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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 dans les mesures de distribution selon la loi de Poisson par approximations normales

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Foreword

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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 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*

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), and secondary ion mass spectrometers(SIMS), gas chromatograph mass spectrometers(GCMS) are of this type. These signals consist of a series of pulses produced at random and irregular intervals that can be understood statistically using a Poisson distribution. Since the variation in a signal follows a Poisson distribution, a 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. It 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 a semi-conductor materials. RoHS(Restrictions on Hazardous Substances) regulation on heavy metals restricts the use of six hazardous materials(e.g, hexavalent Chromium,Lead,Mercury,Cadmium,and flame retardant agents such as PBB and PBDE) in the manufacturing of electronic components and related goods that are sold into the EU. XRF and GCMS are used as testing instruments. The level of hazardous asbestos and crystalline silica present in the environment or building material are detect by XRD. It also allows the condition of an analyzer to be quantified when assessing the limiting performance of an instrument.

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 involved. The need to establish a methodology to determine the minimum detectable value in that area is recognized [9].
This part of ISO 11843 considers the Poisson distribution approximated by the normal distribution, ensuring consistency with the IUPAC approach and, particularly, with the series of ISO 11843 standards. Conventional type of approximation is used for this purpose. Definitions are given for the variance, for the critical value of the response variable, for the capability of detection criteria and for the minimum detectability level [10].

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 state variable is equal to the minimum detectable value(x_d) is not in the basic state.

This standard is fully compliant with ISO 11843, part 1, 3 and 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 provides the methods to determine 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. Conventional type of approximation is used to approximate the Poisson distribution by the Normal distribution to consist with ISO11843-3 and ISO11843-4. This part of ISO 11843 should be applied to a sufficient number of counts of the response variable.

Note The accuracy of the approximation is described to compare with the results of the Poisson exact arithmetic in Annex C.

2 Normative references

The following documents are indispensable for the application of this document. For dated references, only the edition cited is applicable. For undated references, the latest edition of the reference document (including any amendments) is applicable.

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

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

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

I SO 5479: 1 997, 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 Guide 30:1992, *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 5479, ISO 5725-2, ISO 11095, ISO 11843-1, ISO 11843-2, ISO 11843-3, ISO 11843-4, and ISO Guide 30 apply.

4 Symbols (and abbreviated terms)

The meanings of the symbols used here are given in Annex A.

5 Measurement system and data handling

The conditions under which Poisson distribution measurement is 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 being observed. These two parameters should therefore be noted and not changed during the course of the measurement.

The following conditions are essential for determining the minimum detectable value.

(1) Both the signal and the background noise should have Poisson distributions. The signal should be treated as mean value of gross count.

(2) The spectra under consideration should not have received any data treatment, such as smoothing.

(3) Time interval: A measurement over a longer period of time is preferable to several shorter measurements. A measurement taken for over one second is better than 10 measurements over 100 milliseconds each. The approximation of the Poisson distribution by the Normal distribution is more reliable with higher mean values.

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

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

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

NOTE Additional conditions for the interpretation of the data are: the instrument works correctly; the detector works in the linear counting range; both the ordinate and the abscissa axes are calibrated; there is no signal that cannot be identified, except statistical fluctuation; degradation of the specimen during measurement is negligibly small; at least one signal or peak that belongs to an element can be observed.

6 Computation by approximation (Annex B.1)

6.1 Definition of the critical value based on the Normal distribution

The critical value, y_c, is defined as the value of the response variable, y, if the system is considered to move from a dormant or 'basic' state to an 'active' state.

The decision about whether the measured signal is 'significant' or 'not significant' is made by comparing the arithmetic mean of the actual measured values, $\bar{y}_g$, with the critical value, y_c. The probability that $\bar{y}_g$ 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, α.

The critical value, y_c, of the response variable, y, generally satisfies

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

Equation (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

α	the probability that an error of the first kind;
$1-\alpha$	confidence levels;
$z_{1-\alpha}$	$(1-\alpha)$-quantile of the standard normal distribution;
σ_b	standard deviation under actual performance conditions for responses of the basic state;
$\bar{y}_b$	the arithmetic mean of the actual measured response of the basic state
J	number of replications of measurement on the reference material representing the value of the basic state variable (blank sample);
K	number of replications of measurement on the actual state (test sample).

Note that the + sign is used when the response variable increases with increasing level of the state variable. When the response variable decreases with increasing level of the state variable the - sign is used.

The definition of the critical value and its conceptual diagram in Figure 1 in this clause follow ISO11843-1 and ISO11843-3.

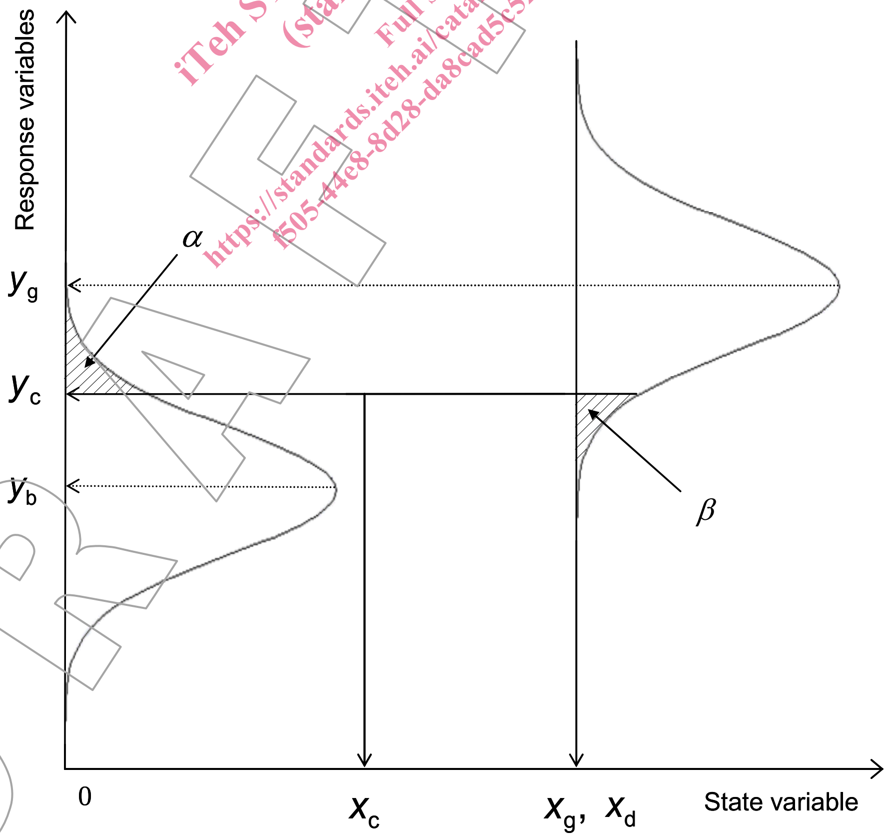

Figure 1

6.2 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 through $\bar{y}_\text{b}$ as $\sqrt{\bar{y}_\text{b}}$ gives an estimate of σ_b and the that of the repeated measurements of the response variable in the actual state of the sample is used as $\sqrt{\bar{y}_\text{g}}$ gives an estimate of σ_g (see Annex B.1).

The critical value, y_c, of the response variable which follows a Poisson distribution approximated by the Normal approximation generally satisfies

$$y_\text{c} = \bar{y}_\text{b} + z_{1\text{-}\alpha}\sigma_\text{b}\sqrt{\frac{1}{J}+\frac{1}{K}} = \bar{y}_\text{b} + z_{1\text{-}\alpha}\sqrt{\bar{y}_\text{b}}\sqrt{\frac{1}{J}+\frac{1}{K}}\,, \tag{3}$$

where

$\bar{y}_\text{b}$ the arithmetic mean of the actual measured response of the basic state

Note that the + sign is preferable in Poisson distribution measurements as the response variable increases with increasing level of the state variable.

6.3 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 may 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 expectation of the response variable, η_g, for which an incorrect decision occurs with a probability, β, that there is no signal, but only background noise. This is termed an ‘error of the second kind’.

If the standard deviation of the responses for a given value x_g is σ_g, the criterion for the probability to be greater than or equal to $1-\beta$ is defined by inequality (4), and it is actually given by inequalities (5) and (6):

$$\eta_\text{g} \geq y_\text{c} + z_{1-\beta}\sqrt{\frac{1}{J}\sigma_\text{b}^2 + \frac{1}{K}\sigma_\text{g}^2}\,, \tag{4}$$

If y_c is replaced by $y_\text{c} = \eta_\text{b} + z_{1-\alpha}\sigma_\text{b}\sqrt{\frac{1}{J}+\frac{1}{K}}$, defined in equation (2) and (3), then

$$\eta_\text{g} - \eta_\text{b} \geq z_{1-\alpha}\sigma_\text{b}\sqrt{\frac{1}{J}+\frac{1}{K}} + z_{1-\beta}\sqrt{\frac{1}{J}\sigma_\text{b}^2 + \frac{1}{K}\sigma_\text{g}^2}\,, \tag{5}$$

where

α the probability that an error of the first kind has occurred;
β the probability that an error of the second kind has occurred;
η_b expected value under the actual performance conditions for the responses of the basic state;
η_g expected value under the actual performance conditions for the responses of a sample with