INTERNATIONAL STANDARD

ISO 11843-7

Second edition
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Capability of detection —

Part 7:
Methodology based on stochastic properties of instrumental noise

Capacité de détection —

Partie 7: Méthodologie basée sur les propriétés stochastiques du bruit instrumental

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Contents

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.

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).

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. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

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 69, *Applications of statistical methods*, Subcommittee SC 6, *Measurement methods and results*.

This second edition cancels and replaces the first edition (ISO 11843-7:2012), which has been technically revised.

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

- created a new 6.2;
- 6.2 of the first edition is renumbered 6.3.

A list of all parts in the ISO 11843 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

The series of ISO 11843 is based on the probability distributions of the net state variable (measurand) for both the linear and nonlinear calibration situations. The focus is implicitly, though sometimes explicitly, on the uncertainty associated with an estimate of the measured response predominantly coming from the baseline noise in instrumental analysis. In many, if not most, analytical instruments, the baseline noise is considered the prime cause of uncertainty when the sample amount is as low as the minimum detectable value. Within its domain of applicability, the method given in this document can dispense with the repetition of real samples, thus helping to improve global environments by saving time and energy that would be required by repetition.

The basic concept of ISO 11843-7 is the mathematical description of the probability distribution of the response variable in terms of mathematically well-defined random processes. This description straightforwardly leads to the minimum detectable value. As for the relation of the response and measurand, linear and nonlinear calibration functions can be applied. In this manner, compatibility with ISO 11843-2 and ISO 11843-5 is ensured.

The definition and applicability of the minimum detectable value are described in ISO 11843-1 and ISO 11843-2; the definition and applicability of the precision profile are described in ISO 11843-5. The precision profile expresses how the precision changes depending on the net state variable. ISO 11843-7 specifies the practical use of the fundamental concepts in ISO 11843 in case of the background noise predominance in instrumental analysis.

The minimum detectable value, x_d, is generally expressed in the unit of the net state variable. If the calibration function is linear, the SD or CV of the response variable estimated in this document can linearly be transformed to the SD or CV of the net state variable, which in turn can be used for the estimation of the minimum detectable value, x_d.

If the calibration function is nonlinear, the precision profile of the response variable in this document needs to be transformed to the precision profile of the net state variable as shown in ISO 11843-5. In this situation, the contents of ISO 11843-5 can be used for this purpose without modification.

INTERNATIONAL STANDARD **ISO 11843-7:2018(E)**

Capability of detection —

Part 7:
Methodology based on stochastic properties of instrumental noise

1 Scope

Background noise exists ubiquitously in analytical instruments, whether or not a sample is applied to the instrument. This document is concerned with mathematical methodologies for estimating the minimum detectable value in case that the most predominant source of measurement uncertainty is background noise. The minimum detectable value can directly and mathematically be derived from the stochastic characteristics of the background noise.

This document specifies basic methods to

- extract the stochastic properties of the background noise,
- use the stochastic properties to estimate the standard deviation (SD) or coefficient of variation (CV) of the response variable, and
- calculate the minimum detectable value based on the SD or CV obtained above.

The methods described in this document are useful for checking the detection of a certain substance by various types of measurement equipment in which the background noise of the instrumental output predominates over the other sources of measurement uncertainty. Feasible choices are visible and ultraviolet absorption spectrometry, atomic absorption spectrometry, atomic fluorescence spectrometry, luminescence spectrometry, liquid chromatography and gas chromatography.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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: General statistical terms and terms used in probability*

ISO 3534-2, *Statistics — Vocabulary and symbols — Part 2: Applied statistics*

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

ISO 5725-1, *Accuracy (trueness and precision) of measurement methods and results — Part 1: General principles and definitions*

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

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

ISO 11843-5, *Capability of detection — Part 5: Methodology in the linear and non-linear calibration cases*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 3534-1, ISO 3534-2, ISO 3534-3, ISO 5725-1, ISO 11843-1, ISO 11843-2, ISO 11843-5 and the following apply. A list of symbols and abbreviated terms used in this document is provided in Annex A.

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 http://www.electropedia.org/

3.1
precision profile
<detection capability> mathematical description of the standard deviation (SD) of the response variable [$\sigma_Y(X)$] or net state variable [$\sigma_X(X)$] as a function of the net state variable

Note 1 to entry: The coefficient of variation (CV) of the response variable or net state variable as a function of the net state variable is also referred to as a precision profile.

Note 2 to entry: Precision means the SD or CV of the observed response variable or SD or CV of the net state variable when estimated by the calibration function (see ISO 11843-5).

[SOURCE: ISO 11843-5:2008, 3.4, modified — “coefficient of variation” has been removed and Note 1 to entry has been added instead. Note 2 to entry has also been added.]

3.2
minimum detectable value of the net state variable
x_d
value of the net state variable in the actual state that will lead, with probability 1 – β, to the conclusion that the system is not in the basic state

Note 1 to entry: Under the assumption that the SD, $\sigma_X(X)$, of the net state variable is constant [$(\sigma_X(X) = \sigma_X]$, the minimum detectable value, x_d, is defined as

$$x_\mathrm{d} = \left(k_\mathrm{c} + k_\mathrm{d}\right)\sigma_X \tag{1}$$

where

k_c denotes a coefficient to specify the probability of an error of the first kind;

k_d is a coefficient to specify the probability of an error of the second kind.

If the SD, σ_Y, of the response variable is assumed to be constant [$\sigma_Y(X) = \sigma_Y$], then the minimum detectable value can be calculated by the following Formula (2):

$$x_\mathrm{d} = \left(k_\mathrm{c} + k_\mathrm{d}\right)\left(\sigma_Y / \left|\mathrm{d}Y / \mathrm{d}X\right|\right) \tag{2}$$

where $|\mathrm{d}Y/\mathrm{d}X|$ denotes the absolute value of the slope of the linear calibration function and is constant.

Note 2 to entry: If the net state variable is normally distributed, the coefficients $k_\mathrm{c} = k_\mathrm{d} = 1{,}65$ specify the probabilities of an error of the first and second kinds (= 5 %) and Formula (1) can simply be written as $x_\mathrm{d} = 3{,}30\sigma_X$.

Note 3 to entry: If $k_\mathrm{c} = k_\mathrm{d} = 1{,}65$, Formula (1) takes the form that $\sigma_X / x_\mathrm{d} = 1/3{,}30 = 30$ %. Therefore, x_d can be found in the *precision profile* (3.1). x_d is located at X, the CV of which is 30 %.

Note 4 to entry: Different types of *precision profiles* (3.1) are defined, but they can be transformed to each other.

For example, the SD, $\sigma_Y(X)$, of the response variable can be transformed to the SD, $\sigma_X(X)$, of the net state variable by means of the absolute value of the derivative, $|\mathrm{d}Y/\mathrm{d}X|$, of the calibration function [$Y = f(X)$]: $\sigma_X(X) = \sigma_Y(X)/|\mathrm{d}Y/\mathrm{d}X|$ (see ISO 11843-5). This treatment is an approximation, the extent of which depends on local curvature, involving $\mathrm{d}^2Y/\mathrm{d}X^2$.

[SOURCE: ISO 11843-5:2008, 3.2, modified — Notes to entry 1 to 4 have been added.]

4 Quantitative analysis and background noise

4.1 Error sources of analysis

The quantitative analysis to obtain a measurand from a sample is generally considered to consist of preparation, instrumental analysis, data handling and calibration. These steps of analysis are mechanically independent of each other and so are probabilistically independent as well.

This document applies only to instrumental analysis. However, the errors from the other steps affect the error of the final value of the measurand, as well. That is, the combined uncertainty associated with an estimate of the measurand depends on the propagation of all uncertainties relating to the relevant steps. The following conditions are necessary for the use of ISO 11843-7.

At concentrations near the minimum detectable value in chromatography, the error from the sample injection into a chromatograph is even less important (e.g. CV = 0,3 % in a recent apparatus) than the background noise (CV = 30 % by definition). If the importance of a factor other than noise is comparable to that of the noise, the methodologies of this document are not applicable.

Data handling is usually a process to extract a signal component from noisy instrumental output such as peak height or area, which is a relative height of a summit of a peak-shaped signal or integration of intensities over a signal region, respectively. The statistical influences of this process are the major concern of this document. The use of a digital or analogue filter can also be taken into account, if the noise after the filtration is analysed for this purpose.

4.2 Random processes in background

Typical examples of the response variable are area and height measured in chromatography. In this document, intensity difference [Formula (6)] and area [Formulae (10) and (11)] are taken as the difference and summation of intensities Y_i of instrumental output. The response variables are usually independent of each other even if they are obtained from consecutive measurement by the same instrument. On the other hand, the consecutive intensities Y_i are formulated as a time-dependent random process, and in many cases, can be considered 1/*f* noise[1].

The power spectrum, $P(f)$, of 1/*f* noise has a slope inversely proportional to frequency, *f*:

$$P\left(f\right) \propto \frac{1}{f} \tag{3}$$

when *f* is near zero.

The simplest model of random processes is the white noise. Let w_i denote the random variable of the white noise at point *i*. By definition, the mean of the white noise is zero and the SD, $\tilde{w}$, of the white noise is constant at every point *i*. A prominent feature of the white noise is that the noise intensities, w_i and w_j, are independent of each other, if $i \neq j$.

The autoregressive process [AR(1)-process] of first order is a mathematical model in which the intensities, M_i and M_j, are not independent of each other ($i \neq j$). The AR(1)-process is treated as a major component of time-dependent changes of instrumental output [see Formula (9)]. The AR(1)-process at point *i* is defined to take the form

$$M_i = \rho M_{i-1} + m_i \tag{4}$$

where

m_i denotes the random variable of the white noise at point i;

ρ is a constant parameter ($-1 < \rho < 1$).

5 Theories for precision

5.1 Theory based on auto-covariance function

A theory has been proposed [2][3][4] based on an auto-covariance function:

$$\psi\left(\tau_s\right) \equiv E\left[Y_{t_0+\tau_s} Y_{t_0}\right] \tag{5}$$

where $E[\cdot]$ denotes the mean of a random variable inside the square brackets over t_0.

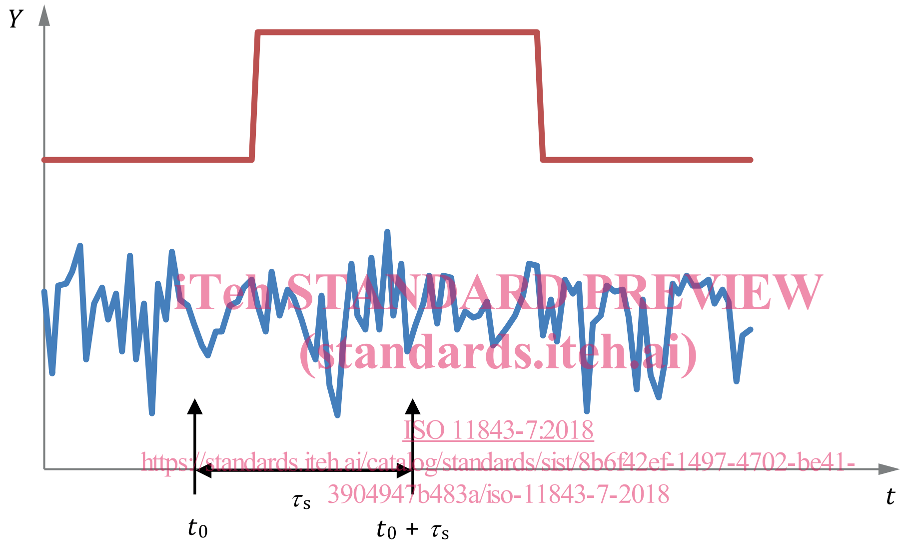

Figure 1 — Signal (upper line) and noise (lower line) with intensity difference

The upper part of Figure 1 depicts the signal as (an approximation to) a rectangular pulse. Noise (constituting background) on the signal is depicted as the oscillatory curve in the lower part of the figure. t_0 denotes a time value on the background portion of the signal and $t_0 + \tau_s$ denotes a time value on the signal itself. The measurement (signal reading) is the difference in intensities at times t_0 and $t_0 + \tau_s$. The value of the signal would be zero at t_0 in the absence of background noise. The signal has a finite value at $t_0 + \tau_s$ when a sample is measured. In the ISO 11843-7 measurement model, the signal and noise are superimposed, and this mixed random process takes the value Y_i at time t_i. The intensities at times t_0 and $t_0 + \tau_s$ are described as Y_{t_0} and $Y_{t_0+\tau_s}$, respectively, and the intensity difference is given by Formula (6).

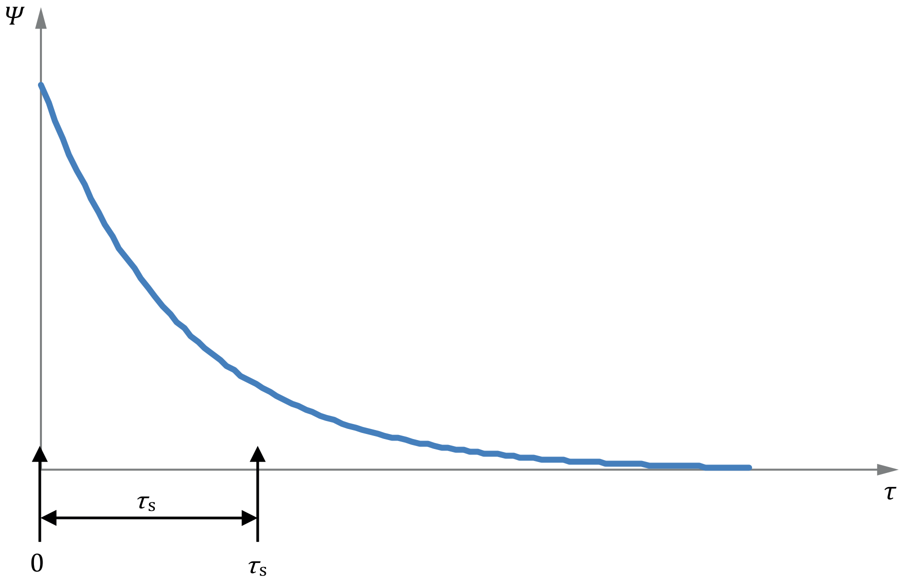

Figure 2 — Auto-covariance function of noise

The difference between the values of the auto-covariance function, $\psi(\tau)$, at 0 and τ_s gives the right side of Formula (7).

Near the minimum detectable value, which is dictated by the background fluctuation, intensity difference often applies in analytical optical spectrometry. The definition of intensity difference, e.g. signal reading corrected for background, is[2][3][4]:

$$\Delta Y = Y_{t_0+\tau_s} - Y_{t_0} \tag{6}$$

Here, ΔY corresponds to the response variable Y. The variance of the intensity difference is written as shown in Formula (7)[2][3][4]. [For the derivation of Formula (7), see Annex B.]

$$\sigma_{\Delta Y}{}^2 = 2\left[\psi\left(0\right) - \psi\left(\tau_s\right)\right] \tag{7}$$

Formula (7) is of practical use when the actual auto-covariance functions, $\psi(0)$ and $\psi(\tau_s)$, are known from the observation of background noise as shown in Figure 2. The substitution of Formula (7) for Formula (2) ($\sigma_Y = \sigma_{\Delta Y}$) leads to the minimum detectable value.

Use can be made of the Wiener-Khintchine theorem[5], which relates the auto-covariance function to the power spectral density through the Fourier transform:

$$\psi\left(\tau_s\right) = \int_0^\infty S_b\left(f\right)\left|G\left(f\right)\right|^2 \cos\left(2\pi f \tau_s\right) \mathrm{d}f \tag{8}$$

where

$S_b(f)$ denotes the power spectrum of the observed background noise;

$G(f)$ is the frequency response of the (linear) read-out system.

Formula (8) indicates the estimation of the measurement SD, Formula (7), through the noise power spectrum.