

PERFORMANCE EVALUATION CRITERIA

Confirmatory analyses:

In confirmatory analysis, the compounds are generally detected by AAS, AES, MS, etc...

Elaboration of laboratory data

In the statistical data processing, all the data submitted by the participants are elaborated considering two decimal places. In case there are not declared decimal places, they are considered as corresponding to "zero" (E.g. 25=25,00 - 25,3=25,30 - 25,32=25,32).

Concerning the use of decimal places, we advise you to consult document EA4/16, point 7.6.

The Assigned Value x_{pt} :

The Assigned Value x_{pt} , is the value attributed to a particular property of proficiency test items (definition from ISO 13528).

The procedure for determining the Assigned Value x_{pt} is described below.

After excluding results that are identified as invalid the data population is checked for normality and for the presence of outliers by applying appropriate statistics and visual presentations. For both spiked and incurred test materials, x_{pt} represents the value of concentration obtained from Algorithm A (ISO 13528) or from the median. The chosen value will be reported in the Final Report.

The value is not assigned when $p < 8$, where "p" is the number of data after invalid results rejection.

The standard uncertainty of the assigned value $u(x_{pt})$

The standard uncertainty $u(x_{pt})$ is calculated as:

$$u(x_{pt}) = s^* / \sqrt{p}$$

where:

- s^* is the robust estimate of the participant standard deviation;
- p is the number of participants.

In case of not negligible effects of inhomogeneity and instability, if $0.1 < [u(x_{pt})]^2 / \sigma_{pt}^2 \leq 0.5$, the standard uncertainty is expanded by the factor 1,25

$$u(x_{pt}) = 1,25 [s^* / \sqrt{p}]$$

In case of median as estimator, the standard deviation is calculated as $s^* = \text{MADe}$ (where MADe is the Median Absolute Deviation).

When the standard uncertainty is too high, the assigned value could be inaccurate.

Therefore:

- In case $[u(x_{pt})]^2 / \sigma_{pt}^2 > 0.5$, the consensus value is not determined and individual laboratory performance scores are not reported. Summary statistics are provided only for information.
- In case $0.1 < [u(x_{pt})]^2 / \sigma_{pt}^2 \leq 0.5$, the uncertainty is not negligible. The effects of uncertainty are introduced in the calculation of the z-score (that will be calculated as z'-score). The standard uncertainty $u(x_{pt})$ is expanded by factor 1.25 only in case inhomogeneity and instability effects are not negligible.

z-score, z'-score and σ_{pt} (standard deviation for proficiency assessment):

When the number of confirmatory quantitative data is $p \geq 8$, the participant's result are converted into a z-score according to the equation:

$$z\text{-score} = (x_i - x_{pt}) / \sigma_{pt}$$

where:

- x_i is the analyte concentration value reported by the laboratory;
- x_{pt} is the assigned value (obtained with confirmatory methods);
- σ_{pt} is the standard deviation for proficiency assessment calculated from b x_{pt} .
- $b = \%RSD / 100$, (RSD = Relative Standard Deviation)
- the $\%RSD$ value comes from the Horwitz equation (Horwitz, W., 1988, Pure Appl. Chem. 60, 855-864)

$$\%RSD = 2(1-0.5 \log X_{pt})$$

where x_{pt} is expressed as a dimensionless concentration.

σ_{pt} is related to the concentration of the analyte: it comes from Horwitz equation (unless otherwise specified); in case of contamination less than 10 ppb the Thompson equation modified Horwitz equation (Thompson, M., 2000, Analyst 125, 385-386). In particular circumstance σ_{pt} is chosen from Proficiency Test provider's (PTp) experience, derived from previous rounds. The adopted criteria is reported in the Final Report.

If $0.1 < [u(x_{pt})]^2 / \sigma_{pt}^2 \leq 0.5$, participant's result are converted into a z' -score according to the equation:

$$z'\text{-score} = (x_i - x_{pt}) / \sqrt{\sigma_{pt}^2 + u^2(x_{pt})}$$

where:

- x_i is the analyte concentration value reported by the laboratory;
- x_{pt} is the assigned value (obtained with confirmatory methods);
- σ_{pt} is the standard deviation for proficiency assessment calculated from b x_{pt}
- $u(x_{pt})$ is the standard uncertainty calculated as previously described.

In case of z' -score, the assigned value will be given in *italics* when the uncertainty is not negligible, with underlined font where inhomogeneity and instability effects are not negligible.

The laboratory performance evaluation was established taking into account the following criteria for z -score and z' -score:

- when $|z| \leq 2$ acceptable (satisfactory)
- when $2 < |z| \leq 3$ warning signal (questionable)
- when $|z| > 3$ action signal (unsatisfactory)