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Capability of detection —

Part 6: Methodology for the determination of the critical value and the minimum detectable value in Poisson distributed measurements by normal approximations

Capacité de détection —

Partie 6: Méthodologie pour la détermination de la valeur critique et de la valeur minimale détectable pour les mesures distribuées selon la loi de Poisson approximée par la loi Normale

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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 11843-6 was prepared by Technical Committee ISO/TC 69, *Application 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*

— *Part 5: Methodology in the linear and non-linear calibration cases*

— *Part 6: Methodology for the determination of the critical value and the minimum detectable value in Poisson distributed measurements by normal approximations*

— *Part 7: Methodology based on stochastic properties of instrumental noise*

This corrected version of ISO 11843-6:2013 incorporates the following correction: in the key of Figure 1, the meanings of *X* and *Y* have been transposed.

Introduction

Many types of instruments use the pulse-counting method for detecting signals. X-ray, electron and ion-spectroscopy detectors, such as X-ray diffractometers (XRD), X-ray fluorescence spectrometers (XRF), X-ray photoelectron spectrometers (XPS), Auger electron spectrometers (AES), secondary ion mass spectrometers (SIMS) and gas chromatograph mass spectrometers (GCMS) are of this type. These signals consist of a series of pulses produced at random and irregular intervals. They can be understood statistically using a Poisson distribution and the methodology for determining the minimum detectable value can be deduced from statistical principles.

Determining the minimum detectable value of signals is sometimes important in practical work. The value provides a criterion for deciding when "the signal is certainly not detected", or when "the signal is significantly different from the background noise level"[1-8]. For example, it is valuable when measuring the presence of hazardous substances or surface contamination of semi-conductor materials. RoHS (Restrictions on Hazardous Substances) sets limits on the use of six hazardous materials (hexavalent chromium, lead, mercury, cadmium and the flame retardant agents, perbromobiphenyl, PBB, and perbromodiphenyl ether, PBDE) in the manufacturing of electronic components and related goods sold in the EU. For that application, XRF and GCMS are the testing instruments used. XRD is used to measure the level of hazardous asbestos and crystalline silica present in the environment or in building materials.

The methods used to set the minimum detectable value have for some time been in widespread use in the field of chemical analysis, although not where pulse-counting measurements are concerned. The need to establish a methodology for determining the minimum detectable value in that area is recognized.[9]

In this part of ISO 11843 the Poisson distribution is approximated by the normal distribution, ensuring consistency with the IUPAC approach laid out in the ISO 11843 series. The conventional approximation is used to generate the variance, the critical value of the response variable, the capability of detection criteria and the minimum detectability level.[10]

In this part of ISO 11843:

— α is the probability of erroneously detecting that a system is not in the basic state, when really it is in that state;

— β is the probability of erroneously not detecting that a system is not in the basic state when the value of the state variable is equal to the minimum detectable value(x_d).

This part of ISO 11843 is fully compliant with ISO 11843-1, ISO 11843-3 and ISO 11843-4.

Capability of detection —

Part 6:
Methodology for the determination of the critical value and the minimum detectable value in Poisson distributed measurements by normal approximations

1 Scope

This part of ISO 11843 presents methods for determining the critical value of the response variable and the minimum detectable value in Poisson distribution measurements. It is applicable when variations in both the background noise and the signal are describable by the Poisson distribution. The conventional approximation is used to approximate the Poisson distribution by the normal distribution consistent with ISO 11843-3 and ISO 11843-4.

The accuracy of the normal approximation as compared to the exact Poisson distribution is discussed in Annex C.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO Guide 30, *Reference materials - Selected terms and definitions*

ISO 3534-1, *Statistics — Vocabulary and symbols — Part 1: General statistical terms and terms used in probability*

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 11843-3, *Capability of detection — Part 3: Methodology for determination of the critical value for the response variable when no calibration data are used*

ISO 11843-4, *Capability of detection — Part 4: Methodology for comparing the minimum detectable value with a given value*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 3534-1, ISO 11843-1, ISO 11843-2, ISO 11843-3, ISO 11843-4, and ISO Guide 30 apply.

4 Measurement system and data handling

The conditions under which Poisson counts are made are usually specified by the experimental set-up. The number of pulses that are detected increases with both the time and with the width of the region over which the spectrum is observed. These two parameters should be noted and not changed during the course of the measurement.

The following restrictions should be observed if the minimum detectable value is to be determined reliably:

a) Both the signal and the background noise should follow the Poisson distributions. The signal is the mean value of the gross count.

b) The raw data should not receive any processing or treatment, such as smoothing.

c) Time interval: Measurement over a long period of time is preferable to several shorter measurements. A single measurement taken for over one second is better than 10 measurements over 100 ms each. The approximation of the Poisson distribution by the normal distribution is more reliable with higher mean values.

d) The number of measurements: Since only mean values are used in the approximations presented here, repeated measurements are needed to determine them. The power of test increases with the number of measurements.

e) Number of channels used by the detector: There should be no overlap of neighbouring peaks. The number of channels that are used to measure the background noise and the sample spectra should be identical (Annex D, Figure D.1).

f) Peak width: The full width at half maximum (FWHM) is the recommended coverage for monitoring a single peak. It is preferable to measurements based on the top and/or the bottom of a noisy peak. The appropriate FWHM should be assessed beforehand by measuring a standard sample. An identical value of the FWHM should be used for both the background noise and the sample measurements.

Additional factors are: the instrument should work correctly; the detector should be operating within its linear counting range; both the ordinate and the abscissa axes should be calibrated; there should be no signal that cannot be clearly identified as not being noise; degradation of the specimen during measurement should be negligibly small; at least one signal or peak belonging to the element under consideration should be observable.

5 Computation by approximation

5.1 The critical value based on the normal distribution

The decision on whether a measured signal is significant or not can be made by comparing the arithmetic mean $\bar{y}_g$ of the actual measured values with a suitably chosen value y_c. The value y_c, which is referred to as the critical value, satisfies the requirement

$$P(\bar{y}_g > y_c | x = 0) \leq \alpha \tag{1}$$

where the probability is computed under the condition that the system is in the basic state ($x = 0$) and α is a pre-selected probability value.

Formula (1) gives the probability that $\bar{y}_g > y_c$ under the condition that:

$$y_c = \bar{y}_b \pm z_{1-\alpha} \sigma_b \sqrt{\frac{1}{J} + \frac{1}{K}} \tag{2}$$

where

$z_{1-\alpha}$ is the $(1 - \alpha)$-quantile of the standard normal distribution where $1 - \alpha$ is the confidence level;

σ_b is the standard deviation under actual performance conditions for the response in the basic state;

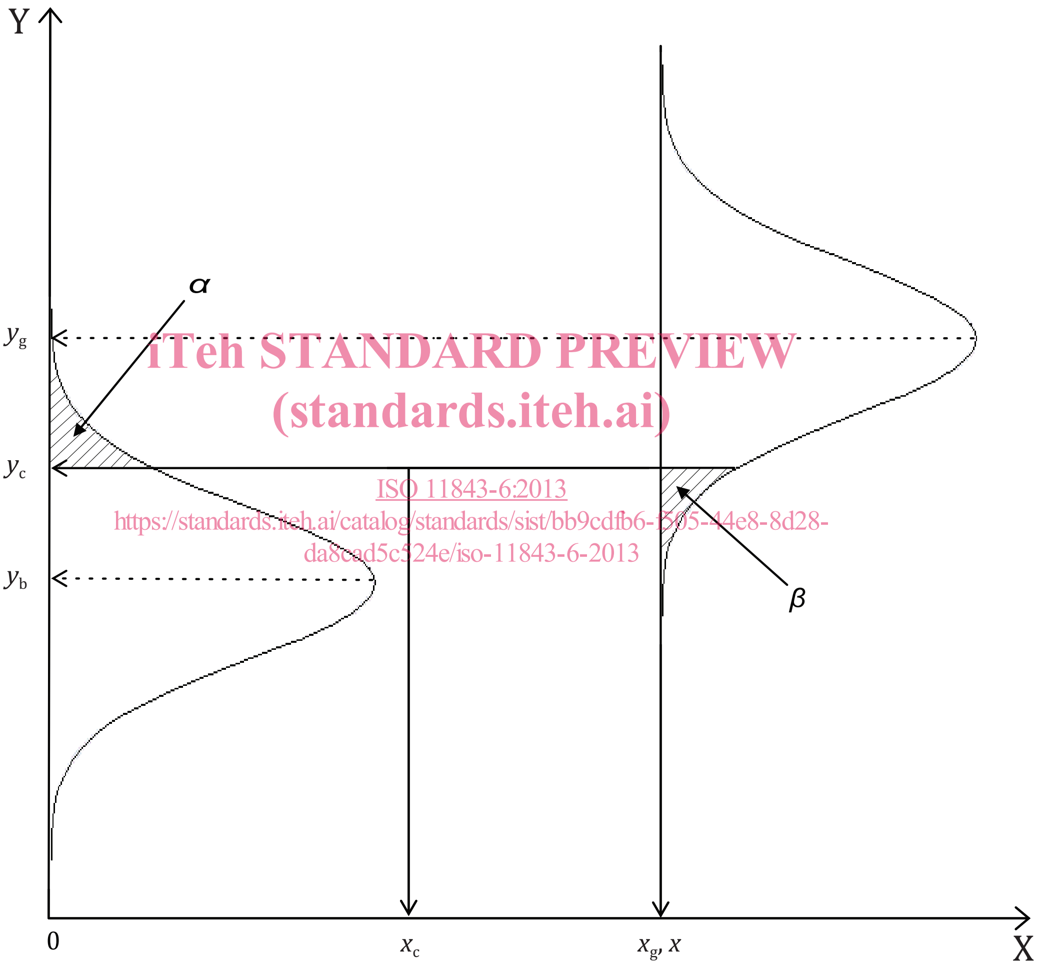
$\bar{y}_b$ is the arithmetic mean of the actual measured response in the basic state;

J is the number of repeat measurements of the blank reference sample. This represents the value of the basic state variable;

K is the number of repeat measurements of the test sample. This gives the value of the actual state variable.

The + sign is used in Formula (2) when the response variable increases as the state variable increases. The − sign is used when the opposite is true.

The definition of the critical value follows ISO 11843-1 and ISO 11843-3. Its relationship to the measured values in the active and basic states is illustrated in Figure 1.



Key

X state variable

Y response variable

α the probability that an error of the first kind has occurred

β the probability that an error of the second kind has occurred

Figure 1 — A conceptual diagram showing the relative position of the critical value and the measured values of the active and basic states

5.2 Determination of the critical value of the response variable

If the response variable follows a Poisson distribution with a sufficiently large mean value, the standard deviation of the repeated measurements of the response variable in the basic state is estimated as $\sqrt{\bar{y}_b}$. This is an estimate of σ_b. The standard deviation of the repeated measurements of the response variable in the actual state of the sample is $\sqrt{\bar{y}_g}$, giving an estimate of σ_g (see Annex B).

The critical value, y_c, of a response variable that follows the Poisson distribution approximated by the normal distribution generally satisfies:

$$y_c = \bar{y}_b + z_{1-\alpha}\sigma_b\sqrt{\frac{1}{J}+\frac{1}{K}} \approx \bar{y}_b + z_{1-\alpha}\sqrt{\bar{y}_b}\sqrt{\frac{1}{J}+\frac{1}{K}} \tag{3}$$

where

$\bar{y}_b$ is the arithmetic mean of the actual measured response in the basic state.

5.3 Sufficient capability of the detection criterion

The sufficient capability of detection criterion enables decisions to be made about the detection of a signal by comparing the critical value probability with a specified value of the confidence levels, $1-\beta$. If the criterion is satisfied, it can be concluded that the minimum detectable value, x_d, is less than or equal to the value of the state variable, x_g. The minimum detectable value then defines the smallest value of the response variable, η_g, for which an incorrect decision occurs with a probability, β. At this value, there is no signal, only background noise, and an ‘error of the second kind’ has occurred.

If the standard deviation of the response for a given value x_g is σ_g, the criterion for the probability to be greater than or equal to $1-\beta$ is set by inequality (4), from which inequalities (5) and (6) can be derived:

$$\eta_g \geq y_c + z_{1-\beta}\sqrt{\frac{1}{J}\sigma_b^2+\frac{1}{K}\sigma_g^2} \tag{4}$$

If y_c is replaced by $y_c = \eta_b + z_{1-\alpha}\sigma_b\sqrt{\frac{1}{J}+\frac{1}{K}}$, defined in Formulae (2) and (3), then:

$$\eta_g - \eta_b \geq z_{1-\alpha}\sigma_b\sqrt{\frac{1}{J}+\frac{1}{K}} + z_{1-\beta}\sqrt{\frac{1}{J}\sigma_b^2+\frac{1}{K}\sigma_g^2} \tag{5}$$

where

α is the probability that an error of the first kind has occurred;

β is the probability that an error of the second kind has occurred;

η_b is the expected value under the actual performance conditions for the response in the basic state;

η_g is the expected value under the actual performance conditions for the response in a sample with the state variable equal to x_g.

With $\beta = \alpha$ and $K = J$, the criterion simplifies to:

$$\eta_g - \eta_b \geq z_{1-\alpha} \sqrt{\frac{1}{J}} \left(\sqrt{2}\sigma_b + \sqrt{\sigma_b^2 + \sigma_g^2} \right) \tag{6}$$

If σ_b is replaced with an estimate of $\sqrt{\bar{y}_b}$ following 5.2 and similarly σ_g is replaced with an estimate of $\sqrt{\bar{y}_g}$ (see Annex B), the criterion becomes inequality (7).

$$\eta_g - \eta_b \geq z_{1-\alpha} \sqrt{\frac{1}{J}} \left(\sqrt{2\bar{y}_b} + \sqrt{\bar{y}_b + \bar{y}_g} \right) \tag{7}$$

NOTE When validating a method, the capability of detection is usually determined for $K = J = 1$ in accordance with ISO 11843-4.

5.4 Confirmation of the sufficient capability of detection criterion

The standard deviations and expected values of the response are usually unknown, so an assessment using criterion inequality (6) has to be made from the experimental data. The expression on the left-hand side of the simplified criterion inequality (6) is unknown, whereas that on the right-hand side is known.

A confidence interval of $\eta_g - \eta_b$ is provided by N repeated measurements in the basic state and N repeated measurements of a sample with the state variable equal to x_g. A $100(1-\alpha/2)\%$ confidence interval for $\eta_g - \eta_b$ is:

$$(\bar{y}_g - \bar{y}_b) - z_{(1-\alpha/2)} \sqrt{\frac{1}{N}\sigma_b^2 + \frac{1}{N}\sigma_g^2} \leq \eta_g - \eta_b \leq (\bar{y}_g - \bar{y}_b) + z_{(1-\alpha/2)} \sqrt{\frac{1}{N}\sigma_b^2 + \frac{1}{N}\sigma_g^2} \tag{8}$$

where $z_{(1-\alpha/2)}$ is the $100(1-\alpha/2)$ quantile of the standard normal distribution.

To confirm the sufficient capability of detection criterion, a one-sided test is used. With $\beta = \alpha$, $100(1-\alpha)\%$ of the one-sided lower confidence bound on $\eta_g - \eta_b$ is:

$$\eta_g - \eta_b \geq (\bar{y}_g - \bar{y}_b) - z_{(1-\alpha)} \sqrt{\frac{1}{N}\sigma_b^2 + \frac{1}{N}\sigma_g^2} \tag{9}$$

where

N is the number of replications of measurements of each reference material used to assess the capability of detection;

$\bar{y}_g$ is the arithmetic mean of the actual measured response in a sample with the state variable equal to x_g;

η_b is the expected value under actual performance conditions for the response in the basic state;

η_g is the expected value under actual performance conditions for the response in a sample with the state variable equal to x_g.