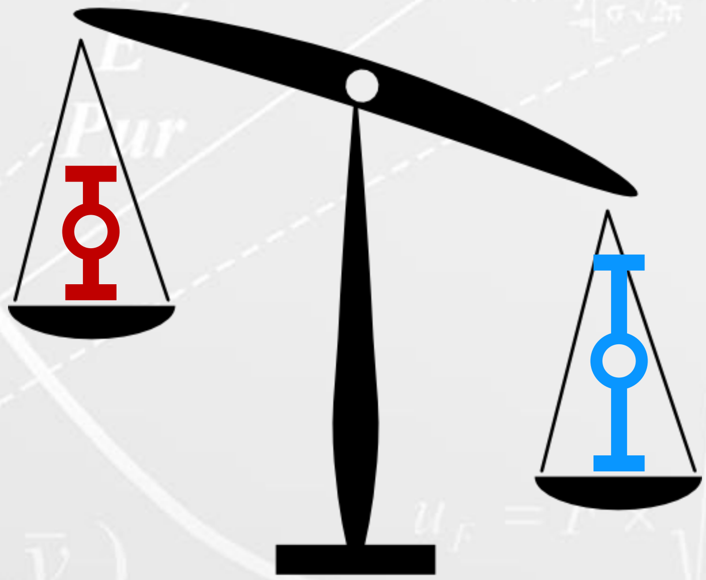
Critical Issues of the Accreditation Standards
Nicosia, 21-22 February 2019

Target uncertainty



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22 Feb. 2019

Overview

1. The measurement process
2. The measurement goal
3. Measurement requirements
4. Setting the target measurement uncertainty (MU)
5. Comparison of the estimated with the target MU
6. Highlights
7. Exercise

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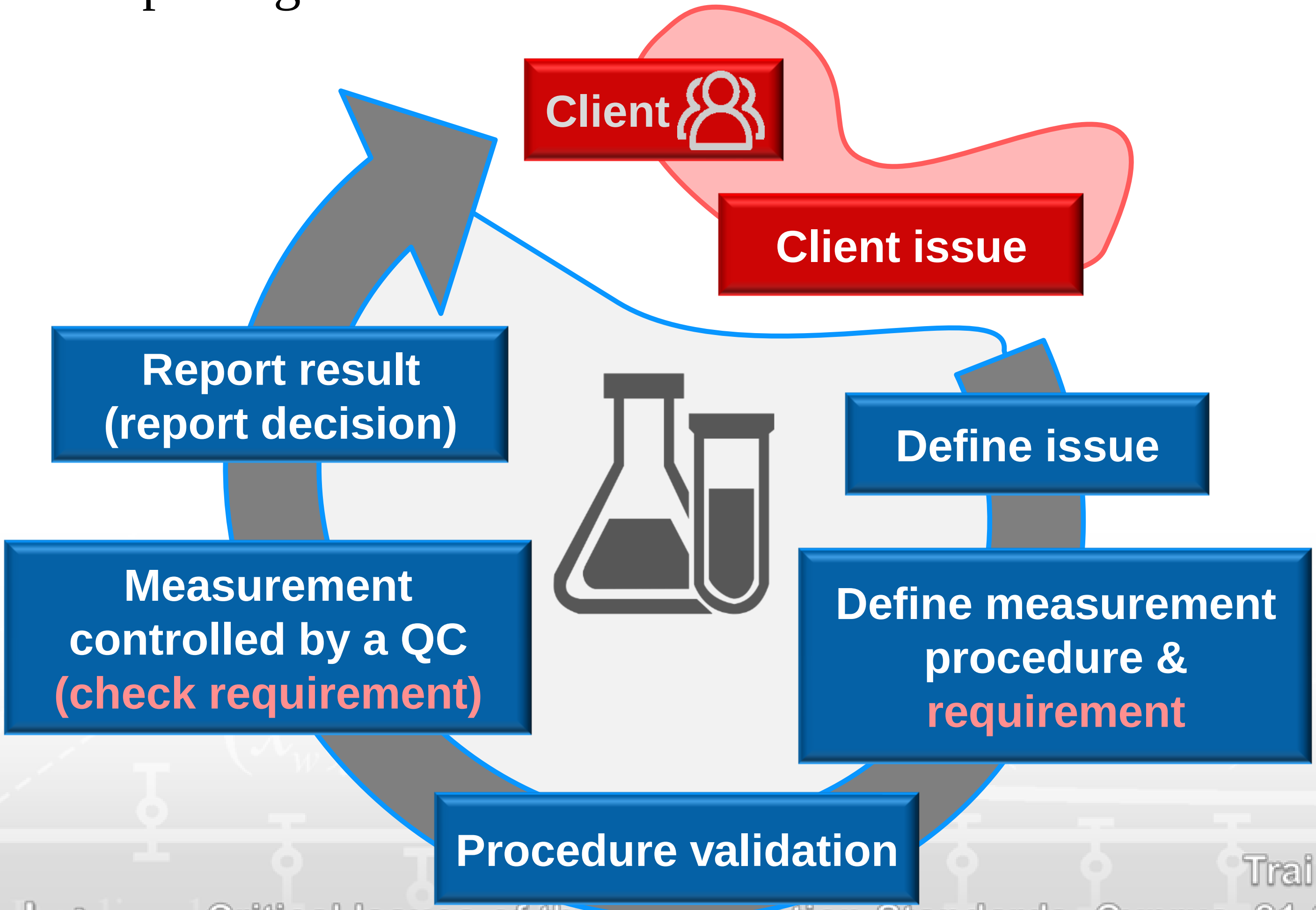
1. The measurement process

The measurement requirements should be defined immediately before measurement procedure validation, to be considered in this validation and when reporting the measurement result.



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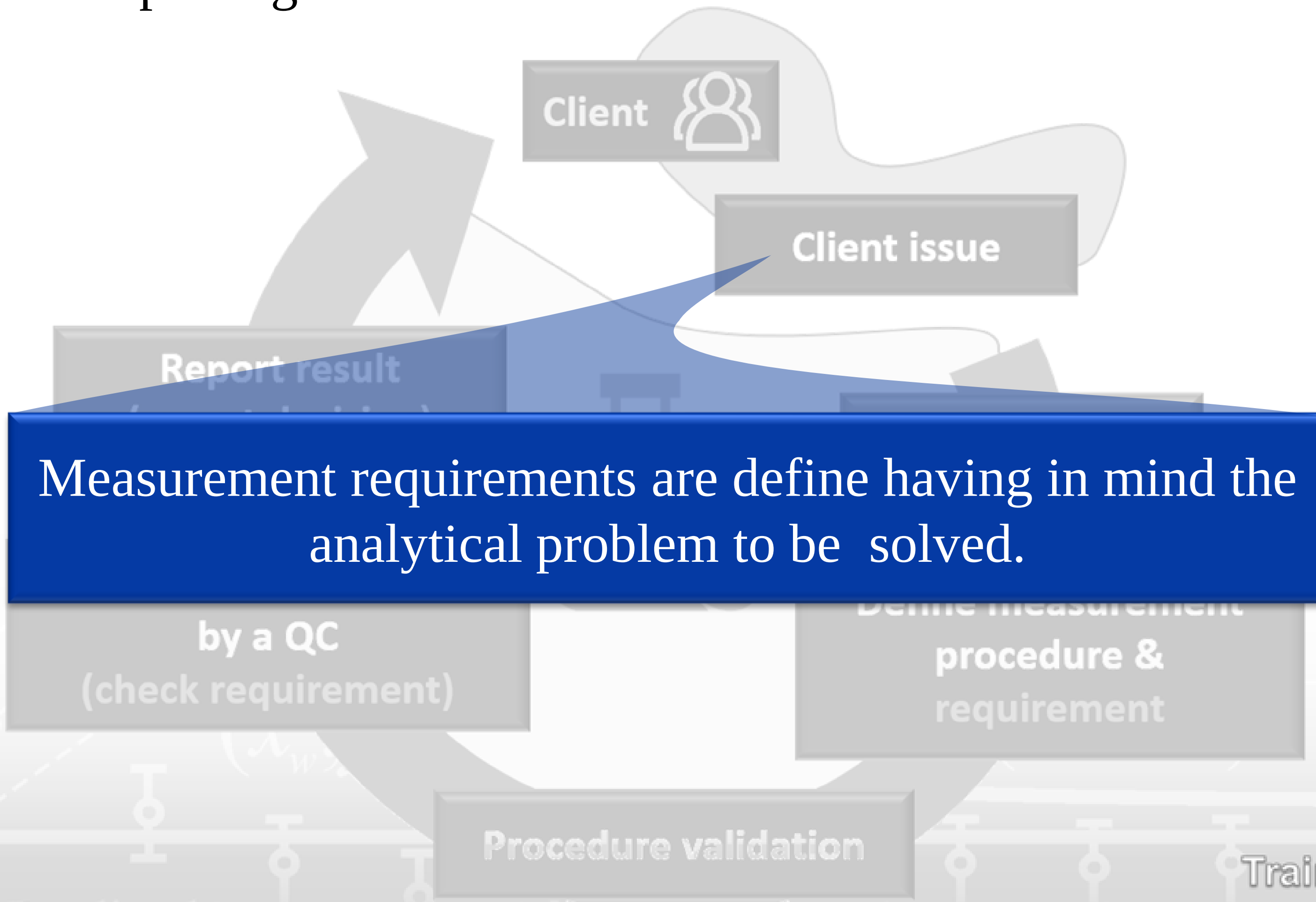

Measurement requirements are define having in mind the analytical problem to be solved.

2. The measurement goal

Measurements are performed for a variety of reasons:

1) To assess compliance with a regulation or specification;
2) To distinguish different items or detect a trend of a system;
3) To characterise a new material.

Compliance of a silver alloy with a specification

Distribution of a drug in test animal organs

Characterisation of a meteorite

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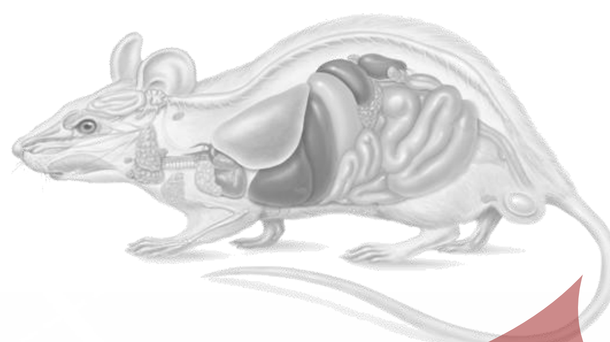
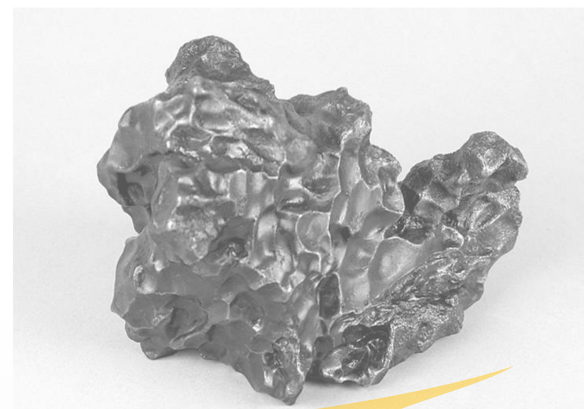


Distribution of a drug in



Characterisation of a

All these analytical applications have specific measurement requirements…

3. Measurement requirements

Examples of measurement requirements:

Technical requirements:

1) Intermediate precision (e.g. maximum coefficient of variation);
2) Analyte recovery (e.g. maximum and minimum analyte recovery);
3) Limit of quantification (e.g. maximum limit of quantification);
4) Measurement uncertainty, MU (e.g. target MU).

Other requirements:

1) Cost of analysis (e.g. maximum cost of analysis);
2) Analysis duration (e.g. maximum analysis duration);
3) Required material and expertise (e.g. volumetric determination).

3. Measurement requirements

The technical requirements needed to assess measurement fitness for an intended purpose are:

1) Analytical range;
2) Measurement uncertainty (i.e. target MU);
3) Measurement traceability ("target" measurement traceability).

Requirements of other performance parameters could be set (e.g. maximum measurement repeatability) to guarantee that measurements uncertainty magnitude will, in the end, be small enough.

4. Setting the target measurement uncertainty

4.1. Target uncertainty from regulation or client

4.2. Range of the compliance interval

4.3. Target values of performance characteristics

4.4. Acceptance limit beyond the specification limit

4.5. Assigned standard deviation in PT

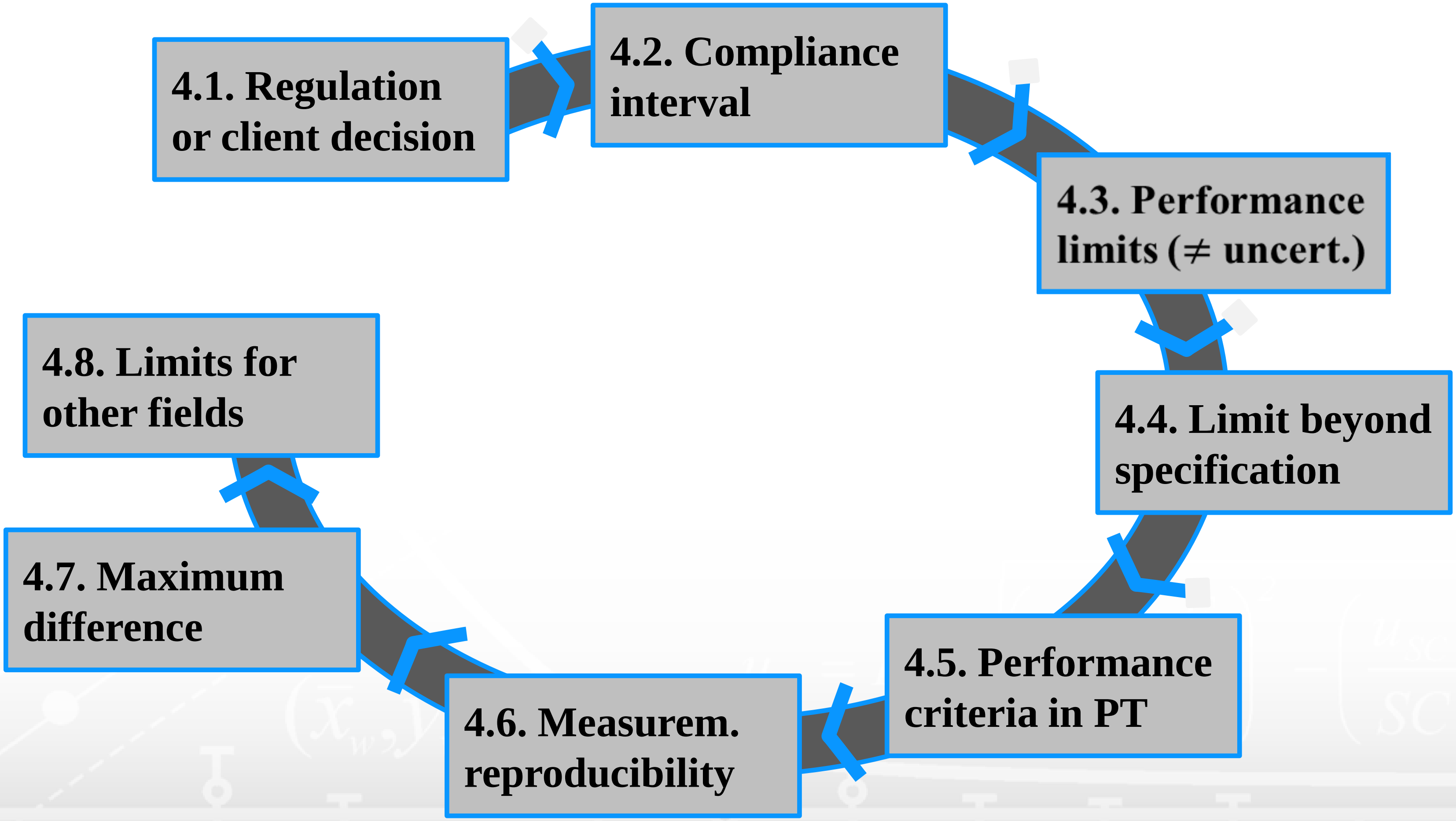
4.6. Measurement reproducibility

4.7. Smallest difference to be distinguished

4.8. Target values from related analytical fields

4. Setting the target measurement uncertainty

This section is organised from the best to the less adequate information to set measurement requirements.



4.1. Target uncertainty from regulation or client

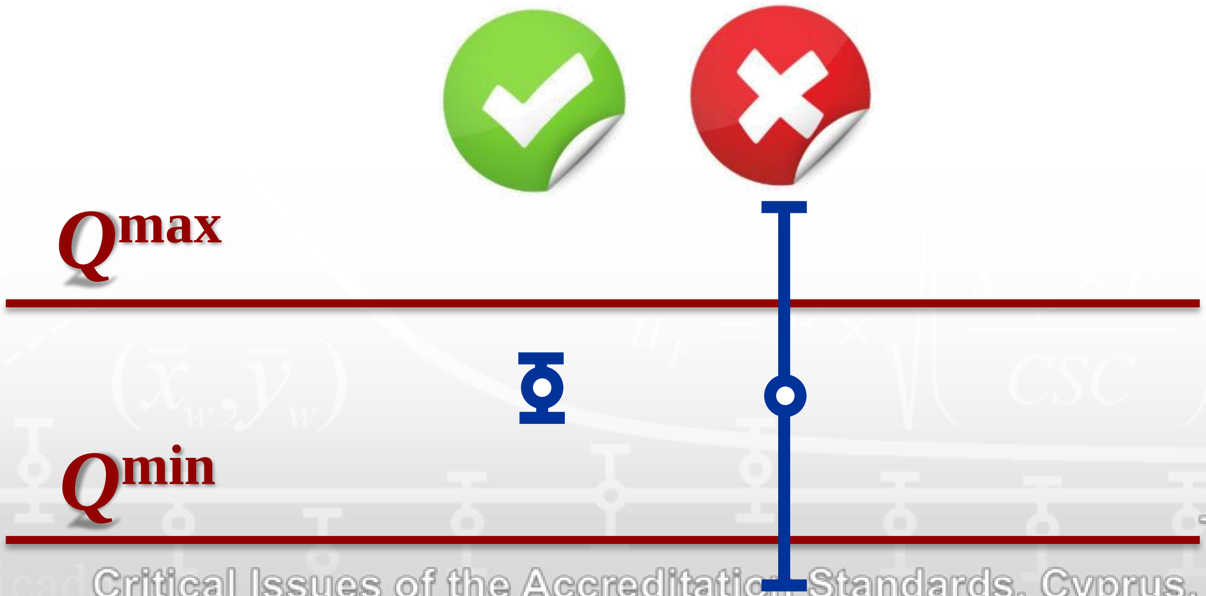
The target measurement uncertainty can be defined in the regulation or by the client. The option of the client does not supersedes the regulation (…)

4.2. Range of the compliance interval

If regulation or specification defines a maximum, $Q^{\max}$, and a minimum, $Q^{\min}$, permissible quantity value, expanded measurement uncertainty, U, should be small enough to distinguish values within this interval:

$$U^{\mathrm{tg}} = \frac{Q^{\max} - Q^{\min}}{8}$$

U^{tg} - Target expanded uncertainty.



4.2. Range of the compliance interval

Example:

Directive 76/160/EEC on quality of bathing water defines that water pH should be between 6-9. Therefore, U^{tg} is:

$$U^{\text{tg}} = \frac{9-6}{8} = 0.38$$

This performance is easily achieved by potentiometric determinations with combined glass electrode.

1. Council Directive 76/160/EEC of 8 December 1975 concerning the quality of bathing water.

4.3. Target values of performance characteristics

In some analytical fields, target values of relevant conventional performance parameters are set, such as the maximum standard deviation of measurement intermediate precision, $s_{\mathrm{I}}^{\mathrm{tg}}$, and the maximum, $\bar{E}_{\mathrm{Max}}$, and minimum, $\bar{E}_{Min}$, mean errors.

Since intermediate precision and mean error can quantify major random and systematic effects, it can be used to estimate the target standard uncertainty, u^{tg}:

$$u^{\mathrm{tg}} = \sqrt{\left(s_{\mathrm{I}}^{\mathrm{tg}}\right)^2 + \left(\frac{\bar{E}_{\mathrm{Max}} - \bar{E}_{\mathrm{Min}}}{2\sqrt{6}}\right)^2}$$

This equation is applicable when no relevant systematic effect is observed and /or no bias correction is performed.

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Half of the error range with assumed triangular distribution

This equation is applicable when no relevant systematic effect is observed and /or no bias correction is performed.

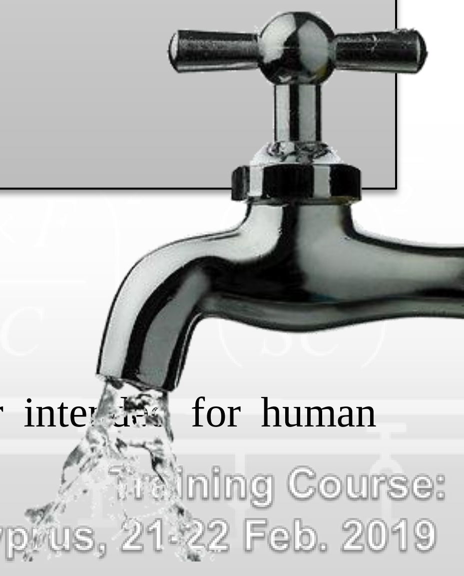
4.3. Target values of performance characteristics

Example:

Assessment of the compliance of cadmium concentration in drinking water with Council Directive 98/83/EC [2].

$$u^{\mathrm{tg}} = \sqrt{\left(s_{\mathrm{I}}^{\mathrm{tg}}\right)^2 + \left(\frac{\bar{E}_{\mathrm{Max}} - \bar{E}_{\mathrm{Min}}}{2\sqrt{6}}\right)^2} =$$

$$= \sqrt{\left(\frac{5 \cdot 0.1}{2}\right)^2 + \left(\frac{5 \cdot 0.1}{\sqrt{6}}\right)^2} = 0.32\ \mu\mathrm{g\ L^{-1}}$$

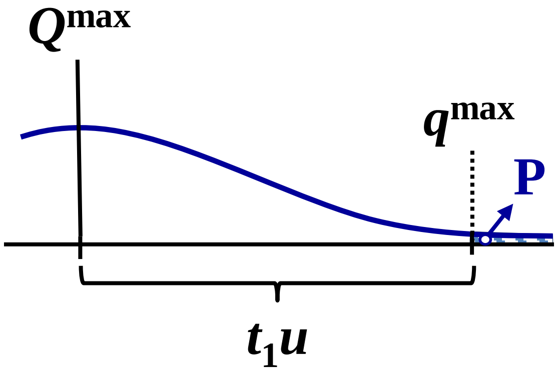


2. Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption.

4.4. Acceptance limit beyond the specification limit

If compliance of an item with a maximum permissible quantity, $Q^{\max}$, is decided by taking measurement uncertainty into account for a confidence level of 1-P, measurement results have an approximate normal distribution and a measured quantity value, $q^{\max}$, is defined beyond which probability of item being non-compliant is larger than 1-P:

$$u^{\mathrm{tg}} = \frac{q^{\max} - Q^{\max}}{t_1}$$



where t_1 is the one-tailed Student's t for (1-P) confidence level and the degrees of freedom of the measurement uncertainty, u.

Equivalent equations can be deduced for a minimum permissible quantity.

4.4. Acceptance limit beyond the specification limit

Example:

Good manufacturing practice of gold/silver/copper alloys, to be used in gold artefacts, are known to produce gold contents with deviations from the target composition not larger than 5 ‰. Therefore, deviations of gold content larger than 5 ‰ are not satisfactory. For this reason, the target standard uncertainty, u^{tg}, of these measurements should be:

$$u^{\text{tg}} = \frac{5‰}{t_1^{99\%}} = \frac{5‰}{2.93} = 1.7‰$$

4.5. Assigned standard deviation in PT

For proficiency tests where performance is assessed by calculating a z-score, z, the target standard uncertainty, u^{tg}, can be equal to the assigned standard deviation of the z-score, σ:

$$z = \frac{q_i - Q_{\mathrm{Ref}}}{\sigma}$$

where q_i is the measured quantity value reported by the laboratory, Q_{Ref} is the reference quantity value and σ the assigned standard deviation (i.e. $u^{\mathrm{tg}} = \sigma$)

4.5. Assigned standard deviation in PT

Example:

In QUASIMEME proficiency tests for the analysis of acid-extractable lead in marine sediments with a mass fraction between (5 mg kg^{-1} and 500 mg kg^{-1}), the z-score is calculated by using:

$$\sigma = \frac{Q_{\mathrm{Ref}} \cdot 12.5}{100} + 0.5 \cdot 2$$

… and $u^{\mathrm{tg}} = \sigma$.

3. QUASIMEME, Quasimeme Laboratory Performance Studies – Programme 2017, Wageningen University, Wageningen, 2017.

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… and $u^{\mathrm{tg}} = \sigma$.

terms that vary with the analyte

3. QUASIMEME, Quasimeme Laboratory Performance Studies – Programme 2017, Wageningen University, Wageningen, 2017.

4.6. Measurement reproducibility

For operationally defined measurement procedures, whenever the standard deviation, s_{R}, of measurement reproducibility is known and considered adequately low for the typical purpose of measurements, the target standard uncertainty, u^{tg} is:

$$u^{\mathrm{tg}} = s_{\mathrm{R}}$$

i.e., the u^{tg} should not be larger than the larger observed dispersion of results produced by the used procedure.

4.6. Measurement reproducibility

Example:

The measurement of pentachlorophenol (PCP) in leather, according to ISO 17070 standard [4], has a reproducibility standard deviation, s_R, of 0.8 mg kg^{-1} between 6.7 mg kg^{-1} and 16.8 mg kg^{-1}. Therefore, the target standard uncertainty, u^{tg}, in this range is:

$$u^{tg} = s_R = 0.8 \text{ mg kg}^{-1}$$

4. ISO 17070:2006, Leather – Chemical tests – Determination of pentachlorophenol content, 2006.

4.7. Smallest difference to be distinguished

If a variation of α % of the analysed system or a difference of α % of characterised items must be distinguished, with a confidence level of 99 %, the α must be larger than its expanded uncertainty, U_α.

$$\alpha = \frac{|x_A - x_B|}{\frac{x_A + x_B}{2}} > U_\alpha = \frac{k\sqrt{u_{x_A}^2 + u_{x_B}^2}}{\frac{x_A + x_B}{2}}$$

where x_A and x_B are the compared measured quantity values, u_{x_A} and u_{x_B} their standard uncertainties, respectively, and k the coverage factor of U_α.

If both standard uncertainties ($u_{x_A} \approx u_{x_B} \approx u$) are equivalent, the u must be smaller than $[\alpha/(k2^{1/2})]$ to distinguish this difference. Therefore, the target standard uncertainty, u^{tg} is:

$$u^{tg} = \frac{\alpha}{k\sqrt{2}}$$

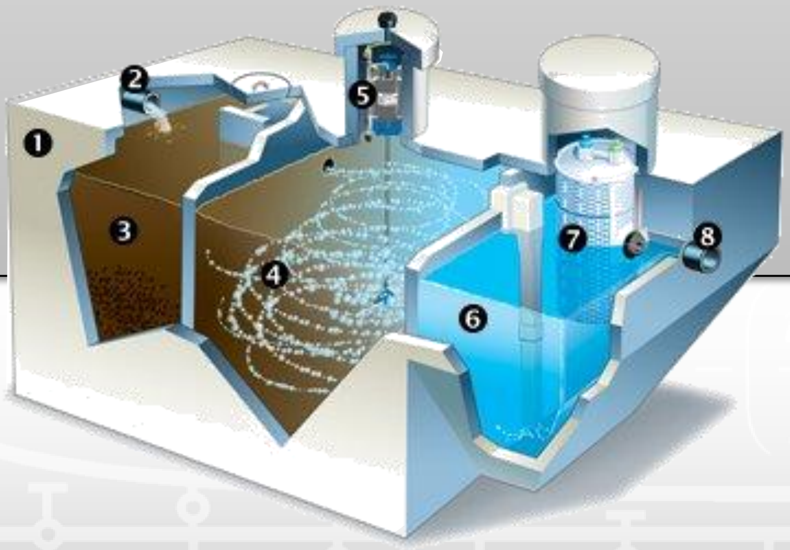
5. R. J. N. Bettencourt da Silva, Water 5 (2013) 1279-1302.

4.7. Smallest difference to be distinguished

Example:

The optimisation of wastewater treatment scheme, by changing conditions in a pilot plan, is controlled by the percentage reduction of the chemical oxygen demand (COD) with the treatment. If COD reduction of 5 % are considered relevant, the determination of COD reduction should be carried out with a standard uncertainty not larger than 1.2 %:

$$u^{\mathrm{tg}} = \frac{5\ \%}{4.2} = 1.2\ \%$$



4.8. Target values from related analytical fields

The target measurement uncertainty can be defined considering target values of performance parameters of similar or related measurements.

Example 1:

The target measurements uncertainty associated with the quantification of gold in pure gold alloys, should be smaller than that defined for the analysis of gold in mining products.

Example 2:

The target uncertainty of measurements of lead in drinking water, should be smaller than that associated with measurements of lead in wastewaters.

5. Comparison of the estimated with the target MU

In principle, the measurement uncertainty, u, should be smaller than the target value, u^{tg}, but if u^{tg} is not defined in a regulation or specification, an additional tolerance of 20 % to 30 % can be considered to allow for the variability of the uncertainty evaluation process.

The GUM [6] *discusses that analysts should be aware of the variability of the uncertainty evaluation process, illustrating it with the variability of the estimation of the standard deviation of a population from a small number of results (paragraph E.4.3 in* [6]*).*

The tolerance of 20 % to 30 % is defined considering critical values of one-tailed χ^2 or F tests use to compare a standard deviation with a fixed value or another standard deviation, respectively.

6. Joint Committee for Guides in Metrology, Evaluation of measurement data – Guide to the expression of uncertainty in measurement (GUM), JCGM 100, BIPM, 2008

6. Highlights

- Measurement fitness for the intended purpose depends on measurement traceability and uncertainty;
- The assessment of the adequacy of measurement uncertainty depends on the comparison with a target (maximum) value;
- The target measurement uncertainty must be defined by the client (regulator) or the analyst;
- In many analytical applications, information for setting the target MU is available;
- The variability of the measurement uncertainty evaluation process should be considered in the comparison with the target value.

7. Exercises

7.1. Define the target uncertainty for the measurement of total hardness in drinking water

7.2. Define the target uncertainty for the determination of nitrites in the water of a river

(discuss the levels at where the target values are applicable)