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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

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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

$u_{j,\mathrm{rel}}$	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
$\overline{u}_{C_{\mathrm{ref}}}$	mean standard uncertainty of the reference values or mean standard uncertainty of the assigned values of the interlaboratory comparison samples
$u_{C_{\mathrm{ref}}}$	standard uncertainty of the reference value
$u_{C_{\mathrm{ref}},i}$	standard uncertainty of the assigned value of the interlaboratory sample i
$u_{R_{\mathrm{w}}}$	standard uncertainty component for the within-laboratory reproducibility
$u_{r,\mathrm{range}}$	standard uncertainty component from the range control chart (obtained under repeatability conditions)
$u_{R_{\mathrm{w}},\mathrm{bat}}$	standard uncertainty component resulting from variations between batches
$u_{R_{\mathrm{w}},\mathrm{stand}}$	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
$u_{V,\mathrm{rep}}$	random standard uncertainty component of the volume added (obtained under repeatability conditions)
$\varepsilon_{V,\mathrm{max}}$	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

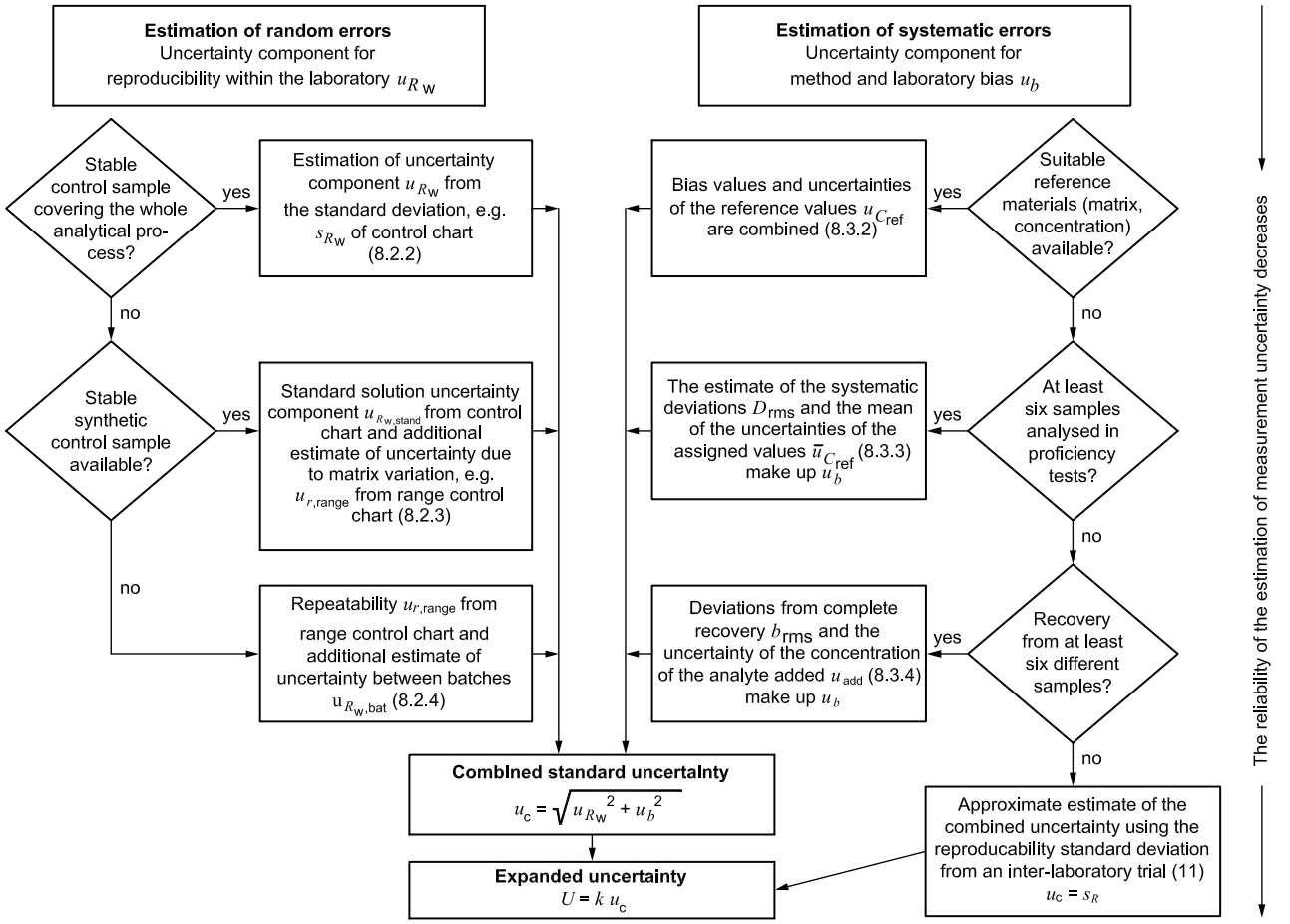
The expanded uncertainty, U, is reported either as an absolute uncertainty value or as a relative uncertainty value. For results near the limit of quantification, the uncertainty is often found to be constant and can therefore be expressed as an absolute value. When results are well above the limit of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



NOTE It is recognized that, while the analysis of at least six samples in the bias estimation is appropriate for the vast number of situations, there are occasions when this is not so. The greater the number of determinations, the greater the confidence in the estimation.

Figure 1 — Schematic procedure for the estimation of measurement uncertainty (including references to appropriate clauses and subclauses within this International Standard)

8 Evaluation of available precision and bias data

8.1 Approach and criteria

In this International Standard, the uncertainty component for the within-laboratory reproducibility, u_{R_w}, and the uncertainty component from method and laboratory bias, u_b, form the basis for the estimation of the measurement uncertainty. Selected validation data and analytical quality control results shall be representative of the measurement specification as described in Clause 7:

— measurement procedure: Are all steps of analysis considered (pretreatment, is the reference sample comparable to test samples)?

— within-laboratory reproducibility: Are all conditions of execution of the measurement procedure considered (e.g. different operators using different equipment)?

— measurement object: Are matrix variations (e.g. drinking water, surface water, sea water, waste water) and all possible interferences considered?

Choose, as a basis for the estimation of the uncertainty, the source of experimental information that provides the best coverage of uncertainty contributions in actual practice. Evaluate whether information exists on missing uncertainty contributions that are not known to be negligible.

If necessary, complete the uncertainty estimation, based on validation data and quality control results, with information from additional experiments or with estimations on the basis of existing knowledge.

If overestimation of the measurement uncertainty is acceptable, i.e. if the target measurement uncertainty is not exceeded, the result of this experimental approach including possible overestimation is still acceptable. If overestimation is not acceptable, a more detailed estimation shall be performed, which can encompass part of a modelling approach described, for example, in QUAM[11].

Figure 1 shows a schematic representation of the procedure.

Uncertainty calculations can be performed using either absolute or relative values (see 7.2).

Annex B contains worked examples of the estimation of measurement uncertainty according to this International Standard.

NOTE Measurement uncertainty can be estimated in several ways. Ideally, the estimates should lead to a statistically identical result. If not, this can be the consequence of not covering all sources of uncertainties. In this case, the uncertainty is underestimated. It can also occur, however, that even applying the method correctly leads to an overestimation of the uncertainty. This high value can be the consequence of uncertainty components not associated with the measurement method under consideration, e.g. those associated with the reference value of a reference material or the uncertainty of the concentration of a solution used in recovery experiments.

8.2 Within-laboratory reproducibility

8.2.1 Within-laboratory reproducibility conditions

The estimation of the random variations of measurement results shall be made under the same conditions as used when routine analysis is carried out.

Thus, it is necessary that the measurements be made under “within-laboratory conditions” (i.e. on different days and, depending on the conditions in the respective laboratory, with different equipment and different operators). These conditions fall between repeatability and reproducibility conditions and are referred to as within-laboratory reproducibility in this International Standard.

These conditions are usually employed when quality control samples are analysed that are similar to test samples.

For the estimation of the uncertainty component for the within-laboratory reproducibility, u_{R_w}, three approaches are described, see 8.2.2, 8.2.3 and 8.2.4, respectively. Examples of each approach are given in Annex B.

8.2.2 Control samples covering the whole analytical process

If stable quality control (QC) samples that cover the whole analytical process, including all sample preparation steps, are analysed regularly using the conditions described in 8.2.1, and if these QC samples are similar in matrix and analyte concentration levels to test samples, then the uncertainty component for the within-laboratory reproducibility, u_{R_w}, at this concentration and for this matrix, can be estimated from the standard deviation of these QC results (e.g. as obtained from quality control charts).

$$u_{R_w} = s_{R_w} \tag{1}$$

where s_{R_w} is the standard deviation of the QC results.

A minimum number of eight measurements is required for the estimation of this uncertainty component.

NOTE It is recognized that, while the analysis of at least eight measurements is appropriate for the vast number of situations, there are occasions when this is not so. The greater the number of measurements, the greater the confidence in the estimation.

If the analytical method covers a broad concentration range or range of matrices, and the uncertainty component for the within-laboratory reproducibility, u_{R_w}, varies with the concentration or matrix, it is necessary to analyse quality control samples comprising different matrices and concentration levels.

8.2.3 Using standard solutions as quality control samples

If quality control samples with an identical matrix to test samples are not available and synthetic standard solutions (with a matrix which differs from that of routine samples) are used, the additional uncertainty component due to possible increased inhomogeneity of the analyte in the matrix should also be considered.

The additional uncertainty due to inhomogeneity can be estimated, e.g. from range control charts using samples of different matrices. For the calculation of the standard deviation from the mean range, see Annex A.

Since the uncertainty component from the range control chart, $u_{r,\text{range}}$, covers only the repeatability component, it shall be combined with the uncertainty of the results from the quality control sample analysed, i.e. the standard solutions, $u_{R_\text{w},\text{stand}}$, to obtain a reliable estimate of the within-laboratory reproducibility.

$$u_{R_\text{w}} = \sqrt{u^2_{R_\text{w},\text{stand}} + u^2_{r,\text{range}}} \tag{2}$$

where

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

$u_{r,\text{range}}$ is the uncertainty component from the range control chart.

A minimum number of eight measurements is required for the estimation of both uncertainty contributions.

NOTE It is recognized that, while a number of at least eight measurements is appropriate for the vast number of situations, there are occasions when this is not so. The greater the number of measurements, the greater the confidence in the estimation.

The uncertainty component from the repeatability is partly included twice in this estimation, repeatability from standard solutions (part of $u_{R_\text{w},\text{stand}}$) as well as repeatability from test samples. However, in general, the repeatability part of the uncertainty component for the within-laboratory reproducibility, u_{R_w}, is small if measurements are performed at a concentration level well above the limit of quantification.

8.2.4 Unstable control samples

Where stable quality control samples are not available, e.g. for the determination of oxygen in water, the uncertainty component from the repeatability can be calculated from the mean of the ranges of replicate analyses (see Annex A). A minimum number of eight samples for the determination of ranges is required.

NOTE It is recognized that, while the analysis of at least eight samples is appropriate for the vast number of situations, there are occasions when this is not so. The greater the number of replicate analyses, the greater the confidence in the estimation.

For the uncertainty component resulting from variations between batches, $u_{R_\text{w},\text{bat}}$, other procedures for the estimation are required. In many cases, this component relies on scientific judgement based on the analyst's experience (see ISO/IEC Guide 98-3:2008, 4.3.1).

$$u_{R_\text{w}} = \sqrt{u^2_{r,\text{range}} + u^2_{R_\text{w},\text{bat}}} \tag{3}$$

where

$u_{r,\text{range}}$ is the uncertainty component from the range control chart;

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

8.3 Method and laboratory bias

8.3.1 General

If possible, sources of bias should always be eliminated. ISO/IEC Guide 98-3 states that if bias is significant and can be reliably estimated, then a measurement result should always be corrected. This is usually specified during development of a measurement procedure.

In many cases, the observed bias can vary depending on the matrix and the concentration of the analyte. This may be taken into account by using several matrix reference materials.

To evaluate the uncertainty associated with method and laboratory bias, u_b, two components shall be estimated:

a) the bias itself (as difference from the nominal or certified reference value);

b) the uncertainty of the nominal or certified reference value.

NOTE The bias uncertainty component can be neglected if it is $< u_{R_w} / 3$.

In 8.3.2, 8.3.3 and 8.3.4, respectively, three approaches to estimating the uncertainty associated with method and laboratory bias are outlined:

— analysis of suitable reference materials;

— participation in interlaboratory comparisons;

— recovery experiments with suitable samples.

8.3.2 Analysis of suitable reference materials

Results from regular analysis of suitable reference materials can be used to estimate the measurement uncertainty component associated with method and laboratory bias, u_b. Therefore each reference material should have been analysed in at least six batches of analyses.

NOTE 1 It is recognized that, while the analysis of the reference materials in at least six batches of analyses is appropriate for the vast number of situations, there are occasions when this is not so. The greater the number of results, the greater the confidence in the estimation.

The uncertainty in the reference value of the certified reference material can be obtained from the producer's certificate. It may be necessary to convert the uncertainty given on the certificate into a standard uncertainty, e.g. if the uncertainty is expressed as an expanded uncertainty or as a confidence interval. For other reference materials, the uncertainty in the reference value is taken from suitable statistical data, e.g. for material from interlaboratory trials from the reproducibility standard deviation (see 8.3.3).

To obtain a reliable estimate of the measurement uncertainty component associated with method and laboratory bias, u_b, it is advisable to use several reference materials covering the scope of the analytical method (different matrices and concentration levels). If only one reference material is used, the uncertainty may be underestimated.

If several reference materials are used, different values for bias are obtained which are used to calculate the uncertainty component b_{rms}. The uncertainty component associated with method and laboratory bias, u_b, is given by:

$$u_b = \sqrt{\bar{u}^2_{C_{\text{ref}}} + b^2_{\text{rms}}} \tag{4}$$

where

$\bar{u}_{C_{\text{ref}}}$ is the mean uncertainty of the reference values;

b_{rms} is the root mean square of the individual bias values, given by

$$b_{\text{rms}} = \sqrt{\frac{\sum (b_i)^2}{n_{\text{r}}}} \tag{5}$$

in which

b_i is the difference between the mean measured value and the accepted reference value of the ith reference material;

n_{r} is the number of reference materials.

If the individual bias values and the uncertainties of the reference values vary significantly, it can be necessary to separately estimate uncertainties for the different cases.

If only one reference material is available, the results of analyses of this reference material are treated as the best available estimate for the measurement uncertainty component associated with method and laboratory bias, u_b.

When only one reference material is used, the uncertainty component associated with method and laboratory bias is given by:

$$u_b = \sqrt{b^2 + \left(\frac{s_b}{\sqrt{n_{\text{M}}}} \right)^2 + u^2_{C_{\text{ref}}}} \tag{6}$$

where

b is the difference between mean measured value and an accepted reference value;

s_b is the standard deviation of the measured values of the reference material;

n_{M} is the number of bias measurements on the reference material;

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

NOTE 2 If only one reference material is used, the uncertainty of the bias estimation $s_b / \sqrt{n_{\text{M}}}$ can also make a significant contribution to u_b and is therefore included in the equation (see Reference [12]).

8.3.3 Participation in interlaboratory comparisons

Results from interlaboratory comparisons may be used in the same way as results from analyses of reference materials, if it is assumed that the assigned value in the interlaboratory comparison is a sufficiently good estimate of the true value.

NOTE 1 For each certified reference material, an estimate of bias, with a mean value based on several measurements performed on different days, can be obtained. In proficiency testing schemes, often, only single measurements are performed on a single day. Therefore, the difference between a laboratory result and the assigned value is calculated for different interlaboratory samples. This difference then includes contributions from both the uncertainty component associated with method and laboratory bias, u_b, and the uncertainty component for the within-laboratory reproducibility, $u_{R_{\text{w}}}$. The contributions from both components can lead to an overestimate of measurement uncertainty.

To determine an estimate of the bias from interlaboratory comparison results, a laboratory should have analysed at least six different samples within one or more rounds of interlaboratory comparisons.

NOTE 2 It is recognized that, while the analysis of at least six different samples is appropriate for the vast number of situations, there are occasions when this is not so. The greater the number of samples, the greater the confidence in the estimation.

The differences, D_i, between the measurement results and the assigned values for the different samples can be both positive and negative. All difference values are used to estimate the root mean square of the differences, D_{rms}:

$$D_{\text{rms}} = \sqrt{\frac{\sum D_i^2}{n_{\text{ilc}}}} \tag{7}$$

where

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

n_{ilc} is the number of interlaboratory comparison samples analysed.

If the individual differences and the uncertainties of the assigned values vary significantly, it may be necessary to separately estimate uncertainties for the different cases.

NOTE 3 Usually the uncertainty of an assigned value of an interlaboratory comparison sample is larger than the uncertainty of the certified reference value of a certified reference material. Thus, usually the estimated uncertainty component is larger. In some cases, the uncertainty of the assigned value of the interlaboratory comparison sample is so large that it cannot be used for the estimation of the uncertainty component associated with method and laboratory bias.

The mean uncertainty of the assigned values of the interlaboratory comparison samples, which have been calculated as robust or arithmetic mean from the results of the participating laboratories (i.e. consensus value), $\overline{u}_{C_{\text{ref}}}$, is calculated as:

$$\overline{u}_{C_{\text{ref}}} = \frac{\sum u_{C_{\text{ref}},i}}{n_{\text{ilc}}} \tag{8}$$

where

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

if the median or robust mean is used as consensus value or

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

if the arithmetic mean is used as consensus value, where

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

n_{ilc} is the number of analysed interlaboratory comparison samples;

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

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

NOTE 4 As specified in ISO 13528,[5] it is necessary to introduce a factor of 1,25 if the median or a robust mean is used for the calculation of the consensus value.

If the assigned value is not established as mentioned above, the uncertainty shall be obtained directly from the organizer of the interlaboratory comparison scheme.

Finally, the standard uncertainty component associated with method and laboratory bias, u_b, is calculated as:

$$u_b = \sqrt{D_{\text{rms}}^2 + \bar{u}_{C_{\text{ref}}}^2} \tag{9}$$

where

D_{rms} is the root mean square of the differences;

$\bar{u}_{C_{\text{ref}}}$ is the mean uncertainty of the assigned values of the interlaboratory comparison samples.

8.3.4 Recovery experiments

Recovery experiments, which estimate the recovery of a known amount of analyte added to a previously analysed sample, can also be used to evaluate bias.

In this case, the uncertainty associated with method and laboratory bias, u_b, consists of two components: the difference between observed and complete recovery of the analyte, and the uncertainty in the concentration of the analyte added.

The recovery experiments should be performed with at least six different samples of the relevant matrix.

NOTE It is recognized that, while the analysis of at least six different samples of the relevant matrix is appropriate for the vast number of situations, there are occasions when this is not appropriate. The greater the number of recovery experiments, the greater the confidence in the estimation.

The standard uncertainty associated with method and laboratory bias, u_b, estimated from recovery experiments is:

$$u_b = \sqrt{b_{\text{rms}}^2 + u_{\text{add}}^2} \tag{10}$$

where

b_{rms} is the root mean square of the deviations from the recovery experiments;

u_{add} is the uncertainty in the concentration of the analyte added.

The root mean square of the deviations from the recovery experiments, b_{rms}, is obtained from:

$$b_{\text{rms}} = \sqrt{\frac{\sum b_i^2}{n_\eta}} \tag{11}$$

where

b_i is the deviation from the complete recovery (100 %) of the ith recovery experiment or from the mean recovery, if the results are corrected with this mean recovery;

n_η is the number of recovery experiments.

If the individual bias values vary significantly, it may be necessary to separately estimate uncertainties for the different cases.

Bias from recovery experiments consists of contributions from both uncertainty components, u_b and $u_{R_{\text{w}}}$. These contributions can lead to measurement uncertainty being overestimated. Therefore each recovery which is used to calculate the deviation, b_i, should ideally be a mean recovery based on six determinations in order to reduce the contribution of the $u_{R_{\text{w}}}$ component.

The uncertainty in the concentration of the analyte added, u_{add}, consists of two components: the uncertainty of the volume added, u_V, and the uncertainty in the concentration of the solution added, u_{conc}.

The uncertainty of the volume added, u_V, can often be estimated from information provided by the manufacturers of volumetric labware. The systematic and the random (repeatability) errors shall be taken into account. The systematic error is often referred to as “maximum deviation”. Where insufficient information is available, it is necessary that a rectangular distribution be assumed and that the systematic standard uncertainty component of the volume, $u_{V,b}$, be added, calculated as:

$$u_{V,b} = \frac{\varepsilon_{V,\max}}{\sqrt{3}} \tag{12}$$

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

If the temperature deviates from that specified by the manufacturer of the volumetric labware, this shall also be taken into account (for further information, see QUAM[11]).

The random uncertainty component of the volume added, $u_{V,\mathrm{rep}}$, provided by the manufacturer is often given as a standard deviation.

The uncertainty component of the volume added, u_V, is given by:

$$u_V = \sqrt{u_{V,b}^2 + u_{V,\mathrm{rep}}^2} \tag{13}$$

where

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

$u_{V,\mathrm{rep}}$ is the random uncertainty component of the volume added (repeatability conditions).

If the solution used in recovery experiments is a certified reference material, the uncertainty of the concentration can be obtained from the certificate. If the solution is prepared by the laboratory, the uncertainty in the concentration shall be estimated in a suitable way (e.g. see B.3).

The uncertainty in the concentration of the analyte added, u_{add}, is calculated as:

$$u_{\mathrm{add}} = \sqrt{u_V^2 + u_{\mathrm{conc}}^2} \tag{14}$$

where

u_V is the uncertainty component of the volume added;

u_{conc} is the uncertainty of the concentration of the addition solution.

Finally, the standard uncertainty component associated with method and laboratory bias, u_b, is calculated according to Equation (10).

The recovery experiment might not cover all possible causes of uncertainty. Relevant ($>u_c/3$) contributions, e.g. those caused by interfering substances, shall be considered separately.

9 Calculation of the combined standard uncertainty

Calculate the combined standard uncertainty, u_c, from the standard uncertainties, u_j, or the combined relative standard uncertainty, $u_{c,\mathrm{rel}}$, from the relative standard uncertainties, $u_{j,\mathrm{rel}}$, respectively, of all J sources of uncertainty:

$$u_c = \sqrt{\sum_{j=1}^{J} u_j^2} \tag{15}$$

$$u_{\mathrm{c,rel}} = \sqrt{\sum_{j=1}^{J} u_{j,\mathrm{rel}}^2} \tag{16}$$

If there are no further uncertainty components, other than u_{R_w} and u_b, the combined standard uncertainty is calculated according to Equation (17).

$$u_\mathrm{c} = \sqrt{u_{R_\mathrm{w}}^2 + u_b^2} \tag{17}$$

10 Calculation of the expanded uncertainty

Calculate the expanded uncertainty, U, or the relative expanded uncertainty, U_rel, using a coverage factor of k = 2. This approximately corresponds to a symmetrical confidence interval of 95 %.

$$U = 2u_\mathrm{c} \tag{18}$$

$$U_\mathrm{rel} = 2u_\mathrm{c,rel} \tag{19}$$

11 Estimation of measurement uncertainty from reproducibility standard deviation

Measurement uncertainty can also be approximately estimated, if data from an interlaboratory comparison for method validation as specified in ISO 5725-2[2] are available, using the reproducibility standard deviation, s_R, from the interlaboratory comparison according to ISO 21748.[6] For this purpose, s_R is multiplied by a factor of 2 and the result is an estimate for the expanded uncertainty, U (for more details see ISO 21748[6]). If data from an interlaboratory comparison are used, it is necessary that the laboratory ensure that the within-laboratory standard deviation from replicate analyses is comparable to the repeatability standard deviation obtained in the interlaboratory comparison. It is also necessary that the laboratory check for gross errors regarding bias.

Reproducibility standard deviations for a method from proficiency tests where no repeatability standard deviation is stated can be used in a similar way.

12 Report

The complete report of measurement uncertainty consists of the uncertainty itself, the chosen confidence level, and the method used for the estimation of the measurement uncertainty.

EXAMPLE Mass concentration of SO_4^{2-} in waste water (ISO 10304-1[4]): (100 ± 8) mg/l

With the following footnote:

The measurement uncertainty was derived from results of interlaboratory trials. It represents the expanded uncertainty and was obtained with a coverage factor of k = 2. This corresponds to a confidence level of approximately 95 %.

Annex A
(normative)

Estimation of the standard uncertainty from range control charts

The standard uncertainty can be calculated from the mean range of a range control chart using Equation (A.1):

$$u_{r,\text{range}} = \frac{\bar{R}}{d_2} \tag{A.1}$$

where

$\bar{R}$ is the mean range;

d_2 is taken from Table A.1 and is dependent on the number of values from which the range is calculated.

Table A.1 — Factors for the calculation of the standard deviation from the mean range (Source: ISO 8258[3])

No. of values from which the range is calculated	Factor d_2
2	1,128
3	1,693
4	2,059
5	2,326

Annex B
(informative)

Examples of the estimation of measurement uncertainty

B.1 Example 1 — Estimation of measurement uncertainty using reference material

NOTE See 8.2.2 and 8.3.2.

B.1.1 Origin of quality control data

For quality control for the determination of orthophosphate in sea water samples, a certified reference material is analysed in 30 batches over a period of about three months.

B.1.2 Calculation of the uncertainty component for the within-laboratory reproducibility

As the analysis of the quality control sample covers the whole analytical process except sampling, the standard deviation of the quality control results, s_{R_w}, is equivalent to the uncertainty component for the within-laboratory reproducibility, u_{R_w}, at this concentration level. As the results are well above the limit of quantification, the uncertainty can be expressed as a relative value. See Table B.1.

Table B.1 — Results of the analyses of the quality control sample

Number	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**
PO_4^{3-}-P , µmol/l	2,16	2,40	2,31	2,33	2,36	2,27	2,37	2,27	2,27	2,10	2,26	2,58	2,23	2,47	2,37
Number	**16**	**17**	**18**	**19**	**20**	**21**	**22**	**23**	**24**	**25**	**26**	**27**	**28**	**29**	**30**
PO_4^{3-}-P , µmol/l	2,39	2,30	2,26	2,42	2,67	2,36	2,37	2,36	2,30	2,50	2,17	2,43	2,35	2,16	2,30

From these quality control data the following values are calculated:

Mean value: $\overline{c}$ = 2,336 µmol/l

Standard deviation: s_{R_w} = 0,122 µmol/l

From this the relative uncertainty component for the within-laboratory reproducibility, $u_{R_w,rel}$, can be calculated as:

$$u_{R_w,rel} = \frac{s_{R_w}}{\overline{x}} = \frac{0,122}{2,336} = 0,052\,1 = 5,21\ \%$$

B.1.3 Calculation of the uncertainty component associated with method and laboratory bias

Since only one reference material is available, it is necessary that three components be considered for the estimation of the uncertainty component associated with method and laboratory bias, u_b:

a) the difference between the mean measured value and an accepted reference value, bias;

b) the standard deviation of the measured values of the reference material, s_b;

c) the uncertainty of the reference value, $u_{C_{ref}}$.

The certificate accompanying the reference material provides the following information:

— certified value, C_{ref}, and confidence interval of orthophosphate-P: (2,43 ± 0,41) µmol/l;

— the confidence interval (±0,41) represents three standard deviations derived from the interlaboratory testing for the generation of the certified reference value.

From this it follows that the uncertainty of the reference value, $u_{C_{ref}}$ is:

$$u_{C_{ref}} = \frac{0,41}{3} \text{ µmol/l} = 0,137 \text{ µmol/l}$$

The relative uncertainty of the reference value, $u_{C_{ref},rel}$, is given by:

$$u_{C_{ref},rel} = \frac{u_{C_{ref}}}{C_{ref}} = \frac{0,137}{2,43} = 0,056$$

The bias, b, is calculated using the mean of the measured values of the control sample $\bar{x}$ (see B.1.2):

$$b = \bar{x} - C_{ref} = 2,336 - 2,43 = -0,094$$

The relative bias, b_{rel}, is given by:

$$b_{rel} = \frac{\bar{x} - C_{ref}}{C_{ref}} = \frac{2,336 - 2,43}{2,43} = -0,0387$$

The coefficient of variation of the measured values of the reference material, $C_{V,b}$, is equal to the relative uncertainty component for the within-laboratory reproducibility, $u_{R_w,rel}$, (see B.1.2):

$$C_{V,b} = u_{R_w,rel} = 0,052\,1$$

and

$$n_M = 30$$

Using these data, the relative uncertainty component associated with method and laboratory bias, $u_{b,rel}$ is calculated as:

$$u_{b,rel} = \sqrt{b_{rel}^2 + \left(\frac{C_{V,b}}{\sqrt{n_M}}\right)^2 + u_{C_{ref},rel}^2} = \sqrt{(-0,038\,7)^2 + \left(\frac{0,052\,1}{\sqrt{30}}\right)^2 + 0,056\,2^2} = 0,068\,9 = 6,89\,\%$$

B.1.4 Calculation of the relative combined uncertainty, $u_{c,rel}$

The relative combined uncertainty is calculated as:

$$u_{c,rel} = \sqrt{u_{R_w,rel}^2 + u_{b,rel}^2} = \sqrt{0,052\,1^2 + 0,068\,9^2} = 0,086\,4 = 8,64\,\%$$

B.1.5 Calculation of the relative expanded uncertainty, U_{rel}

The relative expanded uncertainty is calculated using a coverage factor k = 2:

$$U_{rel} = k u_{c,rel}$$

$$U_{rel} = 2 \times 0,086\,4 = 0,172\,8 \approx 17,3\,\%$$

B.2 Example 2 — Estimation of measurement uncertainty based on data from proficiency tests

NOTE See 8.2.2 and 8.3.3.

B.2.1 Origin of quality control data

The total phosphorus content of sea water samples is routinely determined. For interlaboratory quality control the laboratory regularly participates in proficiency tests. In the period from 2003-07 to 2004-04, the results listed in Table B.2 were obtained.

Table B.2 — Results from proficiency tests

Proficiency test	c_{ass} µmol/l	$\bar{c}$ µmol/l	D_i µmol/l	$D_{i,rel}$ %	$s_{R,i,rel}$ %	$n_{p,i}$	$u_{C_{ref},i,rel}$ %
1	14,080	14,253	0,173	1,23	3,1	28	0,73
2	6,250	6,752	0,502	8,03	4,8	28	1,13
3	2,820	2,582	−0,238	−8,44	7,6	28	1,80
4	5,243	5,414	0,171	3,26	5,3	35	1,12
5	3,600	3,780	0,180	5,00	6,9	35	1,46
6	1,838	1,913	0,075	4,08	8,4	35	1,77

c_{ass}	assigned value of the interlaboratory comparison sample
$\bar{c}$	mean value of the laboratory's test results
D_i	difference of the mean value $\bar{c}$ and the assigned value c_{ass}
$D_{i,rel}$	relative difference as a percentage: $D_{i,rel} = \frac{\bar{c} - c_{ass}}{c_{ass}} \times 100$
$s_{R,i,rel}$	reproducibility standard deviation from the interlaboratory comparison for sample i
$n_{p,i}$	number of participating laboratories
$u_{C_{ref},i,rel}$	relative uncertainty of the assigned value of the interlaboratory sample

Since the robust mean was used as the consensus mean, the single uncertainties are calculated as

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

B.2.2 Calculation of the uncertainty component for the within-laboratory reproducibility

As the results are well above the limit of quantification, the uncertainty can be expressed as a relative value. The relative uncertainty component for the within-laboratory reproducibility, is calculated as the coefficient of variation from the analyses of a stable control sample [ρ(P) = 8 mg/l] used in a mean control chart:

mean value from 20 batches $\bar{\rho} = 8{,}03$ mg/l

standard deviation $s = 0{,}352$ mg/l

coefficient of variation $C_V = u_{R_w,rel} = 0{,}043\,8 = 4{,}38$ %

B.2.3 Calculation of the uncertainty component associated with method and laboratory bias

For the determination of the uncertainty component associated with method and laboratory bias, u_b, two components shall be determined: root mean square of the differences, D_{rms}, and the mean uncertainty of the assigned values $\overline{u}_{C_{\text{ref}}}$.

The relative root mean square of the differences $D_{\text{rms,rel}}$ is calculated as

$$D_{\text{rms,rel}} = \sqrt{\frac{\sum D_{i,\text{rel}}^2}{n_{\text{ilc}}}}$$

$$D_{\text{rms,rel}} = \sqrt{\frac{0{,}012\,3^2 + 0{,}080\,3^2 + 0{,}084\,4^2 + 0{,}032\,6^2 + 0{,}050\,0^2 + 0{,}040\,8^2}{6}} = 0{,}056\,2 = 5{,}62\ \%$$

The mean uncertainty of the assigned values is calculated as

$$\overline{u}_{C_{\text{ref}}} = \frac{\sum u_{C_{\text{ref}},i}}{n_{\text{ilc}}}$$

For calculation of the relative mean uncertainty of the assigned values the $u_{C_{\text{ref}},i,\text{rel}}$ values listed in Table B.2 are divided by a factor of 100 (as tabulated values are expressed as percentages)

$$\overline{u}_{C_{\text{ref}},\text{rel}} = \frac{0{,}007\,3 + 0{,}011\,3 + 0{,}018\,0 + 0{,}011\,2 + 0{,}014\,6 + 0{,}017\,7}{6} = 0{,}013\,4 = 1{,}34\ \%$$

Finally the relative uncertainty component associated with method and laboratory bias, $u_{b,\text{rel}}$, is calculated as:

$$u_{b,\text{rel}} = \sqrt{D_{\text{rms,rel}}^2 + u_{C_{\text{ref}},\text{rel}}^2} = \sqrt{0{,}056\,2^2 + 0{,}013\,4^2} = 0{,}057\,8 = 5{,}78\ \%$$

B.2.4 Calculation of the relative combined uncertainty, $u_{\text{c,rel}}$

The relative combined uncertainty is calculated as:

$$u_{\text{c,rel}} = \sqrt{u_{R_{\text{w}},\text{rel}}^2 + u_{b,\text{rel}}^2} = \sqrt{0{,}043\,8^2 + 0{,}057\,8^2} = 0{,}072\,5 = 7{,}25\ \%$$

B.2.5 Calculation of the relative expanded uncertainty, U_{rel}

The relative expanded uncertainty is calculated using a coverage factor k = 2:

$$U_{\text{rel}} = k u_{\text{c,rel}}$$

$$U_{\text{rel}} = 2 \times 0{,}072\,5 = 0{,}145 = 14{,}5\ \%$$

B.3 Example 3 — Estimation of measurement uncertainty using a standard solution as quality control sample and recovery experiments

NOTE See 8.2.3 and (8.3.4.

B.3.1 Origin of quality control data

The herbicide triflusulfuron-methyl is routinely determined in water samples. A quality control sample covering the whole analytical process is not available. Therefore, a standard solution is used as quality control sample for operation of a control chart. For quality control, recoveries are determined in each batch of analyses.

For this purpose, spiked water samples (triflusulfuron-methyl concentration, ρ = 0,1 µg/l) are analysed. The triflusulfuron-methyl results of the real samples are corrected using averaged recoveries.

B.3.2 Calculation of the uncertainty component for the within-laboratory reproducibility

For calculation of the uncertainty component for the within-laboratory reproducibility, u_{R_w}, the results from the following quality control measurements are required:

a) measurement of a stable quality control standard in organic solvent in each batch of analyses (triflusulfuron-methyl concentration, ρ = 0,50 µg/ml).

b) repeated determination of spiked water samples (triflusulfuron-methyl concentration, ρ = 0,1 µg/l) for range control chart.

As the results are well above the limit of quantification the uncertainty can be expressed as a relative value.

B.3.2.1 Data for calculation of the uncertainty component for the within-laboratory reproducibility

See Table B.3.

Table B.3 — Results of stable quality control standard, assigned value: ρ = 0,50 µg/ml

Number of measurement	ρ µg/ml
1	0,49
2	0,50
3	0,52
4	0,48
5	0,49
6	0,51
7	0,51
8	0,54
9	0,48
10	0,49
Mean value $\bar{\rho}$	0,501
Standard deviation s	0,019 1
Coefficient of variation, $C_V = u_{R_w,\text{stand,rel}}$	0,038 2

For the operation of a range control chart, spiked water samples are analysed in duplicate with each batch of samples. The relative range, $R_{j,\text{rel}}$, which is used as quality control value for the range control chart, is calculated as:

$$R_{j,\text{rel}} = \frac{x_{i,\max} - x_{i,\min}}{\bar{x}_j}$$

where j is the jth batch of i replicates.

See Table B.4 for results from the range control chart (d_2 = 1,128 for duplicate measurements).

Table B.4 — Results from the range control chart (d_2 = 1,128)

Number of batch	$R_{j,\text{rel}}$
1	0,154 4
2	0,168 9
3	0,104 6
4	0,044 5
5	0,116 2
6	0,030 3
7	0,113 5
8	0,025 0
9	0,050 1
10	0,025 5
Mean value $\bar{R}_{\text{rel}}$	0,083 3
Coefficient of variation, $C_V = u_{r,\text{range,rel}} = \frac{\bar{R}_{\text{rel}}}{d_2}$	0,073 8

B.3.2.2 Calculation of the uncertainty component for the within-laboratory reproducibility

For calculation of the relative within-laboratory reproducibility, $u_{R_\text{w},\text{rel}}$, the relative uncertainty from the mean control chart, $u_{R_\text{w},\text{stand,rel}}$, is combined with the relative uncertainty component from the range control chart, $u_{r,\text{range,rel}}$.

$$u_{R_\text{w},\text{rel}} = \sqrt{u^2_{R_\text{w},\text{stand,rel}} + u^2_{r,\text{range,rel}}} = \sqrt{0{,}038\ 2^2 + 0{,}073\ 8^2} = 0{,}083\ 1 = 8{,}31\%$$

B.3.3 Calculation of the uncertainty component associated with method and laboratory bias

For the determination of recoveries, spiked water samples (triflusulfuron-methyl concentration, ρ = 0,1 µg/l) are analysed in each batch of analyses. The uncertainty component associated with method and laboratory bias, u_b, is estimated from these recovery experiments. For the estimation of u_b, it is necessary that two components be determined:

a) the root mean square of the deviations from the recovery experiments, b_{rms};

b) the uncertainty in the concentration of the analyte added, u_{add}.

B.3.3.1 Determination of root mean square of the deviations from the recovery experiments, b_{rms}

See Table B.5.

Table B.5 — Results from 10 recovery experiments and calculation of bias from mean recovery, $\bar{\eta}$

η_i %	$b_{i,\text{rel}}$	$\bar{\eta}$ %
95,1	0,066 1	89,2
84,5	−0,052 7	
98,3	0,102	
86,3	−0,032 5	
85,4	−0,042 6	
92,8	0,040 4	
88,0	−0,013 5	
83,0	−0,069 5	
83,8	−0,060 5	
95,0	0,065 0	

The relative bias from the mean recovery is calculated as:

$$b_{i,\text{rel}} = \frac{\eta_i - \bar{\eta}}{\bar{\eta}}$$

where η_i is the recovery of the single measurement.

NOTE Here $b_{i,\text{rel}}$ refers to the mean recovery and not to the target value 100 %, because for calculation of results an equation with a correction factor derived from averaged recoveries is used.

The relative root mean square of the deviations from the recovery experiments, $b_{\text{rms,rel}}$ is calculated as:

$$b_{\text{rms,rel}} = \sqrt{\frac{\sum (b_{i,\text{rel}})^2}{n_\eta}}$$

$$b_{\text{rms,rel}} = \sqrt{\frac{0{,}066\,1^2 + (-0{,}052\,7)^2 + 0{,}102^2 + (-0{,}032\,5)^2 + (-0{,}042\,6)^2 + 0{,}040\,4^2 + (-0{,}013\,5)^2 + (-0{,}069\,5)^2 + (-0{,}060\,5)^2 + 0{,}065\,0^2}{10}}$$

$b_{\text{rms,rel}}$ = 0,059 1 = 5,91 %

B.3.3.2 Determination of the uncertainty in the concentration of the analyte added, u_{add}

The analyte-added uncertainty, u_{add}, consists of two components:

a) the uncertainty of the concentration of the addition solution, u_{conc};

b) the uncertainty component of the volume added, u_V.

B.3.3.2.1 Determination of the uncertainty of the concentration of the addition solution, u_{conc}

The spiking solutions are prepared in the laboratory. The uncertainty due to weighing is considered to be negligible. For the calculation of the uncertainty of the concentration of the addition solution, u_{conc}, the uncertainties of the volumetric glassware are used.

For the preparation of the spiking solutions, 3 (20 ml) volumetric flasks and 2 (1 ml) pipettes are used. The manufacturer gives details about the maximum deviation of the volumes ($u_{V,b,i}$), which are reported to be 0,2 % for the volumetric flasks and 0,7 % for the pipettes.

For intra-laboratory quality control analyses, the volumetric instruments are checked by weighing and the random uncertainty component ($u_{V,\text{rep}}$) is calculated as a standard deviation. The random uncertainty component for the volumetric flasks is 0,045 % and for the pipettes is 0,14 %.

Since there is no other information available regarding the deviation of the volumes, a rectangular distribution is assumed and the systematic uncertainty component of the volume added, $u_{V,b}$ is calculated as:

$$u_{V,b} = \frac{\varepsilon_{V,\max}}{\sqrt{3}}$$

The relative uncertainty of the concentration of the addition solution, $u_{\text{conc,rel}}$ is calculated by combining the systematic and the random uncertainty components:

$$u_{\text{conc,rel}} = \sqrt{\sum u^2_{V,b,i,\text{rel}} + \sum u^2_{V,\text{rep},i,\text{rel}}}$$

$$u_{\text{conc,rel}} = \sqrt{\left(\frac{0{,}002}{\sqrt{3}}\right)^2 \times 3 + \left(\frac{0{,}007}{\sqrt{3}}\right)^2 \times 2 + (0{,}000\,45)^2 \times 3 + (0{,}001\,4)^2 \times 2} = 0{,}006\,4 = 0{,}64\ \%$$

B.3.3.2.2 Determination of the uncertainty of the volume added, u_V

The uncertainty of the volume added, u_V, consists of two components,

a) the systematic uncertainty component of the volume added, $u_{V,b}$;

b) the random uncertainty component of the volume added, $u_{V,\text{rep}}$.

B.3.3.2.2.1 Determination of the systematic uncertainty component of the volume added, $u_{V,b}$

The spiking solution is added using a microlitre syringe. The maximum variation reported by the manufacturer for the volume is 1 %. Since there is no other information available, a rectangular distribution is assumed and the relative systematic uncertainty component of the volume added, $u_{V,b,\text{rel}}$, is calculated as:

$$u_{V,b,\text{rel}} = \frac{\varepsilon_{V,\max}}{\sqrt{3}} = \frac{0{,}01}{\sqrt{3}} = 0{,}005\,8 = 0{,}58\ \%$$

B.3.3.2.2.2 Determination of the random uncertainty component of the volume added, $u_{V,\text{rep}}$

The component $u_{V,\text{rep}}$ is determined by repeated weighing (see Table B.6) of water, which is pipetted using the same or similar microlitre syringe.

B.3.3.2.2.3 Calculation of the uncertainty of the volume added, u_V

For calculation of the relative uncertainty of the volume added, $u_{V,\text{rel}}$, the systematic and the random uncertainty components of the volume added, $u_{V,b,\text{rel}}$ and $u_{V,\text{rep,rel}}$ are combined as follows:

$$u_{V,\text{rel}} = \sqrt{u^2_{V,b,\text{rel}} + u^2_{V,\text{rep,rel}}} = \sqrt{(0{,}005\,8)^2 + (0{,}002\,7)^2} = 0{,}006\,4 = 0{,}64\%$$

B.3.3.2.3 Determination of the uncertainty in the concentration of the analyte added, u_{add}

For calculation of the relative uncertainty in the concentration of the analyte added, $u_{\text{add,rel}}$, the uncertainties $u_{V,\text{rel}}$ (see B.3.3.2.2.3) and $u_{\text{conc,rel}}$ (see B.3.3.2.1) are combined as follows:

$$u_{\text{add,rel}} = \sqrt{u^2_{V,\text{rel}} + u^2_{\text{conc,rel}}} = \sqrt{(0{,}006\,4)^2 + (0{,}006\,4)^2} = 0{,}009\,1 = 0{,}91\%$$

B.3.3.3 Calculation of the uncertainty component associated with method and laboratory bias, u_b

For calculation of the relative uncertainty component associated with method and laboratory bias, $u_{b,\mathrm{rel}}$, the relative root mean square of the deviations from the recovery experiments, $b_{\mathrm{rms,rel}}$ (see B.3.3.1), and the relative uncertainty in the concentration of the analyte added, $u_{\mathrm{add,rel}}$, are combined as follows:

$$u_{b,\mathrm{rel}} = \sqrt{b^2_{\mathrm{rms,rel}} + u^2_{\mathrm{add,rel}}} = \sqrt{(0{,}059\,1)^2 + (0{,}009\,1)^2} = 0{,}059\,8 = 5{,}98\ \%$$

Table B.6 — Standard deviation of the pipetted volume

Number of measurement	Mass g
1	0,249 6
2	0,249 0
3	0,250 2
4	0,251 0
5	0,249 8
6	0,250 2
7	0,248 9
8	0,249 4
9	0,250 4
Mean value $\bar{m}$	0,249 8
Standard deviation s	0,000 686
Coefficient of variation, $C_V = u_{V,\mathrm{rep,rel}}$	0,002 7 = 0,27 %

B.3.4 Calculation of the relative combined uncertainty, $u_{\mathrm{c,rel}}$

The relative combined uncertainty is calculated as:

$$u_{\mathrm{c,rel}} = \sqrt{u^2_{R_\mathrm{w},\mathrm{rel}} + u^2_{b,\mathrm{rel}}} = \sqrt{(0{,}083\,1)^2 + (0{,}059\,8)^2} = 0{,}102\,4 = 10{,}24\ \%$$

B.3.5 Calculation of the relative expanded uncertainty, U_{rel}

The relative expanded uncertainty is calculated using a coverage factor $k = 2$:

$$U_{\mathrm{rel}} = k u_{\mathrm{c,rel}}$$

$$U_{\mathrm{rel}} = 2 \times 10{,}24\ \% \approx 20\ \%$$

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