

Assigned values and their uncertainties

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According to the standards and guidelines mentioned, following possibilities for the assigned value are given in the increasing order of Uncertainty of Assigned Value X_{pt}

- Known values from formulation
- Certified reference Material
- Results from one Lab
- Consensus values from expert laboratories
- Consensus values from participant results

Regardless of method used to derive A.V, check the validity of A.V for each round

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Uncertainty of Assigned Value – $u(X_{pt})$

- ✓ Competent proficiency test provider should report the uncertainty of the assigned value
- ✓ Participants need it
 - For judgement of their performance
 - For estimation of measurement uncertainty from PT data
- ✓ PT Provider should have criteria for acceptability of an Assigned Value in terms of its uncertainty – i.e $u(X_{pt}) \leq 0.3 \text{ SDPA}$

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Known values from formulation – 7.3 (ISO 13528)

- ☐ If a sample is prepared synthetically by mixing constituents in specified proportions or by adding a specified quantity of a substance to a base material (e.g) **cement content of hardened concrete** (cement, aggregate and water are mixed at definite proportion)
- ☐ The assigned value is derived by calculation from the masses used
- ☐ Caution: The analyte might be more loosely bound than in typical materials

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Known values from formulation – 7.3 CARE TO BE TAKEN WHILE PREPARING PT ITEMS

- ☐ Base material free from added constituent
- ☐ Constituents mixed homogeneously
- ☐ All significant sources of error are identified
- ☐ No adverse interaction between constituents
- ☐ Behaviour of PT items prepared is similar to routinely tested samples

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Known values from formulation – 7.3 Measurement Uncertainty

Calculation of an uncertainty budget according to GUM including

- all volumetric and gravimetric steps
- other uncertainty contributions, e.g. From
 - Purity of substances
 - In-homogeneity
 - Instability
 - Adsorption
 - Reaction with constituents in the base material
 - Concentration of analyte in the base material
- based on the law of uncertainty propagation

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Known values from formulation – 7.3 Advantages/disadvantages

- **Advantage**
 - If the analytical method is biased or the participating labs are biased on average it will be a better estimate for the true value
 - **Uncertainty generally is low**
 - If all uncertainty contributions are covered and the purity of the substances is well defined, the assigned value might be **traceable to SI**
- **Disadvantage**
 - If the analyte is more loosely bound than in typical materials, the **difficulty of the analysis might be lower** (not representative)
 - If there is unrecognized instability, adsorption or reaction with matrix constituents the assigned value will be biased

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Certified reference Materials– 7.4 (ISO 13528)

**If the PT material is a
Certified Reference Material
the certified value can be used**

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Certified reference Materials– 7.4 Uncertainty

- ☐ **Usage of the uncertainty from the certificate**
- ☐ **Caution:** Certificates may report uncertainties on a different confidence level (**coverage factor**)

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Certified reference Materials– 7.4 Advantages/disadvantages

- **Advantage**
 - Traceability
 - Low uncertainty
- **Disadvantage**
 - Might be expensive
 - Suitable CRMs might not be available
 - A CRM may be known to participant – Important to conceal the identity of PT item
 - CRMs are often processed heavily to ensure long term stability which may compromise commutability of samples

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Results from one Laboratory – 7.5

- ✓ Preparation of a reference material- as per **ISO 17034:2016**
- ✓ A number of test portions are randomly selected:
 - Analysis in one lab under repeatability conditions together with a certified reference material
 - Analysis with a primary method
- ✓ The assigned value is derived:
 - from a calibration against the certified reference value
 - from the results of the primary method

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Results from one Laboratory – 7.5

The assigned value is derived from formula:

$$X_{pt} = x_{CRM} + \text{Average "d"}$$

Average "d" = Average of the difference (RM – CRM) for each of the "n" results

(take sign also into consideration)

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Results from one Laboratory – 7.5 Measurement Uncertainty

- ❑ When a suitable CRM is not available for calibrating/characterizing the RM, Reference Value can be obtained from an appropriate source – Ensure metrological traceability & Measurement uncertainty needed
- ❑ If the samples and the CRM are not similar (in matrix, composition and level of results), the additional uncertainty arising from this is also to be included

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Results from one Laboratory – 7.5 Measurement Uncertainty

The assigned value is derived from formula:

$$u(x_{pt}) = \text{SQRT}(u_{CRM}^2 + u_d^2)$$

u_{CRM} = Std. uncertainty derived from the certificate of the CRM

u_d = Standard Error of the "n" differences

Combination of the uncertainty of the certified reference value with the uncertainty of the measurements

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Results from one Laboratory – 7.5 Advantages/disadvantages

- **Advantage**
 - Might be traceable to SI through the CRM or the primary method
 - Low uncertainty
 - **Not as expensive as direct usage of CRM**
- **Disadvantage**
 - It is assumed that there are no interactions between materials used and the test conditions
 - **CRMs that are similar enough to test samples in the required matrix and concentration are often not available**
 - Primary method is not available
 - Results are dependent of one laboratory

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Consensus values from expert laboratories – 7.6

- ✓ Samples are prepared and distributed to expert laboratories first (Similar to approach of ISO Guide 35 – CRM characterization)
- ✓ The results of the expert laboratories are used to estimate Robust Mean using Algorithm A
- ✓ No. of expert labs will normally be small -6 or 8. Hence, use the method with caution

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Consensus values from expert laboratories Uncertainties

- If expert laboratories report reliable standard uncertainties of their measurements, calculation of

$$u_x = \frac{1.25}{p} \cdot \sqrt{\sum_{i=1}^p u_i^2}$$

the factor 1.25 for robust estimation of means will be discussed later

- Otherwise the standard deviation of the results to estimate the uncertainty of the mean is used

$$u_x = 1.25 \cdot \frac{s}{\sqrt{p}}$$

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Consensus values from expert laboratories Advantages/disadvantages

- Advantage
 - Particularly useful with operationally defined measurement methods
 - Under circumstances a good estimate for the "true" value if no CRM and no reference measurements are available
- Disadvantage
 - If the expert labs are biased on average, the assigned value will be biased
 - There might be no consensus (multimodal distribution)
 - The uncertainties from expert labs might be not reliable
 - Potential problem for the PT provider: There might be doubts among the participants regarding the selection of experts, if the consensus from expert labs is deviating from the participants' consensus

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Consensus values from participants – 7.7

- ✓ **Consensus Values from**
 - (a) All participants or
 - (b) Expert participants
- ✓ **If expert participants – predefined criteria** such as accreditation status or on the basis of previous performance
- ✓ **Algorithm A for determining Assigned Value**

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Consensus values from participants Uncertainties

- The standard deviation of the results is used to estimate the uncertainty of the mean

$$u_x = 1.25 \cdot \frac{s}{\sqrt{p}}$$

As Assigned Value and Robust SD are determined from participant results, Uncertainty of Assigned Value can be assumed to include the effects of uncertainty due to in-homogeneity, transport & instability

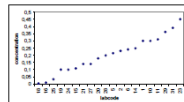
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Consensus values from participants Advantages/disadvantages

- **Advantage**
 - Easy to realize
 - Cheap
 - Particularly useful with operationally defined measurement methods
 - Often the only possibility to estimate the "true" value with natural matrices
- **Disadvantage**
 - If the labs are biased on average, the assigned value will be biased
 - There might be no consensus
 - Precision check, but not trueness check (e.g. analysis of VOC)

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COMPARISON OF THE ASSIGNED VALUE

In case Assigned Value is decided by formulation, certified reference value, reference value (results from one lab) or consensus value of expert labs which are not participants - **compare the A.V with the robust average derived from the results of the round**

In case Assigned Value is decided by consensus value of expert labs or participants, **compare the A.V with the reference value obtained by a competent laboratory (reliable independent estimate)**

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COMPARISON OF THE ASSIGNED VALUE

Std uncertainty of difference $(x^* - x_{pt})$ or $(x_{ref} - x_{pt})$ is calculated using formula

$$\text{SQRT}[u(x_{ref})^2 + u(x_{pt})^2]$$

Difference $(x^* - x_{pt})$ or $(x_{ref} - x_{pt})$ shall not be more than twice the std uncertainty of difference as given above

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IF THE Difference $(x^* - x_{pt})$ or $(x_{ref} - x_{pt})$ IS MORE THAN TWICE ITS UNCERTAINTY THEN,

PT Provider to decide whether to

(A) evaluate the participants results or not

(b) amend the design of subsequent scheme

this difference should be incorporated in the report of the pt round

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PT PROVIDER SHOULD HAVE CRITERIA FOR THE
ACCEPTABILITY OF AN ASSIGNED VALUE INTERMS OF ITS
UNCERTIANTY

$u(x_{pt}) \leq 0.3 \text{ SDPA}$

if this condition is not satisfied,

- a) look for alternate method determination of a.v such that this condition is satisfied
- b) use $u(x_{pt})$ in the interpretation of PT results (z', zeta or E_n score)
- c) if a.v is determined from participant results check for bimodality in the results & if so use separate a.v for each identified sub group
- d) inform participants that $u(x_{pt})$ is not negligible

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