

# Measurement Uncertainty and Material Conformance Probability

Analytical laboratories often request accreditation according to norms such as ISO 17025. This kind of accreditation elevates the importance of estimating and reporting measurement uncertainty. Thermo Scientific™ OXSAS software helps achieve this goal by offering great functions for displaying, reporting and transmitting measurement uncertainty due to the calibration and sample measurement on a Thermo Scientific OES or XRF spectrometer.

## Introduction

Measurement uncertainty plays an important role in making decisions after measuring materials characteristics, managing risk related to non-conform materials, developing tolerances, selecting measurement methods, developing capability statements, achieving laboratory accreditation, testing hypothesis, establishing calibration intervals and communicating technical variables. Therefore, uncertainty estimated should realistically reflect the measurement process under investigation or evaluation.

While the guide to the expression of uncertainty in measurement (GUM<sup>[note 1]</sup>) provides general rules for analyzing and communicating measurement uncertainty, it does not focus on providing step-by-step instructions for evaluating very specific measurement processes. As a result, testing personnel may find the measurement uncertainty assessment difficult or may be confused trying to apply these principles to specific measurement scenarios.

The OXSAS software offers fully integrated solutions to this problem.

## Estimating calibration uncertainty from calibration data

The calibration model of OES spectrometer is based on equation [1]:

$$[1] \quad C = \left( \sum_{i=0}^{\max 3} A_i I^i + \sum_j^n a_j C_j \right) \left( 1 + \sum_k^m m_k C_k \right)$$

In the above equation [1],  $A_i$  are the polynomial coefficients multiplying the powers of the intensity  $I$ ,  $a_j$  ( $a_j < 0$ ) are the additive

correction coefficients multiplying the concentration of the interfering elements  $C_j$  and  $m_k$  are the multiplicative correction coefficients multiplying the concentration of the interfering elements  $C_k$ . All the coefficients (polynomial and corrections) are calculated with the OXSAS multivariable regression (MVR) routine in the same time.

In rare cases the calibration model is linear, without corrections, for example for the calibration curves of ultra-trace concentration levels in pure metals and in precious metals. In all the other cases the calibration model is far from linear and the confidence interval can't be directly calculated. However, despite the complexity of the calibration model, there is an equation that is linear and this is the calibration correlation curve equation [2]:

$$[2] \quad C_{calculated} = a \cdot C_{certified} + b$$

where  $a$  is the slope of the curve and  $b$  is the intercept. For a perfect correlation  $a$  equals 1 and  $b$  equals 0.

The OXSAS method is based on the use of this correlation curve and it calculates the calibration uncertainty through the confidence interval of the curve described by equation [2] instead of trying to calculate for the complex equation described by equation [1].

The confidence interval is noted  $CI$ . Then  $1/2CI(C)$  is calculated as the half width of the confidence interval or the confidence interval's limit at the concentration level  $C$  as a function of the concentration level  $C$ , as described by equation [3]:

$$[3] \quad \frac{1}{2}CI(C) = t_{\alpha/2, n-k} \cdot SEE \cdot \sqrt{\frac{1}{n} + \frac{(C - \bar{C})^2}{\sum_{j=1}^n (C_{certified_j} - \bar{C})^2}}$$

where:

$$[4] \quad SEE = \sqrt{\frac{\sum_{j=1}^n (C_{certified_j} - C_{calculated_j})^2}{n - k}}$$

The  $SEE$  is the Standard Error of Estimate of the calibration curve,  $n$  is the number of samples used in regression,  $k$  is the total number of coefficients for polynomial (curve degree) and corrections (interferences) used in regression,  $t$  is the Student factor for  $\alpha/2$  confidence level (and  $1-\alpha$  double sided probability) and  $n-k$  degrees of freedom,  $C_{certified_j}$  is the certified concentration of sample  $j$  and  $\bar{C}$  is the average of the certified concentrations of the  $n$  samples as calculated by equation [5]:

$$[5] \quad \bar{C} = (\sum_{j=1}^n C_{certified_j}) / n$$

In case of weighted calibration, each pair  $(I_j, C_j)$  is weighted by the weight  $w_j$  and equation [3] changes to equation [6]:

$$[6] \quad \frac{1}{2}CI(C) = t_{\alpha/2, n-k} \cdot SEE \cdot \sqrt{\frac{1}{\sum_{i=1}^n w_i} + \frac{(C - \bar{C})^2}{\sum_{j=1}^n w_j (C_{certified_j} - \bar{C})^2}}$$

with:

$$[7] \quad \bar{C} = (\sum_{j=1}^n w_j \cdot C_{certified_j}) / \sum_{j=1}^n w_j$$

The confidence interval has a minimum difference between the confidence limits at the concentration  $C$  and has maximum values at the low and high concentration ends.

The factors that affect the confidence interval are the desired confidence level  $1-\alpha$ , the number of samples  $n$  and the  $SEE$ . If more samples are used in the calibration and with a better the  $SEE$ , the width of the  $CI$  decreases. This shows the importance of the quality of the calibration process.

The confidence interval estimate gives an indication of how much uncertainty there is in our estimate of the true mean. The narrower the interval, the more precise our estimate.

The advantage of this approach is that the correlation curve is independent on the mathematical model and has the same

$SEE$  as the calibration curve. The number of the degrees of freedom is reported from the concentration versus intensity calibration curve. In fact  $SEE$  is decoupled from the calibration model and reflects the goodness of the fit.

### Combining repeatability and calibration bias uncertainty

The GUM method evaluates and combines the variances of each measurement process error distribution. The combined uncertainty is computed by taking the square-root of the combined variance. In this case, as repeatability and calibration uncertainty are non correlated input quantities, this leads to:

$$[8] \quad U = 2u$$

The expanded uncertainty is defined as:

$$[9] \quad u = \sqrt{SD^2 + CI^2 / 4}$$

which corresponds to a level of confidence of 95%. This is reported in OXSAS software as  $U(95\%)$ .

The measurement result is reported by using equation [10]:

$$[10] \quad C_{result} = C_{measured} \pm U$$

which becomes equation [11]:

$$[11] \quad C_{result} = C_{measured} \pm 2\sqrt{SD^2 + CI^2 / 4}$$

OXSAS software allows also this combined uncertainty to be printed or transmitted to remote computers as desired by the user.

The combined uncertainty is reported in the analysis screen of the analytical software OXSAS as in Figure 1 example.

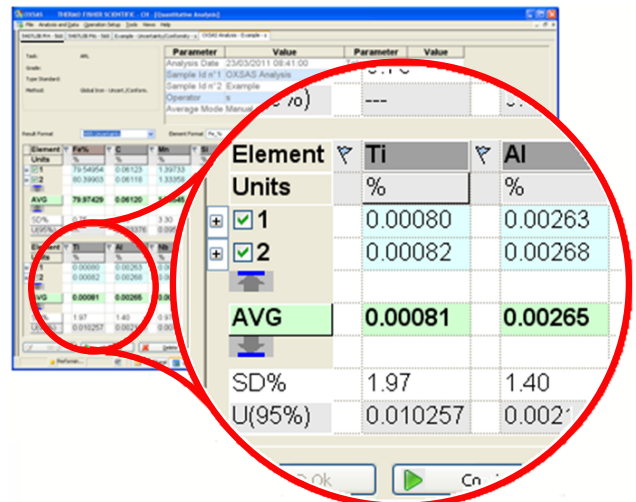


Fig. 1: Example of OXSAS analytical measurement screen reporting the standard deviation along with the Uncertainty  $U(95\%)$

## Evaluating the measurement uncertainty with X-ray instruments

For XRF spectrometry, final results are often calculated based on a single sample measurement. In this case, the uncertainty is evaluated using the theoretical standard deviation calculated by equation [13] where  $a_1$  is the slope of the base curve,  $I$  is the intensity in counts/seconds and  $t$  is the counting time in seconds. Raw intensity from instrument is used when the line is subject to background subtraction or overlap calculation.

$$[12] \quad SD = a_1 \cdot \sqrt{\frac{I}{t}}$$

The equation [13] is used in case of ratio with an internal standard intensity  $I_{std}$

$$[13] \quad SD = a_1 \cdot \frac{I}{I_{std}} \cdot \sqrt{\left(\sqrt{\frac{I}{t}} / I\right)^2 + \left(\sqrt{\frac{I_{std}}{t_{std}}} / I_{std}\right)^2}$$

The Confidence Interval  $CI$  is calculated as described in the previous chapter (equation [3]) if the alphas coefficients are calculated during base curve regression (MVR). If these alphas coefficients are calculated outside the curve regression (Theoretical Alphas), the factor  $k$  refers only to the coefficients of the base curve.

## Compliance probability for conformance testing

The conformance testing procedure used by OXSAS is based on the technical report ASME B89.7.4.1-2005 [note 2]. This approach is applied in work-piece inspections, instrument verification and general conformance tests where uncertain numerical test results are compared with specific requirements.

From chemical composition point of view, a given product for a set of given elements is considered compliant or conforms to a specification, if the result of the analysis is within the specification limits. For a given element, the specification limits are defined by the upper limit  $T_U$  and the lower limit  $T_L$ .

The probability that for a given element the measurement result  $x_m$  is compliant to a specification is expressed through the probability for conformance  $P_c$ :

$$[14] \quad P_c = \Phi\left(\frac{T_U - x_m}{u_c}\right) - \Phi\left(\frac{T_L - x_m}{u_c}\right)$$

where  $\Phi$  is the standard normal cumulative distribution function and  $U_c$  is the combined standard uncertainty defined by the equation [8]. The standard normal cumulative distribution function  $\Phi(z)$  gives the probability that a standard normal variable assumes a value in the interval  $[0, z]$ .

The product is considered to conform to a specification if all the elements are within the specification ranges. However, due to the measurement uncertainty, when the measurements result is near to any specification limit, the conformance probability is less than 100%.

This functionality is also implemented in OXSAS for the official limits of the grade specification and, whenever selected, for the inner control limits.

Figure 2 shows an example of the analysis screen when grade assessment is performed: the elements outside the specification range are highlighted and the compliance probability is shown together with the measurement uncertainty.

As for the Uncertainty, the compliance probability can be printed or transmitted to remote computers as desired by the user.

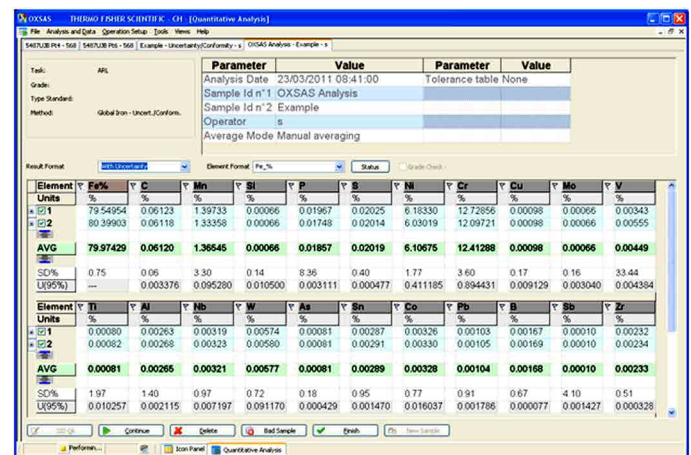


Fig. 2: Example of XRF analysis with theoretical standard deviation and conformance probability together with uncertainty and material (grade) specification limits



In order to understand the case when the measurement results lie near the specification limit, Table 1 shows a numerical example of the analysis made with an ARL OES metals analyzer. It presents the simulation of the conformance probability applied for the elements Cr and Ni in the AISI 304 alloy, for which the specifications for Cr is between 18 and 20% and for Ni is between 8 and 10.5%.

The uncertainties at 19% Cr and at 9.25% Ni (i.e. in the middle of the range) were evaluated as being  $u_{Cr} \sim 0.15\%$  and  $u_{Ni} \sim 0.07\%$ , respectively. With these values the product conformance in function of the measured concentration shows the following probabilities (between 0% and 100%).

The conformance probability is 100% in the middle of the specification range, decreases down to 50% at the limits of the range and further decreases rapidly to 0% outside of these limits. In the example, a probability higher than 95% can for instance be obtained for Cr at 18.3% and for Ni at 8.15%. This information combined with the need to minimize costly alloying elements and assuring at the same time that the product is conform, allows defining safeguard limits for the production.



Cr	Measured Concentrations (%)	18	18.1	18.2	18.3	18.4	18.5	...	19.5	19.6	19.7	19.8	19.9	20
	Conformance Probability (%)	50	74.2	90.3	97.7	99.5	100	100	100	99.5	97.7	90.3	74.2	50
Ni	Measured Concentrations (%)	8	8.05	8.1	8.15	8.2	8.25	...	0.25	10.3	0.35	10.4	0.45	10.5
	Conformance Probability (%)	50	75.8	91.9	98.2	99.7	100	100	100	99.7	98.2	91.9	75.8	50

**Table 1: Conformance probability of AISI 304 in function of the measured content of Cr and Ni with an ARL OES metals analyzer**

[note 1] ISO/IEC Guide 98-3:2008 Guide to the Expression of Uncertainty in Measurement (GUM)

[note 2] ASME B89.7.4.1-2005 (Technical Report) Measurement Uncertainty and Conformance Testing: Risk Analysis

Find out more at [thermofisher.com/oxsas](https://thermofisher.com/oxsas)

**ThermoFisher**  
SCIENTIFIC