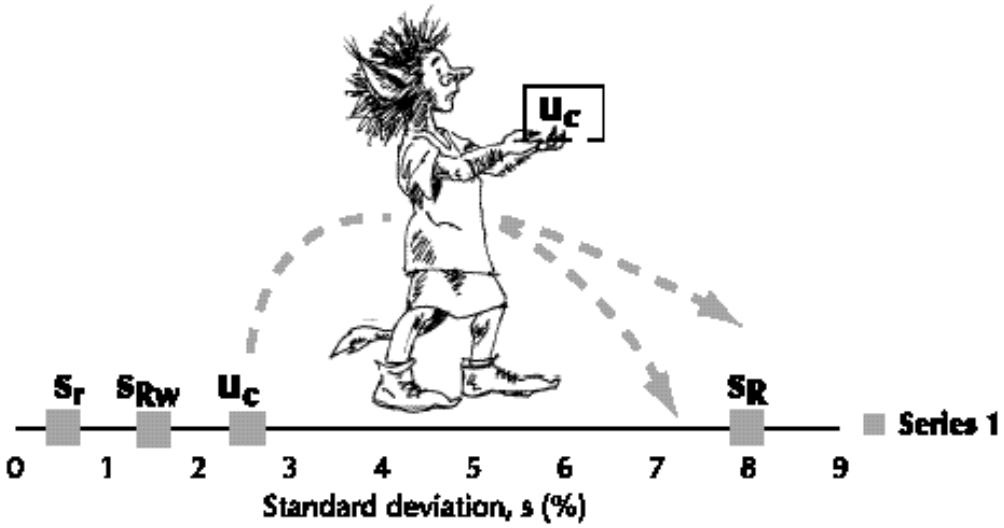
Handbook
for
Calculation of Measurement Uncertainty
in
Environmental Laboratories



Nordtest
Slettetoften 9,
DK-2630 Taastrup
Denmark

Telephone +45 21 21 44 44
nordtest@nordtest.info
www.nordtest.info

NORDTEST

NORDTEST, founded in 1973, is a Nordic institution acting as a joint body in the field competence and expertise in the field of harmonizing of norms and methods, a large Nordic net-work of experts, more than 650 recommended Nordic testing methods and 550 published technical reports.

www.nordtest.info

Nordtest
Slettetoften 9,
DK-2630 Taastrup

Telephone +45 21 21 44 44
nordtest@nordtest.info
www.nordtest.info

Handbook
for
Calculation of Measurement Uncertainty
in
Environmental Laboratories

Edition 4 November 2017

Authors
Bertil Magnusson, Trollboken AB, Sweden
Teemu Näykki, SYKE, Finland
Håvard Hovind, Norway
Mikael Krysell, Swedish Agency for Marine and Water Management
Eskil Sahlin, RISE, Sweden

Drawings by Petter Wang, Norway

Valuable comments on the contents have been provided by:
Rolf Flykt, Sweden
Irma Mäkinen, Finland
Ulla O. Lund, Denmark
Steve Ellison, UK
Ivo Leito, Estonia

Downloading address:
www.nordtest.info

Recommended citation
This document should be cited* as "B. Magnusson, T. Näykki, H. Hovind, M. Krysell, E. Sahlin, Handbook for calculation of measurement uncertainty in environmental laboratories, Nordtest Report TR 537 (ed. 4) 2017. Available from www.nordtest.info.
**Subject to journal requirements*

FOREWORD

The approach of using quality control data and validation data to estimate measurement uncertainty for routine analyses is now well established. This Nordtest handbook TR537, describing the approach is available in several languages at www.nordtest.info. First issued in 2003, this 4th edition is based on experience gained by many laboratories using this approach to estimate measurement uncertainty. Major updates in the 2017 version are as follows:

- Uncertainty over the measurement range – a separate section on estimating measurement uncertainty over the measurement range, in either absolute units or relative units, has been added, this being one of the major difficulties of applying this approach.
- Estimating standard deviation from duplicates – a pooled standard deviation is used instead of a factor applied to the mean range.
- Use of control chart limits for the within-lab reproducibility component *u(Rw)* is pointed out more clearly
- Harmonisation with ISO 11352 *Water quality — Estimation of measurement uncertainty based on validation and quality control data*. The terminology has been harmonised with the ISO standard which applies this approach to measurement uncertainty.

We can also recommend the following resources (see section 2.5) to help users applying this approach to estimate uncertainty:

- Software MUkit – freely available software following this approach to estimate uncertainty. An example of a MUkit report is presented in Appendix 9.
- Online course – a link is given to a course from University of Tartu presenting in detail this approach to estimate uncertainty.

Contents

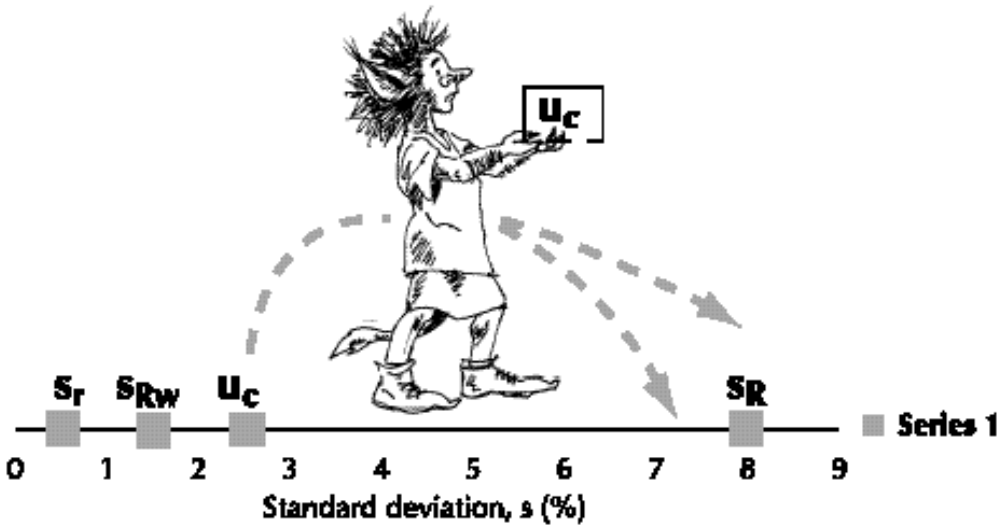
1 Definitions, abbreviations and symbols

The main sources here for edition 4 are edition 3 of this handbook, VIM [10] and the ISO 11352 *Water quality — Estimation of measurement uncertainty based on validation and quality control data* [5].

bias	Estimate of systematic measurement error [10]. Difference between mean measured value from a large series of test results and an accepted reference value (a certified or assigned value). The measure of trueness [10] is normally expressed in term of bias.
CRM	Certified Reference Material
PT	Evaluation of participant performance against pre-established criteria by means of interlaboratory comparisons, also called external quality assessment
Symbols	
RMS_{bias}	The root mean square of the individual bias values [5] (b_{RMS} in ref [5]) $\sqrt{\frac{\sum (bias_i)^2}{n}}$
s	An estimate of the population standard deviation σ from a limited number (n) of observations (x_i)
s_r	Standard deviation under repeatability conditions **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 [5]
s_{Rw}	Standard deviation under within-laboratory reproducibility conditions **within-laboratory reproducibility** intermediate measurement precision where variations within one laboratory alone are included [5] Comment: s_{Rw}, intermediate measure between s_r and s_R. An alternative name is *intermediate precision* [5]. The s_{Rw} can be estimated from a control sample over a certain period of time, preferably at least one year.
s_R	Standard deviation under reproducibility conditions **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 [5]
$\bar{x}$	Mean value
u(bias)	The uncertainty component associated with (possible) method and laboratory bias [5] (u_b in ref [5])

u(Cref)	Standard uncertainty component for the certified or assigned value - a mean value of the individual uncertainties, $u(Cref_i)$ [5] ($\overline{u}_{Cref}$ in ref [5]).
u(Rw)	Standard uncertainty component for the within-laboratory reproducibility [5]
u(x)	Standard uncertainty
u_c	Combined standard uncertainty
U	Expanded uncertainty, normally close to 95 % confidence interval

Repeatability, s_r
Within-lab reproducibility, s_{Rw}
Combined standard uncertainty, u_c
Reproducibility between laboratories, s_R



2 Introduction

2.1 Scope and field of application

This handbook is written for environmental testing laboratories in the Nordic countries. Its purpose is to give support to those implementing the concept of measurement uncertainty following the principles in GUM [1] for routine measurements. However, the approach is very general and should be applicable to most analytical laboratories. The aim is to provide a practical, understandable and common approach of measurement uncertainty calculation.

This approach is mainly based on already existing quality control and validation data, according to the European accreditation guideline [2], the Eurolab Technical Report [3] and the ISO 21748 [4]. The approach is also presented in detail in ISO 11352 [5] and consistent with the requirements of ISO/IEC 17025 [6]. Nordtest has supported this project financially in order to promote and enhance harmonisation between Nordic laboratories.

Practical examples, taken directly from the everyday world of environmental laboratories, are presented and explained. The approach given in this handbook is presented in detail for determination of acrylamide in snacks with LC-MS in an online course "Estimation of measurement uncertainty in chemical analysis" from the University of Tartu[1].

The handbook covers all steps in the analytical chain from the arrival of the test sample in the laboratory to the reporting of the analytical result. It is important to notice that vital parts of the total measurement uncertainty are not included, e.g. sampling, sample transportation and possible gross errors during data storage/retrieval. Regarding sampling uncertainty there is the Nordtest handbook, *Uncertainty from Sampling* [20].

While the recommendations presented do form a valid approach to the evaluation of measurement uncertainty for many purposes, other suitable approaches may also be adopted. Especially the Eurolab Technical Report [3] and the Eurachem/CITAC Guide [7] are useful where several different approaches are presented with detailed examples and the concept of measurement uncertainty is fully described.

Basic knowledge of terminology [10] and the use of quality control and statistics [9] are required to follow the calculations presented here. In order to make it possible for the reader to follow the calculations, raw data is given in appendices.

[1] The presentations are given under heading *10. The single-lab validation approach*, www.sisu.ut.ee/measurement/uncertainty, accessed 2017.

2.2 Comment to data users

Previously, laboratories reported within-laboratory reproducibility s_{Rw}, calculated from data taken from an internal quality control covering the whole analytical process. The expanded measurement uncertainty, *U,* also taking into account method and laboratory bias variation and using a coverage factor of 2, can give values which may be a factor of 2 to 5 times higher. However, this does not reflect a change in the performance of the laboratory, just a much better estimation of the real variation *between* laboratories.

In Figure 1, the ammonium nitrogen, NH_4-N, results from two laboratories are in good agreement – the difference is about 5 %. You can see this to the right of the chart where measurement uncertainty is presented, using the coverage factor of 2, but not on the left, where the s_{Rw} from internal quality control is given.

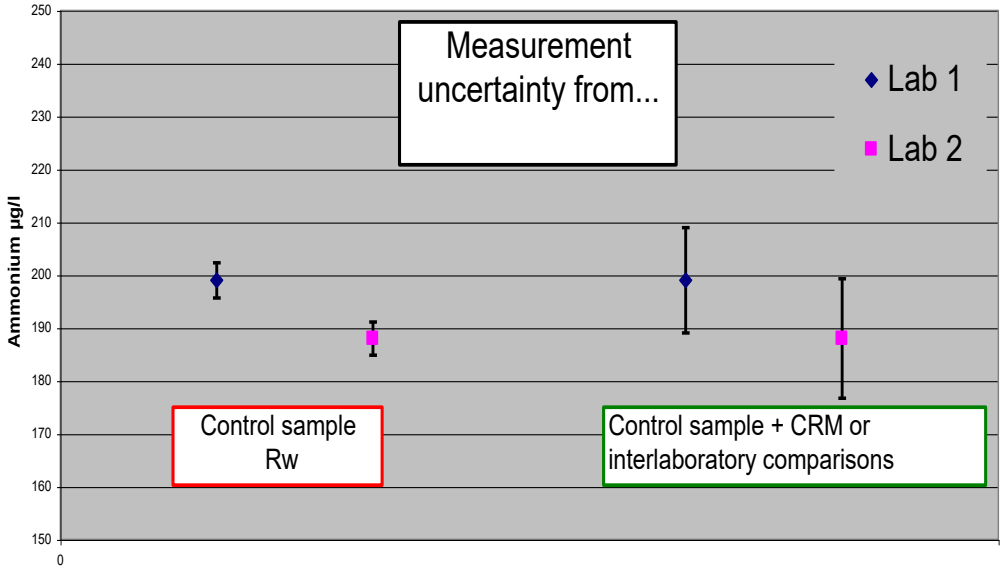


Figure 1. Comparing NH_4-N results from two laboratories, Lab 1 = 199 µg L^{-1} and Lab 2 = 188 µg L^{-1}. To the left the error bars are calculated from internal control, ± s_{Rw}, and to the right the error bars are expanded measurement uncertainty, ± U.

2.3 Ladder of errors

As described in Nordtest TR 569 [9] the sources of errors affecting the possible deviation from a reference value for an analytical result can be described by the ladder presented in Figure 2.

For an individual determination on a test sample in a certain matrix the four different steps in the ladder are as follows: 1) the method as such, 2) the method as it is used in the laboratory, 3) the day-to-day variation in the laboratory, 4) the variation within an analytical run – repeatability.

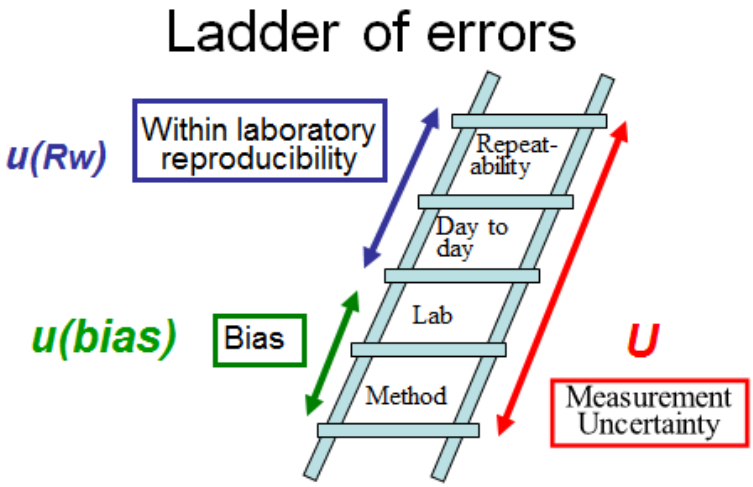


Figure 2. Ladder of errors in a measurement

Step 1 - The method bias – a systematic error owing to the method used

Step 2 - The laboratory bias – a systematic error (for an individual laboratory)

Step 3 - The day-to-day variation – a random error occurring between replicated determinations performed different days in a laboratory over a long period of time

Step 4 - The repeatability – a random error occurring between replicate determinations performed within a short period of time; inhomogeneity is part of the repeatability

Each of these steps on the ladder adds to the uncertainty. The measurement uncertainty normally consists of all four steps. This handbook demonstrates how certified reference materials (or synthetic control samples), proficiency testing or recovery tests are used for estimating *u*(bias), step 1 and 2.

The uncertainty component for within-laboratory reproducibility *u(Rw)* consists of step 3 and 4. The *u(Rw)* can be estimated using repeated measurements of a control sample over a long period of time, provided that the control sample has similar matrix and concentration as the test samples and goes through the whole analytical process. Repeatability can be estimated separately using replicates of routine samples analysed within the same analytical run.

2.4 About Measurement Uncertainty

What is measurement uncertainty?

- The number after ±
- All measurements are affected by a certain error. The measurement uncertainty tells us what size the measurement error **might** be. Therefore, the measurement uncertainty is an important part of the reported result.
- Definition: Measurement uncertainty is ”non-negative parameter characterizing the dispersion of the quantity values being attributed to a measurand, based on the information used” [10]

Who needs measurement uncertainty?

- The data user/customer needs it together with the result to make a correct decision. The uncertainty of the result is important, e.g. when looking at allowable (legal) limits.
- The laboratory, to verify its´ own quality of measurement

Why should the laboratory report measurement uncertainty?

- As explained above, the data user/customer need it in order to be able to make correct decisions
- An estimation of the measurement uncertainty is required in ISO 17025 [6]

How is measurement uncertainty obtained?

- The basis for the evaluation is a measurement and statistical approach, where the different uncertainty sources are estimated and combined into a single value
- “*Basis for the estimation of measurement uncertainty is the existing knowledge (no special scientific research should be required from the laboratories). Existing experimental data should be used (quality control charts, validation, interlaboratory comparisons testing, CRM etc.)*” [2].
- Guidelines are given in GUM [1], further developed in, e.g., EA guidelines [2], the Eurachem/CITAC guide [7], in a Eurolab technical report [3] and in ISO 21748 [4]

How is the result expressed with measurement uncertainty?

- Measurement uncertainty should normally be expressed as U, the expanded measurement uncertainty, with a stated confidence level and a coverage factor, k. In most cases $k = 2$, providing a level of confidence of approximately 95 %
- Measurement uncertainty is expressed normally with one digit, maximum 2 digits. In many cases the uncertainty is rounded up e.g. 6.40 % is rounded to 7 % but common sense should prevail so 6.05 % is rounded down to 6 % - see GUM section 7.2.2 [1]

- It is often useful to state how the measurement uncertainty was obtained Example, where ± 7 % is the measurement uncertainty:

  Concentration of ammonium nitrogen (NH_4-N) = 148 ± 10 µg L^{-1}. The measurement uncertainty, 10 µg L^{-1} (95 % confidence level, coverage factor k = 2) is estimated from internal control and from proficiency testing

How should measurement uncertainty be used?

- It can be used as in Figure 1, to decide whether there is a difference between results from different laboratories
- It is necessary when comparing results to allowable limits, e.g. specifications or allowable (legal) limits, and when using data for classification of ecological or chemical status as required by various EU directives

2.5 External resources

Software

MUkit (Measurement Uncertainty Kit) is a measurement uncertainty software application, its calculation are mainly based on this handbook, Nordtest TR537. It is a user-friendly tool, where a laboratory can utilize results from quality control samples and validation data for uncertainty estimation. MUkit software is available for download free of charge at Envical SYKE website. An example of a MUkit report is given in Appendix 9.
http://www.syke.fi/envical/en

On-line course

University of Tartu gives an on-line course, *Estimation of measurement uncertainty in chemical analysis*. It is an introductory course on estimation of measurement uncertainty in chemical analysis. The course gives the main concepts and mathematical apparatus of measurement uncertainty estimation as well as numerous practical examples. The course contains lectures, practical exercises and numerous tests for self-testing.
https://sisu.ut.ee/measurement/uncertainty

3 Calculation of expanded uncertainty, *U* - overview

A common way of presenting the different contributions to the total measurement uncertainty is to use a so-called fish-bone (or cause-and-effect) diagram. We propose a model (Figure 3), where either the within-laboratory reproducibility is combined with estimates of the method and laboratory bias, (error model in Appendix 3) or the reproducibility s_R is used more or less directly according to ISO 21748 [4]. The alternative way is to construct a detailed fish-bone diagram and calculate/estimate the individual uncertainty contributions. This modelling approach may prove very useful when studying or quantifying individual uncertainty components. However, it has been shown, that in many cases this approach underestimates the measurement uncertainty [11], partly because it is hard to include all possible uncertainty contributions in the modelling approach. By using experimentally determined quality control (QC) and method validation data, there is an increased possibility that all uncertainty components are included in the calculations.

Measurement uncertainty model – fish-bone diagram

Covering the analytical process from sample arrival to report

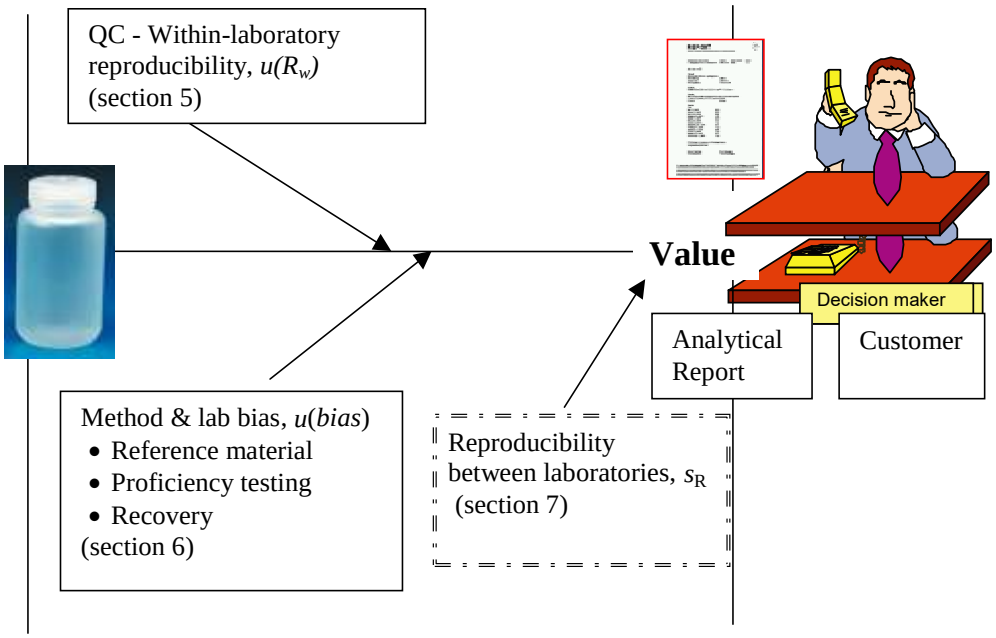


Figure 3. Measurement uncertainty model (fish-bone diagram), where the within-laboratory reproducibility standard deviation is combined with estimates of the method and laboratory bias. Alternatively, according to ISO 21748 [4], the combined standard uncertainty, u_c, can be directly estimated from the reproducibility between laboratories, s_R.

3.1 Customer needs

Customers or data users are in many cases not used to specifying requirements on data quality, so often the requirements have to be set in dialogue. Guidance on how to set the needed uncertainty, the target uncertainty, can be found in the Eurachem Guide *Setting and Using Target Uncertainty in Chemical Measurement* [21].

In cases where no requirements have been established, a guiding principle could be that a tentative expanded uncertainty, U, approximately equal to two times the reproducibility, s_R. The s_R can often be obtained from proficiency testing or from the standard method.

3.2 Flow scheme for uncertainty calculations

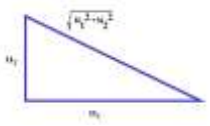
The flow scheme presented in this section forms the basis for the method outlined in this handbook. The flow scheme involves 6 defined steps. The following example with determination of NH_4-N in various types of waters (such as ground, drinking, surface and waste waters) using the automatic photometric method [12] shows the way forward for calculating the measurement uncertainty using this flow scheme. Explanations of the steps and their components will follow in the succeeding chapters. For each step, there may be one or several options for finding the desired information.

Background for the NH_4-N example – automatic photometric method:
Standard uncertainty for within laboratory reproducibility, $u(R_w)$ - For the internal quality control a synthetic control sample at a level of 200 µg L^{-1} is used. Target control limits are used [9]. These limits are wider than if the limits were based on the actual s_{Rw} obtained in the laboratory. NOTE - The $u(R_w)$ is based on the control limits not on the actual $s_{Rw.}$

Standard uncertainty for method and laboratory bias, u(bias) - The laboratory has participated in 6 proficiency testing schemes recently in the concentration range 70 to 270 µg L^{-1}. All results have been somewhat higher than the assigned value. On average, the bias has been +2.2 %. This bias is considered small by the laboratory and is not corrected for in their analytical results, but treated as an uncertainty component. The raw data is given in Appendix 4.

Absolute or relative uncertainty – In the scope of the method EN ISO 11732 [12] is stated*: the method is suitable for ammonium nitrogen in various types of waters in mass concentration ranging from 0.1 to 10 mg L^{-1} in undiluted samples*. Relative uncertainty is here the choice since the starting point of the range is well above the estimated LOQ of 3 µg L^{-1} – see further section 4 where the issue of absolute or relative uncertainty is treated.

For this NH_4-N method, the main sources of uncertainty are contamination and variation in sample handling. These uncertainty sources will be included in the calculations below since we are using experimental data. An output from the calculations below using the MUkit software [13] is given in Appendix 9.

Step	Action	Ammonium NH_4-N by EN ISO 11732
1	***Specify measurand, range, and target U. Decide rel/abs calculations.***	Concentration of NH_4-N > 100 µg L^{-1}. Target uncertainty ± 15 %. Relative uncertainty is calculated.
2	***Quantify $u(R_w)$comp.*** ***A control sample*** ***B possible steps not covered by the control sample***	A: Control sample 200 µg L^{-1}. Control limits (*2s)* are set to ± 6.68 µg L^{-1} or 3.34 % relative. B: The control sample includes all analytical steps.
3	***Quantify u(bias) components***	Proficiency testing results show a % bias[2] of +2.5; +2.7; +1.9; +1.4; +1.8 and +2.9. The root mean square (RMS) of the bias is 2.26 %. The uncertainty of the assigned values, *u(Cref)*, is 1.52 %. (see Appendix 4 for explanations)
4	***Convert components to standard uncertainty u(x)***	Conversion to standard uncertainty [1, 7, 16]. $u(R_w) = 3.34/2 = 1.67$ % $u(bias) = \sqrt{RMS_{bias}^{\ 2} + u(Cref)^2}$ $= \sqrt{2.26^2 + 1.52^2} = 2.73$ %
5	***Calculate combined standard uncertainty, u_c*** 	Standard uncertainties can be combined by taking the square root of the sum of the squares $u_c = \sqrt{u(R_w)^2 + (u(bias))^2} =$ $= \sqrt{1.67^2 + 2.73^2} = 3.20$ %
6	***Calculate expanded uncertainty,*** $U = 2 \cdot u_c$	The reason for calculating the expanded uncertainty is to reach a high enough confidence (app. 95 %) in that the "true value" lies within the interval given by the measurement result ± the uncertainty. $U = 2 \cdot 3.20 = 6.40 \approx 7$ %.

The measurement uncertainty for NH_4-N in water will thus be reported as ± 7 % relative at concentration levels of ammonium > 100 µg L^{-1}.

[2] In case of proficiency testing this is not really a bias since the difference is often based on a single analytical result.

3.3 Summary table for uncertainty calculations

The results of the calculations done in the flow scheme will then be summarised in a summary table.

Concentration of ammonium nitrogen in water by EN ISO 11732

Measurement uncertainty *U* (95 % confidence interval) is estimated to ± 7 % for concentration of NH_4-N > 100 µg L^{-1}. The target uncertainty is ± 15 %. The calculations are based on control chart limits and proficiency testing data.

		Value	***Relative u(x)***	***Comments***
Within-laboratory reproducibility, *u(Rw)*				
Control sample $\overline{X}$ = 200 µg L^{-1}	*u(Rw)*	Control limits is set to ± 3.34 %	1.67 %	
Other components		--		
Method and laboratory, u(bias)				
Reference material	*u(bias)*	--		
Proficiency test	*u(bias)*	RMS_{bias} = 2.26 % *u(Cref)* = 1.52 %	2.73 %	$u(bias) = \sqrt{RMS_{bias}^2 + u(Cref)^2}$
Recovery test	*u(bias)*	--		
Reproducibility between laboratories, s_R				
Proficiency tests 70 to 270 µg L^{-1}.	s_R	--	8.8 %	Data – see section 7.2
Interlaboratory comparison in standard method	s_R		4-10 %	Concentration ranges from 250 to 800 µg L^{-1}.

Combined standard uncertainty, u_c is calculated from the control limits and bias estimation from proficiency tests. The s_R from proficiency testing in a standard method can also be used (see section 7.2).

Measurand	***Combined Standard Uncertainty u_c***	***Expanded Uncertainty U***
Concentration NH_4-N	$\sqrt{1.67^2 + 2.73^2} = 3.20$ %	$2 \cdot 3.20 = 6.4 \approx 7$ %

4 Uncertainty over the measurement range

A measurement uncertainty can be given absolute (with the same unit as the unit of the measured value) or relative (in %) as in the example below.

Measured value	***Measurement uncertainty, U (95 %)***	
	Absolute	***Relative***
20 µg L^{-1}	2 µg L^{-1}	10 %

4.1 Relationship between measurement uncertainty and concentration

The relationship between absolute measurement uncertainty and concentration for many instrumental analytical techniques is shown in Figure 4 below [7, 13, 14].

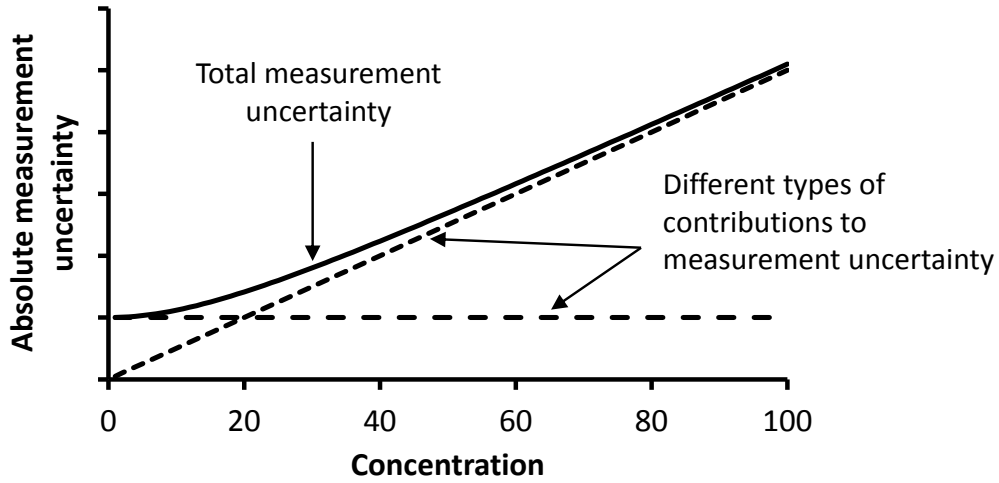


Figure 4. Relationship between absolute measurement uncertainty and concentration for many instrumental analytical techniques.

The total measurement uncertainty (solid line) consists of contributions that are typically proportional to the concentration or independent of the concentration (dashed lines). The relationship between absolute measurement uncertainty and concentration can be approximated with a somewhat simpler relationship shown in Figure 5(a). The corresponding relationship between relative measurement uncertainty and concentration is shown in Figure 5(b).

From Figure 5 it can be seen that it is appropriate to divide the measurement range at the dashed line. In the low range it is appropriate to use an absolute measurement uncertainty, while in the high range it is appropriate to use a relative measurement uncertainty. For methods applied only in the high measurement range a relative uncertainty is most appropriate. For some methods, e.g. titrations and physical methods, it may be appropriate to use an absolute measurement uncertainty in the whole range, but the choice depends on whether the major errors are absolute or relative. For pH we strongly recommend an absolute uncertainty.

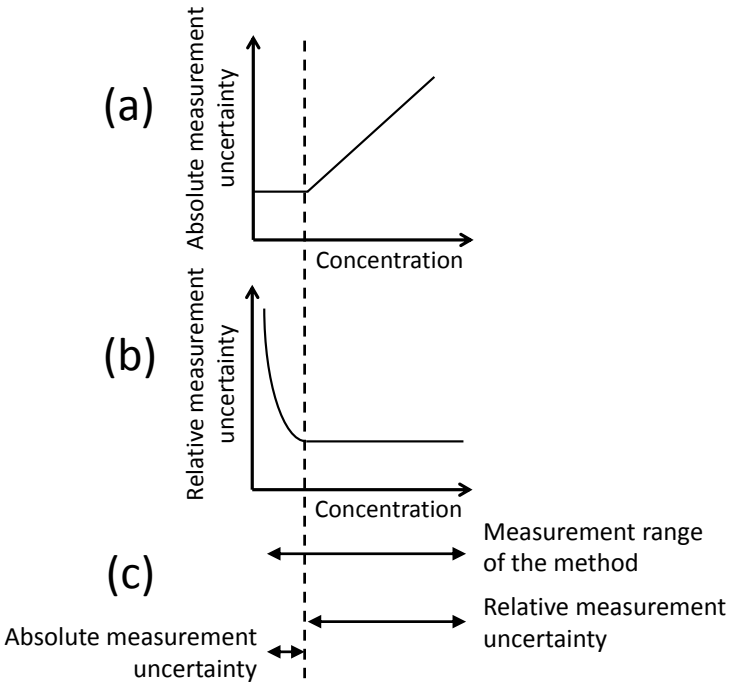


Figure 5. Relationship between (a) absolute measurement uncertainty and concentration, and (b) relative measurement uncertainty and concentration. Division of the measurement range (c) at the dashed line into a low range where the absolute measurement uncertainty is constant and a high range where the relative measurement uncertainty is approximately constant.

4.2 Using replicate results to divide the measurement range

Results from determination of replicates of samples in the whole measurement range can be used to divide the measurement range into a low concentration range where absolute uncertainty is constant and into a high range where relative uncertainty is constant. This is demonstrated below for 73 samples that have been analysed for ammonium nitrogen NH_4-N as two replicates x_1 and x_2. For each sample the calculations shown in the table below were performed.

Table 1 Calculation of relative standard deviation from duplicates. The full data set is given in Appendix 5.

Sample	***x_1 ($\mu g\ L^{-1}$)***	***x_2 ($\mu g\ L^{-1}$)***	***Mean, $\bar{x}$ ($\mu g\ L^{-1}$)***	***Relative s (%)***
1	7.46	7.25	7.35	2.019
2	9.01	9.17	9.09	1.245
3	3.60	3.10	3.35	10.554
I	I	I	I	I
I	I	I	I	I
I	I	I	I	I
73	31.90	32.36	32.13	1.012

Then the graph in Figure 6 is constructed.

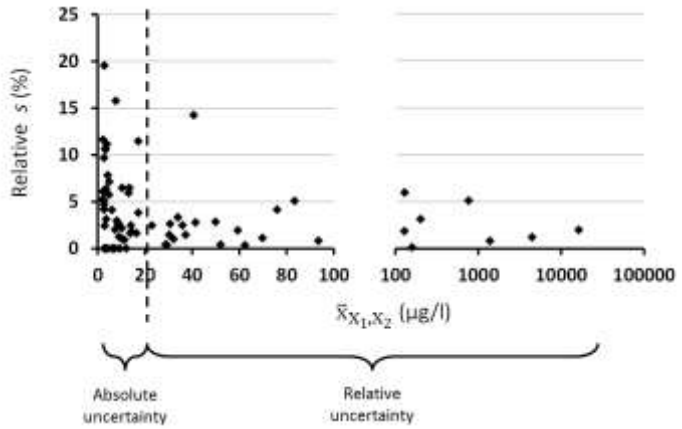


Figure 6. Plot of relative s vs. $\bar{x}$. The dashed line marks a border between two concentration ranges were it is appropriate to use an absolute and a relative uncertainty, respectively. For clarity, the concentration scale above 100 µg L^{-1} is logarithmic.

Figure 6 indicates that the division of the measurement range is at approximately 20 µg L^{-1}, as indicated by a dashed line. Above this concentration the relative standard deviation for the two replicates is independent of the concentration suggesting that it is appropriate to use a relative uncertainty. Furthermore, at concentrations below approximately 20 µg L^{-1} it is appropriate to use an absolute uncertainty. After the uncertainty in the ranges has been calculated the division between the two ranges may be adjusted, see the example in section 4.3.

Sometimes the interpretation is not as straightforward as in Figure 6, however, often useful information about the method is still obtained from such a plot.

4.3 Calculation of uncertainty over the measurement range

After deciding if absolute or relative measurement uncertainty should be used in a certain measurement range, it is important that 1) all uncertainties used in the calculations in that range are either absolute or relative, respectively, 2) only data from that particular measurement range should be used, 3) ideally the data used should cover the major part of the measurement range and 4) the division of the measurement range may be adjusted to fit the results.

For NH_4-N we obtained an expanded uncertainty for the high concentration range of 7 % (see section 3.3) and at the low range an expanded uncertainty of 2 µg L^{-1} was obtained. The level where 2 is about 7 % (2 /0.07) is 28.6 ≈ 30 µg L^{-1} and the division of the measurement range is thus adjusted from 20 to 30 µg L^{-1}. The measurement uncertainty over the measurement range for NH_4-N is given below.

Range	***Measurement Uncertainty, U***
3-30 µg L^{-1}	2 µg L^{-1}
30-1000 µg L^{-1}	7 %
NOTE 1: The absolute uncertainty is equal to the relative uncertainty at 30 µg L^{-1} where the measuring range is divided. NOTE 2: Expanded measurement uncertainty for concentration of NH_4-N in water was achieved by an expert laboratory, which has the method including contamination in full control. Typically routine laboratories can achieve measurement uncertainties 10-20 % at high concentration level.	

5 Within-laboratory reproducibility - *u(Rw)*

In this section two ways of estimating the within-laboratory reproducibility component, *u(Rw)*, for the measurement uncertainty calculation are explained:

- *Control samples covering the whole analytical process – step 3 and 4 of the ladder of errors*. Normally one sample at low concentration level and one at a high concentration level.
  Here *u(Rw)* = s_{Rw}

  NOTE – when wider control limits are used (e.g. target control limits) the *u(Rw)* is based on the s_{target} used to set the limit in the control chart NOT on the actual s_{Rw} obtained for the control sample.
  Here *u(Rw)* = s_{target}

- *Control samples and routine sample replicates.* From control samples not covering the whole analytical process, step 3 of the ladder of errors and from duplicate analyses of test samples with varying concentration levels – step 4 of the ladder of errors.
  Here *u(Rw)* = $\sqrt{s_{Rw}^2 + s_r^2}$

It is of utmost importance that the estimation covers all steps in the analytical chain and all types of matrices – worst-case scenario. The control sample should be run in exactly the same way as the test samples e.g. if the mean of duplicate samples is used for test samples, then the mean of duplicate control samples should be used for the calculations.

It is likewise important to cover long-term variations of some uncertainty components that are systematic in the short-term over time **within** the laboratory, e.g. caused by different stock solutions, new batches of critical reagents, recalibrations of equipment, etc. In order to have a representative basis for the uncertainty estimation and to reflect any such variation the number of results should ideally be more than 60 and cover a time period of at least one year [9].

5.1 Customer demands

Some laboratories choose to use the customer demand when setting the limits in their control charts – target control limits. The actual performance of the method is not interesting, as long as it meets the customer demands on expanded uncertainty. If, for example, the customer asks for data with an (expanded) measurement uncertainty of ± 10 %, then, from our experience, a good starting point is to set the warning control limits (± 2s) to half that value i.e. ± 5 % [9]. The $u(R_w)$ used in the calculations will then be 2.5 %[3], providing that the actual s_{Rw} is lower. This is just a proposal and the measurement uncertainty calculations will show if these control limits are appropriate.

[3] Treating the control limits according to GUM [1] as type B estimate with 95 % confidence limit.

5.2 Control sample covering the whole analytical process

When a stable control sample is available which covers the whole analytical process and has a matrix similar to the samples, the within-laboratory reproducibility at that concentration level can simply be estimated from the measurements of the control samples. If the measurements performed cover a wide range of concentration levels, several control samples at different concentration levels should be used. Example: For NH_4-N two control sample concentration levels (20 and 250 µg L^{-1}) were used. The results for the manual measurement method are presented in the table below. In this case the *u(Rw)* is equal to the s_{Rw}.

		Absolute	***Relative***	***Comments***
Within-laboratory reproducibility, *u(Rw)*				
Control sample 1 $\overline{X}_1$ = 20.01 µg L^{-1}	s_{Rw}	0.5 µg L^{-1}	2.5 %	Measurements in 2002, *n* = 75
Control sample 2 $\overline{X}$ = 250.3 µg L^{-1}	s_{Rw}	3.8 µg L^{-1}	1.5 %	Measurements in 2002, *n* = 50
Other components		--		

5.3 Control samples and routine sample replicates

A synthetic control solution used for quality control would normally not cover the whole analytical process and the matrix type is, in most cases, not similar to the routine samples. Example: To estimate the repeatability in different matrices, duplicate analysis of ammonium in test samples water is performed, and the s_r is estimated. This gives the repeatability for test samples having a normal matrix variation in salt and particles at different concentration levels.

Example – different matrices

The data set consists of 73 duplicate analyses in the range of 2 µg L^{-1} – 16000 µg L^{-1}. Most of the results were below 200 µg L^{-1}. The data, given in Appendix 5, is divided into a lower range, < 30 µg L^{-1} and a higher range > 30 µg L^{-1}.

		Absolute u(x)	**Relative *u(x)***	***Comments***
Repeatability				
Duplicate analyses 2 - 30 µg L^{-1} 30 - 16 000 µg L^{-1}	 s_r s_r	 0.44 µg L^{-1}	 3.8 %	 n = 47 n = 26

As the estimate from duplicate analyses gives the repeatability component (s_r) only, it should be combined with the synthetic control sample results from Section 5.2 to give a better estimate of u *(Rw)*. It can be noticed that the sample matrix has some effect on the variation of the results.

		Value	*u(x)*	*Comments*
Within-laboratory reproducibility , *u(Rw)*				
Low level (2-30 µg L^{-1})	*u(Rw)*	0.5 µg L^{-1} from control sample and 0.44 µg L^{-1} from duplicates	0.7 µg L^{-1}	Absolute *u(Rw)* = $\sqrt{0.5^2 + 0.44^2}$
High level (> 30 µg L^{-1})	*u(Rw)*	1.5 % from control sample and 3.8 % from duplicates	4.1 %	Relative u*(Rw)* = $\sqrt{1.5^2 + 3.8^2}$

Example – unstable control samples

In this example, duplicate samples have been measured with an oxygen probe on 50 occasions over 2 years. The raw data is given in Appendix 6. The concentration variation is limited, so an R-chart approach is chosen. Since it is important to look for systematic differences between the first and the second results the **difference** between the first and the second measurement is calculated and plotted in an R-chart, see Figure 7. The standard deviation for the results can be estimated from the pooled standard deviation of the duplicate samples (see Appendix 6), and in this case becomes 0.025 mg L^{-1}. The control limits ±2s are at $0.025 \cdot 2.83 = 0.07$ mg L^{-1} [9]. Mean value is 7.48 and relative *u(x)* for repeatability is 0.34 %.

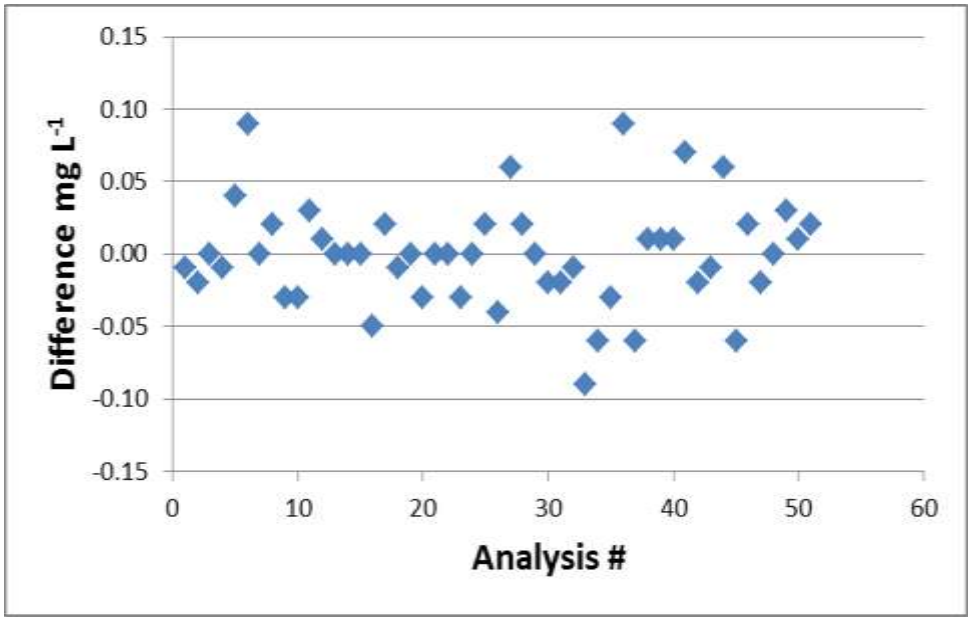


Figure 7. R-chart - Determination of dissolved oxygen in sea water - the difference between the first and the second measurement

However, this only gives the repeatability, s_r for sampling and measurement, but there will also be a "long-term" uncertainty component from the variation in the calibration (here the Winkler titration is used for calibration of the oxygen probe). For this particular measurement, the uncertainty component from the long-term variation in calibration is hard to measure, as no stable reference material is available for dissolved oxygen. One method would be to calculate the standard deviation of differences obtained on different days between the value obtained with the probe and the value obtained with the Winkler method. Here we choose to estimate that component by a qualified guess, but laboratories are encouraged to also try the experimental approach.

The total within-laboratory reproducibility for dissolved oxygen thus becomes:

		Value	***Relative u(x)***	***Comments***
Within-laboratory reproducibility, $u(R_W)$				
Duplicate analyses of natural samples, difference used in R-chart	s_r	s = 0.0252 mg L^{-1} $\overline{X}$ = 7.50 mg L^{-1}	0.34 %	Measurements in 2000-2002, n= 51
Estimated variation from differences in calibration over time		s = 0.5 %	0.5 %	Estimate, based on experience
Combined relative standard uncertainty u_{Rw}				
Repeatability + within-lab reproducibility in calibration		$\sqrt{0.34^2 + 0.5^2}\,\% = 0.60\,\%$		

6 Method and Laboratory bias – *u(bias)*

In this chapter three ways of estimating the uncertainty as a result of the bias component will be outlined, namely; 1) the use CRM, 2) participation in PT and 3) performing recovery tests.

The ISO Guide to the expression of uncertainty in measurement, GUM [1], assumes that "the result of a measurement has been corrected for all recognised significant systematic effects" (GUM 3.2.4). This implies that when developing a measurement method all known sources of bias within the method's scope should be investigated and if possible, eliminated. However, in many cases a developed method may still have a bias and the bias can vary depending on changes in matrix and concentration. Correcting for any observed bias on one reference only cannot be **generally** recommended [15]. The issue of bias correction is also treated in the leaflet *Treatment of an observed bias* from Eurachem, *www.eurachem.org*.

An observed bias can be treated as an uncertainty component as stated in VIM [10][4]. Bias can in many cases be both positive and negative. Even if the measured bias is positive in certain matrices and negative in others, all bias values in a selected concentration range should be used to estimate the uncertainty component, RMS_{bias}. Even if the bias is *not significant* or zero one should treat it as an uncertainty component due to a *possible* bias – the bias may be small or absent, but has to be taken into account.

Two bias components have to be estimated:

1) the root mean square (RMS) of the individual bias values [15]
2) the mean of the standard uncertainty of the assigned/certified values, *u(Cref)* or *u(Crecovery)*[5]

The uncertainty due to bias, *u(bias)* can then be estimated by

$$u(bias) = \sqrt{RMS_{bias}{}^2 + u(Cref)^2} \text{ where } RMS_{bias} = \sqrt{\frac{\sum (bias_i)^2}{n_{CRM}}}$$

where n_{CRM} is the number CRMs used (or PT or recovery tests).

If only one CRM is used also the s_{bias} (standard deviation of the measured values of the CRM) has to be included and *u(bias)* can then be estimated [16, 17] by

$$u(bias) = \sqrt{(bias)^2 + \left(\frac{s_{bias}}{\sqrt{n}}\right)^2 + u(Cref)^2}$$

[4] Measurement Uncertainty NOTE 1…*Sometimes estimated systematic effects are not corrected for but, instead, associated measurement uncertainty components are incorporated*

[5] A mean value is used for simplicity – a pooled value would be more correct.

6.1 Certified Reference Material

Regular measurement of one or several CRM can be used to estimate the bias. Each reference material should be measured in at least 5 different analytical series (e.g. on 5 different days) before the values are used.

One CRM - In this example with one CRM the certified value is 11.5 ± 0.5, with a 95 % confidence interval. The analytical results are on average 11.9 with a standard deviation, s_{bias}, of 2.2 %, n=12.

Uncertainty component from the uncertainty of the certified value	
Step	***Example***
Convert the confidence interval to *u(Cref)*	The confidence interval is ± 0.5. Divide this by 2 to convert it to standard uncertainty: 0.5/2 = 0.25
Convert to relative uncertainty *u(Cref)*	0.25/11.5 · 100 = 2.16 %

3 ***Quantify u(bias) components***

$$\text{bias} = 100 \cdot (11.9 - 11.5)/11.5 = 3.48\,\%$$

s_{bias} = 2.2 % (n = 12)
u(Cref) = 2.16 %

4 ***Convert components to standard uncertainty u(x)***

$$u(bias) = \sqrt{(bias)^2 + \left(\frac{s_{bias}}{\sqrt{n}}\right)^2 + u(Cref)^2} =$$

$$\sqrt{(3.48)^2 + \left(\frac{2.2}{\sqrt{12}}\right)^2 + 2.16^2} = 4.1\,\%$$

Several CRM - If several CRMs are used, we will get different values for bias. The uncertainty due to any bias, $u(bias)$ will be calculated in the following way.

3 ***Quantify u(bias) components***

bias CRM1 is 3.48 %, s=2.2 % (n=12), $u(Cref_1)$=2.16 %
bias CRM2 is -0.9 % s=2.0 % (n=7), $u(Cref_2)$=1.8 %
bias CRM3 is 2.5 %, s= 2.8 % (n=10), $u(Cref_3)$=1.8 %
RMS_{bias} = 2.53 %
mean *u(Cref)*=1,92 %

4 ***Convert components to standard uncertainty u(x)***

$$u(bias) = \sqrt{RMS_{bias}^{\ 2} + u(Cref)^2}$$

$$\sqrt{2.53^2 + 1.92^2} = 3.2\,\%$$

6.2 Proficiency tests

In this case the results from proficiency tests (PT) are used in the same way as reference materials to estimate $u(bias)$. In order to have a reasonably clear picture of the bias from proficiency testing results, a laboratory should participate at least 6 times within a reasonable time interval.

The way forward is very similar to that for reference materials. However, for reference materials a mean value over time is used and for each PT a single laboratory result is used. Therefore the estimated RMS_{bias} from proficiency test will usually be higher. Also the certified value of a CRM normally has a lower uncertainty than an assigned value in a PT. In some cases the calculated uncertainty *u(Cref)* from a proficiency testing becomes too high and is not valid for estimating the *u(bias)*.

Uncertainty component from the uncertainty of the assigned value	
Step	***Example***
Find the between laboratory standard deviations, s_R, and the number of labs, n_{Lab}, for each PT.	In the first PT the s_R is 8.7 % and n_{Lab} is 23. NOTE: If the PT provider reports so called 'robust standard deviation', this value must be multiplied by a factor of 1.25 to correspond to s_R described in this handbook [18].
Calculate $u(Cref_i)$ for each PT	$u(Cref_i) = \frac{s_{Ri}}{\sqrt{n_{Lab,i}}} = \frac{8.7\%}{\sqrt{23}} = 1.8\%$ The other five $u(Cref_i)$ values are e.g. 2.9 %, 1.7 %, 4.1 %, 3.0 % and 2.1 %
Calculate $u(Cref)$ as the average of the individual $u(Cref_i)$ values.	Number of PT: $N = 6$. $u(Cref) = \frac{\sum_{i=1}^{N} u(Cref_i)}{N} = 2.7\ \%$

The bias has been +2 %, +7 %, -2 %, +3 %, +6 % and +5 %, in the 6 PT where the laboratory has participated.

3	***Quantify u(bias) components***	RMS_{bias} = 4.6 %, $u(Cref)$= 2.6 %
4	***Convert components to standard uncertainty u (x)***	$u(bias) = \sqrt{RMS_{bias}{}^2 + u(Cref)^2} =$ $= \sqrt{4.6^2 + 2.6^2} = 5.3\ \%$

If the PT provider estimates the uncertainty, *U*, of the assigned value e.g. according to the procedure described in ISO 13528 [18], then *U*/2 should be used as $u(Cref_i)$ for each PT instead of calculating uncertainty via s_R and n_{Lab}.

NOTE: The drawback with PT is that the laboratory result is based on one measurement which results in an increased uncertainty compared to a mean value. If it is possible to measure several times under a longer time interval on PT samples we recommend using the mean values of these measurements.

6.3 Recovery

Recovery tests, for example the recovery of a standard addition to a sample, can be used to estimate one component[6] of the bias [15]. The guidance given in this section is applicable for test methods that do not include a recovery correction in the procedure.

In an experiment the recoveries for an added spike were 95 %, 98 %, 97 %, 96 %, 99 % and 96 % for 6 **different** sample matrices. The average is 96.8 %. The spike of 0.5 mL was added with a micropipette.

Uncertainty component from recovery, u(Crecovery)	
Step	***Example***
Main components are the uncertainty of the concentration, *u(conc)* of standard and volume added *u(vol)*	*u(conc)* - Certificate ± 1.2 % (95 % conf. limit) gives = 0.6 % *u(vol)* - This value can normally be found in the manufacturer's specifications, or better still use the limits specified in your laboratory. Max bias 1 % (rectangular interval) and repeatability max 0.5 % $u(vol) = \sqrt{\left(\frac{1}{\sqrt{3}}\right)^2 + 0.5^2} = 0.76\,\%$
Calculate *u(Crecovery)*	$\sqrt{u(conc)^2 + u(vol)^2} = \sqrt{0.6^2 + 0.76^2} = 1.0\,\%$

3 ***Quantify u(bias) components***

RMS_{bias} = 3.44 %

u(Crecovery)=1.0 %

4 ***Convert components to standard uncertainty u(x)***

$$u(bias) = \sqrt{RMS_{bias}{}^2 + u(Crecovery)^2} =$$
$$= \sqrt{3.44^2 + 1.0^2} = 3.6\,\%$$

[6] Some bias components are not included in a recovery e.g. bias due to low selectivity, contamination.

7 Reproducibility between laboratories, s_R

If the demand on uncertainty is low, it may be possible to directly use the s_R as an approximation of u_c [3, 4]. The expanded uncertainty $U = 2 \cdot s_R$. This may be an overestimate depending on the quality of the laboratory. It may also be an underestimate due to sample inhomogeneity or matrix variations.

7.1 Data given in a standard method

In order to use a figure taken directly from the standard method, the laboratory must prove that they are able to perform in accordance with the standard method [4], i.e. demonstrating control of bias and verification of the repeatability, s_r. Reproducibility data in the standard method can either be given as a standard deviation s_R or as reproducibility limit R and then $s_R = R/2.8$.

The example below is taken from ISO 15586 *Water Quality — Determination of trace elements by atomic absorption spectrometry with graphite furnace*. The matrix is wastewater. Combined uncertainty in wastewater, u_c, is taken from the s_R from interlaboratory comparisons performed according to ISO 5725 [19] quoted in the ISO method[7].

Table 2. ISO 15586 - Results from the proficiency testing – Cd in water with graphite furnace AAS. The wastewater was digested by the participants.

Cd		***n_{Lab}***	***Outliers***	***Assigned value*** µg L^{-1}	***Mean*** µg L^{-1}	***Recovery*** %	***s_r*** %	***s_R*** %
Synthetic	Lower	33	1	0.3	0.303	101	3.5	17.0
Synthetic	Higher	34	2	2.7	2.81	104	1.9	10.7
Fresh water	Lower	31	2		0.572		2.9	14.9
Fresh water	Higher	31	3		3.07		2.1	10.4
Waste water		27	2		1.00		3.1	27.5

Measurand	***Matrix***	***Combined Uncertainty u_c***	***Expanded Uncertainty U***
Cd	*Waste water*	u_c = 27.5 %	$2 \cdot u_c$ = 55 % ≈ 60 %

[7] In ISO 15586 the relative *s* is given as coefficient of variation, CV.

7.2 Data from proficiency testing

Proficiency tests (PT) are valuable tools in uncertainty evaluation. The reproducibility between laboratories is normally given directly in reports from the exercises as s_R.

Data may well be used by a laboratory having performed satisfactorily in the PT as provided that this PT covers all relevant uncertainty components and steps - see 17025 section 5.4.6.3 [6].

Table 3. Summary results (mean or pooled values) from 10 PT that Lab A has participated in. The reproducibility standard deviation is given in absolute units for pH, s_R and in relative units s_R % for the other parameters.

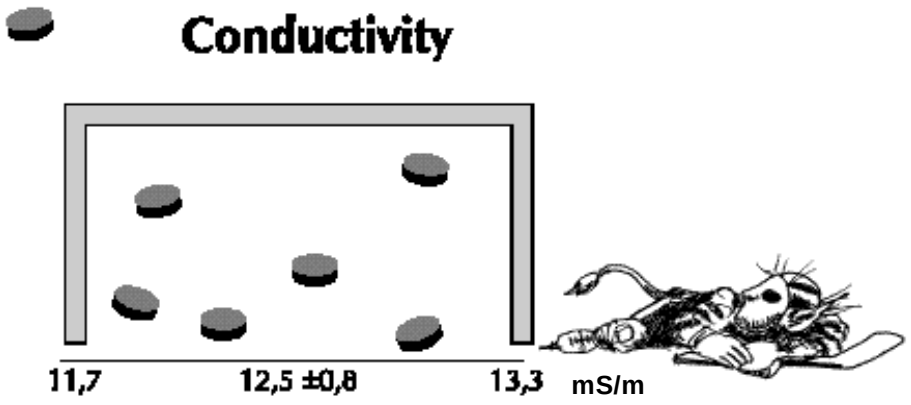
Parameter	Assigned value	Lab A % deviation	s_R (abs)	s_R %	No. of labs	Excluded
pH	7.64	-0.037	0.101	-	90	5
Conductivity, mS/m	12.5	-2.8	-	3.2	86	6
Alkalinity, mmol L^{-1}	0.673	+2.3	-	3.9	60	3
Turbidity, FNU	1.4	-9.1	-	14.2	44	3
NH_4-N, µg L^{-1}	146	+2.2	-	8.8	34	5
NO_3-N, µg L^{-1}	432	-1.6	-	3.7	39	6

In Table 3 we find that for conductivity, the mean assigned value for the results from 10 PT is 12.5 mS/m. The reproducibility standard deviation is 3.2 %, which is a pooled standard deviation between the laboratories in the different PT and this value can be taken as an estimate of combined standard uncertainty i.e.

$$u_c\,(conductivity) = s_R = 3.2\ \%\ \text{and}\ U = 2 \cdot 3.2 = 6.4 \approx 7\ \%\ \text{at}\ 12.5\ \text{mS/m}.$$

If we take the ammonium results, we have a mean value of 146 µg L^{-1}, and we find that the reproducibility, s_R, is 8.8 %. Thus $U = 2 \cdot 8.8 = 17.6 \approx 18$ % at this concentration level.

Comment: In Section 3 the expanded uncertainty, U, for ammonium is 7 % using an automated method in one highly qualified laboratory.



8 Examples

In this chapter, practical examples are presented on how measurement uncertainty can be calculated using the approach in this handbook.

8.1 Ammonium in water

Ammonium in water has already been treated in section 3.2, 4 and section 7.2 . The results in the upper measurement range are summarised in Table 4.

Table 4. Measurement uncertainty of ammonium in water – comparison of different calculations

Uncertainty calculations based on	***Relative expanded uncertainty, U***	***Comment***
Control sample + PT	± 7 %	Uncertainty for one good laboratory- range > 30 µg L^{-1}.
PT	± 18 %	Uncertainty in general among laboratories – level 150 µg L^{-1}

8.2 BOD in wastewater

Biological Oxygen Demand, BOD, is a standard parameter in the monitoring of wastewater. This example shows how data from internal quality control can be used together with CRM results or data from PT to calculate the measurement uncertainty. The results for expanded uncertainty are summarised in Table 5

Table 5. Measurement uncertainty of BOD in water - comparison of different calculations

Uncertainty calculations based on	***Relative expanded uncertainty, U***	***Comment***
Control sample + CRM	± 11 %	
Control sample + PT	± 10 %	n = 3, unreliable estimate
PT	± 16 %	Uncertainty in general among laboratories

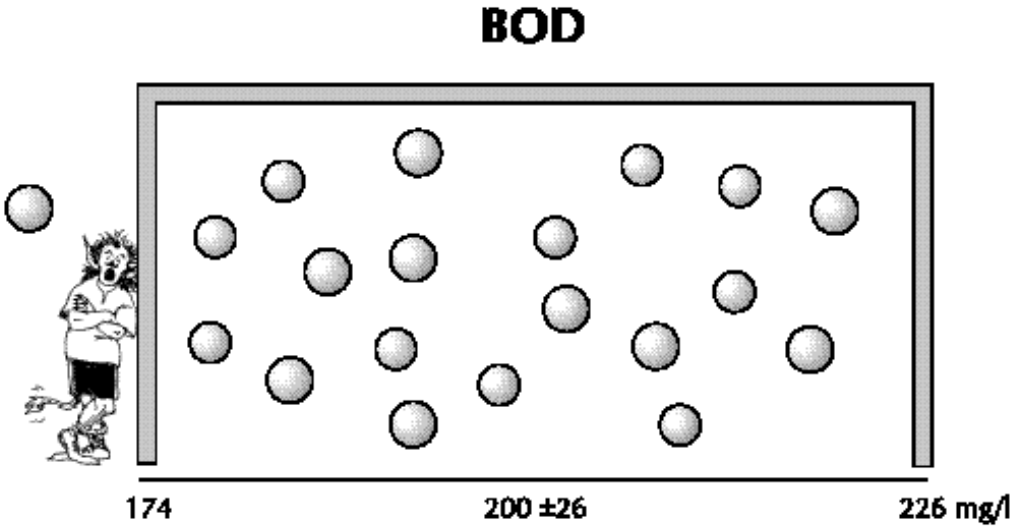
For BOD at high concentrations, using the dilution analytical method, the major error sources are the actual oxygen measurement and variation in the quality of the seeding solution. These errors will be included in the calculations.

Raw data from the internal quality control, using a CRM, is shown in Appendix 7.

The laboratory has only participated in three proficiency testing exercises the last 2 years (Table 6). At least six would be needed, so here we estimate the bias in two different ways – with a CRM and with PT.

Table 6. BOD - results from PT

Exercise	**Assigned value**	**Laboratory result**	**Bias**	s_R	**Number of labs**	$u(Cref_i)$
	mg L^{-1}	mg L^{-1}	%	%		%
1	154	161	+ 4.5	7.2	23	1.50
2	219	210	- 4.1	6.6	25	1.32
3	176	180	+2.3	9.8	19	2.25
$\overline{X}$			+0.9	7.87[8]	$u(Cref)$	1.69
RMS_{bias}			3.76	-	-	-



[8] If s_R or the number of participants vary substantially from exercise to exercise, then a pooled standard deviation will be more correct to use. In this case, where the variation in s_R is limited, we simply calculate the mean s_R (the corresponding pooled standard deviation becomes 7.82, an insignificant difference).

Example A: BOD with internal quality control + one CRM

Step	Action	***BOD in wastewater with*** EN 1899-1 (method with dilution, seeding and ATU)
1	***Specify measurand, range, and target U. Decide rel/abs calculations.***	Concentration of BOD < 2 µg L^{-1} in wastewater. The target uncertainty is ± 20 %. Relative uncertainty is calculated.
2	***Quantify $u(R_w)$comp.*** ***A control sample*** ***B possible steps not covered by the control sample***	A: The control sample, a CRM gives an *s* of 2.6 % at an O_2 level of 206 mg L^{-1}. This *s* is when setting the control chart limits. B: The measurement of the control sample includes all analytical steps.
3	***Quantify u(bias) components.***	The CRM is certified to 206 ± 5 mg L^{-1} O_2. The average result is 214.8 mg L^{-1}. Thus, there is a bias of +8.8 mg L^{-1} or 4.3 %. The s_{bias} is 2.6 % (n=19) The *u(Cref)* is 5 mg L^{-1} / 2 = 2.5 mg L^{-1} and relative $2.5/206 \bullet 100 = 1.2\,\%$
4	***Convert components to standard uncertainty u(x)***	*u (Rw)* = 2.6 % $u(bias) = \sqrt{bias^2 + \frac{s_{bias}}{\sqrt{n}}^2 + u(Cref)^2}$ $= \sqrt{4.3^2 + \left(\frac{2.6}{\sqrt{19}}\right)^2 + 1.2^2} = 4.5\,\%$
5	***Calculate combined standard uncertainty, u_c***	$u_c = \sqrt{2.6^2 + 4.5^2} = 5.2\,\%$
6	***Calculate expanded uncertainty,*** $U = 2 \cdot u_c$	$U = 2 \cdot 5.2 = 10.4 \approx 11\,\%$

Example B: BOD with internal quality control + PT

Step	Action	***BOD in wastewater with*** EN 1899-1 (method with dilution, seeding and ATU)
1	***Specify measurand, range, and target U. Decide rel/abs calculations.***	Concentration of BOD < 2 µg L^{-1} in wastewater. The target uncertainty is ± 20 %. Relative uncertainty is calculated.
2	***Quantify $u(R_w)$comp.*** ***A control sample*** ***B possible steps not covered by the control sample***	A: The control sample, a CRM, gives an *s* of 2.6 % at an O_2 level of 206 mg L^{-1}. The *s* of 2.6 % is also used when setting the limits in the control chart. B: The measurement of the control sample includes all analytical steps after sampling
3	***Quantify u(bias) components.***	***Data from*** Table 6 RMS_{bias} = 3.76 % $u(Cref) = 1.69\,\%$
4	***Convert components to standard uncertainty u(x)***	$u(Rw)$ = 2.6 % $u(bias) = \sqrt{RMS_{bias}{}^2 + u(Cref)^2} =$ $\sqrt{3.76^2 + 1.69^2} = 4.12\%$
5	***Calculate combined standard uncertainty, u_c***	$u_c = \sqrt{2.6^2 + 4.12^2} = 4.87$ %
6	***Calculate expanded uncertainty,*** $U = 2 \cdot u_c$	$U = 2 \cdot 4.87 = 9.7 \approx 10\,\%$

8.3 PCB in sediment

In these examples, the $u(R_w)$ is estimated from a quality control sample and the *u(bias)* is estimated from two different sources: in the first example using a CRM and in the second example by participation in proficiency tests. The sample-work up is a major error source, and it is thus crucial that this step is included in the experimental data. The number of proficiency tests is too few to get a reliable estimate.

Example C: PCB with internal quality control + one CRM

Step	*Action*	*PCB in sediment by GC-MS*
1	***Specify measurand, range, and target U. Decide rel/abs calculations.***	Sum of concentration of 7 PCB analytes. The range is dependent on matrix and analyte. Demand on expanded uncertainty is ± 20 %. Relative uncertainty is calculated.
2	***Quantify $u(R_w)$comp.*** ***A control sample*** ***B possible steps not covered by the control sample***	A: The control sample, which is a CRM, gives a s_{Rw} = 8 % at a level of 150 µg kg^{-1} dry matter. The s_{Rw} of 8 % is also used when setting the control chart limits. B: The measurement of the control sample includes all steps except for drying the sample to determine the dry weight. The uncertainty contribution from that step is considered small.
3	***Quantify u(bias) components.***	The CRM is certified to 152 ± 14 µg kg^{-1}. The average result of the control chart is 144. Thus, there is a bias = 5.3 %. The s_{bias} = 8 % (n=22) *u(Cref)* 14/2, which is 4.6 % relative.
4	***Convert components to standard uncertainty u(x)***	$u(R_w)$ = 8 % $u(bias) = \sqrt{bias^2 + \frac{s_{bias}^2}{\sqrt{n}} + u(Cref)^2}$ $= \sqrt{5.3^2 + \left(\frac{8}{\sqrt{22}}\right)^2 + 4.6^2} = 7.22$
5	***Calculate combined standard uncertainty u_c***	$u_c = \sqrt{8^2 + 7.22^2} = 10.8$ %
6	***Calculate expanded uncertainty,*** $U = 2 \cdot u_c$	$U = 2 \cdot 10.8 = 21.6 \approx 22$ %

Example D: PCB with internal quality control + proficiency testing

Step	Action	PCB in sediment by GC-MS
1	***Specify measurand, range, and target U. Decide rel/abs calculations.***	Sum of concentration of7 PCB analytes. The range is dependent on matrix and analyte. Demand on expanded uncertainty is ± 20 %. Relative uncertainty is calculated.
2	***Quantify $u(R_w)$comp. A control sample B possible steps not covered by the control sample***	A: The control sample, which is a stable in-house material, gives s_{Rw} = 8 % at a level of 150 µg kg^{-1} dry matter. The s_{Rw} of 8 % is also used as s when setting the control chart limits. B: The measurement of the control sample includes all steps except for drying the sample to determine the dry weight. The uncertainty contribution from that step is considered small and is not accounted for.
3	***Quantify u(bias) components.***	Participation in 3 PT with concentration levels similar to the internal quality control. The bias in the 3 exercises has been –2 %, -12 % and –5 %. RMS_{bias} = 7.6 % The $u(Cref_i)$ values in the three exercises have been 2.7 %, 2.5 % and 3.5 %. On average $u(Cref)$ = 2.9 %
4	***Convert components to standard uncertainty u(x)***	The $u(R_w)$ is 8 % $u(bias) = \sqrt{RMS_{bias}^{\ 2} + u(Cref)^2} = \sqrt{7.6^2 + 2.9^2} = 8.1\%$
5	***Calculate combined standard uncertainty, u_c***	$u_c = \sqrt{8^2 + 8.1^2} = 11.4$ %
6	***Calculate expanded uncertainty,*** $U = 2 \cdot u_c$	$U = 2 \cdot 11.4 = 22.8 \approx 23\%$

Summary table for PCB measurement uncertainty calculations

PCB in sediment by extraction and GC-MS

Measurement uncertainty U (95 % confidence interval) is estimated to ± 23 % (relative) for 7 PCB in sediments at a level of 150 µg kg^{-1} dry weight. The target uncertainty is ± 20 %. The calculations are based on internal quality control using a stable sample, CRM and the participation in a limited number of PT.

		Value	***u(x)***	***Comments***
Within-laboratory reproducibility , *u(Rw)*				
Control sample $\overline{x}$ = 160 µg kg^{-1} dry weight	$u(R_w)$	12.8 µg kg^{-1} dry weight	8 %	
Other components		too small to be considered		
Method and laboratory, *u(bias)*				
CRM	*u(bias)*	Bias: 5.3 % s_{bias} = 8 ; n = 22 *u(Cref)* = 4,7 %	*u(bias)* = 7.29	*u(bias)*= $\sqrt{bias^2 + \frac{s_{bias}}{\sqrt{n}}^2 + u(Cref)^2}$
PT n = 3	*u(bias)*	RMS_{bias} = 7.6 *u(Cref)* = 2.9 %	*u(bias)* = 8.1	*u(bias)*= $\sqrt{RMS_{bias}^2 + u(Cref)^2}$

Combined uncertainty, u_c, is calculated from internal quality control and the maximum *u(bias)* from PT.

Measurand	***Combined Uncertainty u_c***	***Expanded Uncertainty U***
PCB	$u_c = \sqrt{8^2 + 8.1^2} = 11.4$	$U = 2 \cdot u_c = 2 \cdot 11.4 = 22.8 \approx 23\,\%$

Conclusion: In this case the calculation of the *u(bias)* gives similar results regardless of whether CRM or proficiency testing results are used. Sometimes proficiency tests will give considerably higher values. If the CRM is similar to test samples and at an appropriate concentration level it might in such cases be more correct to use the CRM results.

9 Reporting uncertainty

This is an example of how an analytical report could look, when measurement uncertainty is reported together with the data. The company and accreditation body logotypes are omitted, and the report does not contain all information normally required for an accredited laboratory. It is recommended to use either relative or absolute values for the benefit of the customer. Here is reported absolute uncertainty.

Analytical Report

Sample identification: P1 – P4

Samples received: 14 December 2002

Analysis period: 14 –16 December 2002

Results

NH_4-N (µg L^{-1}):

Sample	Result	U	Method
P1	103	± 7	23B
P2	122	± 9	23B
P3	12	± 2	23B
P4	14	± 2	23B

TOC (mg L^{-1})

Sample	Result	U	Method
P1	40	± 4	12-3
P2	35	± 4	12-3
P3	10	± 1	12-3
P4	9	± 1	12-3

The laboratory should also prepare a note explaining how the measurement uncertainty has been calculated for the different parameters. Normally, such an explanatory note should be communicated to regular customers and other customers who ask for information. An example is given below:

Note on measurement uncertainty from Dr Analyst's laboratory

Measurement uncertainty:

U = expanded measurement uncertainty, estimated from control sample results, proficiency testing and the analyses of CRMs, using a coverage factor of 2 to reach approximately 95 % confidence level.

NH_4-N: *U* is estimated to 7 % above 30 µg L^{-1} and 2 µg L^{-1} below 30 µg L^{-1}.

TOC: *U* is estimated to 10 % over the whole concentration range.

References:

- B. Magnusson, T. Näykki, H. Hovind, M. Krysell, E. Sahlin, Handbook for calculation of measurement uncertainty in environmental laboratories, Nordtest Report TR 537 (ed. 4) 2017. Available from www.nordtest.info
- ISO 11352:2012 Water quality — Estimation of measurement uncertainty based on validation and quality control data.

10 References

1 Guide to the Expression of Uncertainty in Measurement. ISO, Geneva (1993). (ISBN 92-67-10188-9) Reissued as ISO Guide 98-3 (2008), also available from www.bipm.org as JCGM 100:2008.

2 EA-4/16: EA guideline on the expression of uncertainty in quantitative testing, (2003) www.european-accreditation.org

3 EUROLAB Technical Report 1/2007, Measurement uncertainty revisited: Alternative approaches to uncertainty evaluation. EUROLAB (2007). Available from www.eurolab.org.

4 ISO 21748:2017, Guide to the use of repeatability, reproducibility and trueness estimates in measurement uncertainty estimation. ISO, Geneva.

5 ISO 11352:2012, Water quality -- Estimation of measurement uncertainty based on validation and quality control data, ISO, Geneva.

6 EN ISO/IEC 17025:2005, General Requirements for the Competence of Calibration and Testing Laboratories.

7 S. L. R. Ellison and A. Williams (Eds). Eurachem/CITAC guide: Quantifying Uncertainty in Analytical Measurement, (3rd edition, 2012) ISBN 978-0-948926-30-3. Available from www.eurachem.org.

8 V J Barwick and E Prichard (Eds), Eurachem Guide: Terminology in Analytical Measurement – Introduction to VIM 3 (2011). ISBN 978-0-948926-29-7. Available from www.eurachem.org.

9 H. Hovind, B. Magnusson, M. Krysell, U. Lund, and I. Mäkinen, Internal Quality Control - Handbook for Chemical Laboratories, Nordtest technical report 569 Edition 4 (2011). www.nordtest.info.

10 ISO/IEC Guide 99:2007, International vocabulary of metrology - Basic and general concepts and associated terms (VIM). ISO, Geneva, (2007). Available from http://www.bipm.org as JGCM 200:2008.

11 M. Thompson and S.L.R. Ellison, Dark uncertainty, Accred Qual Assur (2011) 16: 483.

12 ISO 11732:2005, Water quality -- Determination of ammonium nitrogen by flow analysis (CFA and FIA) and spectrometric detection.

13 T. Näykki, A. Virtanen and I. Leito, Software support for the Nordtest method of measurement uncertainty evaluation, Accred Qual Assur, (2012) 6: 603–612.

14 B. Magnusson and M. Koch, Use of characteristic functions derived from proficiency testing data to evaluate measurement uncertainties, Accred Qual Assur (2013) 17:399–403.

15 B. Magnusson, S. L. R. Ellison, Treatment of uncorrected measurement bias in uncertainty estimation for chemical measurements, Anal Bioanal Chem, (2008) 390:201-213.

16 V. J. Barwick and S. L: R. Ellison, Measurement uncertainty: Approaches to the evaluation of uncertainties associated with recovery, Analyst, (1999) 124, 981-990.

17 E. Hund, D.L. Massart and J. Smeyers-Verbeke, Operational definitions of uncertainty. TrAC, (2001) 20 (8).

18 ISO 13528:2015 Statistical methods for use in interlaboratory comparison by proficiency testing.

19 ISO 5725-1-6:1994, Accuracy (trueness and precision) of measurement methods.

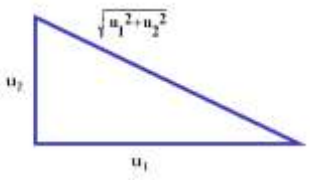
20 C. Grøn, J. Bjerre Hansen, B. Magnusson, A. Nordbotten, M. Krysell, K. Jebjerg Andersen, U. Lund Nordtest 604, Uncertainty from sampling - A NORDTEST handbook for sampling planners on sampling quality assurance and uncertainty estimation Nordtest technical report 604 (2007), www.nordtest.info.

21 R. Bettencourt da Silva and A. Williams (Eds), Eurachem/CITAC Guide: Setting and Using Target Uncertainty in Chemical Measurement, (1st ed. 2015). Available from www.eurachem.org.

11 Appendices

11.1 Appendix 1: Empty flow scheme for calculations

Before starting: Always identify the main error sources, to make sure that they are included in the calculations.

Step	*Action*	*Parameter in matrix by method:*
1	***Specify measurand, range, and target U. Decide rel/abs calculations.***	(measurand) in range xx. The target uncertainty is ± _ %. Relative/absolute uncertainty is calculated.
2	***Quantify u(R_w)comp.*** ***A control sample*** ***B possible steps not covered by the control sample***	A: B:
3	***Quantify u(bias) components***	
4	***Convert components to standard uncertainty u(x)***	
5	***Calculate combined standard uncertainty, u_c*** 	
6	***Calculate expanded uncertainty,*** $U = 2 \cdot u_c$	

11.2 Appendix 2: Empty summary table

(measurand) in (matrix) by (method)

Measurement uncertainty U (95 % confidence interval) is estimated to ± _ (unit) for (measurand) in (matrix) at a level of _ (unit). The target uncertainty is ± _ (unit). The calculations are based on (control samples/control limits/CRM/ /PT/other).

		Value	***u(x)***	***Comments***
Within-laboratory reproducibility, $u(R_w)$				
Control sample $\overline{X}$ = (conc) (unit)	s_{Rw}			
Other components				
Method and laboratory bias				
Reference material	bias			
Proficiency testing	bias			
Recovery test	bias			
Reproducibility between laboratories				
Proficiency testing	s_R			
Standard method	s_R			

Combined uncertainty, u_c, is calculated from __ and bias from __.

Measurand	***Combined Uncertainty u_c***	***Expanded Uncertainty U***
		$2 \cdot u_c$ =

11.3 Appendix 3: Error model used in this handbook

This model is a simplification of the model presented in the ISO guide [4]:

$$y = m + (\delta + B) + e$$

y	measurement result of a sample
m	expected or "true" value for y
δ	method bias
B	laboratory bias
e	random error at within-laboratory reproducibility conditions

Uncertainty estimation in section 3 -6

$$u_c^{\,2} = u(Rw)^2 + u(bias)^2$$

$u(Rw)^2$	The estimated variance of e under within-laboratory reproducibility conditions – intermediate precision. In the ISO guide the repeatability, s_r is used as an estimate of *e*.
$u(bias)^2$	The estimated variance of method bias and laboratory bias.

Uncertainty estimation in section 7

The combined uncertainty u_c can also be estimated from reproducibility data.

$u_c^{\,2} = s_L^{\,2} + s_r^{\,2} = s_R^{\,2}$ - equation A6 ref. [4]

Where s_R^2 is the estimated variance under reproducibility conditions and where s_L^2 is either the estimated variance of B if one method is used by all laboratories or an estimated variance of B and δ if several different methods have been used in the collaborative study (interlaboratory comparison) and s_r^2 is the estimated variance of *e*.

Comment
For samples that are more inhomogeneous and have big variations in matrix opposed to control samples, the estimation of the measurement uncertainty of the method can become too low. However we recommend the use of repeatability limit for duplicate analyses $r = 2.8 \cdot s_r$ in order to control sample inhomogeneity.

11.4 Appendix 4: Uncertainty of bias for NH_4-N in section 3.2

Results for a laboratory from proficiency tests of NH_4-N in water.

PT	***Assigned value x_{ref}***	***Laboratory result x_i***	***Bias[9] (difference)***	***s_R***	***Number of labs***	$u(Cref_i)$
	µg L^{-1}	µg L^{-1}	%	%		%
1999 1	81	83	2.5	10	31	1.80
2	73	75	2.7	7	36	1.17
2000 1	264	269	1.9	8	32	1.41
2	210	213	1.4	10	35	1.69
2001 1	110	112	1.8	7	36	1.17
2	140	144	2.9	11	34	1.89
$\overline{X}$			**+ 2.20**	Mean *u(Cref)*		1.52
RMS_{bias}			**2.26**			

Number of proficiency tests: $N = 6$

$$RMS \text{ of the bias} = \sqrt{\frac{\sum bias_i^{\,2}}{N}} = \sqrt{\frac{2.5^2 + 2.7^2 + ...2.9^2}{6}} = 2.26 \text{ \% (rel)}$$

$$u(Cref) = \frac{\sum_{i=1}^{N} u(Cref_i)}{N} = \frac{1.80+1.17+1.41+1.69+1.17+1.89}{6} = 1.52\%$$

A *t*-test shows that the bias (+2.20 %) is not significant taking into account the standard uncertainty of the assigned value of 1.52 %.

If the assigned value is a median or a robust mean it is recommended to multiply the standard deviation by factor of 1.25 to correspond to s_R described in this handbook [18].

If PT provider reports expanded uncertainty, *U*, of the assigned value according to ISO 13528 [18] or similar , then U/2 should be used as *u(Crefi)* for individual PT instead of calculating uncertainty via s_R and n_{Lab}.

[9] See note in section 6.2.

11.5 Appendix 5: Raw data for NH_4-N - duplicates

Raw data for section 4.2 and 5.3 - Estimation of the s_r from duplicates, absolute *s* at low levels and relative *s* at 'high' levels.

Concentration < 30 µg L^{-1}		
x_1	x_2	*s*
µg L^{-1}	µg L^{-1}	µg L^{-1}
7.46	7.25	0.15
9.01	9.17	0.11
3.60	3.10	0.35
6.48	6.48	0.00
14.49	14.12	0.26
10.84	10.89	0.04
4.61	5.00	0.28
2.60	2.42	0.13
2.80	2.62	0.13
5.84	6.19	0.25
2.12	2.50	0.27
2.30	2.11	0.13
2.52	2.89	0.26
3.71	3.71	0.00
7.43	7.43	0.00
8.83	8.51	0.23
9.12	8.79	0.23
8.24	7.90	0.24
2.62	2.78	0.11
3.33	3.33	0.00
2.69	2.69	0.00
12.09	12.09	0.00
4.24	4.24	0.00
10.49	10.64	0.11
3.68	3.52	0.11
9.37	9.37	0.00
2.22	2.06	0.11
6.10	6.10	0.00
2.96	2.86	0.07
14.02	13.70	0.23
4.24	3.62	0.44
5.10	4.61	0.35
2.78	2.62	0.11
8.52	6.81	1.21
12.82	14.05	0.87
3.17	2.40	0.54
11.28	11.43	0.11
14.31	13.82	0.35
4.01	4.48	0.33
3.27	3.58	0.22
9.98	10.29	0.22
12.56	13.66	0.78
16.2	16.6	0.28
28.8	28.7	0.07
15.8	18.5	1.91
17.7	16.7	0.71
3.35	2.88	0.33
	Pooled s	0.44

Concentration > 30 µg L^{-1}			
x_1	x_2	*s*	***Relative s***
µg L^{-1}	µg L^{-1}	µg L^{-1}	%
37.6	36.9	0.49	1.3
4490	4413	54.45	1.2
136	125	7.78	6.0
62.6	62.3	0.21	0.3
159	159	0.00	0.0
16540	16080	325.27	2.0
31.3	30.1	0.85	2.8
58.5	60.1	1.13	1.9
741	796	38.89	5.1
130	127	2.12	1.7
29.4	29.2	0.14	0.5
1372	1388	11.31	0.8
36.6	44.7	5.73	14.1
22.6	23.4	0.57	2.5
34.8	33.2	1.13	3.3
92.9	94.0	0.78	0.8
40.6	42.2	1.13	2.7
80.4	86.4	4.24	5.1
78.2	73.8	3.11	4.1
48.9	50.9	1.41	2.8
36.6	35.3	0.92	2.6
51.9	52.2	0.21	0.4
198	207	6.36	3.1
70.3	69.2	0.78	1.1
29.9	30.6	0.49	1.6
31.9	32.4	0.35	1.1
		Pooled *s* %	3.8

11.6 Appendix 6: Raw data for dissolved oxygen in Section 5.3

Data plotted in Figure 7 - oxygen in sea water. Range equals the difference between Result 1 and 2. A pooled *s* is calculated from the *s* calculated for each duplicate.

x_1	x_2	Range	*s*
mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}
8.90	8.91	-0.01	0.007
8.99	9.01	-0.02	0.014
8.90	8.90	0.00	0.000
9.11	9.12	-0.01	0.007
8.68	8.64	0.04	0.028
8.60	8.51	0.09	0.064
8.61	8.61	0.00	0.000
8.02	8.00	0.02	0.014
7.05	7.08	-0.03	0.021
6.98	7.01	-0.03	0.021
7.13	7.10	0.03	0.021
6.79	6.78	0.01	0.007
6.55	6.55	0.00	0.000
6.53	6.53	0.00	0.000
4.68	4.68	0.00	0.000
5.28	5.33	-0.05	0.035
7.42	7.40	0.02	0.014
7.62	7.63	-0.01	0.007
5.88	5.88	0.00	0.000
6.03	6.06	-0.03	0.021
6.33	6.33	0.00	0.000
5.90	5.90	0.00	0.000
6.24	6.27	-0.03	0.021
6.02	6.02	0.00	0.000
9.13	9.11	0.02	0.014
9.10	9.14	-0.04	0.028
8.50	8.44	0.06	0.042
8.73	8.71	0.02	0.014
8.09	8.09	0.00	0.000
7.56	7.58	-0.02	0.014
6.30	6.32	-0.02	0.014
6.43	6.44	-0.01	0.007
7.25	7.34	-0.09	0.064
7.25	7.31	-0.06	0.042
8.00	8.03	-0.03	0.021
8.38	8.29	0.09	0.064
9.23	9.29	-0.06	0.042
9.09	9.08	0.01	0.007
9.37	9.36	0.01	0.007
9.38	9.37	0.01	0.007
9.32	9.25	0.07	0.049
8.47	8.49	-0.02	0.014
8.27	8.28	-0.01	0.007
8.37	8.31	0.06	0.042
8.09	8.15	-0.06	0.042
8.05	8.03	0.02	0.014
7.38	7.4	-0.02	0.014
7.49	7.49	0.00	0.000
4.52	4.49	0.03	0.021
4.45	4.44	0.01	0.007
4.29	4.27	0.02	0.014
		Pooled s	0.0252

11.7 Appendix 7: Raw data for BOD in section 8.2

Results in mg L^{-1} O_2 consumption. The certified value and expanded uncertainty of the CRM is 206 ± 5 mg L^{-1}. As the average of two results is always reported for test samples, the s_{Rw} is also calculated from the average of each sample pair in the internal quality control.

Date	**x_1**	**x_2**	**Average**
	mg L^{-1}	**mg L^{-1}**	**mg L^{-1}**
2000-12-09	219	215	217
2001-03-01	206	221	214
2001-03-01	221	210	216
2001-04-01	215	207	211
2001-09-05	199	218	209
2001-09-19	224	212	218
2001-10-16	216	213	215
2001-01-07	196	215	206
2001-11-28	210	207	209
2001-12-11	228	223	226
2001-12-13	207	229	218
2002-01-15	207	208	208
2002-01-22	224	214	219
2002-01-30	201	214	208
2002-02-11	219	223	221
2002-03-06	217	218	218
2002-09-18	206	228	217
2002-10-01	215	226	221
		Average	**214.8**
		s	**5.6**
		***s* %**	**2.6**

11.8 Appendix 8: Template for evaluation of uncertainty

Measurement Uncertainty
from
Quality Control and Validation Data

Name of analytical procedure:	
Analyte:	
Measurement ranges	Calculations - Relative in % or absolute in concentration units
Measurement range 1	
Measurement range 2	
Measurement range 3	
Short description of the analytical procedure	
Corresponding standard procedure/method	
Target uncertainty	

Within laboratory reproducibility $u(R_w)$

Control sample:	**Low**	**Middle**	**High**
Composition of control sample			
Mean value			
Standard deviation, *s*			
Number of determinations, *n*			
Number of months			
Assigned value			

Estimate of s_{Rw} from the warning limits of the control chart

Warning limits ±				
$s_{Rw} = \frac{warning\ limits}{2} =$	Conc. (abs)			
	% (relative)			

List of differences in the procedure/method or property of control samples compared with test samples and if possible also an indication of size. From size an estimate of standard uncertainty, *u* can be made.

	Difference	Size	u
1			
2			
3			
4			

Differences could e.g. be sample amount or matrix, instability, temperature, inhomogeneity, impurities that influence the measurement result. Inhomogeneity of test samples can be assessed by running duplicates. If there are important differences increased, within-lab reproducibility can be calculated below.

Estimation of an increased s_{Rw}

Control sample			
$u(Rw) = \sqrt{(s_{Rw})^2 + s^2_{differences}} =$			

Bias – method and laboratory bias from CRM

Bias is a systematic error or mean difference from an assigned value. Use one page for each matrix or concentration level where appropriate.

(Here you have a choice to do the calculations in concentration (absolute) or relative in %. Please fill in unit used for each column)

Concentration Range:

One CRM. Uncertainty in the assigned value *u(Cref) = U(Cref)/2*.

CRM	Own lab results		Cert. value	*U(Cref)*	*u(Cref)*	*n*	bias = Lab – CRM	*Relative bias = (Lab-CRM)/CRM · 100*
	Mean	s_{bias}						

If there is only **one** CRM there is only one bias value but several measurements and the following equation is applied:

$$u(bias) = \sqrt{(bias)^2 + \left(\frac{s_{CRM}}{\sqrt{n}}\right)^2 + u(Cref)^2}$$

Where n = number of measurement on the CRM and s_{bias} is the obtained standard deviation from measurements on the CRM.

Several CRM – uncertainty in assigned value is *u(Cref) = U(Cref)/2*

CRM	Own lab results		Cert. value	*U(Cref)*	*u(Cref)*	bias = Lab – CRM	*Relative bias = (Lab-CRM)/CRM · 100*
	Mean	s_{CRM}					
					RMS_{bias}		

Number of CRM samples, N =

Root Mean Square is $RMS_{bias} = \sqrt{\frac{\sum (bias_i)^2}{N}}$ =

Mean value of $u(Cref)$ =

Estimate from several CRM: $u(bias) = \sqrt{RMS_{bias}{}^2 + u(Cref)^2}$ =

Bias – method and laboratory bias from PT

Bias is a systematic error or mean difference from an assigned value. Use one page for each matrix or concentration level where appropriate. (Here you have a choice to do the calculations in concentration (absolute) or relative in %. Please fill in unit used for each column)

Concentration range:

Proficiency Testing (PT)

Data from last 10 PT – minimum six!

Year	**Sample ¤**	**Own lab value**	**PT value**	**bias = Lab –PT**	***Relative bias = (Lab-PT)/PT · 100***			s_R[10]	n_{Lab}	$u(Cref_i) = s_R/N_{Lab}$
			RMS$_{bias}$							

Number of PT, N_{PT} =

Root Mean Square, $RMS_{bias} = \sqrt{\frac{\sum (bias_i)^2}{N_{PT}}} =$

Uncertainty in assigned PT value

$u(Cref) = \frac{\sum_{i=1}^{N} u(Cref_i)}{N_{PT}}$ where $u(Cref_i) = \frac{s_{Ri}}{\sqrt{n_{Lab,i}}}$

Calculation of *u(bias)*

See section 6 in Nordtest handbook.

From PT: $u(bias) = \sqrt{RMS_{bias}{}^2 + u(Cref)^2} =$

If PT provider reports expanded uncertainty of the assigned value (U) according to procedure described in ISO 13528, then $U/2$ should be used as $u(Cref_i)$ for individual PT instead of calculating uncertainty via s_R and n_{Lab}.

[10] If the assigned value is a median or if a robust mean PT value is used, the 'robust standard deviation' reported by PT provider must be multiplied by factor of 1.25 [18].

Evaluation of expanded measurement uncertainty

$$U = 2 \cdot u_c = 2 \cdot \sqrt{u(Rw)^2 + \left(u(bias)\right)^2}$$

where u_c= combined standard uncertainty

Low range – Measurement uncertainty:

Bias from	*u(Rw)*	*u(bias)*	u_c	$U = 2 \cdot u_c$
CRM				
PT				
Recovery				

Middle range – Measurement uncertainty:

Bias from	*u(Rw)*	*u(bias)*	u_c	$U = 2 \cdot u_c$
CRM				
PT				
Recovery				

High range – Measurement uncertainty:

Bias from	*u(Rw)*	*u(bias)*	u_c	$U = 2 \cdot u_c$
CRM				
PT				
Recovery				

List over the main contributions to measurement uncertainty and if possible also an indication of size of uncertainty source in concentration (e.g. mg L^{-1}) or in % (relative).

	Source	Size
1		
2		
3		
4		
5		

11.9 Appendix 9: Uncertainty calculations using MUkit.

Step	Action	Determination of ammonium in water	2017-10-22
1	Specify Measurand	Analyte measured: Ammonium Concentration range: 30 – 1000 µg L^{-1} Matrix: Water Analysis method: EN/ISO 11732	
2	Quantify within-laboratory reproducibility, $u(R_w)$ Control sample that covers all the steps in the analytical process	**Control samples:** Matrix: Water Period of measurements: 2001-01-01 - 2002-01-01 Number of control samples: 135 Average concentration: 200 µg L^{-1} Standard deviation, s_{Rw} : 1,67 % $u(R_w) = s_{Rw} =$ 1,67 %	

Step	Action	Determination of ammonium in water	2012-11-22

3 — Quantify method and laboratory bias, $u(bias)$

Method and laboratory bias from Interlaboratory comparisons:

Interlaboratory comparison count, N : 6

I	1	2	3	4	5	6
Assigned concentration, $c_{ref\,i}$	81 µg L^{-1}	73 µg L^{-1}	264 µg L^{-1}	210 µg L^{-1}	110 µg L^{-1}	140 µg L^{-1}
Measured concentration, c_i	83 µg L^{-1}	75 µg L^{-1}	269 µg L^{-1}	213 µg L^{-1}	112 µg L^{-1}	144 µg L^{-1}
$bias_i = \frac{c_i - c_{ref\,i}}{c_{ref\,i}} \cdot 100\%$	2,47 %	2,74 %	1,89 %	1,43 %	1,82 %	2,86 %
Between laboratories standard deviation, $s_{R\,i}$	10,0 %	7,00 %	8,00 %	10,0 %	7,00 %	11,0 %
Consensus value robust mean or median, $s_{R(fixed)i} = 1{,}25 \cdot s_{R\,i}$	No	No	No	No	No	No
Fixed standard deviation, $s_{R(fixed)i}$	10,0 %	7,00 %	8,0 %	10,0 %	7,0 %	11,0 %
Number of participating laboratories, n_i	31	36	32	35	36	34
$u(c_{ref\,i}) = \frac{s_{R(fixed)i}}{\sqrt{n_i}}$	1,80 %	1,17 %	1,41 %	1,69 %	1,17 %	1,89 %
Analyte measured	ammonium					
Matrix	water	water	water	water	water	water
Date	1999-03-01	1999-09-01	2000-03-03	2000-10-04	2001-04-04	2001-10-11
Arranger	NIVA	NIVA	NIVA	NIVA	NIVA	NIVA

		Additional information | | | | | | | $u(c_{ref}) = \frac{\sum_{i=1}^{N} u(c_{ref\,i})}{N}$ = 1,52 % $RMS_{bias} = \sqrt{\frac{\sum_{i=1}^{N} bias_i^{\,2}}{N}}$ = 2,26 % $u(bias) = \sqrt{RMS_{bias}^{\,2} + u(c_{ref})^2}$ = 2,73 %
4	Convert components to standard uncertainty	$u(R_w)$ = 1,67 % $u(bias)$ = 2,73 %
5	Calculate combined standard uncertainty u_c	$u_c = \sqrt{u(Rw)^2 + u(bias)^2}$ = 3,20 %
6	Calculate expanded uncertainty U	$U = 2 \cdot u_c$ = 6,4 %