Determination of assigned value

Consensus values from participants is the method used for the determination of the assigned values. With this approach, the assigned value X for the test material used in a round of a proficiency testing scheme is the robust average of the results reported by all the participants in the round, calculated using Algorithm A in Annex C of ISO 13528:2015.

This algorithm yields robust values of the average and standard deviation of the data to which it is applied.

Outliers are statistically treated with the use of robust statistical methods (determination of the consensus mean and standard deviation, without the need for outlier removal).

- Denote the p items of data, sorted into increasing order, by:
  $x_1, x_2, \ldots, x_i, \ldots, x_p$
- Denote the robust average and robust standard deviation of these data by x* and s*.
- Calculate initial values for x* and s* as:
  $x^* = \text{median of } x_i \ (i = 1, 2, \ldots, p)$
  $s^* = 1.483 \text{ median of } x_i - x^* \ (i = 1, 2, \ldots, p)$
- Update the values of x* and s* as follows. Calculate: $\delta = 1.5s^*$
- For each x_i ($i = 1, 2, \ldots, p$), calculate:

$$x_i^* = \begin{cases} x^* - \delta, & \text{if } x_i < x^* - \delta \\ x^* + \delta, & \text{if } x_i > x^* + \delta \\ x_i, & \text{otherwise} \end{cases}$$

- Calculate the new values of x* and s* from:
  $x^* = \sum x_i^* / p$

$$s^* = 1{,}134\sqrt{\sum\left(x_i^* - x^*\right)^2 / (p - 1)}$$

where the summation is over i.

The robust estimates x* and s* may be derived by an iterative calculation, i.e. by updating the values of x* and s* several times using the modified data, until the process converges. Convergence may be assumed when there is no change from one iteration to the next in the third significant figure of the robust standard deviation and of the equivalent figure in the robust average.

The **standard uncertainty** of the assigned value u_X is estimated as:

$$u_X = 1.25 \times s^* / \sqrt{p}$$

where s is the robust standard deviation of the results and p the number of results*.

Procedure for homogeneity check

a) At least 6 key measurands are chosen which will be sensitive to heterogeneity between the samples. Behavior of these 6 measurands provide a good indication of stability/homogeneity of the remaining measurands, and hence assessment will be limited to that subset of 6 measurands only (ISO 13528:2015, clause 6.1.3).
b) A suitable number of samples (at least 10 for homogeneity and 3 for stability) from each of a high and low concentration batches in their final packaged form are selected at random.
c) The 6 measurands are assayed in 2 test aliquots of each sample in a random order, completing the whole series of measurements under repeatability conditions.
d) The general average $\bar{x}_{..}$, within-samples standard deviation s_w, and between-samples standard deviation s_s, are calculated as shown below:

The data from a homogeneity check are represented by $x_{t,k}$

where

t represents the proficiency test item (t = 1,2........, g)

k represents the test portion (k = 1,2....., m)

Define the sample averages as:

$$\overline{x}_t = \left(x_{t,1} + x_{t,2}\right) / 2$$

and the between-test-portion ranges as:

$$w_t = \left|x_{t,1} - x_{t,2}\right|$$

Calculate the general average:

$$\overline{\overline{x}} = \frac{1}{g}\sum_{t=1}^{g} \overline{x}_t$$

Estimate the standard deviation of sample averages:

$$s_{\overline{x}} = \sqrt{\sum_{t=1}^{g}\left(\overline{x}_t - \overline{\overline{x}}\right)^2 \Big/ (g-1)}$$

and the within-sample standard deviation:

$$s_w = \sqrt{\sum_{t=1}^{g} w_t^2 \Big/ (2g)}$$

Finally, estimate the between-sample standard deviation as:

$$s_s = \sqrt{\max\left(0, s_{\overline{x}}^2 - s_w^2 / 2\right)}$$

Assessment criterion for a homogeneity check

Duplicate values are inspected for a trend or for apparent differences

The between-samples standard deviation s_s is compared with the standard deviation for proficiency assessment σpt. The samples may be considered adequately homogeneous if: $s_s \leq 0.3\ \sigma pt$

A robust estimate of the standard deviation of the results reported by all the participants, calculated using a technique listed in Annex C of ISO 13528:2015, is used to calculate the **standard deviation for proficiency assessment** (σpt) (ISO 13528:2015, clauses B.2.2 and 8.6).

Procedure for a stability check

a) Six months after the homogeneity check, stability study is conducted. This 6-month period is similar to the time delay that is experienced by the samples tested by the participants in the proficiency test.
b) Each of the three stability-coded vial is reconstituted and divided into two similar aliquots
c) Taking the 2 test portions in a random order, obtain a measurement result $y_{t,k}$ on each, completing the whole series of measurements under repeatability conditions. All 23 analytes are measured in the 2 aliquots of each of the three samples.
d) The general average $\bar{y}_{.,.}$ of the measurements obtained in the stability test is calculated.

Assessment criterion for a stability check

The general average of the measurements obtained in the homogeneity check is compared with the general average of the results obtained in the stability check. The samples may be considered adequately stable if:

$|\bar{x}_{.,.} - \bar{y}_{.,.}| \leq 0.3\ \sigma pt.$