

**BOOK OF TUTORIALS AND ABSTRACTS**

---



European Microbeam Analysis Society

---

**EMAS 2009**

11th

**EUROPEAN WORKSHOP**

on

**MODERN DEVELOPMENTS**

**AND**

**APPLICATIONS**

**IN**

**MICROBEAM ANALYSIS**

10 to 14 May 2009

at the

Hotel Spa Faltom

Gdynia/Rumia, Gdansk, Poland

---

Organized in collaboration with  
Silesian University of Technology  
Polish Society for Microscopy (PTMi)  
Polish Academy of Sciences:  
Committee of Materials Science, Institute of Physics,  
Institute of Materials Science and Metallurgy

---



## UNCERTAINTIES IN ELECTRON PROBE MICROANALYSIS

Ryna B. Marinenko<sup>1</sup> and S. Leigh<sup>2</sup>

- 1 National Institute of Standards and Technology (NIST), Surface and Microanalysis Division  
100 Bureau Drive, MS 8371, US-20899-8371 Gaithersburg, Maryland, U.S.A.
- 2 National Institute of Standards and Technology (NIST), Statistical Engineering Division  
100 Bureau Drive, MS 8980, US-20899-8980 Gaithersburg, Maryland, U.S.A.

In 1972 Dr. Marinenko began working at the National Bureau of Standards (now NIST, the National Institute of Standards and Technology) and in 1974 she joined the Microanalysis Section (now the Microanalysis Research Group) where she is a Senior Scientist. Her work and research interests on qualitative and quantitative WDS and EDS X-ray microanalysis with the electron microprobe has concentrated on heterogeneity testing and the certification of standards for microanalysis and the development of digital wavelength-dispersive (WD) compositional mapping for which she received the NIST Bronze Medal in 1988 and shared an IR-100 award in 1987 for WD compositional mapping. Microanalysis standards certified under her leadership include multielement bulk alloys and glasses as well as glass microspheres. Related projects include the micro-characterisation (for composition, heterogeneity, and thickness) of high technology materials such as bulk high-temperature superconductors, thin films used in opto-electronic devices, and bulk and thin film ferroelectric ceramics. She has been an active member of MAS in which she served as a Director and as President, and presently writes the newsletter, MicroNews. She received the MAS Service Award in 2000. She is also the US TAG (Technical Advisory Group) chairman for the ISO TC 202 (International Standards Organisation Technical Committee 202) for Microbeam Analysis. She has about 30 publications.

## 1. ABSTRACT

We determined uncertainties for WDS-EPMA (wavelength-dispersive spectrometry - electron probe microanalysis) data using the globally accepted ISO/GUM (International Standards Organisation / Guide to the Expression of Uncertainty in Measurement). For each calculation, such as the current correction and dead time correction that precedes the calculation of a  $k$ -value (net corrected X-ray counts of unknown / net corrected X-ray counts of standard), uncertainties were calculated from contributing factors and combined until a final combined standard uncertainty for the  $k$ -value was calculated. Our example used data from the analysis of the Ge  $L\alpha$  X-ray line in a SiGe alloy. Additional contributions to uncertainties in EPMA results, such as the matrix correction procedure and mass absorption coefficients (MACs) are considered. All statistical calculations used in the process of arriving at the combined uncertainty are included and the basic steps of the ISO/GUM are described.

## 2. INTRODUCTION

In this report the ISO/GUM is adapted to EPMA data. It provides the basic steps and statistics for determining uncertainties from the equations used in the EPMA community. Hopefully this is a first step in providing a universal system we can all use for reporting uncertainties.

Since the development of the electron microprobe was reported by Castaing in 1949 there have been few publications devoted specifically to uncertainties in EPMA. An early comparison of the calculated compositions from 229 binary alloys, many with well-known compositions, using early matrix correction procedures demonstrated that the deviation in the calculated composition from the accepted values could vary by as much as 18 % relative [1]. A derivation of the variance of the mean for  $k$ -values calculated from wavelength-dispersive spectrometer (WDS) data was reported [2]. This derivation applied only to the counting statistics in the analysis and it can also be used for energy dispersive spectroscopy (EDS) data as demonstrated more recently by Lifshin *et al.* [3], also in Goldstein *et al.* [4]. Both reports applied the results to the determination of the minimum detectable limit (MDL) for an element and to the determination of the optimum X-ray count acquisition time needed to achieve a desired precision for an element. A rigorous application of Poisson counting statistics was described and applied to microanalysis [5]. Again this was applied to the MDL and optimum acquisition time for an element. The difficult task of sorting out uncertainties associated with the individual ZAF (atomic number-absorption-fluorescence) matrix correction factors have also been reported [6].

This report describes the evaluation of uncertainties in electron probe microanalysis according to currently acceptable practices in the scientific community. It includes guidelines and procedures from several references that are recommended reading for anyone involved in

expressing uncertainties for EPMA data. The data and equations used here are from quantitative WDS-EPMA but can be used for quantitative EDS analysis from  $k$ -values extracted from multiple linear least squares fitting procedures.

### 3. ACCURACY AND PRECISION

A distinction between the terms accuracy and precision must be made. These terms **must not** be used interchangeably. Accuracy is a measure of correctness or how close a result or measurand may be to the "true value". Precision is a measure of statistical repeatability or reproducibility. You cannot have good accuracy without good precision but you can have good precision without good accuracy. An enlightening and entertaining discussion on accuracy and precision is available on the web in a National Bureau of Standards (NBS), former name of NIST, Special Publication [7].

### 4. UNCERTAINTIES

Before discussing how to evaluate uncertainties in EPMA, it is important to understand what uncertainty is and its importance in today's global economy. An uncertainty is a "parameter, associated with the results of a measurement that characterizes the dispersion of the values that could reasonably be attributed to the measurand" [8]. It can be reported in either absolute units or relative terms but should always be accompanied by a very clear explanation of how the uncertainty value was determined, including a description of all the contributing factors. John Lyons, former director of the National Institute of Standards and Technology (NIST) stated the need for clear uncertainty statements when he wrote the following in the Foreword to the NIST Technical Note, *Guidelines for evaluating and expressing the uncertainty of NIST measurement results* [9].

"Results of measurements and conclusions derived from them constitute much of the technical information produced by NIST. It is generally agreed that the usefulness of measurement results, and thus much of the information that we provide as an institution, is to a large extent determined by the quality of the statements of uncertainty that accompany them. ... Only if quantitative and thoroughly documented statements of uncertainty accompany the results of NIST calibrations can the users of our calibration services establish their level of traceability to the U.S. standards of measurement maintained at NIST".

The need for clear statements of the uncertainties assigned to reported values had also been discussed as early as 1969, again by C. Eisenhart [10]. The statement above is not just applicable to NIST but also to any laboratory, especially to those issuing standards or experimental results that will be used by others. The ISO and NIST publications cited above

were the result of a global perceived need to evaluate and express uncertainties assigned to standards using a single universally acceptable approach. The ISO publication was a cooperative effort of several international organisations, including the BIPM (International Bureau of Weights and Measures), IEC (International Electrotechnical Commission), IFCC (International Federations of Clinical Chemistry), ISO, IUPAC (International Union of Pure and Applied Chemistry), and OIML (International Organisation of Legal Metrology). Jointly they adopted a provisional standard developed by CIPM (International Committee for Weights and Measures) that we refer to as ISO/GUM. The NIST Technical Note is in full agreement with the ISO Guide but is a more concise version. For any laboratory reporting data with uncertainties, these publications are a definite necessity. They provide a set of statistical terms and concepts with precise definitions and practical guidance. Another highly recommended publication because of its clarity and excellent examples is the EURACHEM/CITAC Guide [11] that is available on the web at no cost. A more recent publication by Kirkup and Frenkel [12] is also recommended.

According to the ISO/GUM a measurement is the approximation of a measurand that is only complete with a quantitative statement of uncertainty. This uncertainty is a combination of several individual uncertainty contributions that are classified as Type A or Type B.

Type A includes statistical evaluations of a series of measurements, such as:

- a series of independent measurements from which a standard deviation of the mean is calculated,
  - parameters calculated for a curve from a set of data with a least squares fit from which a set of standard deviations are calculated,
- and
- analysis of variance (ANOVA) results to identify random effects in some types of measurements.

Type B includes other methods of evaluation, such as:

- scientific judgment based on previous knowledge and understanding of relevant materials and instruments,
  - previous measurement data,
  - data provided in reports and calibrations,
  - uncertainties assigned to reference data,
- and
- manufacturer's specifications.

Each Type A component of uncertainty that contributes to the uncertainty of a measurement result, or what is called a combined standard uncertainty, represented by  $\sigma_c$ , is referred to as a *standard uncertainty*. It is the same as an estimated standard deviation,  $\sigma_i$ , equal to the positive square root of the corresponding estimated variance,  $\sigma_i^2$ . Likewise, the standard uncertainty, or estimated standard deviation for a Type B component of uncertainty is referred to as  $\sigma_j$ , equal to the positive square root of the corresponding estimated variance,  $\sigma_j^2$ . Random and

systematic effects can fall into either type of evaluation. The ISO/GUM discusses random and systematic effects and ways to reduce them in order to minimize uncertainties, and it assumes that every effort is made to identify and correct for all systematic effects in an analysis before calculating the combined standard uncertainty of a measurement.

The combined standard uncertainty,  $\sigma_c$ , is the positive square root of the combined variance,  $\sigma_c^2$ , determined from both Type A and Type B standard uncertainty contributions with propagation of error or RSS (root-sum-of-squares):

$$\sigma_c^2(y) \approx \sum_{i=1}^N \left( \frac{\partial f}{\partial x_i} \right)^2 \sigma^2(x_i) + 2 \sum_{j=1}^{m-1} \sum_{j=i+1}^m \frac{\partial f}{\partial x_i} \frac{\partial f}{\partial x_j} \sigma(x_i, x_j) \quad (1)$$

Here the measurand,  $y$ , is determined from  $N$  other quantities  $x_1, x_2, \dots, x_N$ :

$$y = f(x_1, x_2, \dots, x_N) \quad (2)$$

Equation (1) above is based on a Taylor series approximation and is referred to as the law of propagation of uncertainty. The factors and terms that appear are

$$\frac{\partial f}{\partial x_i} \text{ are the sensitivity coefficients,}$$

$\sigma(x_i)$  is the standard uncertainty of  $x_i$ , and  $\sigma(x_i, x_j)$  is the covariance of  $x_i$  and  $x_j$ .

The second term of eq. (1) is the sum of the covariances between  $x_i$  and  $x_j$  and is sometimes small enough to be excluded, but should be determined when possible.

Explicit formulas for the first and second terms of eq. (1) above for many specific functional forms of the equation used to determine  $y$ , can be readily found in some publications [13] and thus alleviate the need to calculate the partial derivatives. Today partial derivatives of complicated functional expressions can be readily calculated with the use of symbolic calculation facilities of software like *MAPLE* or *MATHEMATICA*.

For EPMA quantification we are first interested in the combined standard uncertainty for the  $k$ -value. This means that a combined standard uncertainty will have to be calculated for the dead time correction, the beam drift correction, and the  $k$ -value determination. The uncertainty associated with the matrix correction procedure will be dealt with later.

For a function that is determined from an addition (or subtraction) where variables  $x_1$  and  $x_2$  are independent and random, such as in equation (3) below,

$$y = a \cdot x_1 + b \cdot x_2 \quad (3)$$

with sensitivity coefficients  $a$  and  $b$ ,

$$\frac{\partial y}{\partial x_1} = a \quad \frac{\partial y}{\partial x_2} = b \quad (4)$$

the standard uncertainties are summed in quadrature as in eq. (5) below to obtain the combined standard variance for  $y$ ,

$$\sigma_c^2(y) = a^2 \cdot \sigma^2(x_1) + b^2 \cdot \sigma^2(x_2) \quad (5)$$

For a function determined by multiplication or division of independent or uncorrelated random variables, the relative standard uncertainties are used to obtain the combined standard uncertainty.

So, for a function such as

$$y = a \cdot x_1 \cdot x_2, \text{ and } \frac{\partial y}{\partial x_1} = a \cdot x_2, \quad \frac{\partial y}{\partial x_2} = a \cdot x_1 \quad (6)$$

The combined relative variance will be the sum of the relative standard uncertainties added in quadrature according to eq. (7) below.

$$\frac{\sigma_c^2(y)}{y^2} = \frac{\sigma^2(x_1)}{x_1^2} + \frac{\sigma^2(x_2)}{x_2^2} \quad (7)$$

For more complicated equations where  $y$  and  $x$  are not correlated, combinations of the two procedures can often be used to calculate the combined standard uncertainty.

## 5. COMBINED STANDARD UNCERTAINTY FOR A $k$ -VALUE

We will proceed stepwise through the calculations used to obtain the  $k$ -value in a WDS-EPMA quantification to determine the combined standard uncertainty for the  $k$ -value of a single element. Eq. (8) is used to correct the dead time of the observed or measured count rate (counts/s),  $I'$ , obtained from a WDS detector.

$$I = \frac{I'}{(1 - \tau I')} \quad (8)$$

where  $I$  is the dead time corrected count rate in counts/s and  $\tau$  is the dead time constant in seconds. Note that this equation should be used with the count rate, not the raw counts. Since the count rate  $I$  is proportional to the beam current,  $i$ ,

$$I = ri \quad (9)$$

eq. (8) can be written as

$$\frac{I'}{i} = r(1 - \tau I') \quad (10)$$

This equation is used to determine the dead time by plotting  $I'/i$  in counts/s/nA versus  $I'$  in counts/s resulting in a straight line plot with intercept  $k$  on the  $I'/i$  axis and slope of  $(-r\tau)$  so that  $\tau$  is estimated as minus the ratio of slope to intercept. We use a linear least squares fit to such data to determine the dead time and the variance. X-ray count data taken from a Cr  $K\alpha$  peak with a PET crystal at currents ranging from 50 to 600 nA was fit to a straight line with a least squares linear fit. The dead time,  $\tau$ , was determined to be 2.098  $\mu$ s with a single standard deviation of 0.087  $\mu$ s. We will use this uncertainty for the dead time when we later calculate a combined uncertainty for the current corrections. But there is the question of whether the component of uncertainty attributable to the covariance between the slope of the fitted line and intercept is large enough to merit incorporation in the variance determination. To do this we use the propagation of error formula Ku (Table 1, page 337-269) [13] for a function form  $\bar{x}/y$ . The second order correction term can be estimated by

$$\left(\frac{\bar{x}}{\bar{y}}\right)^2 \left(-2 \frac{S_{\bar{x}\bar{y}}}{\bar{x}\bar{y}}\right) \quad (11)$$

where  $S_{\bar{x}\bar{y}}$  is the covariance of  $x$  and  $y$ . The correction is -0.0025, which is only about 0.1 % relative to the dead time.

We will use the dead time calculated above and its uncertainty in a propagation of uncertainties for Ge  $L\alpha$  in the WDS-EPMA quantification of a SiGe bulk specimen. The analysis was done at 15 kV, 30nA beam current with a TAP crystal, and a point beam using a Jeol 8600 electron microprobe (*Note*: Certain commercial equipment, instruments, or materials are identified in this paper in order to adequately specify the experimental procedure; such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose). A polished slice taken from the SiGe boule was mounted on carbon tape. The expanded ( $k = 2$ , 95 % coverage) (*Note*: The use of  $k$  here is an ISO/GUM coverage factor used to expand the bounds of the uncertainty) combined heterogeneity

uncertainty for Ge in the SiGe alloy was determined to be 0.92 % mass fraction [14]. Ten points were sampled for 40 s each, and beam current readings were acquired after sampling each point. Backgrounds for each analyzed point were taken from both sides of the Ge  $L\alpha$  peak. All count data reported here for the X-ray peak and background are the average of the 10 readings. The X-ray counts acquired from the 10 points were first corrected for changes in the beam current during the analysis using the equation

$$I_C = I' \times \frac{i_{Sc}}{i_{obs}} \quad (12)$$

where  $I_C$  is the average or raw X-ray counts corrected for beam current drift,  $I'$  is the measured X-ray counts at the observed current,  $i_{obs}$ , and  $i_{Sc}$  is the nominal value chosen to correct all X-ray data readings to in the data set. The nominal value can be a rounded number in the range of the observed current readings or it can be the first current reading in the data set. The calculated value for  $I_C$  is 138927 cts/40 s.

Since eq. (12) uses only multiplication and division, the relative uncertainties of the mean are added in quadrature.

$$\sigma_{I_C} = I_C \sqrt{\frac{\sigma_{i_{obs}}^2}{(i_{obs})^2} + \frac{\sigma_{I'}^2}{(I')^2}} \quad (13)$$

where  $\sigma_{I_C}$  is the combined standard uncertainty of the mean for the X-ray counts corrected for beam drift,  $\sigma_{i_{obs}}$  is the standard uncertainty of the mean for the observed current, and  $\sigma_{I'}$  is the standard uncertainty of the mean for the observed X-ray counts. For the SiGe alloy the average for the 10 values of  $I'$  for Ge was 138953 cts/40 s, with a standard uncertainty of the mean,  $\sigma_{I'}$  equal to 210 cts/40 s. The average observed current,  $i_{obs}$ , for the 10 readings was 30.53 nA with a standard uncertainty of the mean of 0.002 nA. Substitution into eqs. (12) and (13) results in the corrected counts of  $I_C = 138927$  cts/40s with a standard uncertainty of the mean of  $\sigma_{I_C} = 210$  cts/40s. This value is very close to the standard uncertainty of the mean for the observed current. The contribution from the current drift to the uncertainty is minimal and probably could have been ignored.

The evaluation of the combined standard uncertainty from the current drift and dead time can be calculated with the equation

$$\sigma_{CDT} = \sqrt{\left[ \frac{(I_C)^2}{(1 - \tau(I_C))^2} \right]^2 \sigma_{\tau}^2 + \left[ \frac{1}{(1 - \tau(I_C))^2} \right]^2 \sigma_{I_C}^2} \quad (14)$$

where  $\sigma_{CDT}$  is the combined standard uncertainty of the mean for the current-corrected and dead time-corrected X-ray counts. Using the values calculated above for the dead time and the corresponding standard uncertainties of the means, the value of  $\sigma_{CDT}$  for Ge in the alloy was determined to be 211 cts/40 s. For the Ge standard wafer that was used as the standard for Ge in the alloy, the current corrected counts,  $I_c$ , is 497168 cts/40s with a standard uncertainty,  $\sigma_{I_c}$ , of 657cts/40s. The combined uncertainty for the standard,  $\sigma_{CDT}$ , was calculated from eq. (14) to be 675 cts/40s.

Now we can calculate the uncertainty of the mean for the observed  $k$ -value for Ge in the SiGe alloy specimen. The equation for the determination of the  $k$ -value is

$$k = \frac{I_{UCDT} - BG_{UCDT}}{I_{STDCDT} - BG_{STDCDT}} \quad (15)$$

where  $I_{UCDT}$  and  $BG_{UCDT}$  are the beam current corrected and dead time corrected X-ray counts for the peak and the background of the unknown, and  $I_{STDCDT}$  and  $BG_{STDCDT}$  are the beam current corrected and dead time corrected X-ray counts for the peak and background of the standard. The background is determined from interpolation of readings taken from both sides of the X-ray peak where there were no interferences.

The experimental variance of the mean for the intensity of the unknown,  $\sigma_{IU}^2$ , in the numerator of eq. (15) is

$$\sigma_{IU}^2 = \sigma_{IUCDT}^2 + \sigma_{BGUCDT}^2 \quad (16)$$

For the denominator, the experimental variance of the mean for the intensity of the standard,  $\sigma_{ISTD}^2$ , is

$$\sigma_{ISTD}^2 = \sigma_{I_{-STDCDT}}^2 + \sigma_{BG_{-STDCDT}}^2 \quad (17)$$

Then the combined standard uncertainty for the  $k$ -value,  $\sigma_k$ , is

$$\sigma_k = k \sqrt{\frac{\sigma_{IU}^2}{(I_{UCDT} - BG_{UCDT})^2} + \frac{\sigma_{ISTD}^2}{(I_{STDCDT} - BG_{STDCDT})^2}} \quad (18)$$

This equation is the same as reported by Ziebold in 1967 [2] and later used by Lifshin in 1999 [3]. In our case we have included the uncertainties from the dead time and current corrections. From data in the Table 1, below, the  $k$ -value and the  $k$ -value combined standard uncertainty of the mean were calculated to be  $0.2785 \pm 0.00059$  (0.21 %).

This is a small uncertainty, probably attributable to the good homogeneity and counting statistics for the Ge L $\alpha$  X-ray peak from both the unknown and the standard as well as the low

Table 1. Dead time and current corrected X-ray counts  $\pm$  standard uncertainties of the mean for the analysis of Ge L $\alpha$  in a SiGe alloy with Ge wafer standard.

<b>Counts/40 s <math>\pm</math> Standard uncertainty of the mean</b>		
<b>Specimen</b>	<b>Ge L<math>\alpha</math> - on peak</b>	<b>Background</b>
SiGe alloy	136926 $\pm$ 210	841 $\pm$ 25
Ge wafer (Standard)	497167 $\pm$ 657	1262 $\pm$ 23

counting statistics for the background. It is not always possible in EPMA quantification to achieve these favourable conditions. When the element concentration is in minor or trace quantities or when the peak to background ratio is very low, then  $\sigma_k$  can be expected to be greater.

The equations above are the foundation for evaluating Type A uncertainties for EPMA quantification. There may be additional contributing factors not considered here such as overlapping peak corrections or volatile elements that should be accounted for as needed. Spectrometer reproducibility, not specifically mentioned so far, is incorporated into the counting statistics of the original X-ray counts and does not have to be added as a separate standard uncertainty. It was reported in previous heterogeneity studies that spectrometer movement for reading the X-ray peak and two backgrounds during a data acquisition results in a 30 % relative increase in the value of the standard uncertainty than when the spectrometers are stationary [14].

Type B uncertainties, if significant, should be included in the evaluation of the final uncertainties assigned to the  $k$ -values. The manufacturers' specifications such as the uncertainty of the current and the time readings and the impurity of standards are Type B uncertainties that should be included in the combined standard uncertainties determined above. If the information is not available and there is no reliable evaluation of the uncertainty, it should be left out until such time as the information becomes available.

## 6. COMBINED STANDARD UNCERTAINTY OF THE COMPOSITION

From the measured  $k$ -value the composition in mass fraction percent is calculated using a specified ZAF or  $\varphi(\rho z)$  matrix correction procedures. Since no single combination of a correction procedure and MACs produces the best results for all elements and compositions,

care should be taken in selecting a correction procedure/MAC combination that will minimize the uncertainty in the reported composition. This is why it is valuable to be able to evaluate the results from several different combinations of correction procedures and MACs for any given

EPMA quantification. If the composition of the unknown or a material of similar composition is known, comparisons of each of the results to the accepted values will enable selection of the best procedure/MAC combination. Another guideline in selecting the best correction combination is to select one that gives a mass fraction total of  $100 \pm 1\%$  relative; but this is not a guarantee of the best choice (note that it is absolutely not acceptable in EPMA quantification of flat polished samples to normalize data to a total of 100% mass fraction; normalisation is justified only in special situations such as particle analysis where geometry and size have a significant effect on quantification results). Another way to determine the best correction procedure/MAC combination is to conduct the analysis at two or three different voltages, assuming the specimen is homogeneous in depth. The best procedure will produce similar results at all voltages.

Lifshin *et al.* [3] proposed that the  $k$ -value uncertainty of the mean can be converted to mass fraction by applying the equation proposed by Ziebold [2] for the empirical correction procedure. The equation relates the  $k$ -value to composition,  $M$ , in mass fraction, with an  $a$ -factor

$$\frac{1-k}{k} = a \left( \frac{1-M}{M} \right) \quad (18)$$

Knowing the  $a$ -factor, the variance of the mean for the composition due only to counting statistics can be determined from the equation,

$$\sigma_M^2 = M^2 \left[ \frac{I_{UCDT} + BG_{UCDT}}{n(I_{UCDT} - BG_{UCDT})^2} + \frac{I_{STDCDT} + BG_{STDCDT}}{n'(I_{STDCDT} - BG_{STDCDT})^2} \right] \left[ 1 - \frac{(a-1)M}{a} \right]^2 \quad (19)$$

where  $n$  and  $n'$  are the number of measurements from the sample and standard respectively.

If the standard uncertainty of the mean for the matrix correction procedure/MAC combination,  $\sigma_{CP}$ , can be reasonably evaluated, it can be combined in quadrature with the combined uncertainty of the mean for the estimate of the composition,  $\sigma_M$ , to determine a combined standard uncertainty for the element quantification. But if there is no way to evaluate the former standard uncertainty, it should be left out using only  $\sigma_M$  for the uncertainty in the element composition.

Beyond determining the uncertainties, the ISO/GUM also provides guidelines for expanding uncertainties as well as how to report them. Details will not be included here as these are procedures that are already used in the electron probe community.

## 7. CONCLUSIONS

We have applied the ISO/GUM, the universally accepted guide for the evaluation of measurement uncertainties, to EPMA quantification, and we have shown that the ISO/GUM equations agree with those previously published for the evaluation of the counting statistics uncertainty in quantitative EPMA. The ISO/GUM goes beyond the counting statistics uncertainties to include additional factors like manufacturers' specifications and scientific judgment in the evaluation of the uncertainty of a measurand. For basic quantitative EPMA the equations above can conveniently be used in a spreadsheet to facilitate repeated calculation of uncertainties. Not all details of the approach have been included here, so we recommend reading the original references.

## 8. ACKNOWLEDGEMENTS

Thanks to Andrew Rukhin of the NIST Statistics Engineering Division, and to Dale Newbury of the NIST Surface and Microanalysis Science Division for their valuable comments.

## 7. REFERENCES

- [ 1] Poole D M (1968) Progress in the correction for the atomic number effect. in: Quantitative electron probe microanalysis (Heinrich K F J, ed.). Washington DC, US Gov. Print. Office, *NBS Spec. Publ.* **298**: 93-131.
- [ 2] Ziebold T O (1967) *Anal. Chem.* **39**: 858-861.
- [ 3] Lifshin E, Dogonaksoy N, Sirois J and Gauvin R (1999) *Microscopy and Microanalysis* **4**: 598-604.
- [ 4] Goldstein J, Newbury D, Joy D, Lyman C, Echlin P, Lifshin E, Sawyer L and Michael J (2003) Scanning electron microscopy and X-ray microanalysis, 3rd ed. New York, Plenum Press.
- [ 5] Ancey M, Bastenaire F and Tixier R (1978) Microanalysis and scanning electron microscopy. Proc. Summer School, St-Martin-d'Herès, France, Sept. 11-16 (Maurice F, Meny L and Tixier R, eds.). Orsay, Les Editions de Physique, 1979: 319-343.
- [ 6] Heinrich K F J (1981) Electron beam microanalysis. New York, Van Nostrand.

- [ 7] Eisenhart C (1969a) Realistic evaluation of the precision and accuracy on instrument calibration systems. in: Precision measurements and calibration (Ku H H, ed.). Washington DC, US Gov. Print. Office, NBS Special Publ. 300: 21-161 to 47-187; and NBS J. Res. 67C: 161-187.
- [ 8] ISO (1995) Guide to the expression of uncertainty in measurement. Geneva, International Organisation for Standards, Guide 98-3:2008, 101 pp.  
[http://www.iso.org/iso/iso\\_catalogue.htm](http://www.iso.org/iso/iso_catalogue.htm) (listed as a Best-selling Standard)
- [ 9] Taylor B N and Kuyatt C E (1994) Guidelines for evaluating and expressing the uncertainty of NIST measurement results. Washington DC, US Gov. Print. Office, National Institute of Standards and Technology Technical Note 1297, 20 pp.  
<http://physics.nist.gov/cuu/Uncertainty/index.html>
- [10] Eisenhart C (1969b) Expression of uncertainties of final results. in: Precision measurements and calibration (Ku H H, ed.). Washington DC, US Gov. Print. Office, **NBS Special Publ. 300**: 96-1201 to 72-1204.
- [11] Ellison S L R, Rosslein M and Williams A (2000). Quantifying uncertainty in analytical measurement. EURACHEM/CITAC Guide, 2nd ed. 120 pp.  
URL: <http://www.measurementuncertainty.org> (full text html-version, free)
- [12] Kirkup L and Frenkel B (2006) An introduction to uncertainty in measurement. New York, Cambridge University Press.
- [13] Ku H H (1969) Notes on the use of propagation of errors formulas. in: Precision measurements and calibration (Ku H H, ed.). Washington DC, US Gov. Print. Office, **NBS Special Publ. 300**: 331-263 to 342-273; and **NBS J. Res. 70C**: 263-273.
- [14] Marinenko R B, Armstrong J T, Turner S, Steel E B and Stevie F A (2003) Characterization of SiGe bulk compositional standards with electron probe microanalysis. in: Characterization and metrology for ULSI technology. 2003 Conference on Characterization and Metrology for ULSI Technology, Austin, TX , March 24-28. **American Inst. of Physics (AIP) Conf. Proc. 683**: 283-242.

