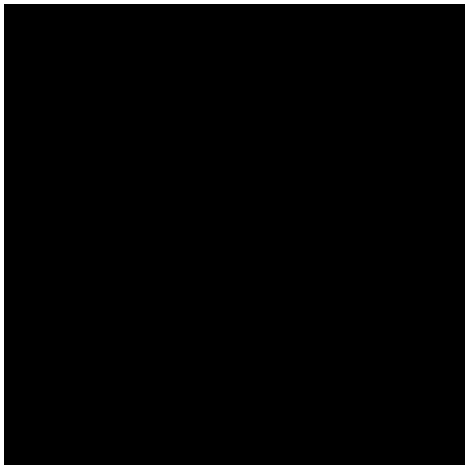
MACPoll Workshop
Novel (S)VOC gas standards for indoor monitoring



Expression of uncertainty – How can reliable measurement results be achieved?

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ISO/IEC 17025

Calibration and testing laboratories shall have and shall apply procedures for estimating uncertainty of measurement.

A statement of the uncertainty in calibration certificates or test reports is necessary

in the case of **calibration laboratories**: principally always

in the case of **testing laboratories**, where applicable,

- when it is relevant to the validity and application of the test results,
- when a customer‘s instruction so requires,
- when the uncertainty affects compliance to a specification limit.

Guide to the expression of uncertainty in measurement (GUM)

GUM concept

Basis principles, e. g.

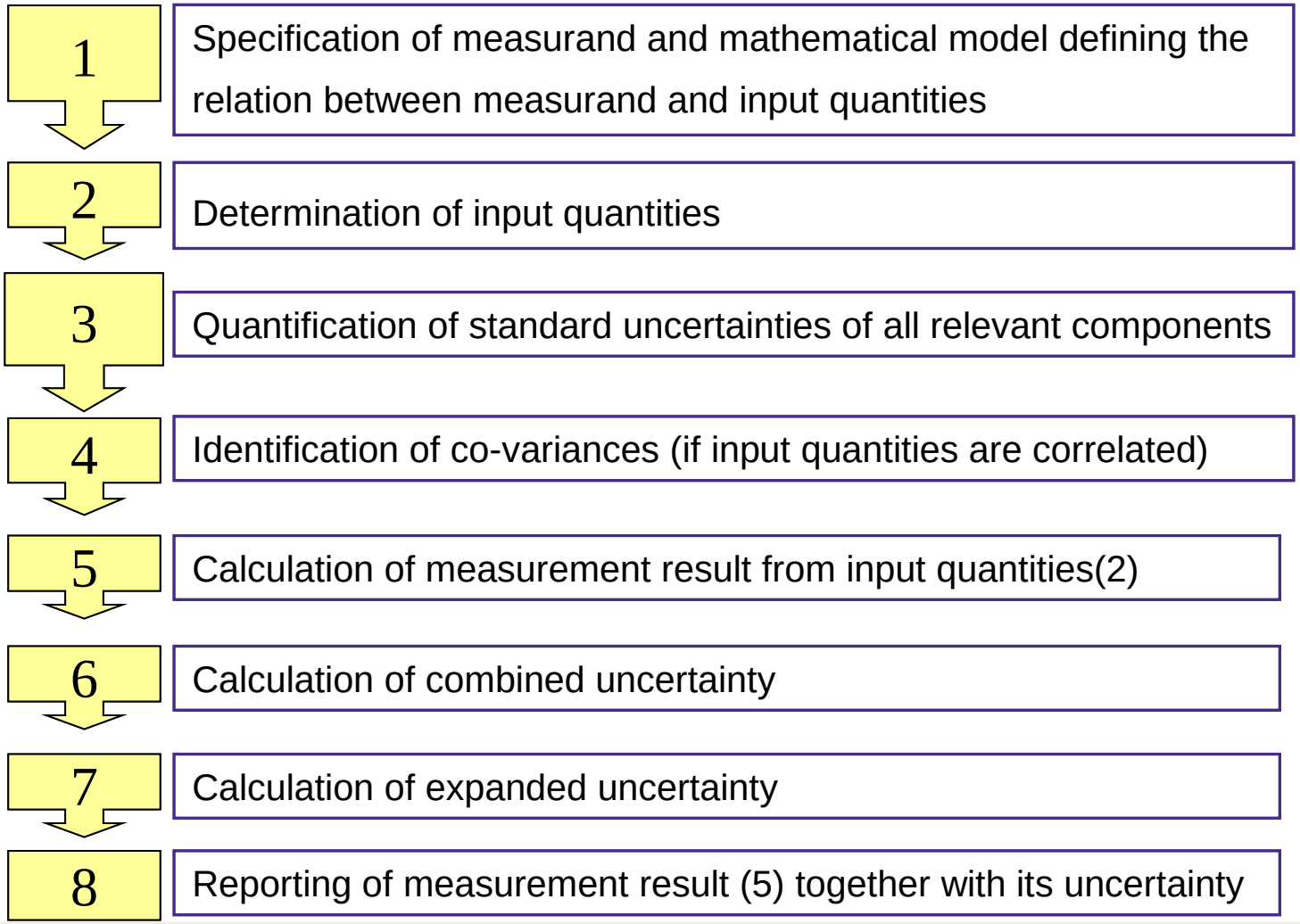
- Correction of known systematic effects, if relevant
- All uncertainty components characterised as standard deviations
- Type A and Type B standard uncertainties

Evaluation procedure:

$$Y = f(x_1, x_2, \ldots, x_n)$$

$$u(y) = \sqrt{\left(\frac{\partial y}{\partial x_1} \cdot u(x_1)\right)^2 + \ldots + \left(\frac{\partial y}{\partial x_n} \cdot u(x_n)\right)^2}$$

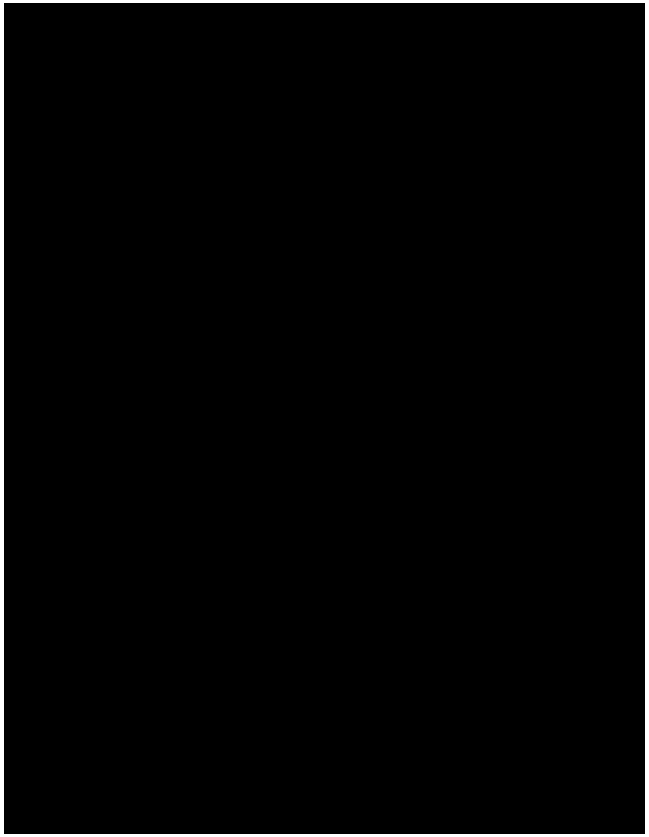
The analytical approach to evaluate MU



Test results and their uncertainty

Measurand: length

Measurand: time



Chemical analysis: example(I)

Typical equation for a spectroscopic measurement:

$$\beta_x = \frac{I_x \cdot \beta_{ref} \cdot R}{I_{ref}}$$

β_x: unknown analyte content in the sample
β_{ref}: analyte content of the reference
I_x: signal of the analyte in the sample
I_{ref}: signal of the analyte in the reference
R: purity of the analyte in the reference

Reference: E DIN 32632-1:2011

Chemical analysis: example(II)

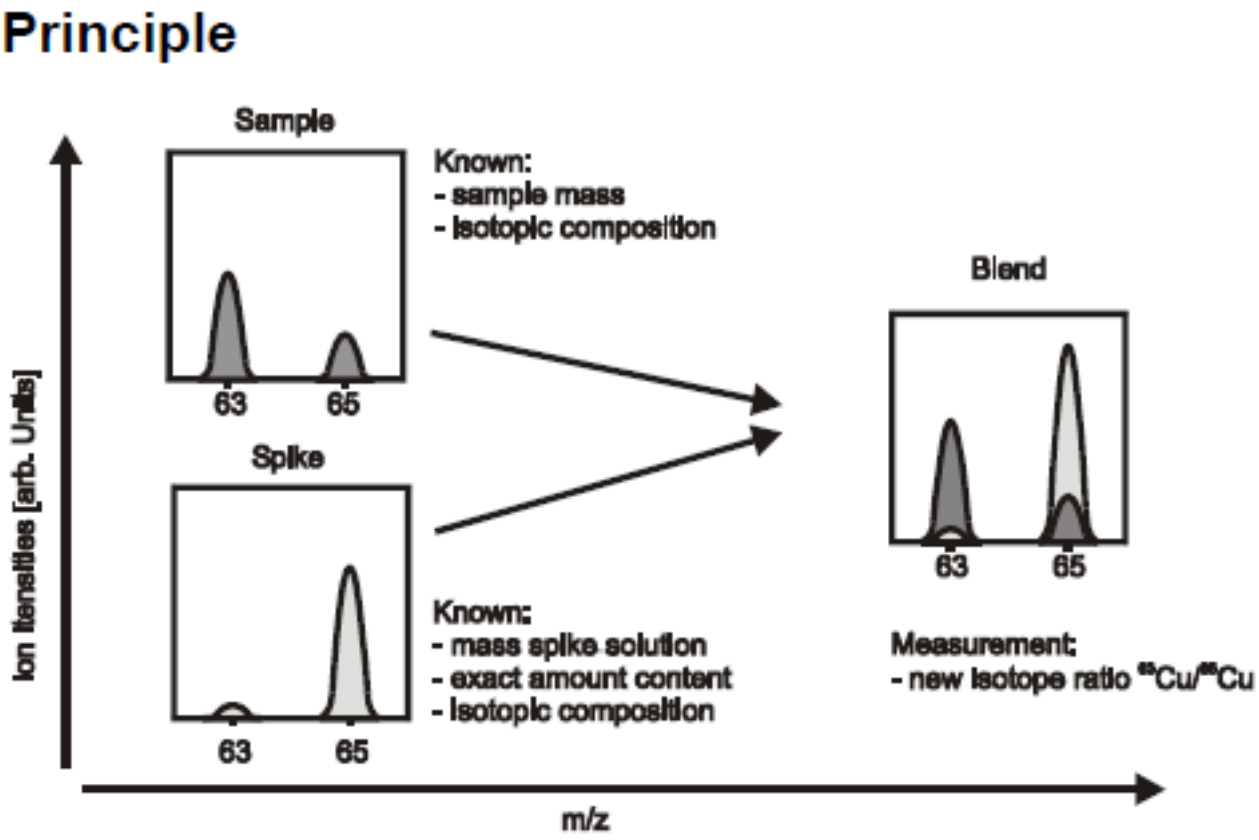
Combined standard uncertainty according to the *law of propagation of uncertainty*:

$$u_{rel}(\beta_x) = \sqrt{u_{rel}^2(I_x) + u_{rel}^2(\beta_{ref}) + u_{rel}^2(R) + u_{rel}^2(I_{ref})}$$

β_x: unknown analyte content in the sample
β_{ref}: analyte content of the reference
I_x: signal of the analyte in the sample
I_{ref}: signal of the analyte in the reference
R: purity of the analyte in the reference

Comparison of „theory“ and experiment

Example: Isotope dilution mass spectrometry



Reference: catalogue of BAM reference procedures

Comparison of „theory“ and experiment

Example: Isotope dilution mass spectrometry

$$c_{sa} = \frac{M_{sa} \cdot m_{sp}}{a_{sa,b} \cdot M_b \cdot m_{sa}} \cdot c_{sp,b} \cdot \left(\frac{R_{sp} - R_B}{R_B - R_{sa}} \right)$$

c_{sa}:	unknown amount of analyte in the sample
$c_{sp.b}$:	amount of isotope B in the spike
M_{sa}, M_b:	molar mass of the analyte element in the sample and of isotope B
m_{sp}, m_{sa}:	weights of spike and sample
$a_{sa,b}$:	abundance of isotope B in the sample
R_{sp}, R_{sa}, R_B:	isotope ratios a/b in the spike, the sample and the blend respectively

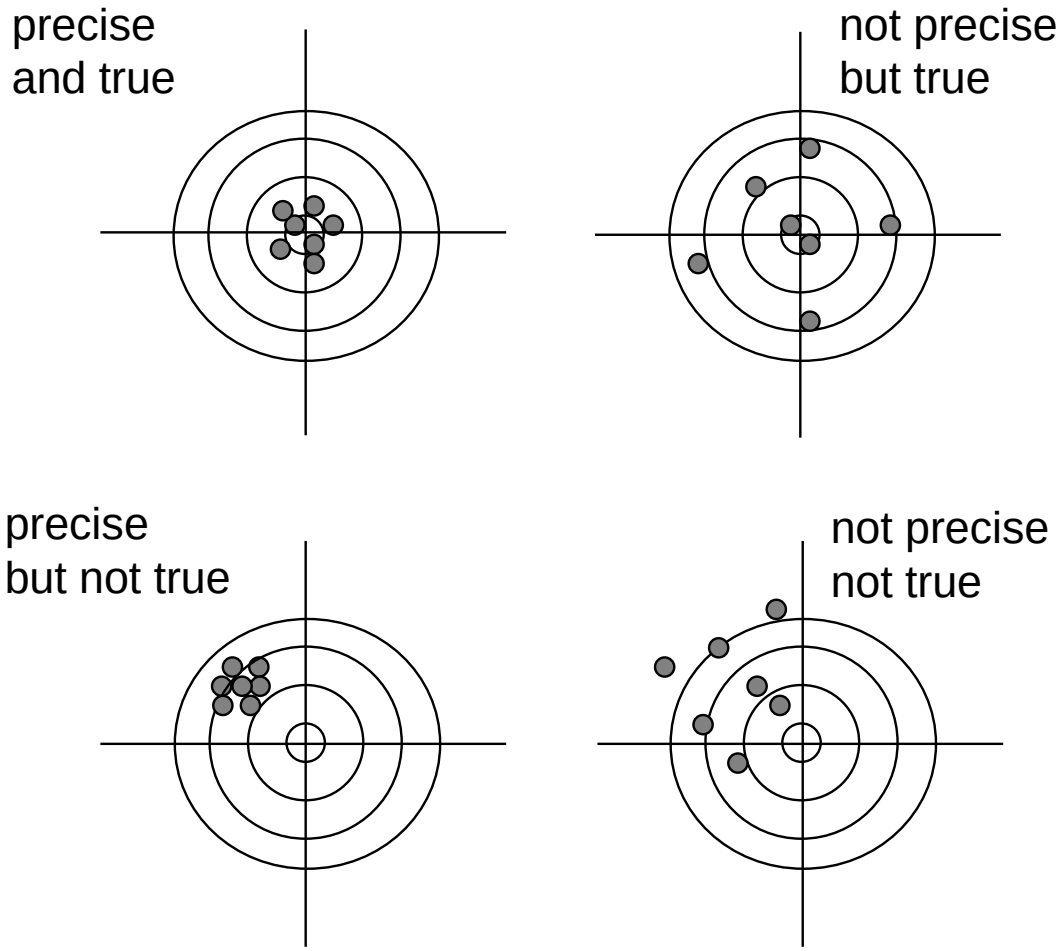
Reference: catalogue of BAM reference procedures

Comparison of „theory“ and experiment

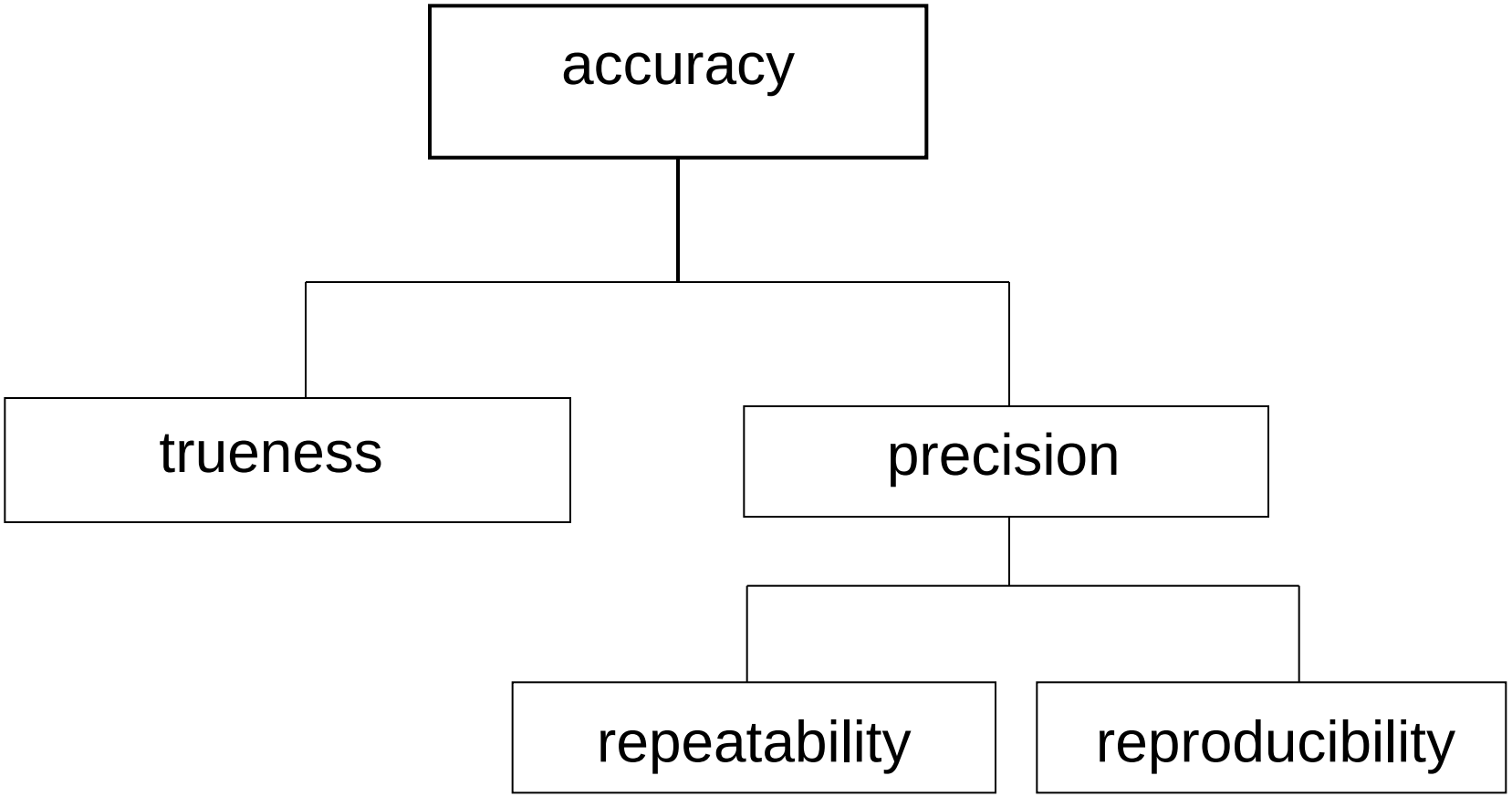
Example: Cd content in sewage sludge
(Measurement uncertainty revisited:
Alternative approaches to uncertainty evaluation,
EUROLAB Technical Report 1/2007)

Measurement uncertainty according to the model: $u_c = 0.017\ \mu g\ g^{-1}$
Experimental standard deviation (n=5): $s_R = 0.041\ \mu g\ g^{-1}$

Accuracy = trueness + precision



Accuracy = trueness + precision



Precision

Repeatability conditions

Measurements on the same or similar objects with the

- same measurement procedure,
- same operator,
- same measuring system,
- same operating conditions,
- same location,

within a short period of time.

Reproducibility conditions

Measurements on the same or similar objects with

- different operators,
- different measuring systems,
- different locations

Intermediate precision conditions

Within-laboratory reproducibility

MU evaluation – empirical approach

Within laboratory reproducibility u_{Rw}

- Stable control sample covering the whole analytical process
- Synthetic control samples + additional information, e.g. from range control charts

Method and laboratory bias u_{bias}

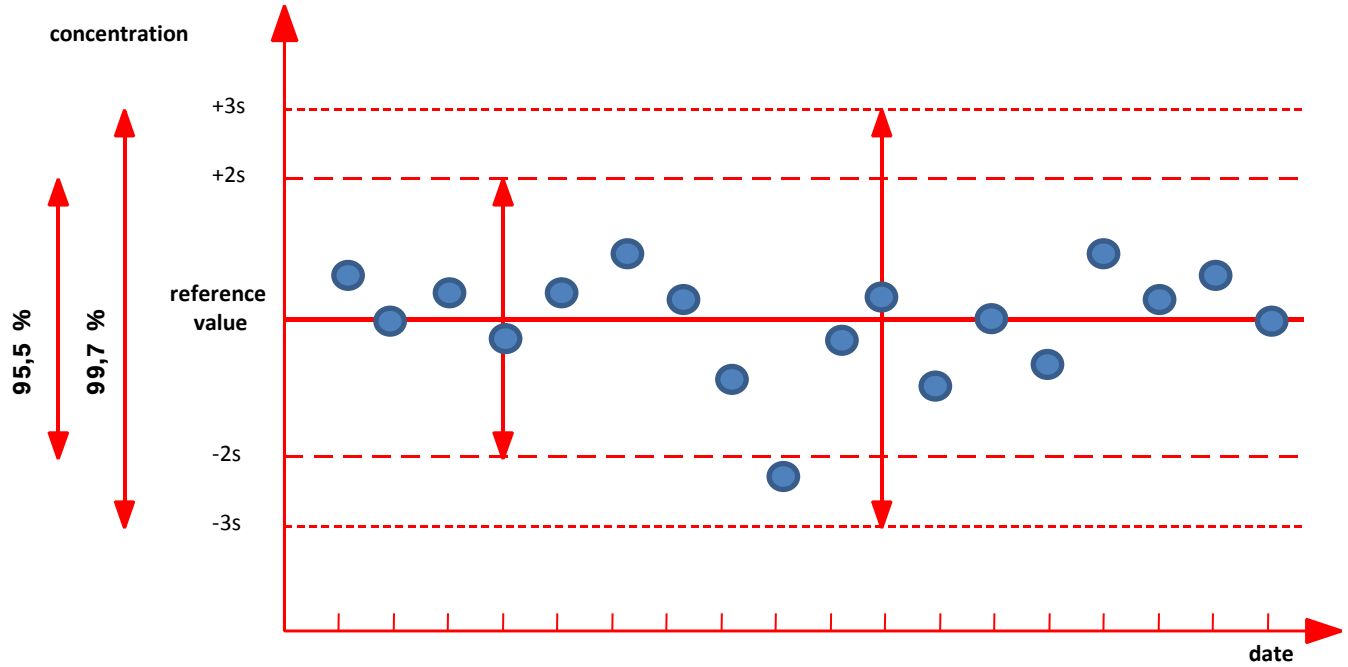
- Suitable reference material (matrix, concentration)
- Results of interlaboratory comparisons (n≥6)

$$u_c = \sqrt{u_{Rw}^2 + u_{bias}^2}$$

Within laboratory reproducibility u_{Rw}

Stable control sample covering the whole analytical process

Measurements on the control sample performed under within laboratory reproducibility (intermediate precision) conditions

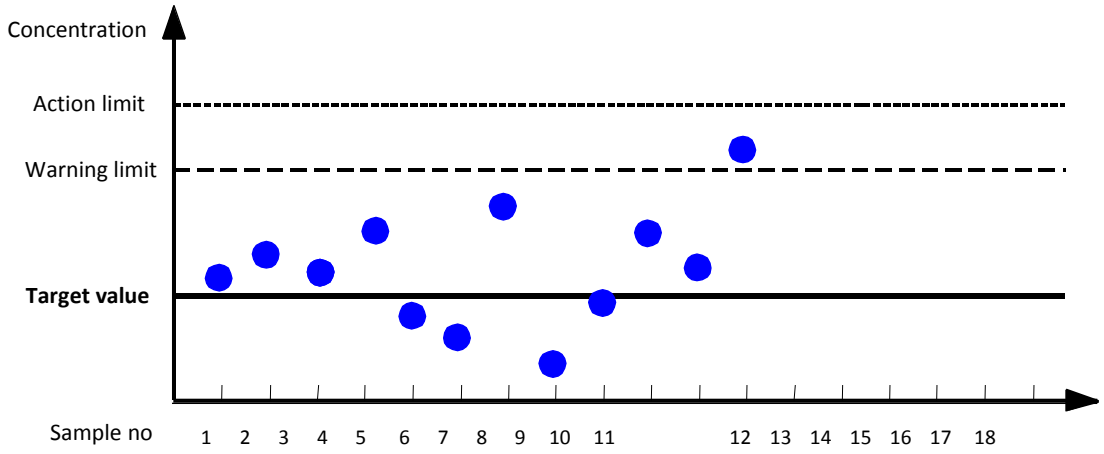


$$u_{Rw} = s_{Rw}$$

Within laboratory reproducibility u_{Rw}

Synthetic control sample + additional information, e.g. from a range chart

Additionally to the measurements on the control sample under within laboratory reproducibility conditions, the real samples are measured twice. The difference between the two results is included in a range control chart.



$$d_i = \left| x_{i,1} - x_{i,2} \right|$$

$$\overline{d} = \frac{\sum_{n} d_i}{n}$$

$$u_{r,range} = \frac{\overline{d}}{1.128}$$

$$u_{Rw} = \sqrt{u^2_{Rw,standard} + u^2_{r,range}}$$

Method and laboratory bias u_{bias}

Suitable reference material(s) (matrix, concentration)

Because of matrix and concentration effects, it is advantageous to measure n≥6 times on n_r different RMs under within laboratory reproducibility conditions.

n_r RM:

$$bias_i = \frac{\sum_j x_{i,j}}{n_j} - x_{C_{ref},i}$$

$$RMS_{bias} = \sqrt{\frac{\sum_i (bias_i)^2}{n_r}}$$

$$\overline{u_{C_{ref}}} = \frac{\sum_i u_{C_{ref},i}}{n_r}$$

$$u_{bias} = \sqrt{\overline{u}_{C_{ref}}^2 + RMS_{bias}^2}$$

only 1 RM:

$$u_{bias} = \sqrt{bias^2 + \left(\frac{s_{bias}}{\sqrt{n}}\right)^2 + u_{C_{ref}}^2}$$

s_{bias}: standard deviation of the measurement series on the RM

n: number of replicates

Method and laboratory bias u_{bias}

Results of interlaboratory comparisons (n ≥ 6)

$$d_i = x_i - x_{C_{ref},i}$$

$$RMS_d = \sqrt{\frac{\sum_i d_i^2}{n}}$$

$$\bar{u}_{C_{ref}} = \frac{\sum_i u_{C_{ref},i}}{n}$$

$$u_{bias} = \sqrt{RMS_d^2 + \bar{u}_{C_{ref}}^2}$$

Evaluation of the uncertainty of the reference value of the ILC, if not explicitly stated by the provider:

Reference value is mean of the participants' values:

$$u_{C_{ref},i} = \frac{s_{R,i}}{\sqrt{n_{p,i}}}$$

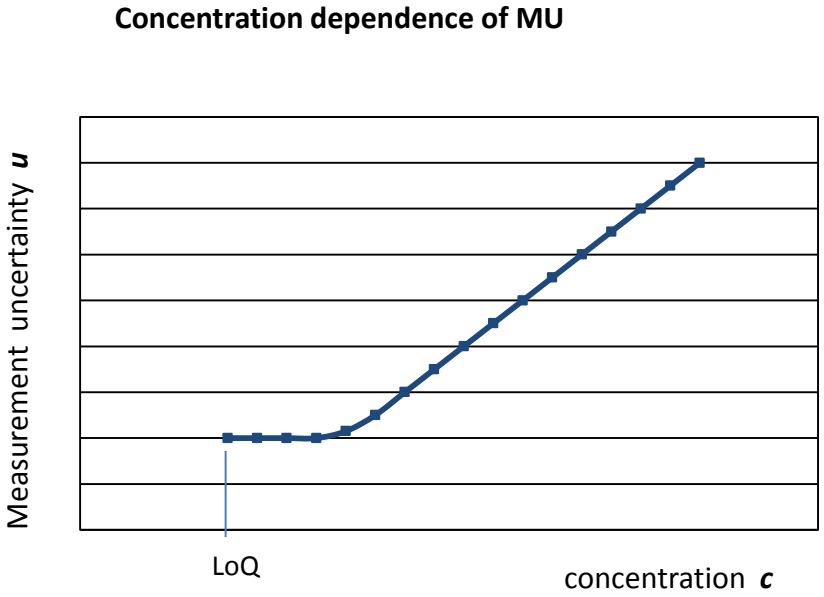
Reference value is median or robust mean:

$$u_{C_{ref},i} = 1{,}25 \cdot \frac{s_{R,i}}{\sqrt{n_{p,i}}}$$

$s_{R,i}$: standard deviation of the ILC_i, $n_{p,i}$: number of participants in ILC_i

Attention

When evaluating u_{Rw} and u_{bias} one should try to simulate the conditions of the real samples as close as possible, e.g. concerning matrix and concentration.



Comparison of both approaches

Analytical approach („GUM“)

pros

- Survey of individual components of MU,
- Evaluation of MU for individual measurements.

cons

- Difficulty of complete modelling.

Empirical approach

pros

- Better chance of a complete budget,
- Use of existing data.

cons

- „Black-box“, i.e. no information about individual MU components,
- MU of the method, not of individual measurement results.

Optimum solution: application and comparison of both approaches

MACPoll

The MACPoll project is dealing among others with measurement of (S)VOC in indoor air.

The provision of **stable control samples** and traceable **reference materials** as well as of **ILCs** could

- help laboratories to implement an improved internal quality assurance,
- improve the comparability/compatibility of measurement results,
- provide a sound basis for the measurement uncertainty evaluation.

References

Handbook for Calculation of Measurement Uncertainty in Environmental Laboratories, Nordtest Report TR 537, Version 3.1, 2012, www.nordtest.info

ISO 11352:2012, Water quality – Estimation of measurement uncertainty based on validation and quality control data

ISO 21748:2010, Guidance for the use of repeatability, reproducibility and trueness estimates in measurement uncertainty estimation

EUROLAB Technical Report 1/2007 „Measurement uncertainty revisited: Alternative approaches to uncertainty evaluations“, www.eurolab.org

Quantifying Uncertainty in Analytical Measurement, EURACHEM / CITAC Guide, 3rd edition, 2012, www.eurachem.org

Thank you for your attention!