Measurement uncertainty in the case of large and heterogeneous variances

Eurachem Workshop – Uncertainty from sampling and analysis for accredited laboratories

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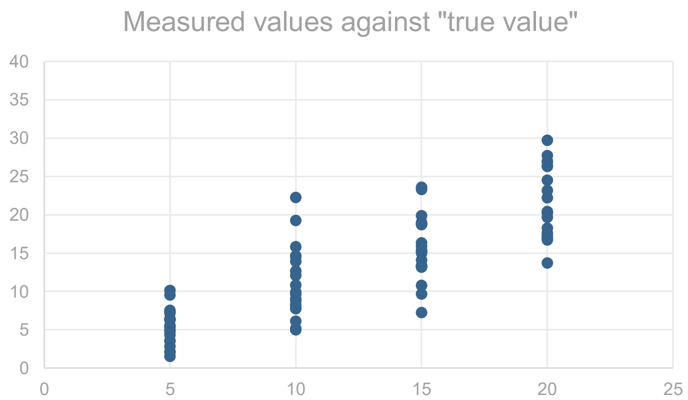
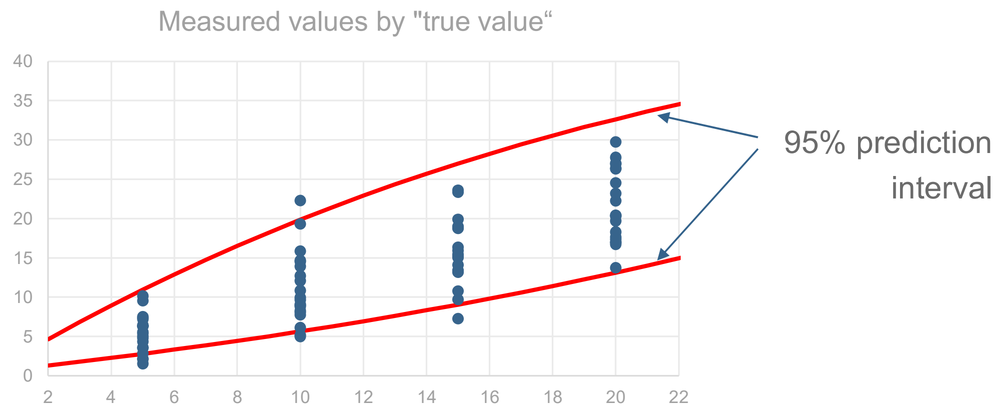
In-house study at four concentration levels

In-house study with 4 spike levels (5, 10, 15 and 20 µg/kg) and 20 replicates



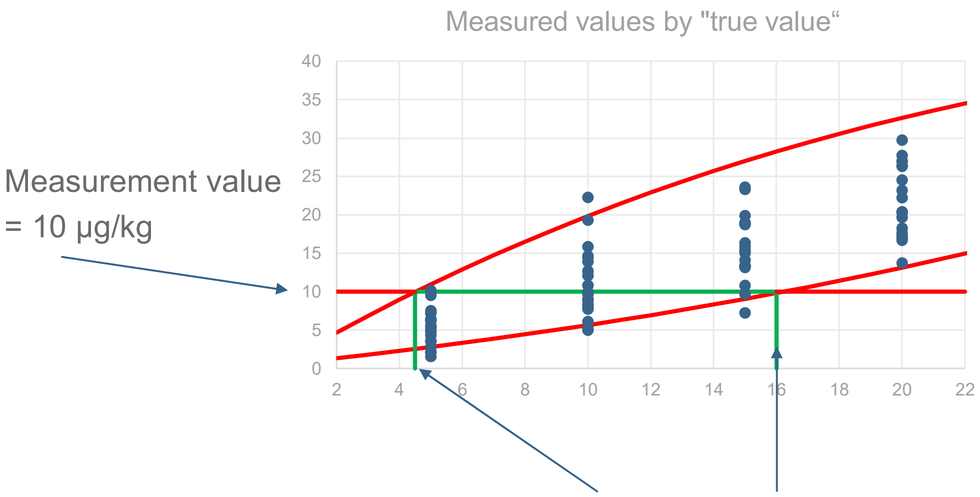
In-house study at four concentration levels

Prediction interval: in which interval does a future measurement fall with a certain probability under a given statistical model and a precision study already carried out? The calculation depends on the statistical model, here the log normal distribution with decreasing standard deviation.



A graphical method for the evaluation of the uncertainty interval

The uncertainty interval can graphically be derived from the prediction interval.

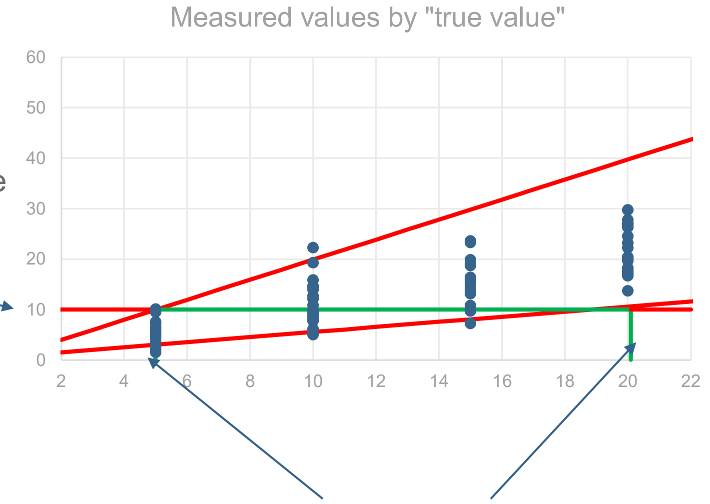


Uncertainty interval belonging to 10 µg/kg: 4.5 µg/kg to 16 µg/kg

A graphical method for the evaluation of the uncertainty interval

Other results will be obtained if the evaluation of the prediction interval is conducted under the assumption of a log normal distribution, here with constant standard deviation (σ = 0,35)

Measurement value = 10 µg/kg

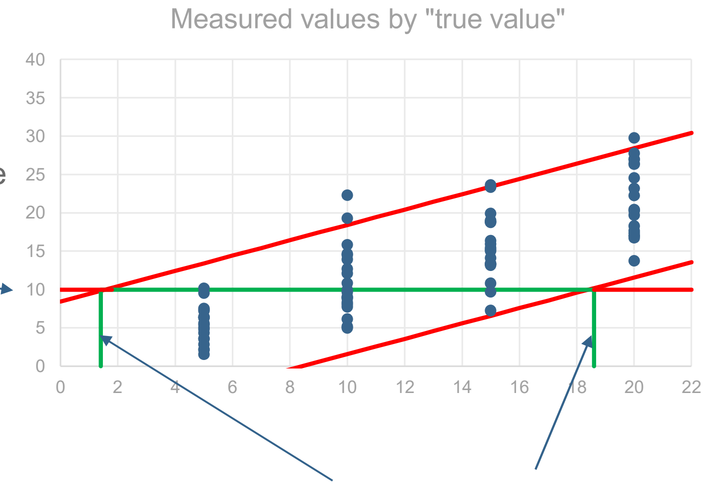


Uncertainty interval belonging to 10 µg/kg: 5 µg/kg to 20.1 µg/kg (uncertainty factor = 2,01)

A graphical method for the evaluation of the uncertainty interval

The evaluation of the uncertainty interval can also be performed with normal distribution and constant standard deviation = 4.3. Then the uncertainty interval corresponds to the conventional measurement uncertainty.

Measurement value = 10 µg/kg



Uncertainty interval belonging to 10 µg/kg: 1.4 µg/kg to 18.6 µg/kg $(10 \pm 2 \cdot 4.3)$

Comparison of results

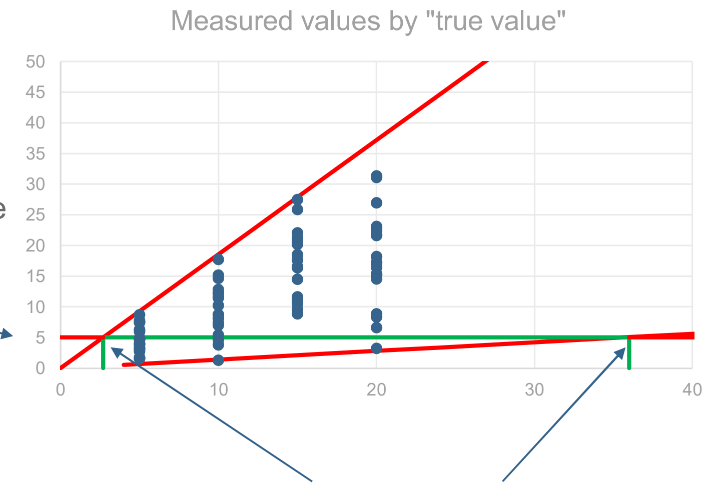
	Uncertainty interval (k=2) for 10 µg/kg
(1) graphical solution based on log-normal with decreasing RSD	4,5 – 16
(2) uncertainty factor $^{F}U=\exp(2s_G)=2.01$	5 – 20.1
(3) conventional measurement uncertainty U(10)=8.6	1.4 - 18.6

Upper limits are similar, whereas the lower limit of the conventional measurement uncertainty (3) is clearly smaller than the lower limits of (1) and (2).

A graphical method for the evaluation of the uncertainty interval: another example

In case of larger RSD, the uncertainty interval becomes highly asymmetric. Here the prediction band is calculated under the assumption of a normal distribution with constant RSD = 0.43.

Measurement value = 5 µg/kg



Uncertainty interval belonging to 5 µg/kg: 2.7 µg/kg to 35.7 µg/kg.

Calculation formula for the case of a normal distribution with constant RSD

Under the assumption of normal distribution with constant RSD there is also a formula for the uncertainty interval:

A given measurement result y obtained at the known concentration level x will lie with 95 % probability in the interval $[x - 1{,}96 \cdot x \cdot RSD, x + 1{,}96 \cdot x \cdot RSD]$.

This is equivalent with

$$x \cdot (1 - \mathbf{1.96} \cdot RSD) \leq y \leq x \cdot (1 + \mathbf{1.96} \cdot RSD)$$

$$\frac{1 - \mathbf{1.96} \cdot RSD}{y} \leq \frac{1}{x} \leq \frac{1 + \mathbf{1.96} \cdot RSD}{y}$$

$$\frac{y}{1 + \mathbf{1.96} \cdot RSD} \leq x \leq \frac{y}{1 - \mathbf{1.96} \cdot RSD}$$

With RSD=0.43, k=2 and y=5: $\frac{5}{1+\mathbf{2}\cdot 0.43} \leq x \leq \frac{5}{1-\mathbf{2}\cdot 0.43}$,

2.7 < x < 35.7 µg/kg

Discussion

- A simple method of calculating the uncertainty interval is the graphical method described in the presentation (based on a prediction band). It can be used for both normal and log normal distribution

- Under the normal distribution with constant standard deviation, the graphical method is equivalent with the conventional measurement uncertainty.

- According to the graphical method, uncertainty intervals are not only depending on the distribution of the data but also on the dependency of the RSD on the concentration level.

- A clear distinction between log normal distribution and normal distribution requires a large number of data points that are not always available.

Discussion

- A worst case solution is as follows: use lower limit from conventional measurement uncertainty, and upper limit from the normal distribution model with constant RSD:

  $$\text{lower limit} = x - 2 \cdot x \cdot \text{RSD}$$

  $$\text{upper limit} = \frac{x}{1 - 2 \cdot x \cdot \text{RSD}}$$

  (x = measured value)

- If RSD>0.5, the upper limit from the normal distribution model with constant RSD becomes infinite. In other words, RSD = 0.5 is an ultimate limit under the assumption of the normal distribution.

- Procedures for the calculation of the prediction interval are described in ISO DTS 23471 (draft to be published in 2020).

Many thanks for your attention!

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