

Implementation of
ISO 11095:1996

Linear calibration using reference materials

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- British Gas plc
- Chemical Industries Association
- Consumers' Association
- GAMBICA (BEAMA Ltd.)
- Institute of Quality Assurance
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- Ministry of Agriculture, Fisheries and Food
- Ministry of Defence
- National Physical Laboratory
- Royal Society of Chemistry
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National foreword

This British Standard reproduces verbatim ISO 11095:1996 and implements it as the UK national standard.

This British Standard is published under the direction of the Management Systems Sector Board whose Technical Committee SS/6 has the the responsibility to:

- aid enquirers to understand the text;
- present to the responsible international committee any enquiries on interpretation, or proposals for change, and keep UK interests informed;
- monitor related international and European developments and promulgate them in the UK.

NOTE International and European Standards, as well as overseas standards, are available from Customer Services, BSI, 389 Chiswick High Road, London W4 4AL.

Cross references

Publication referred to	Corresponding British Standard
ISO 3534-1:1993	BS ISO 3534 <i>Statistics. Vocabulary and symbols</i> Part 1:1993 <i>Probability and general statistical terms</i>
ISO 3534-2:1993	Part 2:1993 <i>Statistical quality control</i>

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Summary of pages

This document comprises a front cover, an inside front cover, pages i and ii, the ISO title page, pages ii to iv, pages 1 to 26, an inside back cover and a back cover.

This standard has been updated (see copyright date) and may have had amendments incorporated. This will be indicated in the amendment table on the inside front cover.

INTERNATIONAL STANDARD

**ISO
11095**

First edition
1996-02-01

Linear calibration using reference materials

Étalonnage linéaire utilisant des matériaux de référence



Reference number
ISO 11095:1996(E)

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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.

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.

International Standard ISO 11095 was prepared by Technical Committee ISO/TC 69, *Applications of statistical methods*, Subcommittee SC 6, *Measurement methods and results*.

Annexes A and B form an integral part of this International Standard. Annex C is for information only.

Introduction

Calibration is an essential part of most measurement procedures. It is a set of operations which establish, under specified conditions, the relationship between values indicated by a measurement system and the corresponding accepted values of some “standards”. In this International Standard, the standards are reference materials.

A reference material (RM) is a substance or an artifact for which one or more properties are established sufficiently well to validate a measurement system. There exist several kinds of RMs:

- a) an internal reference material is an RM developed by a user for his/her own internal use;
- b) an external reference material is an RM provided by someone other than the user;
- c) a certified reference material is an RM issued and certified by an organization recognized as competent to do so.

1 Scope

This International Standard:

- a) outlines the general principles needed to calibrate a measurement system and to maintain that “calibrated” measurement system in a state of statistical control;
- b) provides a basic method
 - for estimating a linear calibration function under either one of two assumptions relating to the variability of the measurements,
 - for checking the assumption of linearity of the calibration function and the assumptions on the variability of the measurements, and
 - for estimating the value of a new unknown quantity by transforming the measured values obtained on that quantity with the calibration function;
- c) provides a control method for extended use of a calibration function
 - for detecting when the calibration function needs to be updated, and
 - for estimating the uncertainty of the measured values after transformation with the calibration function;
- d) provides two alternatives to the basic method under special conditions;
- e) illustrates the basic method and the control method with an example.

This International Standard is applicable to measurement systems for which reference materials are available.

It is applicable to measurement systems with an assumed linear calibration function. It offers a method for examining the assumption of linearity. If it is known that the calibration function is nonlinear, then this International Standard is not applicable unless one uses the “bracketing technique” described in 8.3.

This International Standard does not make a distinction among the various types of RMs and considers that the accepted values of the RMs selected to calibrate the measurement system are without error.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 3534-1:1993, *Statistics — Vocabulary and symbols — Part 1: Probability and general statistical terms*.

ISO 3534-2:1993, *Statistics — Vocabulary and symbols — Part 2: Statistical quality control*.

ISO Guide 30:1992, *Terms and definitions used in connection with reference materials*.

3 Definitions

For the purposes of this International Standard, the definitions given in ISO 3534-1 and ISO 3534-2 and the following definition apply.

3.1 reference material

a substance or an artifact for which one or more properties are established sufficiently well to be used to validate a measurement system

4 General principles

Calibration is a procedure that determines the systematic difference that may exist between a measurement system and a “reference” system represented by the reference materials and their accepted values. In this International Standard, the term system (measurement system or reference system) is used to represent not only a measuring instrument but also the set of procedures, operators and environment conditions associated with that instrument.

The output of a calibration procedure is a calibration function that is used to make transformations of future measurement results. In this International Standard, the term “transformation” refers to

- either a correction of the future measurements if both the accepted values of the reference materials (RMs) and the observed values have the same units,
- or a translation from the units of the observed measurements to the units of the RMs.

The validity of the calibration function depends on two conditions:

- a) that the measurements from which the calibration function was calculated are representative of the normal conditions under which the measurement system operates; and
- b) that the measurement system is in a state of control.

The calibration experiment must be designed to ensure that point a) is met. The control method determines, as soon as possible, when the system has to be considered out of control.

The procedure in this International Standard is only applicable to measurement systems which are linearly related to their reference systems. To check whether the assumption of linearity is valid, more than two RMs must be used during the calibration experiment. This is illustrated in the basic method. Using several RMs, the basic method provides a strategy and techniques to analyse the data collected during the calibration experiment. If linearity is not in question, then an alternative method, simpler than the basic method, can be used to estimate a linear calibration function based on one point. This “one-point calibration” method (following a zero-level transformation) does not allow for any test of assumptions, but it is a quick and easy method to “recalibrate” a system that has been studied more thoroughly during previous experiments. If linearity is in question, then a second alternative can be used, called “bracketing”. The basic method and the one-point method are based on the assumption that the effort invested in calibration will be valid over a period of stability of the process. To study the period over which the calibration is valid, a control method has to be in place. The control method is designed to detect whether changes have taken place in the system that justify an investigation and/or a recalibration. The control method also provides a simple way to determine the precision of the values that have been transformed with a given calibration function.

The bracketing method is labour intensive but may provide greater accuracy in the determination of the values of unknown quantities. This method consists of surrounding as tightly as possible (bracketing) each unknown quantity by two RMs and extracting a transformed value for the unknown quantity from measurements of both the unknown quantity and the values of the two RMs. Only short-term stability of the measurement process is assumed (stability during the measurement of the unknown quantity and of the two RMs). Linearity is assumed solely in the interval between the values of the two RMs.

5 Basic method

5.1 General

This clause describes how to estimate and use a linear calibration function when several (more than two) RMs are available. The availability of several RMs allows the linearity of the calibration function to be verified.

5.2 Assumptions

5.2.1 It is assumed that there is no error in the accepted values of the RMs (this assumption will not be checked in this International Standard). In practice, accepted values of RMs are quoted with their uncertainties. The assumption of no error in the accepted values of the RMs can be considered valid if the uncertainties are small compared to the magnitude of the errors in the measured values of these RMs (see ref. [1]).

NOTE 1 In situations where the RMs have been treated chemically or, in some instances physically, before instrument readings are taken, this International Standard may underestimate the uncertainty associated with the transformation of a new measurement result.

5.2.2 The calibration function is assumed to be linear (this assumption will be examined).

5.2.3 Repeated measurements of a given RM are assumed to be independent and normally distributed, with variance referred to as “residual variance” (the independence and normality assumptions will not be checked in this International Standard). The square root of the residual variance is referred to as the residual standard deviation.

5.2.4 The residual standard deviation is assumed to be either constant or proportional to the accepted value of the RM (this assumption will be examined).

5.3 Calibration experiment

5.3.1 *Experimental conditions*

Experimental conditions should be the same as the normal operating conditions of the measurement system; i.e. if, for example, more than one operator uses the measuring equipment then there should be more than one operator represented in the calibration experiment.

5.3.2 *Choice of RMs*

The range of values spanned by the selected RMs should include (as far as is possible) the range of values encountered during normal operating conditions of the measurement system.

The composition of the selected RMs should be as close as possible to the composition of the targeted material to be measured.

The values of the RMs should be distributed approximately equidistantly over the range of values encountered during normal operating conditions of the measurement system.

5.3.3 *Number of RMs, N*

The number of RMs used to assess the calibration function should be at least 3.

For an initial assessment of the calibration function, a number larger than 3 is recommended (at least 3 over any subinterval where there is a doubt about the linearity of the calibration function).

5.3.4 *Number of replicates, K*

Each RM should be measured at least twice (as many replicates as is possible in practice is recommended).

The number of replicates should be the same for all RMs.

The time and conditions at which the replicates are taken should cover as wide a range as is necessary to ensure that all operating conditions are represented.

5.4 Strategy for analysing the data

5.4.1 Plot the data to check

- a) the state of control of the measurement system during the calibration experiment,
- b) the assumption of linearity, and
- c) the variability of the measurements as a function of the accepted values of the RMs.

5.4.2 Estimate the linear calibration function under the assumption of constant residual standard deviation.

5.4.3 Plot the calibration function and the residuals. The residuals plot is a strong indicator of departure from either the assumption of linearity or from the assumption of constant residual standard deviation. If the assumption of constant residual standard deviation does hold, skip step 5.4.4 and continue with step 5.4.5. Otherwise, execute step 5.4.4.

5.4.4 Estimate the linear calibration function under the assumption of proportional residual standard deviation and plot the calibration function and the residuals.

5.4.5 Evaluate the lack of fit of the calibration function. If the variability due to lack of fit is large relative to the variability due to replication of measurements, investigate the procedures followed during the calibration experiment and re-examine the assumption of linearity of the calibration function. If the assumption of linearity does not hold, then an alternative is to use the bracketing technique described in 8.3.

NOTE 2 There exist other techniques, beyond the scope of this International Standard, that allow the fitting of a quadratic or polynomial curve to the data (see refs. [2] and [3]).

5.4.6 Transform future measured values with the calibration function.

The next clause describes the six steps of this strategy. Clause 9 illustrates the basic method with an example.

6 The steps of the basic method

6.1 Plot of the data collected during the calibration experiment

Figure 1 shows a plot of the measured values versus the corresponding accepted values of the RMs. Figure 1 as well as Figure 2 to Figure 5 are obtained from simulated data. The purpose of these five plots is to illustrate the type of information one can extract from such plots. A complete example is treated in clause 8 with data, plots and analysis.

The major purpose of the plot shown as Figure 1 is to detect visually any unusual behaviour of the measurement system during the calibration experiment, and to identify potential outliers. If possible, label the order of the data points and look for obvious time trends. If some of the data are considered suspicious, or if a time trend is obvious, then an investigation shall take place to discover causes of irregularities. As soon as the causes of irregularities are removed, the calibration experiment should be repeated and new data should be collected to establish a calibration function.