
Capability of detection —

Part 2:

Methodology in the linear calibration case

Capacité de détection —

Partie 2: Méthodologie de l'étalonnage linéaire

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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 3.

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.

Attention is drawn to the possibility that some of the elements of this part of ISO 11843 may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

International Standard ISO 11843-2 was prepared by Technical Committee ISO/TC 69, *Applications of statistical methods*, Subcommittee SC 6, *Measurement methods and results*.

ISO 11843 consists of the following parts, under the general title *Capability of detection*:

— *Part 1: Terms and definitions*

— *Part 2: Methodology in the linear calibration case*

Annex A forms a normative part of this part of ISO 11843. Annexes B and C are for information only.

Introduction

An ideal requirement for the capability of detection with respect to a selected state variable would be that the actual state of every observed system can be classified with certainty as either equal to or different from its basic state. However, due to systematic and random distortions, this ideal requirement cannot be satisfied because:

- in reality all reference states, including the basic state, are never known in terms of the state variable. Hence, all states can only be correctly characterized in terms of differences from basic state, i.e. in terms of the net state variable.

In practice, reference states are very often assumed to be known with respect to the state variable. In other words, the value of the state variable for the basic state is set to zero; for instance in analytical chemistry, the unknown concentration or the amount of analyte in the blank material usually is assumed to be zero and values of the net concentration or amount are reported in terms of supposed concentrations or amounts. In chemical trace analysis especially, it is only possible to estimate concentration or amount differences with respect to available blank material. In order to prevent erroneous decisions, it is generally recommended to report differences from the basic state only, i.e. data in terms of the net state variable;

NOTE In the ISO Guide 30 and in ISO 11095 no distinction is made between the state variable and the net state variable. As a consequence, in these two documents reference states are, without justification, assumed to be known with respect to the state variable.

- the calibration and the processes of sampling and preparation add random variation to the measurement results.

In this part of ISO 11843, the following two requirements were chosen:

- the probability is α of detecting (erroneously) that a system is not in the basic state when it is in the basic state;
- the probability is β of (erroneously) not detecting that a system, for which the value of the net state variable is equal to the minimum detectable value (x_d), is not in the basic state.

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Capability of detection —

Part 2:

Methodology in the linear calibration case

1 Scope

This part of ISO 11843 specifies basic methods to:

- design experiments for the estimation of the critical value of the net state variable, the critical value of the response variable and the minimum detectable value of the net state variable,
- estimate these characteristics from experimental data for the cases in which the calibration function is linear and the standard deviation is either constant or linearly related to the net state variable.

The methods described in this part of ISO 11843 are applicable to various situations such as checking the existence of a certain substance in a material, the emission of energy from samples or plants, or the geometric change in static systems under distortion.

Critical values can be derived from an actual measurement series so as to assess the unknown states of systems included in the series, whereas the minimum detectable value of the net state variable as a characteristic of the measurement method serves for the selection of appropriate measurement processes. In order to characterize a measurement process, a laboratory or the measurement method, the minimum detectable value can be stated if appropriate data are available for each relevant level, i.e. a measurement series, a measurement process, a laboratory or a measurement method. The minimum detectable values may be different for a measurement series, a measurement process, a laboratory or the measurement method.

ISO 11843 is applicable to quantities measured on scales that are fundamentally continuous. It is applicable to measurement processes and types of measurement equipment where the functional relationship between the expected value of the response variable and the value of the state variable is described by a calibration function. If the response variable or the state variable is a vectorial quantity the methods of ISO 11843 are applicable separately to the components of the vectors or functions of the components.

2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this part of ISO 11843. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this part of ISO 11843 are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC 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 3534-3:1999, *Statistics — Vocabulary and symbols — Part 3: Design of experiments.*

ISO 11095:1996, *Linear calibration using reference materials*.

ISO 11843-1:1997, *Capability of detection — Part 1: Terms and definitions*.

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

3 Terms and definitions

For the purposes of this part of ISO 11843, the terms and definitions of ISO 3534 (all parts), ISO Guide 30, ISO 11095 and ISO 11843-1 apply.

4 Experimental design

4.1 General

The procedure for determining values of an unknown actual state includes sampling, preparation and the measurement itself. As every step of this procedure may produce distortion, it is essential to apply the same procedure for characterizing, for use in the preparation and determination of the values of the unknown actual state, for all reference states and for the basic state used for calibration.

For the purpose of determining differences between the values characterizing one or more unknown actual states and the basic state, it is necessary to choose an experimental design suited for comparison. The experimental units of such an experiment are obtained from the actual states to be measured and all reference states used for calibration. An ideal design would keep constant all factors known to influence the outcome and control of unknown factors by providing a randomized order to prepare and perform the measurements.

In reality it may be difficult to proceed in such a way, as the preparations and determination of the values of the states involved are performed consecutively over a period of time. However, in order to detect major biases changing with time, it is strongly recommended to perform one half of the calibration before and one half after the measurement of the unknown states. However, this is only possible if the size of the measurement series is known in advance and if there is sufficient time to follow this approach. If it is not possible to control all influencing factors, conditional statements containing all unproven assumptions shall be presented.

Many measurement methods require a chemical or physical treatment of the sample prior to the measurement itself. Both of these steps of the measurement procedure add variation to the measurement results. If it is required to repeat measurements the repetition consists in a full repetition of the preparation and the measurement. However, in many situations the measurement procedure is not repeated fully, in particular not all of the preparational steps are repeated for each measurement; see note in 5.2.1.

4.2 Choice of reference states

The range of values of the net state variable spanned by the reference states should include

- the value zero of the net state variable, i.e. in analytical chemistry a sample of the blank material, and
- at least one value close to that suggested by a priori information on the minimum detectable value; if this requirement is not fulfilled, the calibration experiment should be repeated with other values of the net state variable, as appropriate.

The reference states should be chosen so that the values of the net state variable (including log-scaled values) are approximately equidistant in the range between the smallest and largest value.

In cases in which the reference states are represented by preparations of reference materials their composition should be as close as possible to the composition of the material to be measured.

4.3 Choice of the number of reference states, I , and the (numbers of) replications of procedure, J , K and L

The choice of reference states, number of preparations and replicate measurements shall be as follows:

- the number of reference states I used in the calibration experiment shall be at least 3; however, $I = 5$ is recommended;
- the number of preparations for each reference state J (including the basic state) should be identical; at least two preparations ($J = 2$) are recommended;
- the number of preparations for the actual state K should be identical to the number J of preparations for each reference state;
- the number of repeated measurements performed per preparation L shall be identical; at least two repeated measurements ($L = 2$) are recommended.

NOTE The formulae for the critical values and the minimum detectable value in clause 5 are only valid under the assumption that the number of repeated measurements per preparation is identical for all measurements of reference states and actual states.

As the variations and cost due to the preparation usually will be much higher than those due to the measurement, the optimal choice of J , K and L may be derived from an optimization of constraints regarding variation and costs.

5 The critical values y_c and x_c and the minimum detectable value x_d of a measurement series

5.1 Basic assumptions

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The following procedures for the computation of the critical values and the minimum detectable value are based on the assumptions of ISO 11095. The methods of ISO 11095 are used with one generalization; see 5.3.

Basic assumptions of ISO 11095 are that

- the calibration function is linear,
- measurements of the response variable of all preparations and reference states are assumed to be independent and normally distributed with standard deviation referred to as "residual standard deviation",
- the residual standard deviation is either a constant, i.e. it does not depend on the values of the net state variable [case 1], or it forms a linear function of the values of the net state variable [case 2].

The decision regarding the applicability of this part of ISO 11843 and the choice of one of these two cases should be based on prior knowledge and a visual examination of the data.

5.2 Case 1 — Constant standard deviation

5.2.1 Model

The following model is based on assumptions of linearity of the calibration function and of constant standard deviation and is given by:

$$Y_{ij} = a + bx_i + \varepsilon_{ij} \quad (1)$$

where

x_i is the symbol for the net state variable in state i ;

ε_{ij} are random variables which describe the random component of sampling, preparation and measurement error.

It is assumed that the ε_{ij} are independent and normally distributed with expectation zero and the theoretical residual standard deviation $\sigma: \varepsilon_{ij} \sim N(0; \sigma^2)$. Therefore, values Y_{ij} of the response variable are random variables with the expectation $E(Y_{ij}) = a + bx_i$ and the variance $V(Y_{ij}) = \sigma^2$, not depending on x_i .

NOTE In the cases in which J samples are prepared for measurement and each of them is measured L times so that $J \cdot L$ measurements are performed altogether for reference state i , then Y_{ij} refers to the average of the L measurements obtained on the prepared sample.

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5.2.2 Estimation of the calibration function and the residual standard deviation

In accordance with ISO 11095, estimates (see note) for a , b and σ^2 are given by:

$$\hat{b} = \frac{\sum_{i=1}^I \sum_{j=1}^J (x_i - \bar{x})(\bar{y}_{ij} - \bar{y})}{s_{xx}} \quad (2)$$

$$\hat{a} = \bar{y} - \hat{b}\bar{x} \quad (3)$$

$$\hat{\sigma}^2 = \frac{1}{I \cdot J - 2} \sum_{i=1}^I \sum_{j=1}^J (\bar{y}_{ij} - \hat{a} - \hat{b}x_i)^2 \quad (4)$$

The symbols used here and elsewhere in this part of ISO 11843 are defined in annex A.

NOTE Estimates are denoted by a symbol ^ to differentiate them from the parameters themselves which are unknown.

5.2.3 Computation of critical values

The critical value of the response variable is given by:

$$y_c = \hat{a} + t_{0,95}(\nu) \hat{\sigma} \sqrt{\frac{1}{K} + \frac{1}{I \cdot J} + \frac{\bar{x}^2}{s_{xx}}} \quad (5)$$

The critical value of the net state variable is given by:

$$x_c = t_{0,95}(\nu) \frac{\hat{\sigma}}{\hat{b}} \sqrt{\frac{1}{K} + \frac{1}{I \cdot J} + \frac{\bar{x}^2}{s_{xx}}} \quad (6)$$

$t_{0,95}(\nu)$ is the 95 %-quantile of the t -distribution with $\nu = I \cdot J - 2$ degrees of freedom.

The derivation of these formulae is given in annex B.

5.2.4 Computation of the minimum detectable value

The minimum detectable value is given by:

$$x_d = \delta \frac{\hat{\sigma}}{\hat{b}} \sqrt{\frac{1}{K} + \frac{1}{I \cdot J} + \frac{\bar{x}^2}{s_{xx}}} \quad (7)$$

where

$\delta = (\nu; \alpha; \beta)$ is the value of the noncentrality parameter determined in such a way that a random variable following the noncentral t -distribution with $\nu = I \cdot J - 2$ degrees of freedom and the noncentrality parameter δ , $T(\nu; \delta)$, satisfies the equation:

$$P[T(\nu; \delta) \leq t_{1-\alpha}(\nu)] = \beta$$

where $t_{1-\alpha}(\nu)$ is the $(1-\alpha)$ -quantile of the t -distribution with ν degrees of freedom.

The derivation of this formula is given in annex B.

For $\alpha = \beta$ and $\nu > 3$, a good approximation for δ is given by

$$\delta(\nu; \alpha; \beta) \approx 2t_{1-\alpha}(\nu) \quad (8)$$

if $\nu = 4$ and $\alpha = \beta = 0,05$, the relative error of this approximation is 5 %; $t_{1-\alpha}(\nu)$ is the $(1-\alpha)$ -quantile of the t -distribution with $\nu = I \cdot J - 2$ degrees of freedom.

Table 1 presents $\delta(\nu; \alpha; \beta)$ for $\alpha = \beta = 0,05$ and various values of ν .

For $\alpha = \beta$ and $\nu > 3$, x_d is approximated by

$$x_d \approx 2t_{0,95}(\nu) \frac{\hat{\sigma}}{\hat{b}} \sqrt{\frac{1}{K} + \frac{1}{I \cdot J} + \frac{\bar{x}^2}{s_{xx}}} = 2x_c \quad (9)$$

Table 1 — Values of the noncentrality parameter for $\alpha = \beta = 0,05$ and ν degrees of freedom

ν	$\delta(\nu; \alpha; \beta)$	ν	$\delta(\nu; \alpha; \beta)$	ν	$\delta(\nu; \alpha; \beta)$
2	5,516	19	3,415	36	3,354
3	4,456	20	3,408	37	3,352
4	4,067	21	3,402	38	3,350
5	3,870	22	3,397	39	3,349
6	3,752	23	3,392	40	3,347
7	3,673	24	3,387	41	3,346
8	3,617	25	3,383	42	3,344
9	3,575	26	3,380	43	3,343
10	3,543	27	3,376	44	3,342
11	3,517	28	3,373	45	3,341
12	3,496	29	3,370	46	3,339
13	3,479	30	3,367	47	3,338
14	3,464	31	3,365	48	3,337
15	3,451	32	3,362	49	3,336
16	3,440	33	3,360	50	3,335
17	3,431	34	3,358		
18	3,422	35	3,356		

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5.3 Case 2 — Standard deviation linearly dependent on the net state variable

5.3.1 Model

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The following model is based on the assumptions that the calibration function is linear and that the standard deviation is linearly dependent on the net state variable and is given by:

$$Y_{ij} = a + bx_i + \varepsilon_{ij} \quad (10)$$

where

x_i , a , b and Y_{ij} are as defined in 5.2.1 and the ε_{ij} are independent and normally distributed with expectation $E(\varepsilon_{ij}) = 0$ and variance:

$$V(\varepsilon_{ij}) = \sigma^2(x_i) = (c + dx_i)^2 \quad (11)$$

i.e., the residual standard deviation is linearly dependent on x

$$\sigma(x_i) = c + dx_i \quad (12)$$

The parameters of the model, a , b , c and d are estimated in a two part procedure as given in 5.3.2 and 5.3.3.

5.3.2 Estimation of the linear relationship between the residual standard deviation and the net state variable

The parameters c and d are estimated by a linear regression analysis with the standard deviations:

$$s_i = \sqrt{\frac{1}{J-1} \sum_{j=1}^J (\bar{y}_{ij} - \bar{y}_i)^2} \quad (13)$$