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**Water quality — Guidance on analytical  
quality control for chemical and  
physicochemical water analysis**

*Qualité de l'eau — Lignes directrices pour le contrôle de qualité  
analytique pour l'analyse chimique et physicochimique de l'eau*

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## Foreword

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

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

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

In other circumstances, particularly when there is an urgent market requirement for such documents, a technical committee may decide to publish other types of document:

- an ISO Publicly Available Specification (ISO/PAS) represents an agreement between technical experts in an ISO working group and is accepted for publication if it is approved by more than 50 % of the members of the parent committee casting a vote;
- an ISO Technical Specification (ISO/TS) represents an agreement between the members of a technical committee and is accepted for publication if it is approved by 2/3 of the members of the committee casting a vote.

An ISO/PAS or ISO/TS is reviewed after three years in order to decide whether it will be confirmed for a further three years, revised to become an International Standard, or withdrawn. If the ISO/PAS or ISO/TS is confirmed, it is reviewed again after a further three years, at which time it must either be transformed into an International Standard or be withdrawn.

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

ISO/TS 13530 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

This first edition of ISO/TS 13530 cancels and replaces ISO/TR 13530:1997, which has been technically revised.

# Water quality — Guidance on analytical quality control for chemical and physicochemical water analysis

## 1 Scope

This Technical Specification provides comprehensive guidance on within-laboratory and between-laboratory quality control for ensuring the production of results with a known level of accuracy in the analysis of waters.

This Technical Specification is applicable to the chemical and physicochemical analysis of all types of waters. It is not intended for application to the analysis of sludges and sediments (although many of its general principles are applicable to such analysis) and it does not address the biological or microbiological examination of water. Whilst sampling is an important aspect, this is only briefly considered.

Analytical quality control, as described in this Technical Specification, is intended for application to water analysis carried out within a quality-assurance programme. This Technical Specification does not address the detailed requirements of quality assurance for water analysis, which can be found in the EURACHEM/CITAC Guide (2002) [20].

The recommendations of this Technical Specification are in agreement with the requirements of established quality-assurance documentation (e.g. ISO/IEC 17025).

This Technical Specification is applicable to the use of all analytical methods within its field of application, although its detailed recommendations may require interpretation and adaptation to deal with certain types of determinands (for example, non-specific determinands, such as suspended solids or biochemical oxygen demand, BOD). In the event of any disparity between the recommendations of this Technical Specification and the requirements of a standard method of analysis, the requirements of the method should prevail.

## 2 Normative references

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

ISO 3534-2:2006, *Statistics — Vocabulary and symbols — Part 2: Applied statistics*

ISO 5725 (all parts), *Accuracy (trueness and precision) of measurement methods and results*

ISO 8466-1, *Water quality — Calibration and evaluation of analytical methods and estimation of performance characteristics — Part 1: Statistical evaluation of the linear calibration function*

ISO 8466-2, *Water quality — Calibration and evaluation of analytical methods and estimation of performance characteristics — Part 2: Calibration strategy for non-linear second-order calibration functions*

ISO 13528:2005, *Statistical methods for use in proficiency testing by interlaboratory comparisons*

ISO/IEC 17025:2005, *General requirements for the competence of testing and calibration laboratories*

ISO Guide 35, *Reference materials — General and statistical principles for certification*

ISO/IEC Guide 43-1, *Proficiency testing by interlaboratory comparisons — Part 1: Development and operation of proficiency testing schemes*

ISO/IEC Guide 43-2, *Proficiency testing by interlaboratory comparisons — Part 2: Selection and use of proficiency testing schemes by laboratory accreditation bodies*

### 3 Terms and definitions

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

#### 3.1 Terms related to measurement methods

##### 3.1.1

##### **validation**

confirmation by examination and the provision of objective evidence that the particular requirements for the specific intended use are fulfilled

[ISO/IEC 17025:2005]

##### 3.1.2

##### **accuracy**

closeness of agreement between a test result or measurement result and the true value

NOTE 1 In practice, the accepted reference value (3.2.6) is substituted for the true value.

NOTE 2 The term “accuracy”, when applied to a set of test or measurement results, involves a combination of random components and a common systematic error or bias component.

NOTE 3 Accuracy refers to a combination of trueness and precision.

[ISO 3534-2:2006]

##### 3.1.3

##### **bias**

difference between the expectation of a test result or measurement result and a true value

[ISO 3534-2:2006]

##### 3.1.4

##### **trueness**

closeness of agreement between the expectation of a test result or a measurement result and a true value

NOTE 1 The measure of trueness is usually expressed in terms of bias.

NOTE 2 Trueness is sometimes referred to as “accuracy of the mean”. This usage is not recommended.

NOTE 3 In practice, the accepted reference value is substituted for the true value.

[ISO 3534-2:2006]

##### 3.1.5

##### **precision**

closeness of agreement between independent test/measurement results obtained under stipulated conditions

NOTE 1 Precision depends only on the distribution of random errors and does not relate to the true value or the specified value.

NOTE 2 The measure of precision is usually expressed in terms of imprecision and computed as a standard deviation of the test results or measurement results. Less precision is reflected by a larger standard deviation.

NOTE 3 Quantitative measures of precision depend critically on the stipulated conditions. Repeatability conditions and reproducibility conditions are particular sets of extreme stipulated conditions.

[ISO 3534-2:2006]

### 3.1.6 limit of detection

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 6107-2:2006]

### 3.1.7 limit of quantification

stated multiple of the limit of detection, for example, two or three times the limit of detection, at a concentration of the determinand that can reasonably be determined with an acceptable level of accuracy and precision

NOTE 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).

[ISO 6107-2:2006]

### 3.1.8 analytical run

group of measurements or observations carried out together, either simultaneously or sequentially, without interruption, on the same instrument by the same analyst using the same reagents

NOTE 1 An analytical run may consist of more than one batch of analyses. During an analytical run, the accuracy and precision of the measuring system is expected to be stable.

NOTE 2 Definition taken from Reference [33] in the Bibliography.

### 3.1.9 batch of analyses

group of measurements or observations of standards, samples and/or control solutions which have been performed together in respect of all procedures, either simultaneously or sequentially, by the same analysts using the same reagents, equipment and calibration

## 3.2 Terms related to measurement results

### 3.2.1 error of measurement

test result or measurement result minus the true value

NOTE 1 In practice, the accepted reference value is substituted for the true value.

NOTE 2 Error is the sum of random errors and systematic errors.

NOTE 3 Adapted from ISO 3534-2:2006.

### 3.2.2 systematic error of result

component of the error of result which, in the course of a number of test results or measurement results, for the same characteristic or quantity, remains constant or varies in a predictable manner

NOTE Systematic errors and their causes can be known or unknown.

[ISO 3534-2:2006]

**3.2.3**

**random error of result**

component of the error of result which, in the course of a number of test results or measurement results, for the same characteristic or quantity, varies in an unpredictable manner

NOTE It is not possible to correct for random error.

[ISO 3534-2:2006]

**3.2.4**

**true value**

value which characterizes a quantity or quantitative characteristic perfectly defined in the conditions which exist when that quantity or quantitative characteristic is considered

NOTE The true value of a quantity or quantitative characteristic is a theoretical concept and, in general, cannot be known exactly.

[ISO 3534-2:2006]

**3.2.5**

**conventional true value**

value of a quantity or quantitative characteristic which, for a given purpose, may be substituted for a true value

NOTE A conventional true value is, in general, regarded as being sufficiently close to the true value for the difference to be insignificant for the given purpose.

[ISO 3534-2:2006]

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**3.2.6**

**accepted reference value**

value that serves as an agreed-upon reference for comparison

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NOTE The accepted reference value is derived as:

- a) a theoretical or established value, based on scientific principles;
- b) an assigned or certified value, based on experimental work of some national or international organization;
- c) a consensus or certified value, based on collaborative experimental work under the auspices of a scientific or technical group;
- d) the expectation, i.e. the mean of a specified set of measurements, when a), b) and c) are not available.

[ISO 3534-2:2006]

**3.2.7**

**certified reference material**

reference material, accompanied by a certificate, one or more of whose property values are certified by a procedure which establishes traceability to an accurate realization of the unit in which the property values are expressed, and for which each certified value is accompanied by an uncertainty at a stated level of confidence

NOTE Definition taken from Reference [36] in the Bibliography.

**3.2.8**

**metrological traceability**

property of a measurement result relating the result to a stated metrological reference through an unbroken chain of calibrations of a measuring system or comparisons, each contributing to the stated measurement uncertainty

[ISO/IEC Guide 99:2007]



### 3.3 Terms related to uncertainty

#### 3.3.1

##### uncertainty of measurement

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]

#### 3.3.2

##### standard uncertainty

$u(x_i)$

uncertainty of the result  $x_i$  of a measurement expressed as a standard deviation

[ISO/IEC Guide 98-3:2008]

#### 3.3.3

##### combined standard uncertainty

$u_c(y)$

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]

#### 3.3.4

##### expanded uncertainty

$U$

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

NOTE 1 The factor depends upon the type of probability distribution of the output quantity in a measurement model and on the selected coverage probability.

NOTE 2 The term “factor” in this definition refers to a coverage factor.

[ISO/IEC Guide 99:2007]

#### 3.3.5

##### coverage factor

$k$

numerical factor used as a multiplier of the combined standard uncertainty in order to obtain an expanded uncertainty

NOTE A coverage factor is typically in the range from 2 to 3.

[ISO/IEC Guide 98-3:2008]

## 4 Performance characteristics of analytical systems

### 4.1 Introduction

ISO/IEC 17025 requires the validation of methods; the validation process is described in detail in EURACHEM Guide (1998) [18]. Primary validation is part of the development of a new analytical method, and is performed during the standardization of the method. Important points to be considered for the primary validation of an analytical method are the following:

- scope of the method;
- calibration;

- limit of detection/limit of quantification;
- interferences;
- estimation of accuracy (trueness and precision);
- uncertainty of measurement;
- robustness;
- fitness for purpose.

According to ISO/IEC 17025, the laboratory shall confirm that it can correctly operate standard methods before applying these methods. This procedure is called secondary validation, where emphasis is laid on calibration and interferences, as well as the laboratory limit of quantitation and measurement uncertainty. In 4.2 to 4.8, the topics calibration and quantification, matrix effects and measurement uncertainty are dealt with especially.

## 4.2 Scope of the method

A clear definition should be given of the forms of the substance that are determined by the procedure and also, when necessary to avoid ambiguity, those forms that are not capable of determination. At this point, it is worth emphasizing that the analyst's selection of an analytical method should meet the user's definition of the determinand. Non-specific determinands need the use of rigorously stipulated analytical methods in order to obtain reliable and comparable results.

Many substances exist in water in a variety of forms or "species" and many analytical systems provide a differential response to the various forms. For example, when a separation of "dissolved" and "particulate" material is required, special care is necessary to define precisely the nature and pore-size of the filter to be used.

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A precise description of the types and natures of samples is important before the analytical system can be chosen. The precautions to be taken when a sample is analysed will depend to a high degree on the sample. The analyst needs information that is as complete as possible on sample types, concentration levels and possible interferences. The scope should contain a clear statement of the types of sample and sample matrices for which the procedure is suitable. If necessary, a statement should also be made of important sample types and matrices for which the procedure is not suitable.

The range of application corresponds to the lowest and highest concentrations for which tests of precision and bias have been carried out using the system without modification. Where an extension can be used to enable the examination of samples containing concentrations greater than the upper limit, such as by analysis after dilution, then it should be regarded as a different procedure but whose performance characteristics may be inferred from the values quoted for the original.

The concentration range of interest can have a marked effect on the choice of analytical technique; of primary concern is the smallest concentration of interest.

## 4.3 Calibration

### 4.3.1 Basics of calibration and quantification

A calibration function is determined from information values  $y_i$ , obtained by measuring given standard concentrations  $x_i$ . The resulting standard deviation of the method  $s_{x_0}$  or confidence interval is a performance characteristic of this calibration, not a performance characteristic of the quantification. Quantification of the analyte content of samples using a calibration function is based on interpolation. The most important performance characteristic for quantification is the estimation of measurement uncertainty (see 4.6) where the uncertainty of calibration is one of the contributions.

Depending on the kind of the functional relationship between the analyte concentration and the measurement response, different mathematical or statistical tools can be used. Mathematical and statistical models are subject to different assumptions; therefore, not only is the performance of the analytical equipment essential but also the kind of mathematical approach. The models should help the analyst to find a clear and reliable functional relationship for calibration. The models should not limit the capabilities of the analytical equipment. Therefore, the selection of the calibration model should be undertaken carefully, taking into consideration the fitness for purpose and the measurement uncertainty required.

- Model of linear regression (ISO 8466-1): the classical model for calibration with the limitations of normal distribution of the responses and a homogeneity of variances over the working range. Normally, this homogeneity of variances is only given in a working range of one or at maximum two decades of concentration. This fact limits the applicability.
- Model of non-linear second-order calibration functions (ISO 8466-2): after discovering a significant non-linearity. This model has the same limitations as linear regression: normal distribution of the responses and homogeneity of variances over the working range.
- Model of weighted regression, weighting the information value with the reciprocal variance, calibration over more than a decade of concentration range is possible.
- Calibration over more than one decade of concentration with at least two concentrations, e.g. for inductively coupled plasma/mass spectrometry (ICP/MS). Linearity must have been checked beforehand with a minimum of five concentrations, e.g. by graphical presentation.

NOTE Detailed instructions on calibration procedures are given in References [26] and [28] in the Bibliography.

All these kinds of calibration should be tested for their contribution to measurement uncertainty. For example, analyse  $N$  times, as a minimum in triplicate, an independent standard or a certified reference material within the concentration range of interest, and calculate the results in accordance with the applied calibration method. The standard uncertainty component,  $s_p$ , representing the deviation of the single results,  $\rho_i$ , from the reference value,  $\rho$ , is calculated as follows:

$$s_p = \sqrt{\frac{\sum_{i=1}^N (\rho_i - \rho)^2}{N - 1}} \quad (1)$$

where

$s_p$  is the standard uncertainty component from calibration;

$N$  is the number of replicate measurements.

$N$  should be chosen with respect to the confidence required.  $s_p$  should be compared with the respective target measurement uncertainty to set the tolerable amount.

### 4.3.2 Calibration strategies

#### 4.3.2.1 Basic or instrument calibration

This type of calibration is carried out without matrix components and without sample preparation; for calibration, pure standard solutions are used. This is inexpensive and directly suited for quantification, if matrix components do not change the slope and the intercept of the calibration function significantly. Normally this calibration is more precise than a calibration including all sample preparation steps.

#### 4.3.2.2 Calibration with matrix material

This kind of calibration is comparable with basic calibration (4.3.2.1). No sample preparation steps are carried out. Instead of the pure solutions of the standards, solutions of the standard substances in analyte-free matrix or artificial matrix are used.

#### 4.3.2.3 Calibration over the total procedure

This type of calibration includes all sample preparation steps, and the calibration solutions are prepared with a representative matrix material. It is suitable to show whether matrix components or sample preparation steps do or do not change the slope and intercept of the calibration function compared to the basic calibration function. Frequently, it is not easy to find a representative matrix material to use it as a basis of calibration solutions. In water analysis, this means that blank free natural water representing the possible matrices of other natural waters has to be found.

If the matrix components significantly change intercept and slope of the calibration function compared to the basic calibration, it is possible to use this calibration over the total procedure for quantification.

### 4.3.3 Internal standardization

#### 4.3.3.1 General aspects

The use of internal standardization for the quantification of concentrations minimizes possible errors made both during injection and by sample losses during sample pre-treatment steps, and also differences in the final sample extract volumes and changes in recoveries caused by matrix effects. Substances used as internal standards should have the following properties.

- Chemical-physical properties should be the same concerning the error-prone procedure steps which should be corrected. If the total procedure should be controlled by the internal standardization, isotopic labelled compounds are recommended; if only final volumes or detection should be controlled, other substances, which are representative concerning these steps, can be used.
- There should not be any measurement interferences with the internal standards.
- No occurrence of the internal standard, neither in real samples nor as blanks, which cannot be avoided.
- Concentration of the added internal standard: in the dynamic range of the method, preferably in the same concentration range as the analytes.
- They should have similar intensities of responses as the analytes.

It is recommended to carry out the internal calibration as a basic calibration, because all multiplicative matrix effects are corrected by the internal standard if it has the properties listed above. Otherwise, an internal calibration over the total procedure has the same disadvantages as described in 4.3.2.3, often there is a lack of representative matrix material. As with all the other possibilities for correcting matrix effects, internal standardization cannot overcome additive matrix effects as well.

#### 4.3.3.2 Calibration with internal standards

Calculation of the calibration function is usually available as an option in the quantification programs of most manufacturers' data analysis software.

Adjust the concentrations according to the sensitivity of the equipment used and the range of determinations required. Evaluate the linear range and, subsequently, set up a calibration. Establish the linear function as a basic calibration of the pairs of values  $y_i/y_{is,i}$  and  $\rho_i/\rho_{is,i}$  of the measured series using Equation (2):

$$\frac{y_i}{y_{is,i}} = a_i \frac{\rho_i}{\rho_{is,i}} + b_i \quad (2)$$

where

- $y_i$  is the measured response of substance i; the unit depends on the evaluation, e.g. area value;
- $\rho_i$  is the mass concentration of substance i (external standard) in the working standard solution, e.g. in nanograms per millilitre, ng/ml;
- $a_i$  is the slope of the calibration function of substance i; the unit depends on the evaluation, e.g. area value millilitres per nanogram, area value·ml/ng.
- $b_i$  is the ordinate intercept of the calibration curve; the unit depends on the evaluation, e.g. area value;
- $y_{is,i}$  is the measured response of the internal standard for the substance i; the unit depends on the evaluation, e.g. area value;
- $\rho_{is,i}$  is the mass concentration of the internal standard, for the substance i, e.g. in nanograms per millilitre, ng/ml.

Calibration can be done as linear regression or as a two point calibration over more than one decade after the previous linearity check.

#### 4.3.3.3 Quantification with internal standards

Add a known amount of the internal standards to the sample prior to sample preparation. Adjust this amount of the internal standards in such a manner that the mass concentration  $\rho_{is,i}$  in the final volume, e.g. of the extract, is nearly the same in the prepared samples as in the calibration solutions. Use the same solvent composition for the standard solutions and the samples.

Calculate the mass concentration  $\rho_{i,\text{sample}}$  of the substance using Equation (3).

$$\rho_{i,\text{sample}} = \frac{\frac{y_{i,\text{sample}}}{y_{is,i,\text{sample}}} - b_i}{a_i} \times \frac{m_{is,i}}{V_{\text{sample}}} = \frac{\rho_{i,\text{sample extract}}}{\rho_{is,i,\text{sample extract}}} \times \frac{m_{is,i}}{V_{\text{sample}}} \quad (3)$$

where

- $y_{i,\text{sample}}$  is the measured response, e.g. peak area, of substance i in the sample extract;
- $y_{is,i,\text{sample}}$  is the measured response, e.g. peak area, of the internal standard, for substance i, of the sample;
- $\rho_{i,\text{sample extract}}$  is the mass concentration of substance i in the sample extract, e.g. in nanograms per millilitre, ng/ml; usually calculated by the software;
- $\rho_{is,i,\text{sample extract}}$  is the mass concentration of the internal standard in the sample extract, for substance i, e.g. in nanograms per millilitre, ng/ml; usually reported by the software;
- $\rho_{i,\text{sample}}$  is the mass concentration of substance i in the water sample, e.g. in micrograms per litre,  $\mu\text{g/l}$ ;
- $m_{is,i}$  is the mass of the added internal standard substance, e.g. in micrograms,  $\mu\text{g}$ ;
- $V_{\text{sample}}$  is the sample volume, in litres, l;