APPLICATION GUIDE 1

Interpretation of measurement results on CETEM certified reference materials

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1. SCOPE

Briefly describes the procedure for assessing measurement bias in a laboratory, recommended in the ISO Guide 33 [1], and exemplifies its application on a CETEM´s certified reference material.

2. INTRODUCTION

Checking bias can be performed as part of ensuring the quality of measurement results, method validation, or both. For bias checking, it is essential that the reference against which the bias is checked is reliable and metrologically traceable[1].

3. CHECKING BIAS

3.1. The certified reference material (CRM) to be used for bias assessment is suitable if the type of material and the properties of interest are relevant for the intended use.

3.2. Independent replicate measurements should be carried out using the same CRM and targeting the same measurand.

3.3. After discarding technically invalid values the measurement results could, if necessary, be scrutinized for possible outliers using the rules described in ISO 5725-2 [2].

3.4. The observed difference between the measured value $\overline{X}_m$ and the property value stated on the certificate V_{CRM} is calculated as

$$\Delta = \left| \overline{X}_m - V_{CRM} \right|$$

3.5. The standard uncertainty associated with the absolute difference u_Δ is calculated according to

$$u_\Delta = \sqrt{u_m^2 + u_{CRM}^2}$$

where:

u_m is the standard uncertainty associated with the value obtained by measuring the CRM.

u_{CRM} is the standard uncertainty associated with the property value of the CRM, that is obtained by dividing the expanded uncertainty by the coverage factor k (both are explicitly stated on the certificates of CETEM CRMs).

3.6. The expanded uncertainty associated with the absolute difference U_Δ with coverage factor 2, corresponding to a level of confidence of approximately 95%, is obtained by

$$U_\Delta = 2 \times u_\Delta$$

3.7. If $\Delta \leq U_\Delta$, then the measured and property values are consistent with one another within their respective uncertainties. As the property value of the CRM is metrologically traceable to some stated reference, ideally the SI, under this condition the result obtained for the CRM confirms the metrological traceability of the results obtained from the measurement procedure [1].

4 STANDARD UNCERTAINTY ASSOCIATED WITH THE MEASURED VALUE

4.1. The Guide to the expression of uncertainty in measurement – GUM 2008 [3] provides general rules for evaluating and expressing uncertainty in measurement. The applications of these concepts in chemical measurement are addressed in the EURACHEM/CITAC Guide CG 4 “Quantifying Uncertainty in Analytical Measurement” [4].

4.2. In practice, the measurement uncertainty may arise from many possible sources, including examples such as incomplete definition of the measurand, sampling, matrix effects and interferences, environmental conditions, uncertainties of masses and volumetric equipment, reference values, approximations and assumptions incorporated in the measurement method and procedure, and random variation. In estimating the overall uncertainty, it may be necessary to take each source of uncertainty and treat it separately to obtain the contribution from that source [4].

4.3. In the absence of an overall uncertainty estimative, one of the following approximations ranked in decreasing usefulness can be used [5]:

- the standard deviation under intermediate precision conditions (e.g. same location and over an extended period of time, but may include other conditions involving changes such as new calibration, calibrators, operators and measuring systems) as determined, for example, from control charts;
- the standard deviation under reproducibility conditions (e.g. combination of various factors

such as operators, equipment, laboratories, time etc) obtained from other sources such as CRM´s certificates or interlaboratory comparison reports, assuming the laboratory's performance is equivalent to the performance of the participants in the study in question.

- the standard deviation of the measurements, which typically underestimates the real uncertainty.

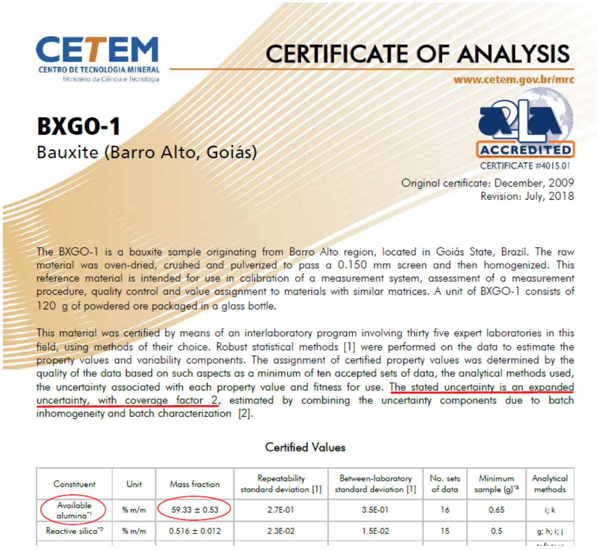
5. EXAMPLE: Checking bias of the measurement of the available alumina content in the CETEM´s bauxite CRM BXGO-1

5.1. Certificate information (Figure1)

$$V_{CRM} = 59.33\ \%\ (m/m)$$

$$U_{CRM} = 0.53\ \%(m/m)$$

$$k = 2$$



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CERTIFICATE OF ANALYSIS

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BXGO-1
Bauxite (Barro Alto, Goiás)

ACCREDITED
CERTIFICATE #4015.01

Original certificate: December, 2009
Revision: July, 2018

The BXGO-1 is a bauxite sample originating from Barro Alto region, located in Goiás State, Brazil. The raw material was oven-dried, crushed and pulverized to pass a 0.150 mm screen and then homogenized. This reference material is intended for use in calibration of a measurement system, assessment of a measurement procedure, quality control and value assignment to materials with similar matrices. A unit of BXGO-1 consists of 120 g of powdered ore packaged in a glass bottle.

This material was certified by means of an interlaboratory program involving thirty five expert laboratories in this field, using methods of their choice. Robust statistical methods [1] were performed on the data to estimate the property values and variability components. The assignment of certified property values was determined by the quality of the data based on such aspects as a minimum of ten accepted sets of data, the analytical methods used, the uncertainty associated with each property value and fitness for use. The stated uncertainty is an expanded uncertainty, with coverage factor 2, estimated by combining the uncertainty components due to batch inhomogeneity and batch characterization [2].

Certified Values

Constituent	Unit	Mass fraction	Repeatability standard deviation [1]	Between-laboratory standard deviation [1]	No. sets of data	Minimum sample (g)*3	Analytical methods
Available alumina*1	% m/m	59.33 ± 0.53	2.7E-01	3.5E-01	16	0.65	i; k
Reactive silica*2	% m/m	0.516 ± 0.012	2.3E-02	1.5E-02	15	0.5	g; h; i; j

Figure 1 – BXGO-1 certificate

5.2. Calculation of the standard uncertainty associated with the property value of the CRM

$$u_{CRM} = \frac{0.53}{2} = 0.265\ \%(m/m)$$

5.3. Measurement results of available alumina content, by caustic digestion (143°C) + CDTA / titimetry, performed under intermediate precision condition, e.g., in six different days

$$Day\ 1 = 60.10\ \%(m/m);\ Day\ 2 = 59.40\ \%(m/m)$$

$$Day\ 3 = 59.60\ \%(m/m);\ Day\ 4 = 59.44\ \%(m/m)$$

$$Day\ 5 = 59.80\ \%(m/m);\ Day\ 6 = 59.35\ \%(m/m)$$

5.4. Calculation of the mean value and standard deviations obtained by measuring the CRM

$$\overline{X} = 59.62\ \%(m/m)$$

$$DP = 0.289\ \%(m/m)$$

$$DP_{\overline{X}} = \frac{0.289}{\sqrt{6}} = 0.118\ \%(m/m)$$

5.5. Estimative of the standard uncertainty associated with the value obtained by measuring the CRM

$$u_m = DP_{\overline{X}} = 0.118\ \%\ (m/m)$$

5.6. Calculation of the difference between the measured value and the property value stated on the certificate

$$\Delta = |59.62 - 59.33| = 0.29\ \%(m/m)$$

5.7. Calculation of the standard uncertainty associated with the absolute difference

$$u_\Delta = \sqrt{0.118^2 + 0.265^2} = 0.29\ \%(m/m)$$

5.8. Calculation of the expanded uncertainty associated with the absolute difference

$$U_\Delta = 2 \times 0.29 = 0.58\ \%(m/m)$$

5.9. As $\Delta \leq U_\Delta$, the mean value obtained by measuring the CRM is not significantly different from the certified property value.

REFERENCES

[1] ISO Guide 33:2015 - Reference materials - Good practice in using reference materials.

[2] ISO 5725-2:2019 - Accuracy (trueness and precision) measurement methods and results – Part 2: Basic method for determination of repeatability and reproducibility of a standard measurement method.

[3] BIPM JCGM – 100:2008 - Evaluation of measurement data - Guide to the expression of uncertainty in measurement.

[4] Ellison S.L.R. & Williams A. eds., Eurachem/CITAC guide: Quantifying Uncertainty in Analytical Measurement, Third edition (2012). ISBN 978-0-948926-30-3. Available on www.eurachem.org/index.php/publications/guides.

[5] Linsinger T. ERM Application Note 1 (2010) - Comparison of a measurement result with the certified value. Available on https://crm.jrc.ec.europa.eu/e/132/User-support-Application-Notes.