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# Capability of detection —

## Part 3:
## Methodology for determination of the critical value for the response variable when no calibration data are used

*Capacité de détection —*

*Partie 3: Méthodologie pour déterminer la valeur critique d'une variable de réponse lorsque aucun étalonnage n'est utilisé*



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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.

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 11843-3 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*

— *Part 3: Methodology for determination of the critical value for the response variable when no calibration data are used*

— *Part 4: Methodology for comparing the minimum detectable value with a given value*

 

# 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 variations, this ideal requirement cannot be satisfied because:

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

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

— Furthermore, the calibration and the processes of sampling and sample preparation add random variation to the measurement results.

In this part of ISO 11843, the symbol $\alpha$ is used for the probability of detecting (erroneously) that a system is not in the basic state when it is in the basic state.



 

# Capability of detection —

## Part 3:
## Methodology for determination of the critical value for the response variable when no calibration data are used

## 1 Scope

This part of ISO 11843 gives a method of estimating the critical value of the response variable from the mean and standard deviation of repeated measurements of the reference state in certain situations (see 5.1) in which the value of the net state variable is zero, for all reasonable and foreseeable purposes. Hence, it can be decided whether values of the response variable in an actual state (or test sample) are above the range of values attributable to the reference state.

General procedures for determination of critical values of the response variable and the net state variable and of the minimum detectable value have been given in ISO 11843-2. Those procedures are applicable in situations in which there is relevant straight-line calibration and the residual standard deviation of the measured responses is either constant or is a linear function of the net state variable. The procedure given in this part of ISO 11843 for the determination of the critical value of the response variable only is recommended for situations in which no calibration data are used. The distribution of data is assumed to be normal or near-normal.



The procedure given in this part of ISO 11843 is recommended for situations in which it is difficult to obtain a large amount of the actual states although a large amount of the basic state can be prepared.

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

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

ISO 3534-3, *Statistics — Vocabulary and symbols — Part 3: Design of experiments*

ISO 5479:1997, *Statistical interpretation of data — Tests for departure from normal distribution*

ISO 5725-2:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*

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

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

ISO 11843-2:2000, *Capability of detection — Part 2: Methodology in the linear calibration case*

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

 

## 3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 3534 (all parts), ISO Guide 30, ISO 5479, ISO 5725-2, ISO 11095 and ISO 11843-1 apply.

## 4 Experimental design

### 4.1 General

The measurement method is assumed to be standardized and known to have been calibrated for measurements of a similar type, although calibration under the specific conditions being studied and at very low levels of the net state variable has not been undertaken or is not possible. The same complete measurement method shall be used for all replicated measurements of the reference state in which the state variable is zero as well as for actual states (test samples) within the measurement series for which a critical value of the response variable is required.

Measurements of actual states shall be randomized among the measurements of the basic state.

Negative values of the response variable shall not be discarded or altered if these arise. For example, negative values shall not be replaced by zeros.

### 4.2 Choice of the reference state in which the value of the net state variable is zero



One of the assumptions in the procedure described in this part of ISO 11843 is that the value of the net state variable is zero in the reference state chosen. The certainty that can be expected in relation to such an assertion is discussed in ISO 11843-2:2000, Subclause 4.1. In reality, reference states are not known in absolute terms of the state variable but only in terms of differences from a (hypothetical) basic state. For this part of ISO 11843, it is sufficient for the reference level to be well below that likely to be measured by the method being used.



In cases in which the basic state is represented by a preparation of a reference material, the composition should be as close as possible to the composition of the material to be measured, i.e. in analytical chemistry the blank matrix material chosen should be very similar in every way to, if not identical with, the samples being examined in that measurement series. Influences due to the presence of other substances or elements, or due to the physical state of samples, can be highly significant. In particular, when solutions are being investigated, the use of pure solvents rather than the solvent extracts normally encountered in the measurement method is unacceptable.

### 4.3 Replication

#### 4.3.1 Number of replications, $J$

The response from the method used on the basic state shall be measured for a sufficient number of replicates $J$ of the entire procedure so as to give a good estimate of the mean and of the standard deviation. It is important to have sufficient data to examine the distribution of data to see whether the response variable is normally, or near-normally, distributed. About 30 measurements should usually ensure that the estimate of the standard deviation will not differ more than 30 % from the true standard deviation with approximately 95 % probability.

NOTE In some situations, it is not possible to perform the number of measurements outlined above because of constraints on the amount of material available or for other reasons. In such situations, the estimate of the standard deviation obtained is markedly uncertain. When such an estimate $s$ (see $s_b$ in 5.2) of a true standard deviation $\sigma$ is to be made, conclusions can be drawn as to the range about the interval based on $s$ within which the estimate of $\sigma$ can be expected to lie with prespecified probability $1 - \alpha$. This is a statistical problem usually solved (if assumption of normality is valid and $s$ is the sample standard deviation) by the use of the chi-squared distribution for the number of results on which the estimate of $s$ was based to give a confidence interval for the value of $\sigma$ of

 

$$s\sqrt{\frac{\nu}{\chi^2_{1-\frac{\alpha}{2}}(\nu)}} < \sigma < s\sqrt{\frac{\nu}{\chi^2_{\frac{\alpha}{2}}(\nu)}}$$

where $\nu = J - 1$, values of quantiles of $\chi^2$-distribution are obtainable from standard tables and $\alpha$ is as defined in the introduction.

Replications of measurements $K$ on the actual states (test samples) using the entire method will lower the critical value of the response variable to some extent [see Equation (4)], although cost constraints will have to be carefully considered.

### 4.3.2 Uniformity of replication

When taking samples of the basic state in order to measure the response variable, it is essential to follow in every way the sampling procedure in the overall method.

If standard reference materials are available, they should be used because their homogeneity will have been carefully studied.

The possibilities of some surface phenomena, of electrostatic effects, of settling-out, etc., giving non-identical samples should always be borne in mind.

### 4.3.3 Possible disturbing factors

Variation of possible disturbing factors during the runs should be minimized, as outlined in ISO 11843-2:2000, Subclause 4.1.



## 5 Computation of the critical value of the response variable $y_c$



### 5.1 Basic method

ISO 11843-1 defines the critical value $y_c$ as the value of the response variable $y$ such that, if it is exceeded, the decision will be made that the system is not in the basic state. The critical value is chosen so that, when the system is in the basic state, this decision will be made with only a small probability $\alpha$. In other words, the critical value is the minimum significant value of a measurement or signal, applied as a discriminator against background (noise).

The decision "detected" or "not detected" is made by comparison of the arithmetic mean of the determinations obtained for the actual state $\bar{y}_a$ with the critical value $y_c$ of the respective distribution. The probability that the arithmetic mean of measured values $\bar{y}_a$ exceeds the critical value $y_c$ for the distribution in the basic state ($x = 0$) should be less than or equal to an appropriate pre-selected probability $\alpha$.

The critical value $y_c$ of the response variable can be expressed generally as follows:

$$P(\bar{y}_a > y_c \mid x = 0) \leqslant \alpha \tag{1}$$

NOTE $P(\bar{y}_a > y_c \mid x = 0)$ is the probability that $\bar{y}_a > y_c$ under the condition that $x = 0$.

The definition may be stated as an equality, although the inequality accommodates discrete distributions, such as the Poisson distribution, for which not all values of $\alpha$ are possible.

If

a) $y$ is normally distributed with standard deviation $\sigma_0$,

b) samples of actual states are as homogeneous as possible,

c) the measurements are unbiased,