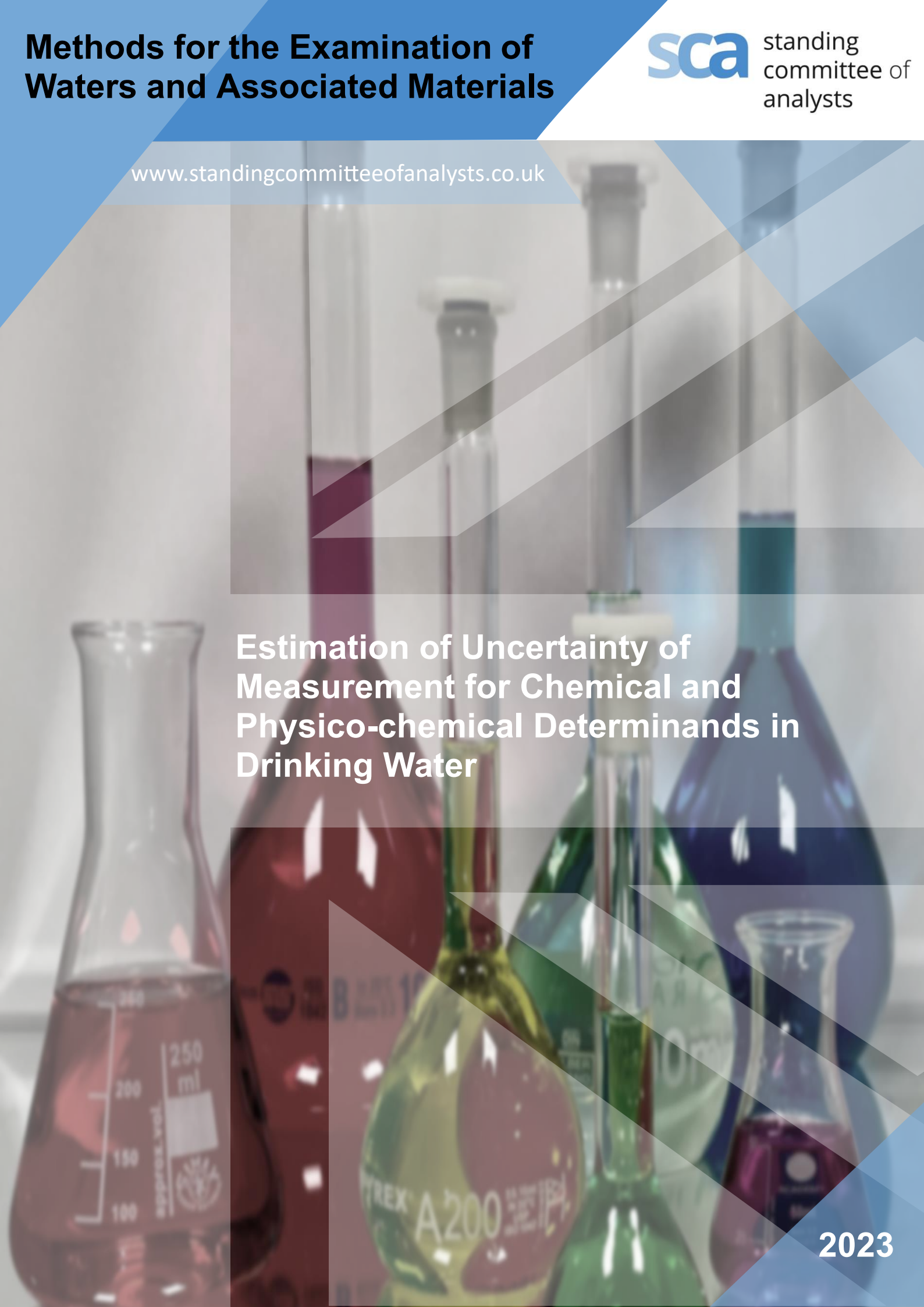


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Estimation of Uncertainty of Measurement for Chemical and Physico-chemical Determinands in Drinking Water

2023

Estimation of Uncertainty of Measurement for Chemical and Physico-chemical Determinands in Drinking Water

This booklet contains guidance on calculating uncertainty of measurement for chemical and physico-chemical determinands relevant to the tests carried out on drinking water for regulatory compliance.

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About this series

Introduction

This booklet is part of a series intended to provide authoritative guidance on recommended methods of sampling and analysis for determining the quality of drinking water, ground water, river water and sea water, wastewater and effluents as well as sewage sludges and biota.

In addition, short reviews of the most important analytical techniques of interest to the water and sewage industries are included.

Performance of methods

Ideally, all methods should be fully evaluated with results from performance tests. These methods should be capable of establishing, within specified or pre-determined and acceptable limits of deviation and detection, whether or not any sample contains concentrations of parameters above those of interest.

For a method to be considered fully evaluated, individual results from at least three laboratories should be reported. The specifications of performance generally relate to maximum tolerable values for total error (random and systematic errors) systematic error (bias) total standard deviation and limit of detection - often, full evaluation is not possible and only limited performance data may be available.

In addition, good laboratory practice and analytical quality control are essential if satisfactory results are to be achieved.

Standing Committee of Analysts

The preparation of booklets within the series "Methods for the Examination of Waters and Associated Materials" and their continuing revision is the responsibility of the Standing Committee of Analysts (SCA) - Established 1972 by the Department of the Environment.

At present, there are several working groups, each responsible for one section or aspect of water quality analysis:

1. General principles of sampling and accuracy of results
2. Microbiological methods
3. Inorganic and physical methods, metals and metalloids
4. Organic methods
5. Biological, biodegradability and inhibition methods
6. Radiochemistry methods

The actual methods and reviews are produced by smaller panels of experts in the appropriate field, in co-operation with the working group and main committee. The names of those members principally associated with these methods are listed at the back of this booklet.

Publication of new or revised methods will appear on our website – the library for which serves as a record of the bona fide methods developed and produced by the Standing Committee of Analysts.

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Every effort is made to avoid errors appearing in the published text. If, however, any are found, please notify the Secretary.

secretary@standingcommitteeofanalysts.co.uk

Users should ensure they are aware of the most recent version they seek.

Warning to users

The analytical procedures described in this booklet should only be carried out under the proper supervision of competent, trained analysts in properly equipped laboratories.

All possible safety precautions should be followed, and appropriate regulatory requirements complied with. This should include compliance with the Health and Safety at Work etc. Act 1974 and all regulations made under the Act, and the Control of Substances Hazardous to Health Regulations 2002 (SI 2002/2677). Where particular or exceptional hazards exist in carrying out the procedures described in this booklet, then specific attention is noted.

Numerous publications are available giving practical details on first aid and laboratory safety.

These should be consulted and be readily accessible to all analysts. Amongst such resources are:

HSE: [Information about health and safety at work](#)

RSC: [Laboratory best practices](#)

The Approved List of Biological Agents. (2023) Advisory Committee on Dangerous Pathogens of the Health and Safety Executive (HSE).

A Estimation of Uncertainty of Measurement for Chemical and Physico-chemical Determinands in Drinking Water

A1 Foreword

The European Union (EU) Commission Directive 2015/1787, amending Annexes II and III to the EU Drinking Water Directive (98/83/EC), was officially adopted by the European Commission on 6 October 2015 and came into force in the UK by amendments to the Water Supply (Water Quality) Regulations. The amending regulations introduced a requirement for uncertainty of measurement and limit of quantification as performance characteristics for analysis for the purposes of regulatory monitoring. The regulations removed the regulatory requirement for trueness, precision and limit of detection.

It is Drinking Water Inspectorate's (DWI) role to regulate water companies in England and Wales to ensure the requirements of the Water Supply (Water Quality) Regulations, including analysis, are met. There is already a requirement for laboratories undertaking analysis for the purpose of compliance assessment to incorporate uncertainty of measurement calculations as part of the requirements of EN ISO/IEC 17025 (2017).

However, DWI concluded that there was ambiguity regarding the specifics of how uncertainty of measurement and limit of quantification shall be applied and that this would result in a lack of comparability between laboratories.

This document will ensure a consistent approach to calculation of uncertainty of measurement and limit of quantification across all laboratories in England and Wales that undertake analysis for the purposes of drinking water compliance.

A2 Introduction

This guide is written to assist technical and quality managers in laboratories undertaking the analysis of water to estimate the uncertainty of measurement in a way that conforms to ISO 11352 (2012) Water Quality: Estimation of Measurement Uncertainty Based on Validation and Quality Control Data. Some aspects of other internationally recognised standards for calculating uncertainty of measurement have been included and referenced where they were considered necessary to enhance or clarify the method, but ISO 11352 (2012) shall be the main reference document for UK laboratories.

Definitions and symbols used throughout this blue book are described in Section 3.

Regulatory requirements have transferred from using precision, bias and limit of detection (LoD) to prescribe the quality of analytical results to uncertainty of measurement (UoM) and limit of quantification (LoQ). This guide specifies how these shall be calculated by the UK water industry to ensure consistency of interpretation. The structure of this guide closely follows the international standard ISO 11352 (2012). ISO 11352 has worked examples of many of the calculations.

Although LoD and LoQ are not discussed in ISO 11352, they are fundamental values for evaluating analytical methods and for setting regulatory limits in the UK and guidance to their calculation is included in this document.

A3 Scope

The Prescribed Concentrations or Values (PCV) as defined in Schedule 1 of the Water Supply (Water Quality) Regulations, or the Specification Concentrations or Values (SCV) for indicator parameters as defined in Schedule 2 of the Water Supply (Water Quality) Regulations, are also fundamental values in setting the concentrations at which estimates of uncertainty shall meet regulatory standards of quality.

The objectives of this guide are to:

- meet the WFD regulatory requirements
- ensure results are comparable across laboratories
- assist in the assessment and comparison of laboratories, typically by the United Kingdom Accreditation Service (UKAS) and the DWI
- ensure the additional resources required by laboratories are proportional to the regulatory benefit
- provide the water industry with a tool to facilitate adoption of uncertainty of measurement for regulatory purposes

The relative expanded uncertainty (except for pH), U_{rel} , will be quoted as the UoM and used to provide an interval around the laboratory result that contains the true value with approximately 95% confidence (unless another level is specified).

A4 Principle and Limitations

A laboratory result is an estimate of the true value of the determinand. There is an uncertainty associated with the method of measurement arising from a combination of a systematic error or bias in the system and a random error. In most cases, the same estimate of UoM may be applied to all results from a controlled method irrespective of the sample matrix, analyst or instrument of the same type so long as these have been incorporated into the estimate (see section A7). In cases where the matrix or other aspect of the analysis is not well controlled, there will be additional sources of uncertainty that shall be taken into account.

The estimate of the UoM shall be based on validation data in the first instance. Continuing analytical quality control (AQC) data shall provide a more robust estimate once enough values are available and the method has become well established in the laboratory. Proficiency test schemes provide an independent confirmation of the uncertainty due to bias but may include sources of uncertainty not appropriate to the internal laboratory uncertainty.

The estimation of UoM should reflect current performance and be based on a maximum of one year's worth of data. An exception to this is where proficiency testing data is used in the estimation of bias and is infrequent.

This blue book covers the calculation of the measurement uncertainty for the physico-chemical and chemical determinands in the Water Framework Directive (WFD), the Drinking Water Directive (DWD) and the UK water regulations. Microbiological parameters are not included. Neither does it consider the uncertainties associated with sampling and transportation to the laboratory.

Everything from receipt of the sample and storage in the laboratory contributes to the laboratory's combined uncertainty of measurement and shall accompany the analytical result.

Although written for laboratory methods, the procedures also cover the uncertainties in online monitoring measurements when under the control of the laboratory.

A5 Procedural Overview

The random and systematic errors are estimated separately and combined as the square root of the sum of squares of the uncertainties for within laboratory reproducibility, the method and the laboratory bias. The combined uncertainty, U_c , is multiplied by a coverage factor (usually $k = 2$) to produce the expanded uncertainty.

In brief:

- (a) Estimation of random error shall be obtained directly if there is a stable sample that can be used for a quality control chart. Failing that, a stable synthetic control sample shall be combined with the uncertainty due to matrix variation. Only where a stable standard is not available shall the repeatability be used, combined with an estimate of the between batch uncertainty.

- (b) ISO 17025 requires the AQC standard to be taken through the entire analytical procedure. If for some reason this does not happen an additional estimate of uncertainty shall be needed to combine with the quality control chart data. An estimate of all of the contributions to uncertainty, represented by a 'fishbone' diagram is a useful aid to determine this.
- (c) Estimation of the systematic error is more complex. Where a certified reference material in a matrix exists the uncertainties due to the estimated bias and concentration of the reference material shall be combined. Alternatively the uncertainty from at least six recovery tests shall be combined with the uncertainty in the amount of analyte added. A third method is to estimate uncertainty from at least six deviations obtained from a suitable proficiency testing scheme, combined with the mean uncertainty in the reference value.

The uncertainty of measurement for new methods cannot be estimated from control chart data as it is very unlikely that a chart with sufficient points will be available until the method is in general use. A preliminary estimate from the initial validation exercise shall be made. Note that regulatory requirements are that all estimates have at least ten degrees of freedom. Using the calculation scheme described in NS30 (Cheeseman and Wilson, 1989) requires at least eleven duplicate measurements to be sure of achieving ten degrees of freedom under all circumstances. Once the method has been in use for an appropriate time period, data from the quality control chart shall then be used to calculate uncertainty.

Laboratories shall complete proficiency testing (PT) schemes for new methods within an appropriate time scale. Non-participation in PT schemes, and responding appropriately to the outcome, shall be justified to the accreditation body. There may only be a few PT rounds per year, so the initial validation could be used for two years or more before data from six rounds are available for a robust comparison with the internal estimate of bias. Whilst laboratories will still be expected to participate in PT schemes and act on any failing rounds, PT scheme data are not compulsory for calculation of uncertainty of measurement as long as other suitable data are available from the methods specified in this document.

A6 Preparative stages for the estimation of measurement uncertainty

A6.1 Specification of the measurement

The laboratory shall properly define the analytical method and verify it as fit for purpose before estimating the uncertainty. The method shall specify:

- the determinand
- the analytical system
- calculation of the results
- the valid concentration range of the method
- the extent of matrix interference.

Some measuring equipment may have internal sensors for processing measurements, such as for temperature compensation. This may add additional uncertainty to measurements and

laboratories shall consider this when there are unusual changes in quality control data or uncertainty of measurement values.

A6.2 Specification of the form in which the measurement uncertainty is reported

The uncertainty is to be reported as the absolute value for concentrations near the LoQ (up to 3 times the LoQ). At higher concentrations the uncertainty of measurement will be expressed as a percentage of the measured concentration. In particular, it shall be estimated close to the regulatory value (the PCV or SCV $\pm 25\%$) unless other levels of interest are agreed between the laboratory, their client and the regulatory body.

Note:- values for pH are expressed in pH units.

A7 Evaluation of available precision and bias data

A7.1 Approach and criteria

The estimate of UoM is based on the within-laboratory reproducibility (u_{RW}) of the method and the laboratory bias (u_b). The source of the data shall be representative in that it covers:

- the complete determination procedure, including pre-treatment, matrix adjustment, calibration and measurement
- the conditions of execution, including different operators, equipment and environments
- matrix variations and possible interferences.

The accompanying spreadsheets contain calculation blocks for estimating the magnitude of various sources of uncertainty and combining the results. These are referenced below by capital letters. The output of these blocks are the relative uncertainty, indicated by the subscript 'rel' in the symbol at the head of the column. The results from individual blocks are combined in a summary table at the bottom of the worksheet. The data here is in a form that is suitable for copying into the second spreadsheet to calculate the combined and expanded uncertainty for all determinands analysed in the laboratory. Formulae in the calculation blocks are the same as those specified in ISO 11352 (2012) which has worked examples of the calculations. Note that in a few cases the results of these calculations differ slightly from the spreadsheets due to differences in rounding. The laboratory shall choose at least one calculation block and enter appropriate data generated using the specified method. However, not all calculation blocks within the spreadsheet need to be filled in for every determinand. The following sections refer to calculation blocks within the accompanying spreadsheet where relevant.

A7.2 Within-laboratory reproducibility (u_{Rw})

The estimation of reproducibility shall be made under the conditions of routine analysis. The best estimate will therefore come from quality control charts or similar data. The laboratory shall choose at least one of the following three options:

- a. Where there is a stable standard to use for AQC and the construction of a quality control chart, the reproducibility will be the standard deviation of these results (**s_{Rw} block A in the accompanying spreadsheets**). The solution of the stable standard shall have the similar matrix as the samples and be taken through the whole analytical process with each batch. A minimum of eight values are required for a recently validated method. However, if the laboratory is carrying out validation in accordance with NS30 (Cheeseman and & Wilson, 1989), then a minimum of 22 data points will be available and shall be used. When a method has been in use for a reasonable time, a minimum of 60 points shall be used from different batches, from all instruments used for the method operated by all analysts competent in the method.
- b. If quality control samples with the same matrix as samples are not available, then synthetic standard solutions are used (**s_{Rw} from block B**). AQC standards with a matrix differing from routine samples will require an additional estimation of the repeatability from a range chart using samples from different matrices (**$u_{r,range}$ block C**) to combine with the uncertainty of the standard ($u_{Rw,stand}$) and take into account the additional uncertainty due to the increased inhomogeneity of the analyte in the matrix. At least eight values are required.

$$u_{Rw} = \sqrt{u_{Rw,stand}^2 + u_{r,range}^2}$$

(refer to appendix 3 for definitions of the symbols)

- c. When control samples would be unstable the uncertainty can be estimated from the range of replicate analyses (**$u_{Rw,range}$, block C**) and between-batch variation ($u_{Rw,bat}$). At least eight values are required.

$$u_{Rw} = \sqrt{u_{r,range}^2 + u_{Rw,bat}^2}$$

The between-batch variation may be estimated in various ways. For instance, the calculation in NS30 (Cheeseman and & Wilson, 1989) separates the between-batch standard deviation from the validation data (**block N**).

A7.3 Method and laboratory bias (u_b)

Bias shall be eliminated if at all possible, or if this is not possible, it shall be minimised. The Eurachem/CITAC Guide (Ellison and Williams, 2012) notes 'Where the bias ...and the precision associated with the bias check, are all small compared to s_R , no additional allowance need be made for bias uncertainty'. The spreadsheet returns 'no bias' if data are not entered into one of the options. The Eurachem/CITAC Guide (Ellison and Williams, 2012) also notes that component uncertainties less than a third of the largest need not be evaluated in detail. However it is advisable to enter the data obtained at validation. The combined

uncertainty will increase by a very small amount when the bias uncertainty meets the above conditions.

Statistically justifiable outliers shall be excluded from estimates of the bias uncertainty. Advice in some standards is that results should be corrected for bias (for example ISO/IEC Guide 98-3) but this is not acceptable when reporting results for compliance purposes in the UK. When the uncertainty contribution from the bias is too large the combined uncertainty will not meet the target, the inference being that the method is inadequate and it shall not be used. The uncertainty associated with the method and the laboratory has two components: the standard deviation of the measured bias and the uncertainty of the nominal concentration of the reference material. The laboratory shall choose at least one of the following three options for estimation:

- a. Regular analysis of a suitable reference material to provide a reliable estimate of the bias and its uncertainty ($u_{b,rel}$ **blocks D1/D2 for relative bias and D3/D4 for absolute bias**). At least six values are required from analyses on different days. The uncertainty in the reference material (u_{Cref}) may be derived from the producer's certificate. It may be necessary to convert the given value for the semi-range to a standard uncertainty. Systematic errors are best treated as having a rectangular distribution; thus the uncertainty is the given value divided by $\sqrt{3}$ (Eurachem/CITAC Guide, Ellison and Williams, 2012).

Blocks D1 and D2 are provided in the spreadsheet, depending on whether single or multiple CRMs are used in the estimation (ie CRMs with different test certificate values). The equivalent blocks (D3 and D4) are also included for the determination of pH bias in absolute terms.

For single CRMs the following equation is applied (D1 and D3, for absolute U_b)

$$u_{b,rel} = \sqrt{b^2 + \left(\frac{s_b}{\sqrt{n_M}}\right)^2 + u_{Cref}^2}$$

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_{Cref} is the uncertainty of the reference value

For estimations of bias using more than one CRM, the following equation is used (D2 and D4 for absolute U_b).

$$u_{b,rel} = \sqrt{u_{Cref}^2 + b_{rms}^2}$$

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

$$b_{rms} = \sqrt{\frac{\sum(b_i)^2}{n_r}}$$

b_i is the difference between the mean measured value and the accepted reference value of the i th reference material

n_r is the number of reference materials

- b. Recovery experiments which measure the concentration of added analyte to provide an estimate of the bias (based on a nominal recovery of 100%) and its uncertainty (**blocks E and F**). Ideally these would be 'blind spikes', thus the analyst cannot be influenced by knowledge of the amount added. There are two components: the difference between the observed and calculated values (**block F**) and the uncertainty in the amount of analyte added (**block H**). At least six values within a relevant matrix are required.

The standard uncertainty associated with method and laboratory bias (u_b) estimated with recovery experiments is

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

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

$$b_{rms} = \sqrt{\frac{\sum b_i^2}{n_n}}$$

b_i is the deviation from the complete recovery (100%) of the i th recovery experiment or from the mean recovery, if the results are correct with the mean recovery

n_n is the number of recovery experiments

Note: recovery experiments for **turbidity and colour** in **raw water** matrices containing appreciable concentrations of the parameter of interest are challenging as high background levels in the raw water matrix make spiking experiments difficult to undertake. Any such experiment is likely to lead to falsely low recoveries and an associated large estimation of uncertainty due to the incorrect estimate of bias.

It is therefore permitted to undertake sample pre-treatment (e.g. filtration and/or acidification) for these parameters, to allow realistic recoveries to be obtained from the sample spikes.

Where pre-treatment is applied to the method for a matrix requiring it, the procedure should be comprehensively documented and details recorded in the relevant procedure.

- c. Interlaboratory comparisons, or proficiency testing data (**block G1 for relative and G2 for pH absolute values**) may be used in the same way as a reference material when it can be assumed that the assigned value is a good estimate of the true value. At least six values are required from analyses on different days. The organising laboratory shall provide the uncertainty in the nominal value ($u_{Cref,i}$).

Note if s_R (reproducibility standard deviation) or the number of participants varies substantially between PT rounds then the following equation (from Nord test document TR537) may be applied for a pooled standard deviation (not provided in the example spreadsheets).

$$\% Pooled = \sqrt{\frac{(n_1 - 1) \times \%S_1^2 + (n_2 - 1) \times \%S_2^2 + (n_3 - 1) \times \%S_3^2}{(n_1 + n_2 + n_3) - 3}} \dots$$

$$u_{Cref,rel} = \frac{(\% Pooled)}{\sqrt{\text{mean No. participating labs}}}$$

When interlaboratory and proficiency testing schemes calculate the assigned or nominal value from the average of all participants, differences that are laboratory-specific may adversely influence the uncertainty estimate of all laboratories. The returns from rounds of the proficiency tests shall be used as an independent confirmation of the bias estimated by options (a) or (b) above. They do not need to be included in laboratories' regulatory estimates of uncertainty of measurement as long as data from methods (a) or (b) above are available. Laboratories shall set out how data from interlaboratory trials and proficiency testing schemes will be used in procedures for each analytical method and include a justification for the approach. **Block P** compares the proficiency test scheme returns with the laboratory estimate from comparison with a traceable standard and recovery experiments and applies simple statistical tests of significance, however the use of these tests is not mandatory.

A8 Calculations

A8.1 Calculation of the combined standard uncertainty

The combined uncertainty (u_c or $u_{c,rel}$) is the square root of the sum of squares of the standard uncertainties (or the relative standard uncertainties).

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

Usually it is simply the combination of the laboratory precision (u_{RW}) and bias uncertainty (u_b):

$$u_c = \sqrt{u_{R_w}^2 + u_b^2}$$

A9 Calculation of the expanded uncertainty

Whilst individual and combined uncertainties are standard deviations, the expanded uncertainty is a range. The expanded uncertainty (U or U_{rel}) is obtained from the combined uncertainty by multiplication with a coverage factor of $k = 2$ unless there are exceptional reasons for choosing another value for k . This is a symmetrical confidence interval ($\pm U$ or $\pm U_{rel}$) of about 95%. However, this value of k may be insufficient where the combined uncertainty is based on statistical observations with relatively few degrees of freedom (fewer than six). The choice of k then depends on the effective number of degrees of freedom (Eurachem/CITAC Guide, Ellison and Williams, 2012).

In the UK DWI, through water quality regulations, will set the PCV and SCV and an acceptable uncertainty of measurement for all determinands of interest in wholesome water. With few exceptions this will be in terms of the relative expanded uncertainty. The acceptable uncertainty of measurement for other determinands not specified in the regulations will need to be decided by the laboratory to suit the intended use of the analytical data.

A10 Calculation of Limit of Quantification (LoQ)

For methods where the discrimination of the method is insufficient to record values other than zero for most blank determinations, the within-batch standard deviation of either the low standard, low spiked standard or the within-batch standard deviation of the sample shall be used to calculate the limit of quantification. Some methods, particularly those involving simple titrations or the use of comparators, may be incapable of measuring any within-batch differences less than the limit of quantification (LoQ). In such cases the LoQ shall be quoted as the lowest measurable concentration or value.

All estimates of standard deviation used to estimate limit of quantification or precision or used in significance tests shall have at least 10 degrees of freedom for regulatory purposes in the UK (derived from using an 11x2 validation scheme). Uncertainty estimates for other purposes are also likely to require many more degrees of freedom than the minimum specified in ISO 11352 (2012).

A11 Records

The laboratory shall have a procedure covering the calculation of UoM from the data collected during validation of the analytical method, subsequent monitoring and re-validation testing. The laboratory shall maintain a register of the characteristics of each analytical method in use and this shall accompany the expanded uncertainty. Components of the register of characteristics shall be:

- Units
- Coverage factor
- Confidence level
- LoQ and the factor used to derive it from the within laboratory reproducibility.

Other parameters of the method needed by users of the data may be conveniently included in the register and kept available for inspection. A table of the estimates and the date ranges to which they apply shall be maintained by the laboratory.

When quality control data indicates there has been a significant change in the precision or bias of the method, or if the laboratory makes significant changes to the method, the UoM shall be reviewed and if necessary recalculated. This will include:

- when changes are made in control chart limits due to a significant change in precision following control chart review
- when new PT data are available after each round (if used in the estimation of UoM)
- when new estimates of bias are made from CRM or recovery data (if used in the estimation of UoM)

A12 Associated Spreadsheets

Two spreadsheets to facilitate the calculations are provided:

UoM-BB calculations: a set of calculation blocks, identified by letters, for the validation and on-going AQC data.

UoM-BB determinands: a sheet for all determinands that combines the random and systematic uncertainty

Each calculation block is identified by a letter. Not all blocks will be used; it depends on the route chosen to calculate UoM. Where there is a worked example in ISO 11352 (2012) the section reference is below the block. The blocks are self-contained with the exception of the coverage factor (k). This is clearly displayed near the top of the sheet and will be 2 except in exceptional cases. Where appropriate the ISO 11352 (2012) symbol is at the head of the column and the formula at the foot of the column. The sheets are unprotected so that laboratories can import the parts they need into their own systems. It is the laboratory's responsibility to protect their working spreadsheets to prevent corruption of the formulae and to maintain a set of test data to demonstrate they are functioning correctly.

The coloured cells contain formulae; these formulae shall not be changed. Data shall be entered into the white cells within the blocks. The worked example in the spreadsheets shall be used to confirm the active formulae have not been corrupted.

A12.1 UoM-BB calculations

It is intended that this workbook will be used to capture all the data for a single determinand. There are separate sheets for precision and bias calculations. At the foot of each sheet the results of the calculations are gathered into a summary table with a row that may be copied into the second spreadsheet (UoM-BB determinands) where uncertainty components are combined and expanded to provide the regulatory statistic.

There are four worksheets:

Worksheet: precision

- A. Precision estimate using a matrix standard
- B. Precision estimate using a synthetic standard
- C. Range calculations

Worksheet: bias

- D. Bias uncertainty using a traceable standard or certified reference material (D1-D4)
- E. Bias uncertainty from recovery tests
- F. Recovery calculations
- G. Bias uncertainty using proficiency test data (G1 and G2)
- H. Standard addition calculations
- J. Replicates calculations
- K. Standard addition, summary

- M. Concentration of reference materials
- N. Validation summary of statistics (NS30)
- P. Comparison of bias estimates with PT results

Worksheet: tables, data

Calculation blocks C, F, G, J and P are repeated in this sheet for more general use. The new blocks are:

- L. Control chart data
- Q. The look-up table for the range chart factors

At the foot of the sheet is a table of terms and symbols used in the other spreadsheet (**UoM-BB determinands**) with some explanation of their meaning. The order of the terms and colour of the blocks is the same as the columns in the second spreadsheet (**UoM-BB determinands**).

Worksheet: control chart

The data in calculation block L is copied into the first two columns and plotted as a control chart. If it is to be used properly the nominal concentration of the standard, the desired central value and standard deviation will need to be entered in 'Chart set-up values' cells.

A12.2 UoM-BB determinands

This is intended to form a table of uncertainty estimates of all determinands analysed in the laboratory. Columns A to F may be copied into laboratory reports as needed. The remaining columns contain the laboratory data and intermediate results needed to calculate the relative expanded uncertainty in column F. The data for these columns may be entered directly or copied from the previous spreadsheet (UoM-BB calculations). A consistent colour fill is used to aid this.

A13 References

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A15 Symbols

b	bias estimated as the difference between mean measured value and an accepted reference value
b _i	bias of the i th reference material; the deviation from the complete recovery (100 %) of the i th recovery experiment
b _{rel}	relative bias; i.e. the bias divided by the reference concentration expressed as a percentage.
b _{rms}	root mean square of individual bias values respectively of the deviations from recovery experiments
c	mean value of the laboratory's test results
C _{ass}	assigned value of the interlaboratory comparison sample
c _j	measured concentration of the j th solution
C _{ref}	concentration of the reference standard
C _{V,b}	coefficient of variation of the measured values of the reference material
D _i	the difference between the measurement result and the assigned value of the i th sample of the interlaboratory comparison
D _{i,rel}	relative difference as a percentage: $D_{i,rel} = \frac{c - C_{ass}}{C_{ass}} \times 100$
D _{rms}	root mean square of the differences
d ₂	factor for the calculation of the standard deviation from the mean range 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
U _{Cref,i,rel}	relative uncertainty of the assigned value of the interlaboratory sample
n _{ilc}	number of analysed interlaboratory comparison samples
n _M	number of measurements
n _{p,i}	number of participating laboratories for sample i
n _r	number of reference materials
n _η	number of recovery experiments
R	mean range
R _{j,rel}	relative range of the j th batch of replicates
s	standard deviation
S _b	between-batch standard deviation
S _j	standard deviation of measurements of the concentration of solution j
S _t	total standard deviation
S _w	within-batch standard deviation
S _{R,i}	reproducibility standard deviation from the interlaboratory comparison for sample i
S _{R,i,rel}	relative reproducibility standard deviation from the interlaboratory comparison of samples
S _{Rw}	standard deviation of the quality control results

U	expanded uncertainty
U_{rel}	relative expanded uncertainty
U_c	combined standard uncertainty
$U_{c,rel}$	combined relative standard uncertainty
U_j	standard uncertainties from different sources j
$U_{j,rel}$	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
$U_{b,rel}$	relative standard uncertainty component associated with method and laboratory bias
U_{conc}	standard uncertainty of the concentration of the addition solution
U_{Cref}	mean standard uncertainty of the reference values or mean standard uncertainty of the assigned values of the interlaboratory comparison samples
U_{Cref}	standard uncertainty of the reference value
$U_{Cref,j}$	standard uncertainty of the assigned value of the interlaboratory sample i
U_{Rw}	standard uncertainty component for the within-laboratory reproducibility
$U_{r,range}$	standard uncertainty component from the range control chart (obtained under repeatability conditions)
$U_{Rw,bat}$	standard uncertainty component resulting from variations between batches
$U_{Rw,stand}$	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
$U_{V,rep}$	random standard uncertainty component of the volume added (obtained under repeatability conditions)
$\epsilon_{V,max}$	maximum deviation of the volume from the specified value (producer information)
η	recovery

A16 Definitions

The definitions are in accordance with ISO standards where available and sources are referenced where applicable.

Batch	A series of measurements made under repeatability conditions
Bias or measurement bias	The estimate of a systematic measurement error (ISO/IEC Guide 99, 2007). The difference between the mean measured value and the accepted reference value (b).
Combined standard uncertainty or combined standard measurement uncertainty	A 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).
Coverage factor	A number larger than one by which a combined standard measurement uncertainty is multiplied to obtain an expanded measurement uncertainty (ISO/IEC Guide 99, 2007).
Error or measurement error	The measured quantity value minus a reference quantity value (ISO/IEC Guide 99, 2007).
Expanded uncertainty or expanded measurement uncertainty	The product of a combined standard measurement uncertainty and a factor larger than the number one. Note 1 to entry: The term “factor” in this definition refers to a coverage factor (ISO/IEC Guide 99, 2007).
Limit of detection (LoD)	<p>The true amount of analyte which leads with high probability to the conclusion that the analyte is present, given a particular decision criterion. The decision criterion (‘critical value’) is usually set to ensure a low probability of declaring the analyte present when it is in fact absent (Eurachem/CITA Guide, Ellison and Williams, 2012).</p> <p>The output signal or value above which it can be affirmed with a stated level of confidence, for example 95 %, that a sample is different from a blank sample containing no determinand of interest (ISO 13530, 2009).</p> <p>ISO/TS 13530 defines LoD as 4.65 times within-batch standard deviation. In previous regulatory documents this has been simplified to 3 times within batch standard deviation of a low standard or 5 times if a blank is used.</p>
Limit of quantification (LoQ)	A stated multiple of the limit of detection at a concentration of the determinand that can reasonably be determined with an acceptable level of accuracy and precision. The limit of quantification can be calculated using an appropriate standard or sample and may be obtained from the lowest calibration point on the calibration curve, excluding the blank (EU directive 2009/90/EC).

	<p>ISO/TS 13530 does not define LoQ but suggests 3 times the LoD, which will have a relative uncertainty of approximately 33%. In practice this is close to 10 times the within-batch standard deviation of a matrix blank or sample with a low concentration of the determinand.</p> <p>For regulatory purposes in the UK the LoQ shall be calculated directly as 10 times the within-batch standard deviation with at least ten degrees of freedom.</p>
Precision	The 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).
Prescribed concentration or value (PCV)	The regulatory limit for parameters listed in Schedule 1 of the Water Supply (Water Quality) Regulations.
Random error or random measurement error	The component of measurement error that in replicate measurements varies in an unpredictable manner (ISO/IEC Guide 99, 2007).
Relative Standard Deviation (RSD)	An estimate of the standard deviation of a population from a statistical sample of n results divided by the mean of that sample. Often known as coefficient of variation (CV). Also frequently stated as a percentage (Eurachem/CITA Guide, Ellison and Williams, 2012).
Relative standard measurement uncertainty	The standard measurement uncertainty divided by the absolute value of the measured quantity value (ISO/IEC Guide 99, 2007).
Repeatability conditions	Observation conditions where independent test or measurement results are obtained with the same method on identical test or 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).
Reproducibility conditions	Observation conditions where independent test or measurement results are obtained with the same method on identical test or measurement items in different test or measurement facilities with different operators using different equipment (ISO 3534-2, 2006).
Standard uncertainty or standard measurement uncertainty.	The measurement uncertainty expressed as a standard deviation (ISO/IEC Guide 99, 2007).
Specification concentration or value	The regulatory limit for indicator parameters listed in Schedule 2 of the Water Supply (water Quality) Regulations.
Systematic error or systematic measurement error	The component of measurement error that in replicate measurements remains constant or varies in a predictable manner (ISO/IEC Guide 99, 2007).
Uncertainty of measurement (UoM) or measurement uncertainty	A 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).

Within-laboratory reproducibility	Intermediate measurement precision where variations within one laboratory alone are included.
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Correspondence

However well procedures may be tested, there is always the possibility of discovering hitherto unknown problems. Analysts with such information are requested to contact the Secretary of the Standing Committee of Analysts:

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Amendment History

This blue book (No.282) supersedes No.276 and the following key changes are highlighted for your convenience:

Version	Section	Amendment
282	A7.2a	Block A or B changed to Block A to remove “or B” “The same changed” to ‘a similar’
282	A7.2b	Added “If quality control samples with the same matrix as samples are not available, then synthetic standard solutions are used (sRw from block B).”; “an additional”; and “and take into account the additional uncertainty due to the increased inhomogeneity of the analyte in the matrix.”
282	A7.3a	“(brms block F)” removed “Ubrel” added
282	A7.3 b	Added: The standard uncertainty associated with method and laboratory bias (u_b) estimated with recovery experiments is $u_b = \sqrt{b_{rms}^2 + u_{add}^2}$ 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 $b_{rms} = \sqrt{\frac{\sum b_i^2}{n_n}}$ b_i is the deviation from the complete recovery (100%) of the i th recovery experiment or from the mean recovery, if the results are correct with the mean recovery n_n is the number of recovery experiments
282	General	Number of editorial changes to update publication dates and grammatical errors.

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