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Water quality — Estimation of measurement uncertainty based on validation and quality control data

Qualité de l'eau — Estimation de l'incertitude de mesure basée sur des données de validation et de contrôle qualité

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 11352 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

Introduction

The basic principles of the estimation of measurement uncertainty are set out in ISO/IEC Guide 98-3. There are several ways of estimating measurement uncertainty depending on the purpose of the estimation and the available data; Eurolab TR 1[9] gives an overview of the main approaches.

This International Standard specifies a set of procedures to enable laboratories to estimate the measurement uncertainty of their results, using an approach based on quality control results and validation data. It is structured in a way that is applicable to analysts that do not have a thorough understanding of metrology or statistics.

NEN 7779[8] and Nordtest TR 537[10] have been used as a basis for developing this International Standard. The approach taken is "top-down", contrary to the mainly "bottom-up" strategy adopted in ISO/IEC Guide 98-3.

It is statistically acceptable to combine a precision estimate and the uncertainty associated with the bias into one uncertainty measure. The sources of data for this approach are method validation and analytical quality control. The experimental approach specified in this International Standard enables a greater coverage of the sources of variation observed during routine use of the analytical method.

Water quality — Estimation of measurement uncertainty based on validation and quality control data

1 Scope

This International Standard specifies methods for the estimation of measurement uncertainty of chemical and physicochemical methods in single laboratories based on validation data and analytical quality control results obtained within the field of water analysis.

NOTE 1 The principles of the estimation of uncertainty specified in this International Standard are consistent with the principles described in ISO/IEC Guide 98-3.

In this International Standard, the quantification of measurement uncertainty relies on performance characteristics of a measurement procedure obtained from validation and the results of internal and external quality control.

NOTE 2 The approaches specified in this International Standard are mainly based on QUAM[11], NEN 7779[8], Nordtest TR 537[10], and Eurolab TR 1[9].

NOTE 3 This International Standard only addresses the evaluation of measurement uncertainty for results obtained from quantitative measurement procedures. The uncertainties associated with results obtained from qualitative procedures are not considered.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO/IEC Guide 98-3:2008, *Uncertainty of measurement — Part 3: Guide to the expression of uncertainty in measurement* (*GUM:1995*)

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

NOTE 1 The terms and definitions listed are generally reproduced without the Notes which are associated with the terms and definitions in the respective references.

NOTE 2 The terms concerning precision data from interlaboratory trials are taken from ISO 3534-2:2006[1] because the definitions in ISO/IEC Guide 99:2007[7] are wider than those in ISO 3534-2:2006 as they include different measurement procedures, which is not appropriate for this International Standard.

3.1
trueness
closeness of agreement between the average of an infinite number of replicate measured quantity values and a reference quantity value

[ISO/IEC Guide 99:2007[7], 2.14]

3.2
precision
closeness of agreement between indications or measured quantity values obtained by replicate measurements on the same or similar objects under specified conditions

[ISO/IEC Guide 99:2007[7,] 2.15]

3.3
error
measurement error
measured quantity value minus a reference quantity value

[ISO/IEC Guide 99:2007[7], 2.16]

3.4
systematic error
systematic measurement error
component of measurement error that in replicate measurements remains constant or varies in a predictable manner

[ISO/IEC Guide 99:2007[7], 2.17]

3.5
bias
measurement bias
estimate of a systematic measurement error

[ISO/IEC Guide 99:2007[7], 2.18]

3.6
random error
random measurement error
component of measurement error that in replicate measurements varies in an unpredictable manner

[ISO/IEC Guide 99:2007[7], 2.19]

3.7
repeatability conditions
observation conditions where independent test/measurement results are obtained with the same method on identical test/measurement items in the same test or measuring facility by the same operator using the same equipment within short intervals of time

[ISO 3534-2:2006[1], 3.3.6]

3.8
repeatability
precision under repeatability conditions

[ISO 3534-2:2006[1], 3.3.5]

3.9
batch
series of measurements made under repeatability conditions

3.10
intermediate precision conditions
conditions where test results or measurement results are obtained with the same method, on identical test/measurement items in the same test or measurement facility, under some different operating condition

NOTE There are four elements to the operating condition: time, calibration, operator and equipment.

[ISO 3534-2:2006[1], 3.3.16]

3.11
intermediate precision
precision under intermediate precision conditions

[ISO 3534-2:2006[1], 3.3.15]

3.12
within-laboratory reproducibility
intermediate measurement precision where variations within one laboratory alone are included

3.13
reproducibility conditions
observation conditions where independent test/measurement results are obtained with the same method on identical test/measurement items in different test or measurement facilities with different operators using different equipment

[ISO 3534-2:2006[1], 3.3.11]

3.14
reproducibility
precision under reproducibility conditions

[ISO 3534-2:2006[1], 3.3.10]

3.15
uncertainty
measurement uncertainty
non-negative parameter characterizing the dispersion of the quantity values being attributed to a measurand, based on the information used

[ISO/IEC Guide 99:2007[7], 2.26]

3.16

standard uncertainty
standard measurement uncertainty

measurement uncertainty expressed as a standard deviation

[ISO/IEC Guide 99:2007[7], 2.30]

3.17
combined standard uncertainty
combined standard measurement uncertainty
standard measurement uncertainty that is obtained using the individual standard measurement uncertainties associated with the input quantities in a measurement model

[ISO/IEC Guide 99:2007[7], 2.31]

3.18
relative standard measurement uncertainty
standard measurement uncertainty divided by the absolute value of the measured quantity value

[ISO/IEC Guide 99:2007[7], 2.32]

3.19
target measurement uncertainty
measurement uncertainty specified as an upper limit and decided on the basis of the intended use of measurement results

[ISO/IEC Guide 99:2007[7], 2.34]

3.20
expanded uncertainty
expanded measurement uncertainty
product of a combined standard measurement uncertainty and a factor larger than the number one

NOTE The term “factor” in this definition refers to a coverage factor.

[ISO/IEC Guide 99:2007[7], 2.35]

3.21
coverage factor
number larger than one by which a combined standard measurement uncertainty is multiplied to obtain an expanded measurement uncertainty

[ISO/IEC Guide 99:2007[7], 2.38]

4 Symbols

b bias estimated as the difference between mean measured value and an accepted reference value

b_i bias of the ith reference material respectively deviation from the complete recovery (100 %) of the ith recovery experiment

b_{rms} root mean square of individual bias values respectively of the deviations from recovery experiments

D_i difference between the measurement result and the assigned value of the ith sample of the interlaboratory comparison

D_{rms} root mean square of the differences

d_2 factor for the calculation of the standard deviation from the mean range $\bar{R}$

i variable related to an observation of a series

j variable related to a source of uncertainty

J total number of sources of uncertainty

k coverage factor

n_{ilc} number of analysed interlaboratory comparison samples

n_{M} number of measurements

$n_{\text{p},i}$ number of participating laboratories for sample i

n_{r} number of reference materials

n_{η} number of recovery experiments

$\bar{R}$ mean range

s standard deviation

s_b standard deviation of the measured values of the reference material

$s_{R,i}$ reproducibility standard deviation from the interlaboratory comparison for sample i

$s_{R_{\text{w}}}$ standard deviation of the quality control results

U expanded uncertainty

U_{rel} relative expanded uncertainty

u_{c} combined standard uncertainty

$u_{\text{c,rel}}$ combined relative standard uncertainty

u_j standard uncertainties from different sources j

$u_{j,\text{rel}}$ relative standard uncertainties from different sources j

u_{add} standard uncertainty in the concentration of the analyte added

u_b standard uncertainty component associated with method and laboratory bias

u_{conc} standard uncertainty of the concentration of the addition solution

$\bar{u}_{C_{\text{ref}}}$ mean standard uncertainty of the reference values or
mean standard uncertainty of the assigned values of the interlaboratory comparison samples

$u_{C_{\text{ref}}}$ standard uncertainty of the reference value

$u_{C_{\text{ref}},i}$ standard uncertainty of the assigned value of the interlaboratory sample i

u_{R_w} standard uncertainty component for the within-laboratory reproducibility

$u_{r,\text{range}}$ standard uncertainty component from the range control chart (obtained under repeatability conditions)

$u_{R_\text{w},\text{bat}}$ standard uncertainty component resulting from variations between batches

$u_{R_\text{w},\text{stand}}$ standard uncertainty component of the results from the standard solution which is used as quality control sample

u_V standard uncertainty component of the volume added

$u_{V,b}$ systematic standard uncertainty component of the volume added

$u_{V,\text{rep}}$ random standard uncertainty component of the volume added (obtained under repeatability conditions)

$\varepsilon_{V,\max}$ maximum deviation of the volume from the specified value (producer information)

η recovery

5 Principle

A measurement result of a laboratory is an estimate of the value of the measurand. The quality of this estimate depends on the inevitable uncertainty that is inherent to the measurement result. In principle, the measurement uncertainty is a property of individual measurement results. The estimation of the measurement uncertainty for each individual measurement result is usually not necessary, if the measurement result originates from a controlled measurement process. In this International Standard, the measurement uncertainty is, therefore, determined for a set of similar measurement results. Generally, it is assumed that the set of measurement results obtained with a specific analytical method is obtained under controlled conditions. The estimation of the measurement uncertainty applies to all of the measurement results within the set, independently of, for example, sample matrix or analyst, provided that the measurement is carried out under a quality assurance programme.

This International Standard specifies procedures for the estimation of measurement uncertainty within the scope of the analytical method, and generally, random and systematic errors need to be considered. The estimation of measurement uncertainty is based on analytical quality control results and validation data which represent the within-laboratory reproducibility, and the method and laboratory bias.

6 Procedure

The procedure for the estimation of measurement uncertainty consists of the steps shown schematically in Figure 1. The figure gives references to appropriate clauses and sub-clauses within this International Standard.

In general, the method and laboratory bias (systematic error) and the within-laboratory reproducibility (random error) are determined independently using suitable data from method validation and analytical quality control results.

The combined measurement uncertainty, i.e. the root of the quadratic sum of the uncertainty component for the within-laboratory reproducibility and the uncertainty component associated with method and laboratory bias, is multiplied by a factor of 2 to obtain the expanded uncertainty at a confidence level of approximately 95 %.

If the measurement uncertainty varies significantly, depending on the matrix and/or concentration range, the uncertainty estimation shall be made separately for each matrix and/or concentration range.

7 Preparative considerations for the estimation of measurement uncertainty

7.1 Specification of the measurement

Before starting the estimation of measurement uncertainty, it is necessary that the analyst specify the analytical method under consideration, and the objectives and purposes of the measurement. The following list is a minimal checklist for this specification.

The specification comprises:

— the measurand;

— the measurement procedure;

— the field of application (matrices, concentration range).

7.2 Specification of the parametric form in which the measurement uncertainty is reported

The expanded uncertainty, U, is reported either as an absolute uncertainty value or as a relative uncertainty value. For results near the limit of quantification, the uncertainty is often found to be constant and can therefore be expressed as an absolute value. When results are well above the limit of quantification, the uncertainty is often proportional to the analyte concentration and can therefore be expressed as a relative value.

EXAMPLE Determination of a heavy metal (limit of quantification: 5 µg/l).

for concentration range 5 µg/l to 20 µg/l	U = 1 µg/l
for concentration >20 µg/l	U_{rel} = 5 %

Usually, the measurement uncertainty is determined for a certain matrix and concentration range. In some situations, an interpolation function may be applied between different concentration ranges (see QUAM:2000[11], E.4).

