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Water quality — Calibration and evaluation of analytical methods —

Part 1:
Linear calibration function

Qualité de l'eau — Étalonnage et évaluation des méthodes d'analyse —

Partie 1: Fonction linéare d'étalonnage

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

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

This second edition cancels and replaces the first edition (ISO 8466-1:1990), which has been technically revised.

The main changes compared to the previous edition are as follows:

— the title has been modified;

— the scope of the document is the calibration for routine analysis;

— calculation of performance characteristics has been moved to the informative Annex A;

— the calibration range has been extended to several decadeorders of magnitudes;

— the verification of the homogeneity of variances has been deleted;

— the linearity test has been modified;

— various calibration strategies have been described;

— the document has been editorially revised.

A list of all parts in the ISO 8466 series can be found on the ISO website.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

Calibration is a prerequisite for the quantification of analytes by means of physicochemical and chemical methods. In most cases, simple linear regression is applied because many measuring methods show a linear relationship between the indicated value and the sample content.

Since the publication of ISO 8466-1 in 1990, a huge progress has been made in the field of instrumental analysis, a consequence of which is that various calibration strategies have been developed in order to make best use of the equipment. The calibration range of many analytical methods was constrained to a maximum of one order of magnitude by the theoretical statistical requirement to only apply simple linear regression if homogeneity of variances exists across the selected working range. Due to the estimation of measurement uncertainty by calculation of the confidence interval in ISO 8466-1:1990, it had been necessary to conform to the required homogeneity of variances. Meanwhile, other methods for the estimation of measurement uncertainty that are independent of calibration have been established (e.g. ISO 11352).

Calibration is always done in two steps. The first step comprises the determination of the linear range, the second step is the calculation of the calibration function. The calibration strategies that are described in this document enable the analyst to individually define the calibration effort according to specified requirements. The method that is described in ISO 8466-1:1990 remains part of the informative annex since it can still be useful for specific purposes (e.g. method validation).

Water quality — Calibration and evaluation of analytical methods —

Part 1:
Linear calibration function

1 Scope

This document specifies various calibration strategies for physicochemical and chemical analytical methods and specifies the calculation of analytical results.

It defines the general context for linear calibration so that individual standards dealing with analytical methods for the examination of water quality can make reference to it.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

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

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

3.1
working range
interval, determined by calibration, between the highest and the lowest content, where the lowest possible limit of the working range is the limit of quantification of the analytical method

3.2
one-point calibration
calibration between the origin and the indicated value corresponding to the content in the *calibration sample* (3.8)

3.3
two-point calibration
calibration using two *calibration samples* (3.8) with different contents at the upper and at the lower working range limit

3.4
indicated value
y
quantity value provided by a measuring instrument or a measuring system

Note 1 to entry: In accordance with definition 4.1 "indication" of ISO/IEC Guide 99[6].

3.5
content
general term for the quantitative expression of the concentration or fraction of a substance in or of a substance mixture

Note 1 to entry: For example, it is the generic term for mass concentration, molar concentration, mass fraction.

3.6
total procedure
analytical method comprising all steps from sample pretreatment to the report of results

3.7
calibration solution
standard solution without a matrix

3.8
calibration sample
standard solution with a matrix

3.9
measurement procedure
comprises all details of a measurement including all calculations for obtaining the measurement result

3.10
responsivity
R
input–output gain of a detector system, i.e. indicated value divided by the corresponding content in the *calibration sample* (3.8)

Note 1 to entry: For a system that responds linearly to its input, there is a unique responsivity. For nonlinear systems, the responsivity is the local slope.

4   Symbols

A_s recovery rate for the sample

A_{Is} recovery rate of the internal standard

a intercept of the calibration line or the regression line for standard addition

b slope of the calibration line or the regression line for standard addition or the coefficient of the linear term of the second-order calibration function

b_i point-to-point slope i

b_m median of the slopes b_i

c regression coefficient of the quadratic term of the second-order calibration function

F factor (taking into account sample preparation, e.g. enrichment factor)

f conversion factor (e.g. 100 for expression in %)

f_1 or f_2 degree of freedom

i index of the calibration solutions (1, 2, ..., N)

m number of replicate measurements per spiking level for standard addition

N number of calibration solutions

n	number of spiking levels for the method of standard addition (including unspiked sample)
P	confidence level
R	responsivity
R_0	responsivity threshold
R_m	responsivity median
V_{ssi}	volume of the spiking solution i
V_M	volume of the measurement solution
V_s	volume of the sample
V_{su}	volume of the sub-samples
x	analyte content
$\bar{x}$	mean value of the contents x_i
x_e	analyte content in the calibration solution
x_{eg}	analyte content in the spiked calibration sample
x_g	analyte content in the sample after calibration of the total procedure
x_{Ie}	content of the internal standard I in the calibration solution
x_{Ieg}	content of the internal standard I in the calibration sample
x_{Ig}	content of the internal standard I in the sample
x_{IM}	measured content of the internal standard I in the measurement solution
x_i	analyte content in the calibration solution i
x_M	analyte content in the measurement solution
x_o	analyte content in the original sample
x_s	analyte content in the sample
x_{sp}	content of the spiked sample
x_{ss}	content of the spiking solution
x_z	spiked content in the sample
x_{zi}	spiked content in the sub-samples i
y	indicated value
$\bar{y}$	mean value of the indicated values y_i
y_e	indicated value for external calibration
y_{eg}	indicated value for external calibration of the total procedure
y_g	indicated value of the analyte in the sample

y_{Ie}	indicated value of the internal standard I for calibration of the measuring method
y_{Ieg}	indicated value of the internal standard I for calibration of the total procedure
y_{Ig}	indicated value of the internal standard I in the sample
y_i	indicated value of the calibration solution i or indicated value of the sub-sample i for standard addition
y_s	indicated value of the (unspiked) sample
Δb_{i-m}	difference between the slope b_i and the median of the slopes b_m

5 Determination of the linear working range and establishment of the calibration range

5.1 General

Linearity of the analytical measuring method is tested within the practice-oriented working range in accordance with the following pattern:

a) First step: Establishment of the preliminary working range.

Prepare and analyse calibration solutions (with or without internal standards, analyte-dependent but matrix-independent) over one or more orders of magnitude.

b) Second step: Test linearity and establishment of the linear working range.

Calculate the linear calibration function.

5.2 Preliminary choice of working range

Each calibration starts with the selection of a preliminary working range. This is subject to:

— the objective with respect to the practical application;

— the technically feasible possibilities;

— the linearity of the functional relationship between the indicated values and the contents.

The working range should largely cover a wide application range for the purpose in hand.

The available measuring instruments often allow the choice of a wide linear working range (sometimes over several orders of magnitude). On the other hand, it is required that the indicated values obtained near the lower limit of the working range can be at least distinguished from the indicated values of the procedure blank. A lower limit of the working range is only reasonable if it is greater than or equal to the limit of quantification of this method. Moreover, dilution and concentration steps are required to be feasible and accurate.

5.3 Estimation of the linear working range

5.3.1 General

For testing the linearity of a working range covering one or more orders of magnitude, the following procedure which is based on the first-order calibration function has proved to be effective.

Prepare a minimum of five calibration solutions with different contents (x_i) and determine the corresponding indicated values (y_i). Subsequently, plot both the measuring points and the point-to-point slopes in a diagram and visually estimate the linear working range (see 6.3.1).

Here, the contents may be equidistant or be based on geometric series (e.g. 1; 2; 4; 8; …) or, when testing linear working ranges that are expected to be large, such as for ICP-MS, be based on the power of ten.

Multiple measurements increase the reliability of the statement.

For many measuring methods showing a linear behaviour over two to five orders of magnitude, a series of contents (x_i) in the form of … 0,1; 0,2; 0,5; 1; 2; 5; 10; 20; 50; 100; … is suitable.

NOTE 1   For the recommended series of contents, the measuring points for the contents are nearly equidistant on a logarithmic scale. Instead of a series of contents of e.g. [… 0,2; 2; 20; …], the series of contents of [… 0,25; 2,5; 25; …] can also be applied.

NOTE 2   Multiple calibration solutions increase the reliability more than multiple determination.

5.3.2   Visual testing of measurement data — Testing using the x/y-diagram

The measuring points are plotted in a content/indicated value-diagram and the developing of the measuring points is visually assessed.

NOTE 1   When using a spreadsheet programme, the additional presentation of a linear regression function and a comparing second-order regression function (stating the correlation coefficient or the coefficient of determination) can be helpful.

NOTE 2   Analysis of residuals using a preliminary linear regression can give additional information.

5.3.3   Estimation of the linear range by calculating the point-to-point slope

For estimation of the linear working range calculate section-wise the slope b_i from the data sets of each two consecutive measuring points.

In case of a linear calibration function, a constant slope can be expected. Since there might be a non-linear sub-section, the median of the slope values should be used instead of the arithmetic mean value. In case of a linear working range, the section-wise calculated slopes should scatter around the median. A non-linear range at the beginning or at the end will be recognised by systematically increasing or decreasing deviations from the median of the slopes b_m.

For evaluation, plot the differences ($\Delta b_{i-m} = b_i - b_m$) between the slopes b_i and the median of the slopes b_m in a diagram.

If the procedure is linear across the selected working range, the differences will be normally distributed around zero (vary unsystematically around zero). Emerging trends indicate a non-linear relationship between content and indicated value.

If, in addition, a tolerance range with limiting lines above and below the zero-line is entered, then the working range that is accepted to be linear can be easily estimated. The tolerance range is defined in accordance with the accuracy requirements for analysis. The linear working range ends (or starts) at the measuring point (characterized as continuous index) that is just located within the accepted scatter around the zero-line or from which a systematic trend is recognized.

Annex B describes this procedure and gives examples.

NOTE 1   The tolerance range can affect measurement uncertainty.

NOTE 2   Especially in the case of measuring points not being equidistantly distributed, single points can visually lead to a false estimation of linearity. The limit of the linear working range can be specified more precisely by adding further measuring points.

As an alternative to the estimation of the linear range by determining the point-to-point slope, Annex C describes the testing of the linear working range by means of the empirical test of curvature. Both methods lead to the same result.

NOTE 3   An Excel spreadsheet for the testing of the linear working range can be downloaded from the website of the Water Chemistry Society[10]. It includes several sample data sets.

6   Calibration strategies

6.1   General

The calibration function that has been determined for a substance is only valid for the covered working range. Moreover, it depends on the operating condition of the measuring instrument and shall be tested within each series of measurements (see Clause 7). The calibration function is valid as long as the requirements for the measurement uncertainty are fulfilled.

The measurement uncertainty of analytical results comprises contributions from random and systematic deviations. The determination of the measurement uncertainty using quality assurance data is described in ISO 11352. Calibration itself contributes to the random and systematic deviations depending on the number of calibration levels applied and the number of parallel determinations, or to what extent a correction of matrix-related systematic deviations is done during calibration. Therefore, more or less complex calibration strategies can be selected according to the required measurement uncertainty for analysis. In this context, this document does not clearly specify the number of calibration levels, the number of standard additions or the number of parallel determinations.

For establishing the calibration functions, five modes of operation are described:

a)   calibration of the measuring method using an external standard;

b)   calibration of the measuring method using an internal standard;

c)   calibration of the total procedure using an external standard;

d)   calibration of the total procedure using an internal standard;

e)   calibration according to the method of standard addition.

The following options for working ranges and for the number of calibration levels can be applied:

—   for one-point calibration, selection of a content level at the upper working range limit. Blanks shall be negligible (below the limit of detection);

—   if blanks are not negligible or are varying, measurement of at least one more content level near the lower working range limit and exclusion of the origin for the calculation of the calibration function;

—   for multi-point calibration, distribution of content levels across the calibration range;

—   for one-point and two-point calibration, a minimum of three measurements for each content level.

The lowest content level of the calibration range shall be greater than or equal to the limit of quantification. The determination of the limit detection and of the limit of quantification is carried out in accordance with documented procedures, for example according to ISO/TS 13530.

Table 1 summarizes the basic conditions and application ranges of various calibration strategies.

For large working ranges, some software packages offer the possibility of weighting by means of $1/x$ in order to improve trueness in the lower part of the working range, if necessary. This weighting procedure is presented in Annex D, including formulae for calculation.

Table 1 — Summary of various calibration strategies

Calibration method	Subclause	Characteristics/basic conditions	Preferred application range
a) calibration of the measuring method using an external standard, including determination of the recovery rate of the analyte	6.3	— matrix-free calibration solution; — abscissa: content values; — ordinate: indicated values; — regardless of the sample matrix, the content value of the sample is determined from the indicated value of the sample and the calibration function; — matrix effects or process-related effects are corrected by the recovery rate of spiked real or synthetic samples, if necessary	Analytical methods for which it is known due to experience from the standardization process or intralaboratory validation that the recovery rate is predominantly constant.
b) calibration of the measuring method using an internal standard, including determination of the recovery rate of the internal standard	6.4	— matrix-free calibration solution with internal standard; — abscissa: ratio of the analyte content in the calibration solution to the content of the internal standard in the calibration solution; — ordinate: ratio of the corresponding indicated value of the standard substance to the indicated value of the internal standard; — the content value of the sample is determined from the ratio of the indicated values of the analyte and the internal standard and the calibration function; — matrix effects are corrected by addition of the internal standard to the sample prior to sample preparation	Analytical methods for which the matrices influence the measurement results during preparation of different samples to an extent that is not negligible and not predictable
c) calibration of the total procedure using an external standard	6.5	— synthetic samples or analyte-free real samples are spiked with an analyte in order to prepare calibration samples and are subjected to the total procedure; — abscissa: content values; — ordinate: indicated values; — regardless of the sample matrix, the content value of the sample is determined from the indicated value of the sample and the calibration function; — the matrix effect is corrected by the recovery rate of spiked samples	Analytical methods for which it is known due to experience from the standardization process or intralaboratory validation that matrix-related interferences are present which, however, have a similar impact on the indicated values regarding amount and direction.

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