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Guidance for estimation of measurement uncertainty according to the requirements of DIN EN ISO/IEC 17025 for testing laboratories in the subject of chemical analytics in the fields of health-related consumer protection, agricultural sector, chemistry and environment

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Scope of application:

This guidance document contains general rules, guidelines and examples for procedures for estimation of measurement uncertainties. They are intended to ensure interdisciplinary harmonisation of the requirements and approach to accreditation of testing laboratories in the subject of chemical analytics in the fields of health-related consumer protection, agricultural sector, chemistry and environment.

They are directed both to the testing laboratories and the DAkkS auditors.

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1 Purpose / scope of application

Section 5.4.6.2 of DIN EN ISO/IEC 17025:2005 requires that testing laboratories must have available and apply procedures for assessment of measurement uncertainties.

This guidance document contains general rules, guidelines and examples for procedures for estimation of measurement uncertainties. They are intended to ensure interdisciplinary harmonisation of the requirements and approach to accreditation of testing laboratories in the subject of chemical analytics in the fields of health-related consumer protection, agricultural sector, chemistry and environment.

They are directed both to the testing laboratories and the DAkkS auditors.

2 Terms

Analysis sample	Sample(s) or partial sample(s) taken from the lab sample
Dimension	Property of a phenomenon, a body or a substance, with such property having a value which can be expressed by a number and a measurement unit/reference [2]
Quantity value	A combination of a number and a measurement unit/reference attributed to a dimension [1]
Lab sample	Sample(s) or partial sample(s) provided to the laboratory
Error of measurement	Measured value minus a reference value [2]
Measuring result	Amount of quantity values allocated to a measured variable, in combination with any available relevant information [2]
Measured variable	Dimension to be measured [2]
Measuring accuracy	Amount of congruence of indicators or measured variables obtained by repeated measurement of the same or similar objects subject to predefined conditions [2]
Measuring sample	Sample(s) or partial sample(s) obtained from the analysis sample used for measurement
Trueness of measurement	Amount of approximation of the average of an infinite number of repeated measured values in a reference value [2]

Measurement	Process in which one or several quantity values which may be reasonably allocated to a dimension are experimentally determined 1) [2]
Measurement uncertainty	Non-negative parameter identifying the distribution of values associated with the measured variable based on the information used [2]
Measured value	Quantity value representing a measuring result [2]
Reference value	Quantity value used as the basis for comparison of values of dimensions of the same type [2] e.g.: - Value of a certified reference material; - Uncertified reference value of a defined sample provided by the customer; - Reference value determined by a performance test (e.g. ring trial) - Reference value determined by a different procedural principle or also gravimetric weighted sample; The reference value is not necessarily the real value.
Real value	Quantity value identical with a definition of a dimension [2] Note: The real value would be obtained by perfect measurement. Due to their nature, real values cannot be determined.

[1)] in analytics, a sample submitted for analysis is frequently submitted to a series of chemical and/or physical treatments to bring it into a form in which it may be used in a measuring instrument. These steps are deemed part of the measuring process. (Source: EURACHEM – Terminology in Analytical Measurement: Introduction to VIM 3; edition: 2013)

3 Basics

Knowing the measurement uncertainty is essential in order to determine whether a measured value is suitable for a certain purpose.
“When estimating the uncertainty of measurement, all uncertainty components which are of importance in the given situation shall be taken into account using appropriate methods of analysis” (DIN EN ISO/IEC 17025, 5.4.6.3). This applies to both systematic and accidental components of uncertainty.

The measurement uncertainty of a measurement procedure may contain numerous components. In order to provide assistance in step with actual practice, various aspects of determination of the measurement uncertainty are outlined in this document.

The measurement uncertainty can be assessed indirectly by means of a modelling approach or an integrative approach or by means of a direct approach:

Modelling approach:

In the modelling approach, a model of the measurement is created, as described in GUM [1] and a EURACH/CITACT guidance document [3]. In the course of such action, the measurement procedure can be divided into individual modules for which individual uncertainties can be determined. The modelling approach either delivers a measurement uncertainty for the overall procedure or uncertainty contributions from individual modules of the overall procedure which are combined for a total uncertainty pursuant to the law of propagation of uncertainty.

Integrative approach:

In this indirect approach, several sources of uncertainty are determined in an integrative manner. Examples for this approach are described in detail in NORDTEST Technical Report TR 569 “Handbook for Calculation of Measurement Uncertainty in Environmental Laboratories” [4] and in the international standard DIN ISO 11352 “Water quality - Estimation of measurement uncertainty based on validation and quality control data” [5]

Direct approach:

In the direct approach, the distribution and systematic deviations of measurement results are examined as a bundle in one experiment. This approach is described in detail in the international standard DIN EN ISO 20988 “Air quality - Guidelines for estimating measurement uncertainty” [6].

In general, the following applies:

Primarily, the effort and the procedure for determination of the measurement uncertainty is subject to the requirements for the measured value. They may result from statutory provisions, risk assessments, the customer's requirements, etc.

4 Domains of measurement uncertainty

Significant uncertainty contributions may arise from the following domains:

A) Sample taken from the entirety of the test object

B) Obtaining an analysis sample as a representative partial sample

C) Preparing the measuring sample from the analysis sample

D) Determining the measured value from the measuring sample

In order to assess the measurement uncertainty, all steps of the process performed under the conformity assessment body's responsibility must be considered.

While determining the measurement uncertainty, contributions to the domains of A to D must be considered individually, if applicable. It must be clear which domains the indicated measurement uncertainty refers to when stating the measurement uncertainty in the test report. The domains C and D must be considered while stating the measurement uncertainty on principle.

4.1 Uncertainty contributions arising from sampling (A)

Determining the contributions arising from sampling can be particularly complex.

If the contributions arising from sampling cannot be determined, it should be noted that uncertainty arising from sampling has not been determined and therefore was not taken into account within the course of determining the measurement uncertainty.

Frequently, the uncertainty arising from sampling may only be determined by expert opinion, in particular with regard to systematic deviations and due to heterogeneity of the test object. If this is the case, the basis of such assessment must be indicated.

If specific measured values are available, e.g. the results of a number of independent lab values representative for the test object to be sampled which were determined individually, an uncertainty contribution subject to sampling may be estimated.

4.2 Uncertainty contributions arising from obtaining an analysis sample (B)

The uncertainty resulting from distribution of the analyte in the lab sample must be considered. If technical measures are required to reduce a possibly existing inhomogeneity (such as e.g. milling the lab sample), the resulting uncertainty must also be considered.

4.3 Preparing the measuring sample from the analysis sample (C)

The contributions to the measurement uncertainty resulting from preparation of the sample must be considered, e.g. those arising from decompositions, extractions, concentrations, derivatisations and clean-ups.

4.4 Determining the measured value from the measuring sample (D)

The contributions to the measurement uncertainty resulting from determination of the measured value must be considered, e.g. those arising from the following:

- Weighing
- Volume measurements
- Dilution steps (calibration of pipettes, in particular air displacement pipettes, volumetric flasks)
- Precision of the measurement signal of the sample solution (depending on the analyte concentration, the procedural steps, homogeneity of the sample)
- Purity of calibration substances
- Moisture contents
- Calibration solutions, reference materials
- Non-linearity of the calibration function
- Selectivity of the measuring signal
- Physical and chemical interferences of the measuring signal
- Background corrections
- Drifting of the measuring signal, long- and short-term time stability
- Contaminations (blank values)
- Loss of analytes (recovery rates)

5 Determination of measurement uncertainty in practice

5.1 Relevant and significant uncertainty contributions

The basis of determination is the systematic summary of all sources of uncertainty relevant for the assessed examination procedure. Based on such summary, the sources of uncertainty are assessed; such uncertainty contributions having no significant influence on the total uncertainty can be disregarded.

Thus, the following inherently relevant sources of uncertainty could be compiled for a certain examination procedure, among others:

(1) Weighing uncertainties
(2) Volume uncertainties of pipettes and volumetric flasks
(3) Fluctuations of density
(4) Temperature effects
(5) Metrological traceability
(6) Homogeneity of the sampling material
(7) Matrix of the sampling material
(8) (Complex) steps in preparation of the sample
(9) Stability of the measuring signal
(10) Calibration of measuring device

If the assessment finds that e.g. the uncertainty contributions 1) to 5) do not have significant influence on the overall uncertainty in comparison to the uncertainty contributions 6) to 10), they may be disregarded.

5.2 Indirect approaches

Modelling approach:

This approach is described in detail in GUM [1] and for chemical analytics specifically in the EURACHEM/CITAC guidance document “Quantifying Uncertainty in Analytical Measurement” [3].

The first step is preparing a model of the measurement. Then, the individual uncertainty is determined for each individual step of such model. A cause-effect diagram (fishbone or Ishikawa diagram) is recommended for depicting the individual components. Using the sensitivity coefficient, the uncertainty values for the measurement are deduced from the influencing factors’ uncertainty components. Some individual components result from validation; for others, expert opinions are required. For details on the procedure, see [3].

Particular attention should be directed to determining the trueness of measurement since it is frequently difficult to identify such deviations in the individual steps.

Primarily, trueness of measurement is determined by comparing the results with certified reference materials with as similar a composition as the sample material as possible, applying the standard addition procedure or by recovery experiments. Systematic deviations should be corrected as far as possible by optimising the analysis procedure, e.g. by using suitable defined calibration substances (certified), using the up-and-down method to determine the calibration function, chemical separation of the analyte, masking of interfering matrix components, avoiding contamination/loss, adjustment of the matrix in the calibration solutions, use of internal standards, etc. If deviations can be quantified with sufficient accuracy, they are corrected mathematically. In such case, the uncertainties of the corrections must be taken into account.

Integrative approach:

In this indirect approach, several sources of uncertainty are determined in an integrative manner. Examples for this approach are described in detail in NORDTEST Technical Report TR 569 “Handbook for Calculation of Measurement Uncertainty in Environmental Laboratories” [4] and in the international standard DIN ISO 11352 “Water quality - Estimation of measurement uncertainty based on validation and quality control data” [5]

Usually, the results of the quality assurance sample analytics are used to determine the measuring accuracy. Uncertainty components not sufficiently considered during quality assurance must be determined in addition.

Trueness of measurement is determined using the results of analytics of certified matrix reference material if possible. The results from comparative measurements, performance tests or recovery experiments may also be used. For a description of the procedure in detail, see [4] and [5].

The integrative approach frequently only covers the domains C and D (see section 4); if applicable, additional estimations for the domains A and B may be required.

5.3 Direct approach

This approach is described in detail in the international standard DIN EN ISO 20988 “Air quality - Guidelines for estimating measurement uncertainty” [6].

In the direct approach, the distribution and systematic deviations of measurement results are examined as a bundle in a single experiment. The input data are a single series of observations and the associated reference values. DIN EN ISO 20988 describes eight suitable experiments with execution examples. If necessary, deviations not considered by the series of measuring results are determined by expert opinion.

5.4 Frequency of determination of the measuring uncertainty

On principle, the measurement uncertainties of the observed measured variables determined with a test procedure shall be assessed once; this can be performed e.g. within the scope of validation.

The assessment must be reviewed, e.g. if

- internal or external quality assurance measures indicate there are issues
- new findings are determined
- significant changes are made to the analysis procedure
- new or other analytical equipment is used

6 Calculation of measurement uncertainty

The law of propagation of uncertainty describes the combination of independent uncertainty components by addition of the variances. The root of the sum of total variances is the combined uncertainty “uc” which is multiplied with the coverage factor k to obtain the expanded measurement uncertainty “U”.

Frequently, a value of k = 2 can be used which corresponds to a coverage interval (confidence interval) of about 95%. K = 2 may be chosen only if the values have a normal distribution and the number of effective degrees of freedom is of a sufficient size.

Note: Other distributions have other k values. If a small number of degrees of freedom and almost normal distribution of values is present, the t (student) distribution may be used.

7 Presentation of measurement uncertainty

The measurement uncertainty’s presentation must provide an overview of the following information:

- the method used to determine the measurement uncertainty,
- the used coverage factor k or the underlying coverage interval,
- the domains included in the assessment (e.g. with or without sampling) and
- possibly present legal, normative or otherwise mandatory basics for the determination of measurement uncertainty

Example for expression of the measured value and expanded measurement uncertainty, with the contribution of sampling being disregarded:

Iron: 1.78 mg/kg ± 0.10 mg/kg (k = 2)* *: The expanded measurement uncertainty does not include sampling.

Measured value and measurement uncertainty must be stated with the same unit and the same number of decimals.

8 References

[1] “guide to the expression of uncertainty in measurement”, German translation of Guide to the Expression of Uncertainty in Measurement (GUM), DIN V ENV 13005, June 1999, Beuth Verlag

[2] “International dictionary of metrology”, basic and general terms and associated terms (VIM) [International vocabulary of metrology – Basic and general concepts and associated terms] – German-English edition ISO/IEC-guideline 99:2007, August 2012, Beuth Verlag

[3] “Quantifying Uncertainty in Analytical Measurement”, QUAM:2012.P1, EURACHEM/CITAC Guide, 3rd edition, 2012, http://www.eurachem.org/

[4] NORDTEST Technical Report TR 537 ed. 3.1 “Handbook for Calculation of Measurement Uncertainty in Environmental Laboratories”. http://www.nordtest.info.

[5] DIN ISO 11352:2013 – Water quality - Estimation of measurement uncertainty based on validation and quality control data

[6] DIN EN ISO 20988:2007 – Air quality - Guidelines for estimating measurement uncertainty