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Minimizing Errors in Electron Microprobe Analysis

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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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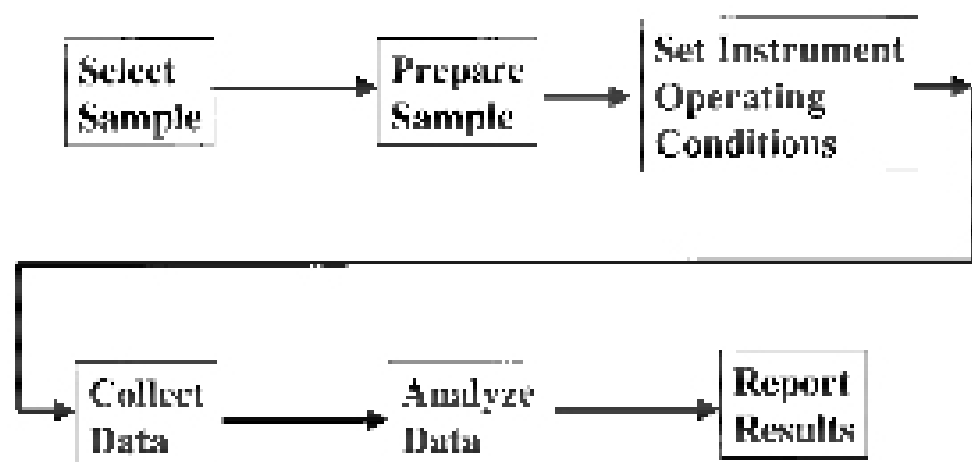

Figure 1. Microanalysis process map.

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 be 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.

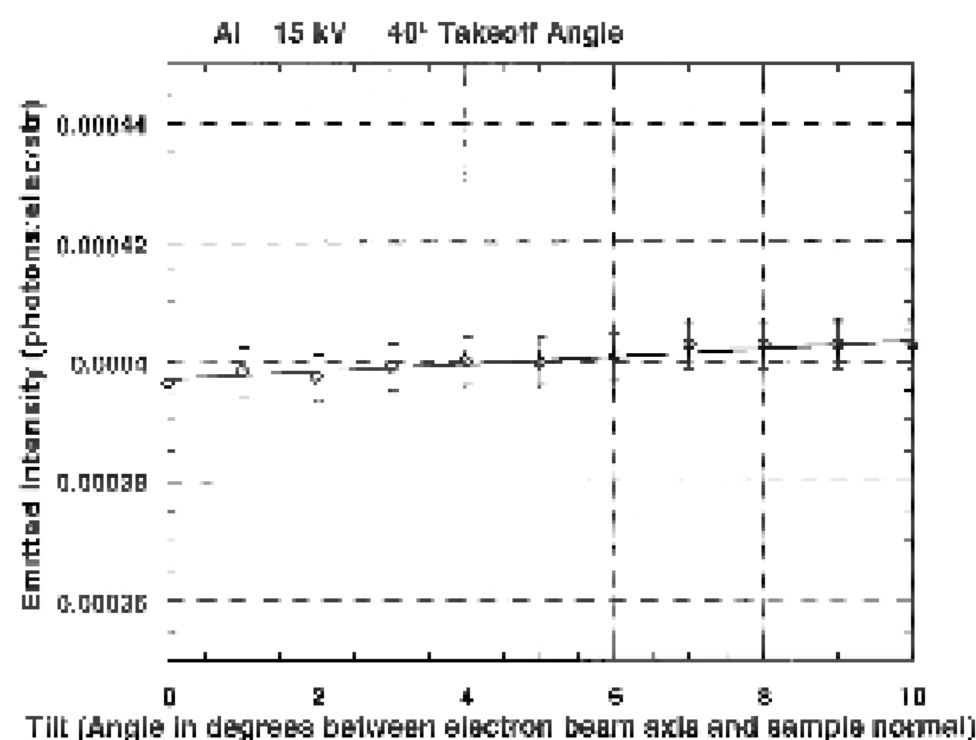

Figure 2. Variation of X-ray emission with sample tilt, based on Monte Carlo calculation using 10,000 electrons.

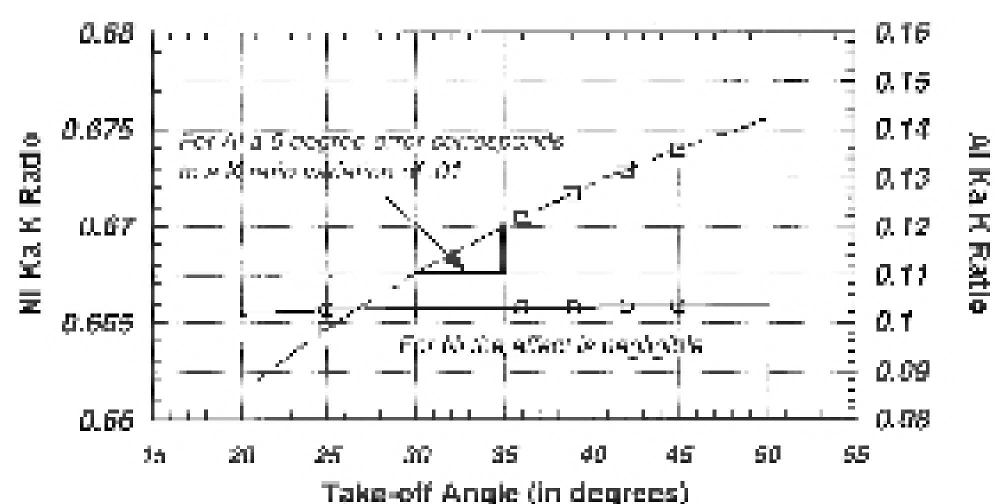

Figure 3. Effect of takeoff angle on *k*-ratios for NiAl, values calculated by ZAF at 20 kV. Squares, Al data; circles, Ni data.

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 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 Ni$K\alpha$ and Al$K\alpha$ 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 Ni$K\alpha$, but a significant effect on the Al$K\alpha$ *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 Al$K\alpha$ in NiAl relative to the Ni$K\alpha$ 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