \bar{N} , the intensity measured on the sample; $\bar{N}(B)$, the corresponding background at the same energy; \bar{N}_s , the intensity measured on the standard; and $\bar{N}_s(B)$, the corresponding background for the standard.

$$K = \frac{\bar{N} - \bar{N}(B)}{\bar{N}_s - \bar{N}_s(B)} \quad (1)$$

The corresponding precision in the K ratio is given by:

$$\sigma_K^2 = K^2 \left[\frac{\bar{N} + \bar{N}(B)}{n(\bar{N} - \bar{N}(B))^2} + \frac{\bar{N}_s + \bar{N}_s(B)}{n'(\bar{N}_s - \bar{N}_s(B))^2} \right] \quad (2)$$

where n and n' refer to the number of measurements made on the sample and standard. Finally, the precision in the C is given by:

$$\sigma_c^2 = C^2 \left[\frac{\bar{N} + \bar{N}(B)}{n(\bar{N} - \bar{N}(B))^2} + \frac{\bar{N}_s + \bar{N}_s(B)}{n'(\bar{N}_s - \bar{N}_s(B))^2} \right] \left[1 - \frac{(a-1)C}{a} \right]^2 \quad (3)$$

where “ a ” is the parameter used in the following (Ziebold and Ogilvie, 1964) equation:

$$\frac{1-K}{K} = a \frac{1-C}{C}. \quad (4)$$

If “ a ” is not known, then either ZAF or $\phi(\rho z)$ methods can be used to calculate a value of K for a given C , and then “ a ” can be calculated from equation (4). With suitably long counting times, the standard deviation in a composition due to counting statistics can be reduced to less than 1% relative.

The next question, however, is: Are there errors introduced in repeated measurements greater than what would be expected based on counting statistics due to repositioning of samples and standards? With WDS measurements, samples and standards must be accurately placed on the

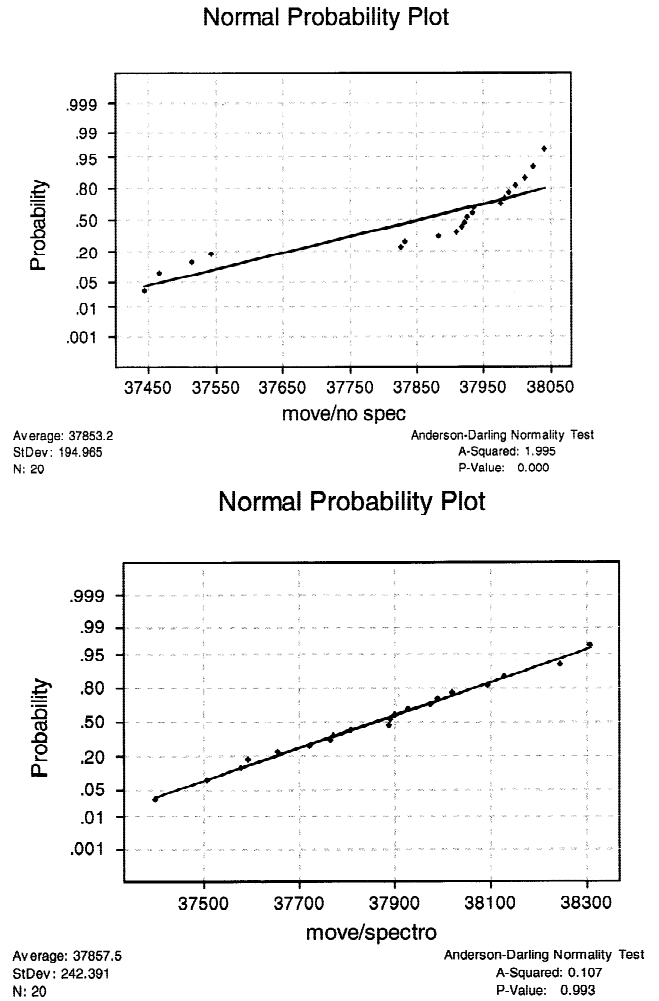


Figure 7. Effect of sample and spectrometer repositioning. **Top:** Sample repositioned, spectrometer not repeaked. **Bottom:** Sample repositioned, spectrometer repeaked.

focusing circle of the spectrometer. This is done in practice in electron microprobes by placing the sample or standard in focus in the coaxial light microscope present in all instruments. Since the depth of field of the microscope is generally less than a micron, the act of focusing generally assures proper specimen placement. Without such placement, the X-ray intensity can change with specimen position introducing another uncertainty factor between standard and sample measurements.

Figure 7 addresses the question: How well can an operator return to the same focus point if a sample is moved out of the field of view and then repositioned? In the top of the figure, no attempt was made to repeak the spectrometer following repositioning of the specimen to place the point of interest in focus in the coaxial light optical microscope.

Automatic repeaking was done, however, in the study on the bottom. Automatic repeaking is commonly performed on fully automated electron microprobes. In each study, 20 repeat measurements were made and the range of counts displayed on the horizontal axis. The vertical axis is the cumulative probability less than, or equal to, corresponding value on the horizontal axis. This type of plot, known as a probability plot, is used to determine if a distribution is normal, as indicated by the degree of fit to a straight line. It can be seen that the plot on the top is definitely not normal, but the calculated standard deviation is very close to what would be expected from the square root of the number of counts. Because the distribution is very far from normal, it would not be very suitable for propagation of error calculations described previously. The figure on the bottom, however, shows that the standard deviation is larger than what would be expected from normal counting statistics, but the distribution is, in fact, close to normal. Therefore, for the example shown, data from full automation in which both the focus and spectrometer settings are reset could more easily be used to predict symmetric confidence intervals around the composition, but those intervals will be somewhat larger than that predicted by counting statistics alone. This effect, however, may be dependent on the peak finding algorithm used.

In addition to counting statistics and mechanical reproducibility, there are a number of other factors that can influence precision and accuracy from a data collection perspective. If not controlled, beam drift is often the largest. Most electron microprobes use feedback apertures that sample the beam current and send a signal to readjust the condenser lens setting in the event of drift. This is critical, because any variation in beam current will produce a directly proportional change in X-ray intensity. Obviously, if samples and standards are measured at different currents, and those currents are not known accurately, then the error in resulting k -ratios can be sizable. Many electron microprobes have beam stabilizers capable of minimizing drift to less than 0.1% relative per hour. Therefore, even for long automated runs, drift may not be an important factor. However, it can be a problem for SEMs not equipped with beam stabilizers.

Drift in beam position is also a concern. A critical requirement of both quantitative and qualitative analysis is that the X-ray excitation volume be well contained in the region to be analyzed to avoid spurious signals from the surrounding environment. If the beam moves during an analysis, or is not actually positioned on the correct region

to be analyzed, then results can be significantly compromised. Reducing a cathode ray tube (CRT) display to spot mode, and observing the spot on what appears to be the correct location on the persistent image, is in no way a guarantee that you are where you want to be. Even if it is the correct location, X-ray excitation volume may exceed the size of the phase analyzed, unless some knowledge is known about both. While the size of the phase can be estimated from the microscopic image providing it is not too thin, either electron range calculations or Monte Carlo calculations should be used to estimate the X-ray excitation volume in cases where phases to be analyzed are less than several microns.

Details of the X-ray measurement process itself depend on whether WDS or EDS is used. Extensive descriptions of these systems can be found in the texts cited earlier, so only a few of the top areas of concern will be described here. With WDS systems, analyzing crystals with high reflectivity and energy resolution are desirable for good signal intensity and high peak-to-background ratios. However, the higher the energy resolution, the more important it is that the spectrometer be at the same energy setting when measuring samples and standards, so mechanical reproducibility and stability becomes a very important factor. As mentioned previously, spectrometer repeaking may be necessary, but with some loss of precision as well as analysis time. The detector itself and associated pulse electronics are also areas of concern. If single channel analyzers are used to avoid higher order reflections, great care must be exercised in selecting energy windows. Figure 8 shows pulse height distribution curves as a function of count rates on a relatively modern instrument. The higher the count rate, the broader the pulse height distribution curve and also the possibility of a peak shift with count rate. These effects can be particularly pronounced in older instruments. A tight pulse height window can cause errors in k -ratios because the fraction of X-rays detected will be different between sample and standard. The lower left part of the figure is a reminder to check that the count rate increases linearly with intensity even after dead time correction. In this case, the beam current was varied and the intensity from a standard was measured. Regression analysis shows the intensity to be linear with beam current, but that may not always be the case, so it is worthwhile to test the linearity of your pulse counting electronics.

With EDS analysis, one of the biggest sources of potential error, if standards are used, is placing the sample and standard at the same location when each is measured. With-

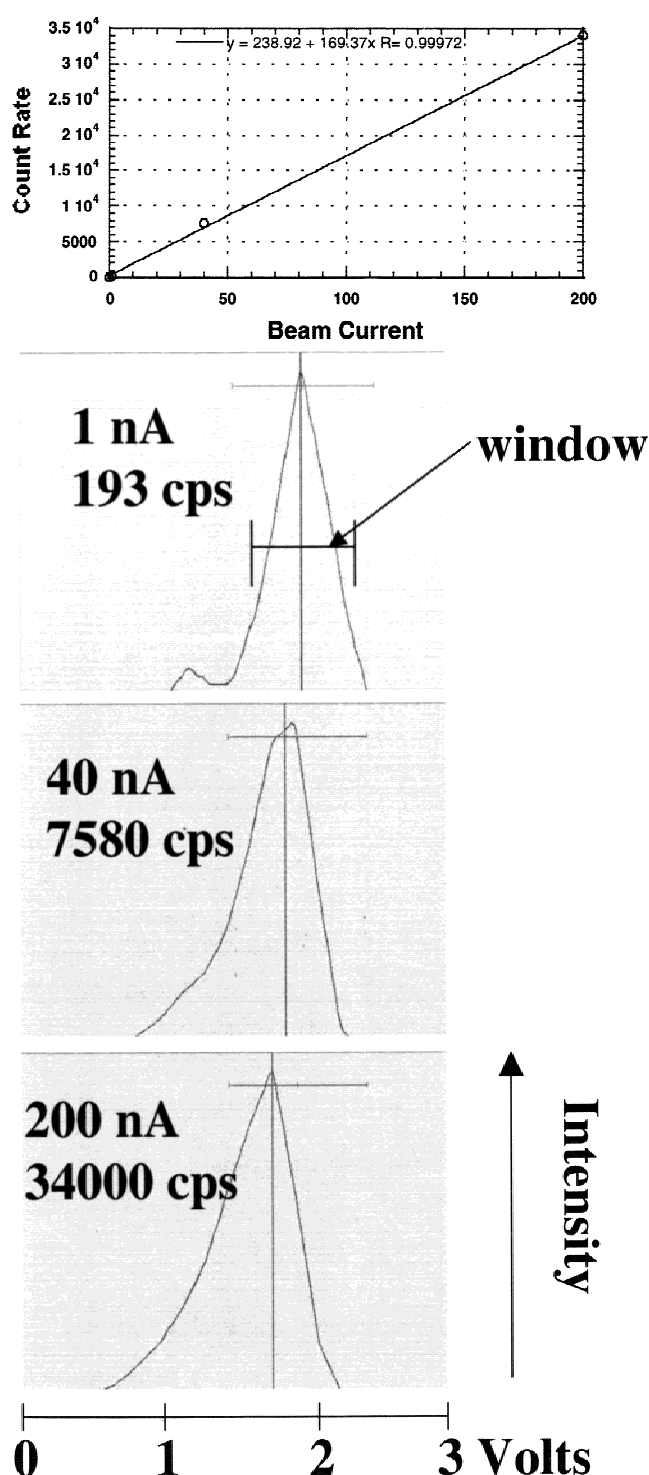


Figure 8. Effect of count rate on pulse height distribution. Mean shifts with count rate; full width at half maximum (FWHM) increases with count rate. Do not set a tight pulse height distribution window.

out a coaxial light microscope, as is the case in most SEMs, getting the same position can be difficult. The best approach is to go to high magnification, and possibly use a larger objective lens aperture to reduce the depth of focus, and

then position the sample or standard only with the stage controls to give the sharpest image. Under no circumstances should the objective lens setting be changed during this process. A change in sample position with respect to the detector can cause changes in both the takeoff angle and the solid angle from which X-rays are detected. The problems associated with beam drift and repositioning are probably the main reasons why so much standardless analysis is done in SEM/EDS systems since only one spectral measurement needs to be made. A single measurement is, of course, also faster. Other limitations of standardless analysis have already been discussed.

ERRORS ASSOCIATED WITH CORRECTION PROCEDURES

Much effort has been expended in the detailed development of quantitative correction analysis procedures and comparing results obtained with different models. To determine which gives the best results, it is necessary to compare them with the results of other more reliable analytical methods. The analytical methods of choice are traditional classical analysis techniques developed for bulk samples. The reason is that many microanalytical techniques are spectroscopic, and spectroscopic techniques are usually limited in accuracy to two significant figures. Techniques like gravimetric analysis and titration provide chemical measurement to three or even more significant figures because we are generally better at measuring weight and volume than collecting spectral data. If analytical techniques for bulk samples are used to check microprobe analysis on standards, then those standards must not only be subjected to classical analytical techniques, but they must also be shown to be homogeneous, as has been reported for the National Institute of Standards and Technology (NIST) Cu-Au and Ag-Au standards (Heinrich et al., 1971). Unfortunately very few studies with the rigor of this one have ever been performed.

Just how different are the results using different correction procedures? Table 1 shows calculated k -ratios for stoichiometric NiAl calculated by various correction procedures. In the case of NiK α , the percent standard deviation is only about 1% relative, and for Al it was 2.49% relative due to the large absorption effect. While this is only one system at one voltage and takeoff angle, the fact is that if analysis conditions are selected so as to minimize correction effects, like lower voltage to limit absorption, the results of different models currently used are really not all that dif-

Table 1. Variability with Correction Procedure: NiAl 40 kV, 20° Takeoff Angle

Correction procedure	Ni Kα	Al Kα
Frame (ZAF)	0.6658	0.1285
Pouchou and Pichoir	0.6583	0.123
Armstrong	0.6508	0.1242
Love and Scott	0.6654	0.1208
Packwood	0.6664	0.1213
Average	0.66134	0.12356
SD	0.006751	0.003076
% Relative SD	1.02	2.49

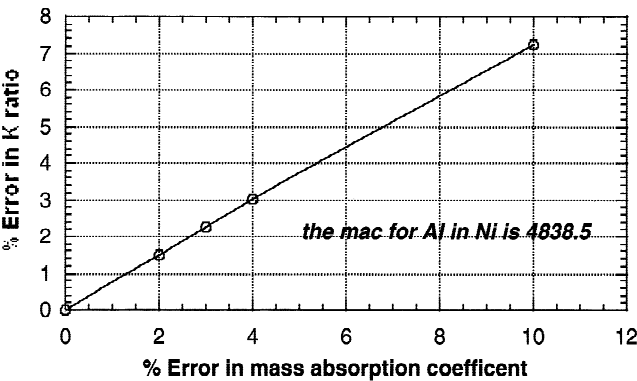


Figure 9. Effect of variability in the absorption correction, with errors in the mass absorption coefficient (mac) NiAl 20 kV, 40° takeoff angle.

ferent. This was not always the case, however, but the result of the hard work of many researchers who improved both the quality of the models and refined them with solid experimental data.

The selection of the models used may actually be less important than the choice of some of the values of some of the parameters used in those models. Figure 9 shows the error in the AlKα *k*-ratio as a function of the percent error in the mass absorption coefficient in the case of NiAl examined at 20 kV with a 40° takeoff angle. It can be seen, for example, that a 4% error in the mass absorption coefficient will result in a 3% relative error in the AlKα *k*-ratio. That error is larger than the difference in the correction models presented in Table 1. Today, as interest grows in going to low voltage and soft X-rays for higher spatial resolution, myriad sources of errors present themselves that will require considerable attention, including peak overlaps, background uncertainty, the need for peak integration, and surface contamination. There is also a need for new fluores-

Table 2. Adding Up the Effects

Source of error	Magnitude
Sample selection	Critical, but can be small
Sample preparation	Critical, but can be small
kV	Generally small
Tilt angle	Generally small
Beam current	Major unless system stabilized
Takeoff angle	Generally small
Detector electronics	Small unless poor use of SCA or system is nonlinear
Counting statistics	Can be minimized by adequate counting times
Background subtraction	Effect increases as concentration decreases
Quantitative model selection	Small for systems with low absorption effects
Mass absorption coefficient	Can be significant with soft X-rays
Reporting results	Should be zero with proper data transcription

SCA, single channel analyzer.

cence and absorption data at low kVs, and possibly even new correction models.

SUMMARY

Table 2 summarizes all of the factors described thus far with the addition of any errors in reporting. These comments are admittedly qualitative in nature, and are intended to serve as a way of approaching error analysis rather than provide an all encompassing quantitative model to predict confidence limits and percent accuracy. Relative accuracy and precision of 1 to 2% relative is possible for major components on samples with well-prepared surfaces assuming that the factors described previously are considered. As the variability of the surface topography increases, and/or specimen orientation becomes more poorly defined, the accuracy and precision will become worse. Accuracy and precision will also become poorer at low concentrations where background characterization is more difficult or at energies below 1 kV.

It should always be remembered that experimental conditions should be chosen to reduce errors whenever possible. There are many modeling tools that can be used to calculate *k*-ratios from concentration for a given set of operating conditions and show expected correction factors.

These tools can be used to predict the sensitivity of a planned measurement to different operating conditions and parameters, as well as predict precision as in the case of counting statistics. Finally, although it is not always possible, having standards close in composition to that of an unknown can be used to develop useful calibration curves from which the composition of the unknown can be determined with high accuracy.

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