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Capability of detection —

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

Capacité de détection —

Partie 4: Méthodologie de comparaison de la valeur minimale détectable avec une valeur donnée

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Foreword

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ISO 11843-4 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 for the following reasons.

a) 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.

b) 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 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.

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

In this part of ISO 11843

— 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.

Capability of detection —

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

1 Scope

This part of ISO 11843 deals with the assessment of the capability of detection of a measurement method without the assumptions in ISO 11843-2 of a linear calibration curve and certain relationships between the residual standard deviation and the value of the net state variable

NOTE These assumptions are often doubtful for values of the net state variable close to zero.

Instead of estimating the minimum detectable value, this part of ISO 11843 provides

— a criterion for judging whether the minimum detectable value is less than a given level of the net state variable, and

— the basic experimental design for testing the conformity of this criterion.

For assessment of the capability of detection, for instance as part of the validation of a measurement method, it is often sufficient to confirm that the method has a minimum detectable value that is less than a given value.

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:—[1)], *Statistics — Vocabulary and symbols — Part 2: Applied statistics*

ISO 3534-3:1999, *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 Guide 30:1992, *Terms and definitions used in connection with reference materials*

1) To be published. (Revision of ISO 3534-2:1993)

3 Terms and definitions

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

4 Experimental design

4.1 General

The measurement method is assumed to be standardized. The same complete method shall be used for all measurements, whether of the reference states or of actual states (test samples).

4.2 Choice of reference states and reference materials

The reference states shall include two values of the net state variable

- the value zero of the net state variable (i.e. in analytical chemistry, a sample of the blank material), and
- a given value, x_g, which will be tested to determine whether it is greater than the minimum detectable value.

The composition of the reference materials representing the reference states should be as close as possible to the composition of the material to be measured in order to satisfy the requirement that reference and test materials behave in the same way in the measuring system.

4.3 Number of replications

It is assumed that the capability of detection is assessed in a separate experiment with the same number of replications for both reference states specified in 4.2. In an application of the method, measurements are performed for the reference material (representing the value zero of the net state variable) and the actual state. The number of replications used in applications of the method are usually smaller than the number of replications used in the assessment of the capability of detection of the method. The following notations are used:

- J is the number of replications of measurements on the reference material representing the value zero of the net state variable (blank sample) in an application of the method;
- K is the number of replications of measurements on the actual state (test sample) in an application of the method.
- N is the number of replications of measurements on each reference material (see 4.2) in assessment of the capability of detection;

The value of N should preferably be at least 5.

NOTE In validation of a method, the capability of detection is usually determined for $J = K = 1$.

5 The criterion for sufficient capability of detection

5.1 Basic assumptions

Basic assumptions in this part of ISO 11843 are

- the measurements of the response variable of all materials are assumed to be independent and normally distributed, and
- the reference and test materials behave in the same way in the measurement system.

5.2 Critical value of the response variable

When a test of the hypothesis that the net state variable of a test sample is zero is based on a comparison (in a randomized experiment) of the responses of the test sample and a sample in the basic state (blank sample known to have the net state variable equal to zero), the critical value of the response for the test sample (the mean of K measurements) is given by

$$y_{\text{c}} = \bar{y}_{\text{b}} + z_{1-\alpha}\,\sigma_{\text{b}}\sqrt{\frac{1}{J}+\frac{1}{K}} \tag{1}$$

The meanings of the symbols used here and in the rest of this part of ISO 11843 are given in Annex A.

When the response variable decreases with increasing level of the net state variable, the critical value of the response is given by

$$y_{\text{c}} = \bar{y}_{\text{b}} - z_{1-\alpha}\,\sigma_{\text{b}}\sqrt{\frac{1}{J}+\frac{1}{K}} \tag{2}$$

where y_{c} now is a lower limit.

In this situation, the expressions $\eta_{\text{g}} - \eta_{\text{b}}$ and $\bar{y}_{\text{g}} - \bar{y}_{\text{b}}$ in 5.3, 5.4 and Clause 6 are changed to $\eta_{\text{b}} - \eta_{\text{g}}$ and $\bar{y}_{\text{b}} - \bar{y}_{\text{g}}$ respectively.

5.3 Probability of detecting a given value of the net state variable

Instead of estimating the minimum detectable value of the net state variable (i.e. the value of the net state variable for which the power of the test in 5.2 has a specified value $1-\beta$), this part of ISO 11843 provides a criterion for the power to be greater than or equal to $1-\beta$ for a given value, x_{g}, of the net state variable. If this criterion is satisfied, it may be concluded that the minimum detectable value is less than or equal to x_{g}.

If the standard deviation of the response for a given value x_{g} of the net state variable is σ_{g}, the criterion for the power to be greater than or equal to $1-\beta$ is given by

$$\eta_{\text{g}} - \eta_{\text{b}} \geqslant z_{1-\alpha}\sigma_{\text{b}}\sqrt{\frac{1}{J}+\frac{1}{K}} + z_{1-\beta}\sqrt{\frac{1}{J}\sigma_{\text{b}}^2 + \frac{1}{K}\sigma_{\text{g}}^2} \tag{3}$$

where η_{b} and η_{g} are the expected values under the actual performance conditions for the responses of the basic state and a sample with the net state variable equal to x_{g}.

NOTE Criterion (3) follows from the definition of net state variable and Figure 1 of ISO 11843-1:1997.

With $\beta = \alpha$, $K = J$ and under the assumption that $\sigma_{\text{g}} \geqslant \sigma_{\text{b}}$ (it is unusual for the standard deviation to decrease as the net state variable increases), the criterion is simplified to

$$\frac{\eta_{\text{g}} - \eta_{\text{b}}}{\sqrt{\sigma_{\text{b}}^2 + \sigma_{\text{g}}^2}} \geqslant \frac{2z_{1-\alpha}}{\sqrt{J}} \tag{4}$$

5.4 Confirmation of the criterion for sufficient capability of detection

The standard deviations and expected values of the responses in Criterion (3) are usually unknown and the fulfilment of the criterion has to be confirmed from experimental data. Thus, the expression on the left-hand side of the simplified Criterion (4) is an unknown constant, while the expression on the right-hand side is a known constant.

From a validation experiment with N observations of the responses for the basic state and a sample with the net state variable equal to x_g, the expression on the left-hand side of Criterion (4) is estimated by

$$\frac{\bar{y}_g - \bar{y}_b}{\sqrt{s_b^2 + s_g^2}} \tag{5}$$

where the meanings for the symbols are as given in Annex A.

An approximate 100(1–γ) % lower confidence limit (CL) for $\left(\eta_g - \eta_b\right) \Big/ \sqrt{\sigma_b^2 + \sigma_g^2}$ is given by

$$\mathrm{CL} = \frac{\bar{y}_g - \bar{y}_b}{\sqrt{s_b^2 + s_g^2}} - \frac{t_{1-\gamma}(\nu)}{\sqrt{N}} \tag{6}$$

where

$t_{1-\gamma}(\nu)$ is the (1–γ)-quantile of the t-distribution with $\nu = 2(N-1)$ degrees of freedom, when the hypothesis $\sigma_b = \sigma_g$ is not rejected;

$\nu = \dfrac{(N-1)\left(s_b^2 + s_g^2\right)^2}{s_b^4 + s_g^4}$ degrees of freedom according to the Welch-Satterthwaite formula, when the hypothesis $\sigma_b = \sigma_g$ is rejected.

If the lower confidence limit for $\left(\eta_g - \eta_b\right) \Big/ \sqrt{\sigma_b^2 + \sigma_g^2}$ satisfies Criterion (4), a minimum detectable value less than or equal to x_g is confirmed.

NOTE For relatively large values of N (at least 20), it may be considered as sufficient for confirmation if either of the inequalities (3) or (4) are satisfied with the estimates $\bar{y}_b$, $\bar{y}_g$, s_b and s_g inserted.

6 Reporting of results from an assessment of the capability of detection

From an assessment of the capability of detection, usually as part of a validation of a method, report the following:

a) all relevant information about the reference materials, including the reference state value x_g;

b) the number of replicates N for each reference state;

c) the mean values, $\bar{y}_b$ and $\bar{y}_g$, and the standard deviations, s_b and s_g, for the responses of the basic state and the sample with the net state variable equal to x_g, respectively;

d) the chosen values of α, β, J and K;

e) the left- and right-hand sides of Criterion (3) with the estimates inserted, i.e. $\bar{y}_g - \bar{y}_b$ and

$$z_{1-\alpha}\, s_b \sqrt{\frac{1}{J} + \frac{1}{K}} + z_{1-\beta} \sqrt{\frac{1}{J} s_b^2 + \frac{1}{K} s_g^2}$$

or, when applicable ($\beta = \alpha$, $K = J$ and $\sigma_g \geqslant \sigma_b$), the statistic $\left(\bar{y}_g - \bar{y}_b\right) \Big/ \sqrt{s_b^2 + s_g^2}$ with its confidence interval and its lower acceptable limit $2z_{1-\alpha} \big/ \sqrt{J}$ according to Criterion (4);

f) the conclusion concerning the capability of detection.

7 Reporting of results from an application of the method

Report the observed values (responses or interpolated values of the net state variable). The fact that an observed value has been used for testing a hypothesis about the true value is no reason to discard the estimate of the true value (i.e. the observed value) and replace it by an upper limit equal to the critical value of the test or the minimum detectable value. In addition to the waste of information, it is also misleading as none of these limits may be interpreted as an upper confidence limit. Report also the applied critical value and, if possible, the minimum detectable value.

Annex A
(normative)

Symbols used in this part of ISO 11843

J number of replications of measurements on the reference material representing the value zero of the net state variable (blank sample) in an application of the method

K number of replications of measurements on the actual state (test sample) in an application of the method

N number of replications of measurements on each reference material (see 4.2) in assessment of the capability of detection

y_c critical value of the response variable

x_g given value which will be tested to determine whether it is greater than the minimum detectable value

η_b expected value under actual performance conditions for responses of the basic state

η_g expected value under actual performance conditions for responses of a sample with the net state variable equal to x_g

σ_b standard deviation under actual performance conditions for responses of the basic state

σ_g standard deviation under actual performance conditions for responses of a sample with the net state variable equal to x_g

$\bar{y}_b$ observed mean response of the basic state

$\bar{y}_g$ observed mean response of a sample with the net state variable equal to x_g

s_b estimate of the standard deviation of responses for the basic state

s_g estimate of the standard deviation of responses for a sample with the net state variable equal to x_g

$z_{1-\alpha}$ $(1-\alpha)$-quantile of the standard normal distribution

$z_{1-\beta}$ $(1-\beta)$-quantile of the standard normal distribution

$t_{1-\gamma}(\nu)$ $(1-\gamma)$-quantile of the t-distribution with ν degrees of freedom

Annex B
(informative)

Example of calculation

Low levels of “quickly reacting aluminium” in natural waters, expressed as mass concentration in micrograms per litre, were measured by connecting a continuous flow system to a graphite furnace atomic absorption spectrometer (see [2]). The absorbance values for five measurements of two samples representing the blank concentration $x_b = 0$ and the net concentration $x_g = 0{,}5$ µg/l are given in Table B.1. Thus, in the assessment of the method $N = 5$. The capability of detection is to be calculated for $J = K = 1$ and $\alpha = \beta = 0{,}05$.

Table B.1 — Absorbance values for the blank concentration $x_b = 0$ and the net concentration $x_g = 0{,}5$ µg/l

Net concentration of aluminium x	**Absorbance** y				
0	0,074	0,081	0,075	0,076	0,074
0,5	0,126	0,126	0,125	0,108	0,130

The statistical analysis yields

$$\bar{y}_b = 0{,}076\,0$$

$$\bar{y}_g = 0{,}123\,0$$

$$s_b = 0{,}002\,9$$

$$s_g = 0{,}008\,6$$

These values give

$$\frac{\bar{y}_g - \bar{y}_b}{\sqrt{s_b^2 + s_g^2}} = 5{,}17$$

The hypothesis $\sigma_b = \sigma_g$ is not rejected with an F-test at the 5 % significance level.

For $\gamma = 0{,}05$ and the number of degrees of freedom $\nu = 8$, then $t_{1-\gamma}(8) = 1{,}86$, and for $\alpha = 0{,}05$ then $z_{1-\alpha} = 1{,}645$.

A 95 % lower confidence limit of $\left(\eta_g - \eta_b\right) \Big/ \sqrt{\sigma_b^2 + \sigma_g^2}$ calculated according to Equation (6) is 4,34, which is greater than $2z_{1-\alpha} \Big/ \sqrt{J} = 3{,}29$ in Equation (4).

Thus, the evaluation shows that the minimum detectable value is less than $x_g = 0{,}5$ µg/l.

Bibliography

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

[2] DANIELSSON, L.-G. and SPARÉN, A. A mechanized system for the determination of low levels of quickly reacting aluminium in natural waters. *Analytica Chimica Acta*, **306**, 1995, pp. 173-181

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