Precision and Sensitivity in Electron Microprobe Analysis

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Sources of variation in microprobe data, other than the obvious fluctuations in x-ray photon emission, are delineated. It is shown that the precision obtained in composition determinations is not generally the same as the precision of x-ray measurements. A convenient method for estimating precision before actually performing an analysis is presented.

THE ELECTRON MICROPROBE has found wide application in the fields of metallurgy, geology, and biology. The design of associated instrumentation has advanced to the point of highly sophisticated and rapid readout of data, and elaborate programs have been written to accomplish the data reduction with high speed digital computers (*1*, *2*). It is somewhat disturbing, therefore, to realize that, although there is an active and continuing dialogue concerning the accuracy of microprobe analysis, little attention is given to the precision of reported measurements. It is the author's opinion that the precision, when reported, is grossly overstated. Most estimates of the relative standard deviation are taken as "one over the square root of the number of counts." Because x-ray count rates achieved with the microprobe are relatively high, such a figure of precision is usually impressive.

This paper shows that there are sources of variation in microprobe data other than the Poisson distribution of x-ray photon emission; further, that the precision obtained in composition determinations is not generally the same as the precision of x-ray measurements; and further, that the x-ray measurements required for even a single composition determination involve four (or at least three) different signals which, by propagation of errors, increases the variance.

Several of these points have been discussed by Heinrich (*3*), but the approach taken in this paper is somewhat different. It is one question to take proper cognizance of statistical variations when an experiment has been performed and the data are in hand. It is another question to make an *a priori* estimate of the precision to be expected when an experiment is to be carried out in a certain way. The latter question is commonly asked of the analyst when he is given a sample, and this paper suggests a method of estimating precision before the analysis is actually made.

Factors Affecting Precision and Accuracy. Table I summarizes the various factors which influence precision and accuracy of microprobe data. Most important, of course, is the time-dependent nature of x-ray photon emission, which follows Poisson statistics. To make a single determination, however, requires four x-ray signals from the unknown sample, a suitable reference standard, background for the unknown sample, and background for the reference standard. These four signals define the corrected relative intensity

$$K = \frac{I(C) - B(C)}{I(1) - B(1)} \quad (1)$$

where $I(C)$ and $B(C)$ are signal and background for the unknown (containing weight fraction C of the element being measured), and $I(1)$ and $B(1)$ are the corresponding measurements on the reference standard (here assumed to be a pure sample—i.e., $C = 1$—of the element being measured). The variance in the relative intensity due only to fluctuations in the x-ray intensities, therefore, involves the four individual variances.

In addition to the inherent x-ray intensity fluctuations, other sources of random variations in the observed signal may be present. It is the author's experience that the primary source of this additional variance is in placing the sample in proper elevation within the instrument. If the effective "depth of focus" for the x-ray spectrometer is smaller than the depth of focus of the viewing system (light optics), then, although the operator reproduces optical focus, there tends to be a random fluctuation in the measured x-ray intensity. This can easily be measured by taking repeated counts at one point on a stationary sample and then taking repeated counts at the same spot but defocusing and refocusing the sample (optically) between each count interval. In the first case, the observed variance should be that expected from the Poisson distribution, but with the latter procedure the standard deviation has been observed to be two to three times larger than that expected from the x-ray statistics alone.

In addition to variance in the measurements on the unknown sample, there will be a variance involved in the measurements of calibration standards when these are used to effect the conversion of x-ray data to chemical composition. As dis-

Table I. Factors Affecting Precision and Accuracy in Electron Probe Microanalysis

PRECISION: Measurements which relate to scatter of dispersion among test results without assumption of any prior information.

1. Statistics of x-ray counting (Poisson statistics)
   a. Signal from unknown
   b. Signal from reference standard
   c. Background measurements
   d. Calibration measurements
2. Other sources of scatter
   a. Stability of electronics
   b. Sample positioning (reproducibility of "focus")
   c. Sample preparation (surface roughness or irregularities)

ACCURACY: Measurements which relate to difference between average test results and true result when the latter is known or assumed.

1. Error in relative intensity
   a. Sample preparation
   b. Background measurements
   c. Counting system errors (dead time error, peak shift)
2. Error in calibration
   a. Empirical method: accuracy of equations; uncertainty in true composition
   b. Computational methods: accuracy of equations; uncertainty in physical properties (absorption coefficients; x-ray yields; etc.)

(1) E. Lifshin and R. E. Hanneman, "An Automated Method for the Collection and Analysis of Microprobe Data," paper presented to the First National Conference on Electron Microprobe Analysis, College Park, Md., May 1966.
(2) J. Z. Frazer, "Computer Program for Microprobe Conversions," *Ibid.*
(3) K. F. J. Heinrich, "Advances in X-Ray Analysis," W. M. Mueller, ed., Vol. 3, p. 95, Plenum Press, N. Y., 1960.

cussed elsewhere (*4*, *5*), this conversion may be done with either calibration standards or by computation from semi-theoretical formulas. Both of these methods are primarily involved in questions of accuracy, as summarized in the lower part of Table I, and this point will not be discussed at any length in the present paper. In general, the measurement of calibration standards should be repeated until the precision of these values is good enough to have little influence on the overall precision of the unknown sample determination. This will be assumed in the following discussion, but the development presented may easily be extended to include variance in the calibration measurements.

To comment briefly on the remaining items in Table I, it is stated that the accuracy of microprobe measurements involves errors in the measured relative intensity as well as the more obvious problem of errors in the calibration. The x-ray signals may be in error as a result of sample preparation (smearing across the surface of an inhomogeneous alloy, tarnishing or other chemical attack on the surface, and so forth), inaccurate correction for background signals, or count loss arising from the finite resolving time of the counting system. With either calibration method, empirical or computational, there is a question of the accuracy of the equations used, but there is also a considerable uncertainty in the known (or true) composition of calibration standards used in the empirical method and in the many physical properties which are required in the computational expressions. However, even if absolutely accurate equations were known, these latter errors might still exist.

Development of an Estimate of Precision. For n measurements of an x-ray signal whose true average count rate is I, each measurement requiring a fixed time interval τ, the mean number of counts is

$$\bar{N} = \sum_{i=1}^{n} N_i/n \cong I\tau \tag{2}$$

and the variance of the mean is

$$s_{\bar{N}}^2 = \sum_{i=1}^{n} (N_i - \bar{N})^2/n(n-1) \geq \sigma_{\bar{N}}^2 = \bar{N}/n \tag{3}$$

The equality on the extreme right of Equation 3 is the definition of Poisson statistics, and the inequality in this equation expresses the previously stated fact that there may be other sources of random fluctuation in the measurements. (Throughout this paper, σ will be taken as the standard deviation due solely to Poisson statistics, and s will be used to denote the actual measured standard deviation.) From Equation 3 it is seen that the relative standard deviation of the mean value is

$$s_{\bar{N}}/\bar{N} \geq \sigma_{\bar{N}}/\bar{N} = 1/\sqrt{n\bar{N}} \tag{4}$$

Using this equation and the rules for propagation of errors, the variance in the corrected relative intensity is given by

$$\left(\frac{s_K}{K}\right)^2 \geq \left(\frac{\sigma_K}{K}\right)^2 = \frac{\bar{N}(C) + \bar{N}_B(C)}{n[\bar{N}(C) - \bar{N}_B(C)]^2} + \frac{\bar{N}(1) + \bar{N}_B(1)}{n'[\bar{N}(1) - \bar{N}_B(1)]^2} \tag{5}$$

where $\bar{N}(C)$ and $\bar{N}_B(C)$ are the mean counts for the sample and its background, $\bar{N}(1)$ and $\bar{N}_B(1)$ are the mean counts for the pure element reference and its background, n is the number of measurements made on the sample and its background, and n' is the number of measurements made on the standard and its background. It is implicit in Equation 5 that the same fixed-time counting interval, τ, is used for the sample and its background and that another fixed time interval, τ', is used for the pure standard and its background. Gaylor (*6*) has shown that using the same count time interval for a signal and its background is an efficient procedure in terms of the total counting time involved.

We are ultimately interested not in the precision of x-ray measurements but rather in the precision of the determined composition and, since the intensity-composition relationship is not usually linear, the relative standard deviations of these two distributions are not equal. The only tractable expression relating composition and intensity is the empirical fit proposed by Ziebold and Ogilvie (*4*). This is

$$\frac{1 - K_1}{K_1} = a_{12}\,\frac{1 - C_1}{C_1} \tag{6}$$

for the measurement of element 1 in a mixture of elements 1 and 2. C_1 is the weight fraction of element 1 in the mixture. (Hereafter the subscripts will be dropped since no ambiguity should arise.) To establish the variance in composition which depends on a given variance in the relative intensity, we use

$$\sigma_C^2 = \sigma_K^2\left(\frac{\partial C}{\partial K}\right)^2 + \sigma_a^2\left(\frac{\partial C}{\partial a}\right)^2 \tag{7}$$

As stated before, calibration measurements should be made a sufficient number of times that the second term in the above equation is negligibly small. Hence, using Equation 6,

$$\frac{s_C}{C} \geq \frac{\sigma_C}{C} = \frac{\sigma_K}{K}\left(1 - \frac{a-1}{a}\,C\right) \tag{8}$$

Here as before s_C is meant in the same context as s_K.

The significance of Equation 8 should be noted, namely, that the conversion parameter a depends on what other elements are present in the sample. Consequently, the precision of composition determinations also depends on what other elements are present.

Analytical sensitivity usually denotes the ability to distinguish between two compositions which are close together. If we determine two compositions, C and C', by n repetitions of each measurement, then we can say that these two values are significantly different with a certain confidence if

$$C - C' > \sqrt{2}\, s_C\, t \tag{9}$$

in which t is Student's factor and depends on the specified confidence level and the number of repetitions n. The analytical sensitivity for a specified confidence level of 95% is, thus,

$$(\Delta C)_{\min} = \sqrt{2}\, s_C t_{0.95} \geqslant 2.33\, s_C \geqslant 2.33\, \sigma_C \tag{10}$$

To estimate the sensitivity it is convenient to make the simplifying assumption (which is commonly valid) that

$$\bar{N}_B(C)/\tau \cong \bar{N}_B(1)/\tau' \ll \bar{N}(1)/\tau'$$

Returning with this approximation to Equation 5 gives

$$\left(\frac{\sigma_K}{K}\right)^2 \cong \frac{1}{n'\bar{N}(1)}\left[1 + \left(\frac{n'\tau'}{n\tau}\right)\frac{1}{K} + 2\left(\frac{n'\tau'}{n\tau}\right)\frac{N_B(1)}{K^2\bar{N}(1)}\right] \tag{11}$$

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(4) T. O. Ziebold and R. E. Ogilvie, Anal. Chem., 36, 322 (1964).
(5) T. D. McKinley *et al.*, eds., "The Electron Microprobe," pp. 95–714, Wiley, N. Y., 1965.
(6) D. W. Gaylor, Anal. Chem., 34, 1670 (1962).

By introducing the definitions

$$I_o = \bar{N}(1)/\tau'$$

and

$$R = \bar{N}(1)/\bar{N}_B(1)$$

for the pure element line intensity and peak-to-background ratio, and using Equation 6 to relate C and K, we obtain

$$\frac{(\Delta C)_{min}}{C} \geq 2.33\frac{\sigma_C}{C} = \frac{2.33}{\sqrt{n\tau I_o R}}\frac{a-(a-1)C}{aC}\left\{RC\left[a-\left(a-1-\frac{n\tau}{n'\tau'}\right)C\right]+2[a-(a-1)C]^2\right\}^{1/2} \quad (12)$$

This equation indicates that, if we know what elements are present in the sample [and, therefore, can estimate the value of a (4)], then we can select an appropriate combination of count times (τ and τ'), repetitions (n and n'), peak intensity (I_o), and peak-to-background ratio (R) to achieve the desired sensitivity. Note that the total work required in terms of the total counting time is equal to $2n\tau + n'\tau'$ because we must count the sample, the reference element, and the background.

When the composition of the measured element goes to small values, the terms within braces in Equation 12 take the approximate value $a\sqrt{2}$ (the parameter a is usually on the order of unity). Expressed as an absolute deviation, for small values of C, Equation 12 gives a measure of the detectability limit—that is, the sensitivity at trace levels:

$$C_{DL} \geqslant 3.29\ a/\sqrt{n\tau I_o R} \quad (13)$$

The same expression may be derived from Theisen's treatment (7) of the detectability limit. His development is based on using a standard with a low but known content of the element under study. Because the reference standard composition is low, the intensity-composition relation may be taken as linear (as long as the other constituents remain in fixed proportions); that is, the composition of the unknown, C, is related to the composition of the standard, C_s, by

$$C = \frac{\bar{N}(C) - N_B}{\bar{N}_s - N_B}C_S \quad (14)$$

if $\bar{N}_S$ is the mean count obtained from the standard and $\bar{N}(C)$ and $\bar{N}_B$ are, as before, the mean counts taken from the unknown and from the background (fixed time counting is assumed).

Defining the detectability limit as that minimum composition for which the signal can be distinguished from background with a specified statistical confidence, Theisen's result is

$$C_{DL} = \frac{C_S}{\bar{N}_s - \bar{N}_B}\frac{s_D t\sqrt{2}}{\sqrt{n}} \quad (15)$$

Here n is the number of repeated counts on both the unknown and the background, and s_D is the measured deviation of the means difference $\bar{N}(C) - \bar{N}_B$.

There is more than one way to define a detectability limit. For quantitative microprobe analysis the statement given above is, in the author's opinion, a sensible definition, but it should be noted that the limit is meaningless unless the confidence level is stated.

Equation 15, with a specified confidence level (which fixes the value of t for the given sample size), is a valid measure of the detectability limit for a particular experiment. As before, however, if we want to estimate this limit before the experiment is carried out, we may approximate the expression by assuming Poisson statistics, using the asymptotic limit for t ($t = 1.64$ for $n = \infty$ and 95% confidence), and using Equation 6 for the intensity-composition relation. With these stipulations, we have

$$\bar{N}_S - \bar{N}_B = C_S\tau I_o/a$$

and

$$s_D = \sqrt{\bar{N}(C) + \bar{N}_B}$$

so that, from Equation 15,

$$C_{DL} \geqslant \frac{2.33\ a}{\sqrt{n\tau I_o R}}\sqrt{RK+2} \quad (16)$$

Because we are considering trace levels, K is small and this expression becomes the same as Equation 13.

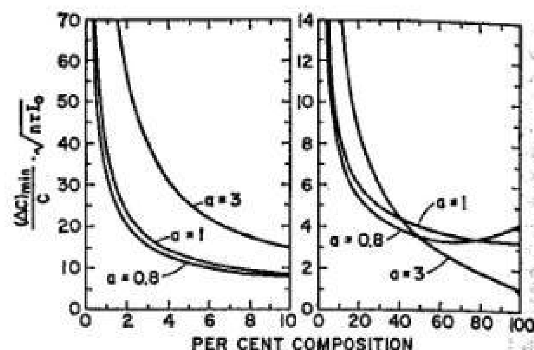

Figure 1. Curves for estimating the sensitivity of analyses with the electron microprobe

For assumed values of $R = 100$ and $n\tau = n'\tau'$. See Equation 12 for definition of symbols

Sample Calculation. To illustrate the use of the relations developed above, the following sample calculations are presented. The numbers used are representative of actual microprobe experience.

The function given by Equation 12 is plotted in Figure 1 for assumed values of $R = 100$ and $n\tau = n'\tau'$. Suppose that we are asked to analyze a sample containing about 3% of the element of interest and that our instrument will produce 10,000 count per second from a pure standard of this element. We elect to repeat the measurements three times with a fixed-time count interval of 60 seconds. From the graph of Figure 1 for compositions around 3%, and assuming $a = 1$, the ordinate is

$$\frac{(\Delta C)_{min}}{C}\sqrt{n\tau I_o} \cong 15$$

We expect, from past experience, that the actual standard deviation in the individual measurements will be two to three times larger than the standard deviation due solely to x-ray statistics, so we estimate that

$$\frac{(\Delta C)_{min}}{C}\sqrt{n\tau I_o} \cong 35$$

For the supposed experimental conditions,

$n = 3$
$\tau = 60$ seconds
$I_o = 10{,}000$ counts per second

(7) R. Theisen, "Quantitative Electron Microprobe Analysis," Springer-Verlag, N. Y., 1965.

so that

$$\sqrt{n\tau I_o} \cong 1300$$

and

$$(\Delta C)_{min}/C \cong 35/1300 = 0.026$$

or, since $C \cong 3$ weight %, then

$$(\Delta C)_{min} \cong 0.08 \text{ weight } \%$$

In this case, then, we may expect to distinguish between 2.96 and 3.04% compositions with 95% confidence. Note, however, that if the other constituents in the sample were strong absorbers of the x-ray line emitted by the element under study, so that $a = 3$, for example, then from Figure 1

$$\frac{(\Delta C)_{min}}{C} \sqrt{n\tau I_o} \cong 40$$

Now the sensitivity under the same instrument setup would be

$$(\Delta C)_{min} \cong 0.21 \text{ weight } \%$$

This indicates that the precision in terms of composition measurements depends strongly on the aggregate composition of the sample, particularly for analyses at levels below about 5%.

Another significant conclusion may be drawn from this sample calculation. The total number of counts taken on the sample would have been (for the case of $a = 1$)

$$n\tau I_o C = 54{,}000 \text{ counts}$$

An estimate of the precision on the basis of "one over the square root of the number of counts" would yield

$$\sigma_{\bar{N}}/\bar{N} = 1/\sqrt{54{,}000} = 0.0043$$

or about a factor of six better performance than the 2.6% relative error predicted by the previous computation.

Concluding Remarks. The sample calculations have shown that neglect of such factors as propagation of errors (Equation 5), aggregate sample composition (Equation 8), and other random fluctuations than simple x-ray statistics can lead to a gross overstatement of the precision of a given microprobe analysis. The method presented in this paper allows the analyst to arrive at a more realistic estimate of his capabilities or, conversely, to plan his experimental procedure so as to approach a desired precision. It is to be hoped that, as digital computer programs are applied to the rapid and automatic treatment of microprobe output, increasing attention will be given to a rigorous statistical analysis of these data. Nevertheless, the relations presented here should continue to provide a useful means of estimating precision before the experiment has actually been carried out.

ACKNOWLEDGMENT

The author is grateful to Dr. K. F. J. Heinrich and Dr. R. E. Michaelis for several precise and accurate comments on this paper.

RECEIVED for review December 27, 1966. Accepted March 31, 1967. Presented at MIT Symposium on "Electron Microprobe Analysis" Houston, Texas, Jan. 30, 1967, and Los Angeles, Calif., Feb. 1, 1967.