

# Uncertainties in Electron Probe Microanalysis

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# What will we talk about?

- **publications on accuracy & precision applied to EPMA quantification results**
- **accuracy or precision?**
- **what is uncertainty and its importance**
- **universally accepted expression of uncertainty – ISO/GUM**
- **ISO/GUM types of uncertainties**
- **calculation of combined standard uncertainties for EPMA quantification results with examples**

# Publications

- Poole (1968), 229 binary alloys many with known comps. with WDS analysis
  - early matrix correction procedures, deviations up to 18 % rel.
- Ziebold (1967), variance of mean for WDS k-values
  - used for MDL calc. and time to achieve desired statistics
- Ancey et. al. (1979), Poisson counting statistics applied to microanalysis data
  - also applied to MDL & time
- Heinrich (1981), uncerts. assoc. with ZAF corrections
- Lifshin et. al. (1999), applied Ziebold work to EDS
  - also MDL & time, derived equation for conc. uncertainty

# Accuracy and Precision

**Accuracy and Precision are not synonymous and these terms should 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 variability, repeatability, or reproducibility.**

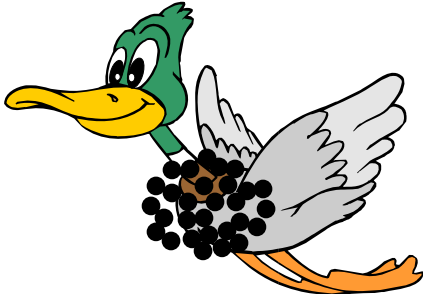
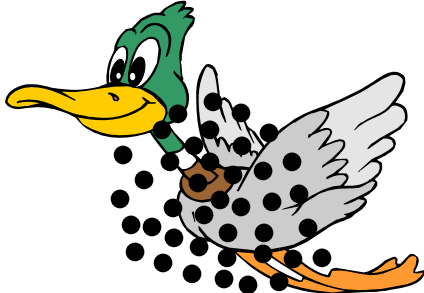
# Accuracy and Precision - Example

## Precision

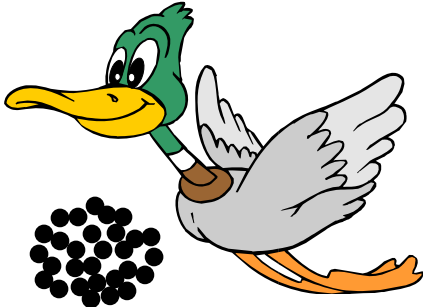
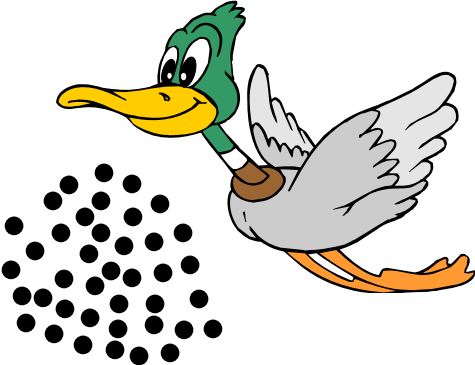
Low

High

High



Low



Accuracy

# Uncertainty

## ISO Definition –

**"parameter, associated with the results of a measurement that characterizes the dispersion of the values that could reasonably be attributed to the measurand"**

- report in either absolute units or relative terms**
- must be accompanied by a very clear explanation of how the uncertainty value was determined**

**- especially important for laboratories issuing standards or experimental results that will be used by others**

- **In the late 1980's – early 1990's there was a perceived need to evaluate and express uncertainties assigned to standards using a single universally acceptable approach.**
- **Several international organizations adopted a provisional standard developed by CIPM (International Committee for Weights and Measures) that we now refer to as ISO/GUM**

# Publications

- **ISO (1995) *Guide to the expression of uncertainty in measurement.***
- **Taylor BN, Kuyatt CE (1994) *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*, NIST Technical Note 1297(free on web).**
- **Ellison SLR, Rosslein M, Williams A, eds (2000) *Quantifying Uncertainty in Analytical Measurement*, EURACHEM/CITAC Guide. (free on web)**

# According to ISO/GUM

- a measurement is the approximation of a measurand which is only complete with a quantitative statement of uncertainty
- a combined uncertainty is a combination of multiple individual uncertainty contributions that are classified as Type A or Type B
- random and systematic effects can fall into either type of uncertainty, although Type A is generally random and Type B is generally systematic
- systematic effects should be minimized as much as possible

# **Type A –statistical evaluation 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,**
- manufacturer's specifications**

# Standard Uncertainties

- Combined standard uncertainty,  $\sigma_C$ , is a combination of standard uncertainties,
  - $\sigma_i$  for Type A components, and
  - $\sigma_j$  for Type B components
  - where  $\sigma_i$  and  $\sigma_j$  are typically estimated standard uncertainties of the mean for Type A and Type B components and are equal to the positive square roots of their respective variances,  $\sigma_i^2$  and  $\sigma_j^2$
  - likewise,  $\sigma_C$  is the positive square root of the variance,  $\sigma_C^2$

# Propagation of Uncertainty

For measurand  $y$  determined from  $N$  other quantities

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

the combined standard variance is defined as

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

a Taylor series approximation where

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

$\sigma(x_i)$  is the standard uncertainty of  $x_i$ ,

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

2<sup>nd</sup> term - sum of covariances of  $x_i$  and  $x_j$  sometimes small enough to be excluded, but should be determined, if possible

# Rules for Calculating Combined Uncertainties

For functions where variables  $x_1$  and  $x_2$  are uncorrelated and random -

determined from an addition or subtraction, where

$$y = a \cdot x_1 + b \cdot x_2$$

with sensitivity coefficients  $a$  and  $b$

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

standard uncertainties are summed in quadrature to obtain combined standard variance for  $y$

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

determined by multiplication or division, where

$$y = a \cdot x_1 \cdot x_2$$

with sensitivity coefficients  $ax_2$  and  $ax_1$

$$\frac{\partial y}{\partial x_1} = a \cdot x_2 \quad \frac{\partial y}{\partial x_2} = a \cdot x_1$$

standard relative uncertainties are summed in quadrature to obtain standard relative variance for  $y$

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

# Calculating Uncertainties in EPMA Quantification

- **Need a combined standard uncertainty for**
  - **dead time correction,**
  - **beam drift correction,**
  - **k-value determination**
  
- **Calculating the uncertainty of the mean**
  - $\sigma^2/N$  = **standard variance of the mean**
  - $\sigma/(N)^{1/2}$  = **standard uncertainty of the mean**

# Calculation of Deadtime

Equation for calculating deadtime-corrected count rate,  $I$ , is

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

$\tau =$  deadtime  
 $I' =$  observed or measured count rate  
in counts/s

the count rate,  $I$ , is proportional to the beam current,  $i$

$$I = ri \quad r = \text{constant}$$

so the equation can be written

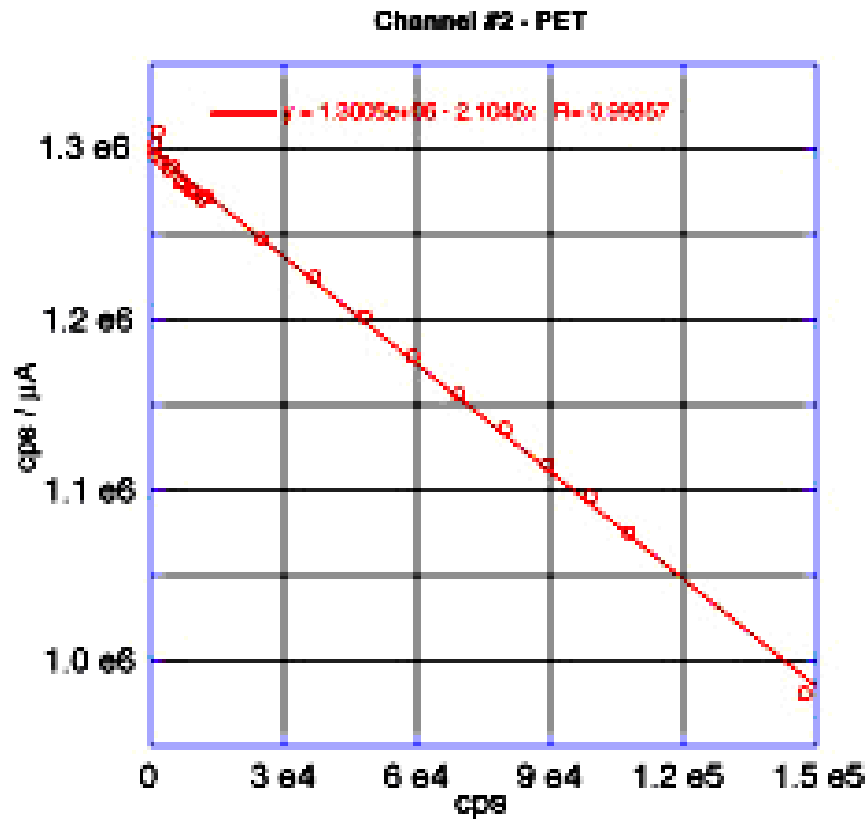
$$\frac{I'}{i} = r(1 - \tau I')$$

plot of  $I'/i$  in cts/s/nA vs  $I'$  in cts/s det. at diff. values of  $i$  – get straight line plot with slope of  $(-r\tau)$  and intercept  $r$ , so  $\tau$  estimated as minus ratio of slope to intercept

# A Deadtime Determination

CrK $\alpha$  with a PET crystal, 15 kV

Data fit to a straight line with a least squares linear fit



Channel 2 - PET

Slope = 2.1045

Intercept =  $1.3005 \times 10^6$

Dead time =  $1.62 \mu$ s

# Calculation of Deadtime Uncertainty

Results of the DT calculation for  $\text{CrK}\alpha$  with PET crystal,  
15 kV, 10 pts. at 50 nA to 600 nA

$$\tau = 2.098 \mu\text{s} \quad \sigma_{\tau} = 0.087 \mu\text{s}$$

Calculations—

1<sup>st</sup> term of the variance calculation by propagation of uncertainty (Taylor Series above) for the functional form where  $\bar{x} = I'$  and  $\bar{y} = I''/i$

$$\frac{\bar{x}}{\bar{y}} \text{ from Ku (1969) is } \left( \frac{\bar{x}}{\bar{y}} \right)^2 \left( \frac{s_{\bar{x}}^2}{\bar{x}^2} + \frac{s_{\bar{y}}^2}{\bar{y}^2} \right)$$

using mean values of variables  $x$  and  $y$ , and variances of the mean (or std variances of the mean),  $s_{\bar{x}}^2$  and  $s_{\bar{y}}^2$  respectively.

**From linear ordinary least squares,**

**the equation for the variance of the slope,  $-r\tau$ , is**

$$\text{Var}(-r\tau) = \sigma^2 \left( \frac{1}{\sum_{i=1}^n (x_i - \bar{x})^2} \right) = s_{\bar{x}}^2$$

**the equation for the variance of the intercept,  $r$ , is**

$$\text{Var}(r) = \sigma^2 \left( \frac{1}{n} + \frac{\bar{x}^2}{\sum_{i=1}^n (x_i - \bar{x})^2} \right) = s_{\bar{y}}^2$$

**where  $\sigma^2$  is the residual variance from the least squares fit.**

**Covariance between slope of fitted line and intercept should be determined. For function form**

$$\frac{\bar{x}}{\bar{y}} \quad \begin{array}{l} 2^{\text{nd}} \text{ order correction term} \\ \text{(Ku, 1969) estimated by} \end{array} \quad \left( \frac{\bar{x}}{\bar{y}} \right)^2 \left( -2 \frac{S_{\bar{x}\bar{y}}}{\bar{x}\bar{y}} \right)$$

**where  $S_{\bar{x}\bar{y}}$  is the covariance of  $\bar{x}$  and  $\bar{y}$ , or, in our case, between the slope and intercept. From ordinary least squares fit,**

$$Cov(S_{\bar{x}\bar{y}}) = \sigma^2 \left( \frac{-\bar{x}^2}{\sum_{i=1}^n (x_i - \bar{x})^2} \right)$$

**Calc. covariance correction is -0.0025  $\mu\text{s}$ , or  $\sim 0.1\%$  rel. to the DT, that is very small.**

# Application of ISO/GUM to WDS-EPMA Data

## Quantitative Analysis of $\text{GeK}\alpha$ in a SiGe bulk specimen

- 15 kV, 30 nA, TAP crystal, 10 points, 40 s each
- heterogeneity tested – 0.92 % mass fraction
- background (BG) from both sides of peak
- beam current (BC) read after each set of peak + BG readings

# Beam Current Drift Correction

$$I_C = I' \times \frac{i_{Sc}}{i_{obs}}$$

$I_C$  = avg. X-ray cts. corrected for BC drift  
 $I'$  = measured X-ray cts. at the observed current,  $i_{obs}$ , and  $i_{Sc}$  is the nominal current, or the 1st current reading in the data set (treated as a known constant)

$$I_C = 138,927 \text{ cts/40 s for the Ge K}\alpha \text{ peak}$$

**Uncertainty – add relative uncertainties of mean in quadrature**

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

$\sigma_{I_C}$  = combined std. uncertainty of mean for corrected X-ray cts.

$\sigma_{i_{obs}}$  = std. uncertainty of mean for obs. current

$\sigma_{I'}$  = std. uncertainty of mean for the obs. X-ray cts.

$$\sigma_{I_C} = 210 \text{ cts/40s}$$

# Comparison of Corrected and Uncorrected GeK $\alpha$ X-ray Counts

	Symbol	Mean Value (cts/40 s)	Std. Uncertainty of the mean (cts/40 s)
Uncorrected on-peak X-ray cts.	$I'$	138953	210
Beam Current Drift Corrected X-ray cts.	$I_C$	138927	210

# Combined Standard Uncertainty Calculation for Deadtime and Current Drift Correction for GeK $\alpha$

Combined standard uncertainty of mean for current and deadtime-corrected X-ray counts,  $\sigma_{CDT}$ , is

$$\sigma_{CDT} = \sqrt{\left[ \frac{(I_C)^2}{(1 - \tau(I_C))^2} \right]^2 \sigma_{\tau}^2 + \left[ \frac{1}{(1 - \tau(I_C))^2} \right]^2 \sigma_{I_C}^2} = 211 \text{ cts/40 s}$$

For the Ge standard wafer,  $I_C = 497168 \text{ cts/40 s}$

$$\sigma_{I_C} = 657 \text{ cts/40 s}$$

$$\sigma_{CDT} = 675 \text{ cts/40 s}$$

# Uncertainty of the Mean Ge k-value in SiGe Alloy

**Determination of k-value where  $I_{UCDT}$  and  $BG_{UCDT}$  are the beam current corrected and deadtime corrected X-ray counts for the peak and the background of the unknown, and  $I_{STDCDT}$  and  $BG_{STDCDT}$  are the beam current corrected deadtime corrected X-ray counts for the peak and background of the standard.**

$$k = \frac{I_{UCDT} - BG_{UCDT}}{I_{STDCDT} - BG_{STDCDT}}$$

**BG taken from interpolation of readings from both sides of peak.**

# Uncertainty of the mean Ge k-value (cont'd)

experimental variance of mean for intensity of unknown (numerator)

$$\sigma_{IU}^2 = \sigma_{I-U_{CDT}}^2 + \sigma_{BG-U_{CDT}}^2$$

experimental variance of mean for intensity of standard (denominator)

$$\sigma_{I_{STD}}^2 = \sigma_{I-STD_{CDT}}^2 + \sigma_{BG-STD_{CDT}}^2$$

combined standard uncertainty for the k-value

$$\sigma_k = k \sqrt{\frac{\sigma_{IU}^2}{\left(I_{UCDT} - BG_{UCDT}\right)^2} + \frac{\sigma_{I_{STD}}^2}{\left(I_{STD_{CDT}} - BG_{STD_{CDT}}\right)^2}}$$

# Uncertainty of the mean Ge k-value (cont'd)

Equation above same as reported by Ziebold in 1967 and later used by Lifshin in 1999, but we have included the deadtime and current drift corrections. The data below was used to calculate the k-value with the combined std. uncertainty of the mean.

$$\text{k-value} = 0.2785 \pm 0.00059 (0.21 \%)$$

<b>Counts/40 s <math>\pm</math> Standard Combined Uncertainty of Mean</b>		
<b>Specimen</b>	<b>GeL<math>\alpha</math> - on Peak</b>	<b>Background</b>
<b>SiGe Alloy</b>	136926 $\pm$ 210	841 $\pm$ 25
<b>Ge Wafer (Standard)</b>	497167 $\pm$ 657	1262 $\pm$ 23

# Comments

- **We have obtained a very small uncertainty**
  - **favorable sample homogeneity**
  - **good on-peak counting statistics and low BG counting statistics**
  - **no spectral interferences**
  - **good current stability**
- **Not always possible in EPMA quantification— so this is where detailed calculation of uncertainties will be important**
  - **on-peak counting statistics are low**
    - **element concentration is minor or trace**
    - **peak/BG ratio is low**
    - **sample sensitive to electron beam (use low currents)**
  - **deadtime change between sample and standard**
  - **current drift during data acquisition**

# Type B Uncertainties

- **So far we have considered Type A**
- **Will need to include Type B**
  - **manufacturer's specs**
    - uncertainty in current and time readings
  - **purity of standard**
  - **matrix correction procedure**

# Evaluate Matrix Correction Procedures

- **Want to minimize uncertainty in final result**
- **Evaluate multiple ZAF or  $\phi(\rho z)$  matrix correction procedures with different MACs**
  - **use a similar material of known composition to the unknown**
  - **look for a mass fraction total of 100 %  $\pm$  1 % rel. with no normalization (not acceptable in EPMA quantification unless special case, like particle analysis)**
  - **analyze at different voltages (sample homogeneous in depth)**

# Expression of Uncertainty in Mass Fraction

Lifshin proposed using the Ziebold empirical correction equation

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

relating the k-value to composition, M, in mass fraction, with an a-factor. If M is known or calculated from the measured k-value,  $\alpha$  can be determined. Then the uncertainty in mass fraction,  $\sigma_M$ , can be determined from another Ziebold equation,

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

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

**If the standard uncertainty of the mean,  $\sigma_{CP}$ , for the matrix correction procedure/MAC combination can be reasonably evaluated (in mass fraction), 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.**

# Conclusions

- **Applied ISO/GUM to EPMA quantification**
- **Shown that ISO/GUM calculations agree with previously published equations of Ziebold and Lifshin**
- **Discussed that ISO/GUM goes beyond counting statistics uncertainties to include other factors in the evaluation of uncertainties**
  - **scientific judgement, manufacturers specs, reports, previous calculations**
- **Recommend establishing a spreadsheet for calculations that can be used repeatedly**
- **Not all details of ISO/GUM, like expanded standard uncertainties and report procedures, have been included so please read original references**