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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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ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Fax: +41 22 749 09 47
Email: copyright@iso.org
Website: www.iso.org

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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.

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

This second edition cancels and replaces the first edition (ISO 11843-6:2013, corrected version issued in 2014), of which it constitutes a minor revision. The changes compared to the previous corrected version are as follows:

— the following updates have been made to add clarity or to correct typographic and obvious errors:

  — in Formula (2) and the related Note, "±" is replaced with "+";

  — in 5.4, 2nd paragraph, "100(1-α/2)%" is replaced with "100(1-α)%", and "described below by the general theory of estimation" is inserted at the end,

  — in Clause 6 e), Figure 1, and Annex C 3rd paragraph, the average values ($\bar{y}_b$, $\bar{y}_d$ and $\bar{y}_g$) are used;

  — in Annex C, 3rd paragraph, 1st sentence, "independent" is inserted before "variables";

  — in the line below Formula (C.1), $I_k(\bullet)$ is consistently replaced with $I_y(\bullet)$;

  — in E.2, 2nd paragraph, the text has been slightly reworded for clarity;

— thorough the text, minor editorial modifications have been made in line with the 2018 edition of the ISO/IEC Directives, Part 2.

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

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 document 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 document:

— 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 document 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 document 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 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 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.

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/

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:

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

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;

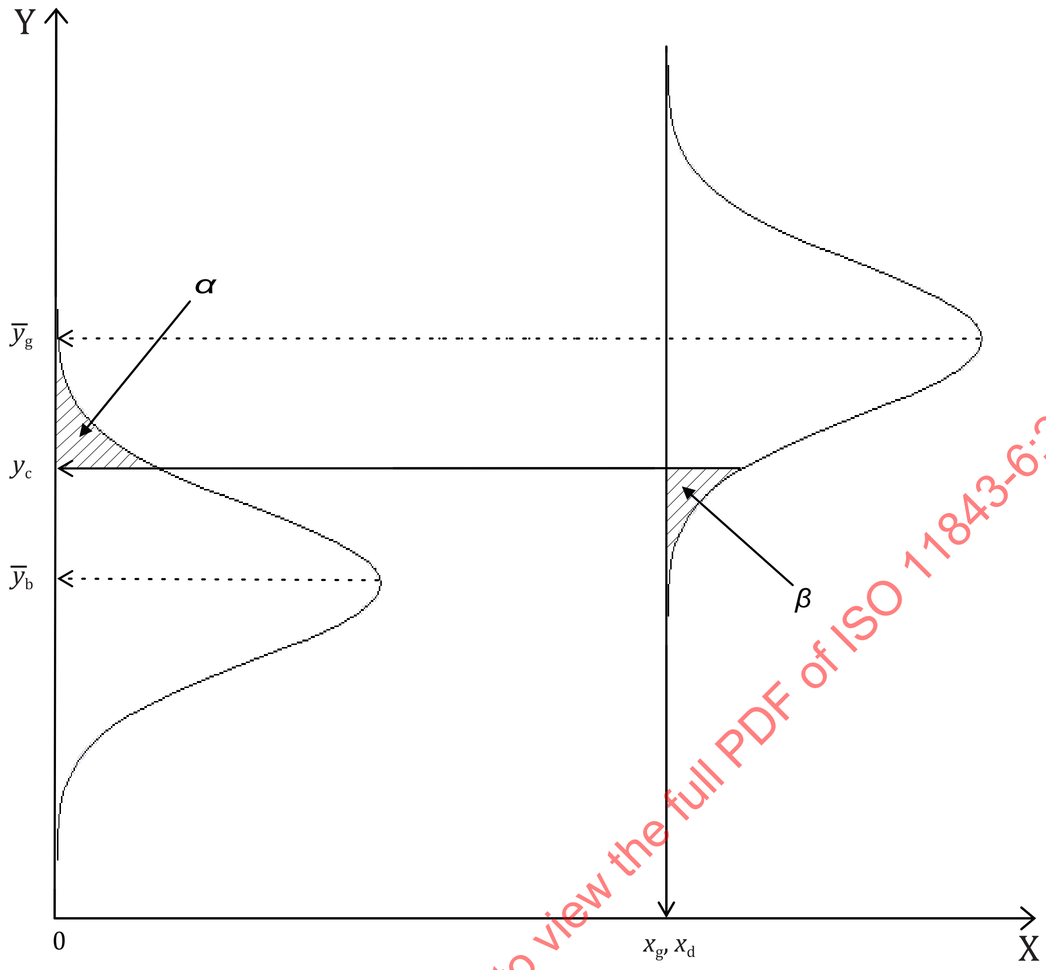
$\bar{y}_b$ is the arithmetic mean of the actual measured response in the basic state;

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.

NOTE Only the + sign is used in Formula (2). In the pulse counting method, the response variable is a positive integer and always increases as the state variable increases.

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 Formula (4), from which Formulae (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 Formula (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 Formula (6) has to be made from the experimental data. The expression on the left-hand side of the simplified criterion Formula (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 − α) % confidence interval for $\eta_g - \eta_b$, described below by the general theory of estimation, is:

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

where $z_{(1-\alpha/2)}$ is the 100(1 − α/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 − α) % of the one-sided lower confidence bound on $\eta_g - \eta_b$ is:

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

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.

The one-sided lower confidence bound on $\eta_g - \eta_b$ of Formula (9) is compared to the right-hand side of Formula (6), giving:

$$\eta_g - \eta_b = (\bar{y}_g - \bar{y}_b) - z_{(1-\alpha)}\sqrt{\frac{1}{N}\sigma_b^2 + \frac{1}{N}\sigma_g^2} \ge z_{(1-\alpha)}\sqrt{\frac{1}{J}}\left(\sqrt{2}\sigma_b + \sqrt{\sigma_b^2 + \sigma_g^2}\right) \quad (10)$$

An approximate 100(1 − α) % lower confidence limit T_0 for $\eta_g - \eta_b$ is obtained by replacing σ_b and σ_g with $\sqrt{\bar{y}_b}$ and $\sqrt{\bar{y}_g}$, respectively, as defined in Formula (3) and Formula (7):

$$T_0 = (\bar{y}_g - \bar{y}_b) - z_{(1-\alpha)}\sqrt{\frac{1}{N}}\sqrt{\bar{y}_b + \bar{y}_g} \quad (11)$$

If the lower confidence limit T_0 satisfies Formula (7), it is concluded that the minimum average detectable response value, $\bar{y}_g$, is less than or equal to the minimum detectable response value, y_d. x_d is therefore less than or equal to x_g and, for relatively large values of N, the lower confidence limit Formula (11) will suffice.

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

The capability of detection assessment is usually carried out as a part of the initial validation of the method. It provides the following:

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

b) the number of replications, N, for each reference state;

c) the mean values, $\bar{y}_b$ and $\bar{y}_g$;

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

e) values for the left- and right-hand sides of Formula (7) using the estimates, i.e. $\bar{y}_g - \bar{y}_b$ or, when both $\beta = \alpha$ and $K = J$ are applicable, the difference $(\eta_g - \eta_b)$ with the confidence interval and the lower acceptable limit, $z_{1-\alpha}\sqrt{\frac{1}{J}}\left(\sqrt{2}\sigma_b + \sqrt{\sigma_b^2 + \sigma_g^2}\right)$, can also be calculated;

f) the conclusion concerning capability of detection;

g) if necessary, the minimum detectable value for a given background value. This is obtained by replacing N and J with infinity and 1, respectively, in Formula (10).

7 Reporting the results from an application of the method

The observed values should be reported as they represent the response of the state variable. The fact that these observed values are used to test for the true values is no reason to discard them and replace them by an upper limit (equal to the critical value of the test) or a minimum detectable value. Report also the applied critical value and, if possible, the minimum detectable value.

Annex A
(informative)

Symbols used in this document

X state variable

Y response variable

J number of replications of measurements on the reference material representing the value of the basic state variable (blank sample)

K number of replications of measurements on the actual state (test sample)

N number of replications of measurements of each reference material in assessment of the capability of detection

x a value of state variable

y a value of response variable

y_c critical value of the response variable defined by ISO 11843-1 and ISO 11843-3

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

x_d minimum detectable value of the state variable

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

σ_g standard deviation under actual performance conditions for the response in a sample with the state variable equal to x_g

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

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

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

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

y_d minimum detectable response value with the state variable equal to x_d

λ mean value corresponding to the expected number of events in Poisson distribution

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

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

$1 - \alpha$ confidence level

$1 - \beta$ confidence level

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

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

T_0 lower confidence limit

Annex B
(informative)

Estimating the mean value and variance when the Poisson distribution is approximated by the normal distribution

The probability function for the Poisson distribution is $p(y, \lambda)$. It is described by the following equation:

$$p(y,\lambda)=\frac{\lambda^{y}}{y!}\mathrm{e}^{-\lambda} \quad \text{(B.1)}$$

where

λ is the mean value corresponding to the expected number of events in a given time;

y is the actual number of events recorded in that time.

Since random variable, Y, follows the Poisson distribution with parameter λ, both the expected value and the variance of this random variable are equal to λ, that is $E(Y) = \lambda$ and $\mathrm{Var}(Y) = \lambda$. Only one parameter, λ, needs to be estimated. This estimate, based on J independent measurements, is:

$$\hat{\lambda}=\bar{y}=\frac{\sum_{i=1}^{J} y_i}{J} \quad \text{(B.2)}$$

When the Poisson distribution is approximated by the normal distribution, the random variable Y is replaced by the random variable Z, which has a normal distribution, $N(\lambda, \lambda)$.

Annex C
(informative)

An accuracy of approximations

In this Annex, the minimum detectable response values, calculated by the conventional approximation, are compared with those obtained by the exact Poisson calculation. These provide estimates of how the accuracy of the approximation varies with the number of counts.

The minimum detectable response value according to the exact Poisson method is calculated by the following procedure.

The summation of independent variables following a Poisson distribution also follows a Poisson distribution, but the difference does not. When this difference is exactly described, the following probability function is used. The response value in the basic state corresponds to the background noise of the measurement, y_b, and the response variable in the actual state, y_d, expresses each two-sample, under the null hypothesis.

This means that the distribution follows Formula (C.1) where y is $\left|\bar{y}_b - \bar{y}_d\right|$.

$$\Pr\left[y\right]=e^{-2\theta}\sum_{j=y}^{\infty}\theta^{j+(j-y)}\left[j!(j-y)!\right]^{-1}=e^{-2\theta}I_y(2\theta) \quad \text{(C.1)}$$

$I_y(\bullet)$ is a modified Bessel function of the first kind. The distribution follows Formula (C.2) under an alternative hypothesis.

$$\Pr\left[y\right]=e^{-(\theta_1+\theta_2)}\sum_{j=y}^{\infty}\theta_1^j\theta_2^{j-y}\left[j!(j-y)!\right]^{-1}=e^{-(\theta_1+\theta_2)}\left(\frac{\theta_1}{\theta_2}\right)^{y/2}I_y(2\sqrt{\theta_1\theta_2}) \quad \text{(C.2)}$$

The minimum detectable response in the actual state value can be derived from these two equations. Alternatively the minimum detectable response value via approximation can be derived by Formulae (7) and (11) when the number of replications of measurements, *N*, is replaced by infinity.

Table C.1 shows the minimum detectable value when the parameter y_b, corresponding to basic state value, is from 1 to 200 together with the differences from the exact Poisson calculation[11].

The exact Poisson calculation and the normal approximation are fairly consistent and within one count of each other over a wide range.

When the minimum detectable response value is to be determined with a precision of 5 % or less, the measurement conditions should be adjusted so that a minimum of 18 discrete counts are used to set the background values.

Table C.1 — Comparison between the Poisson distribution and the normal approximation

Back-ground	Poisson exact	Normal approximation	Difference	Back-ground	Poisson exact	Normal approximation	Difference
y_b	y_d	y_d		y_b	y_d	y_d	
1	8,2	8,4	−0,1	51	87,8	86,9	0,9
2	11,3	11,3	0,0	52	88,9	88,3	0,7
3	14,1	13,8	0,3	53	90,1	89,6	0,5
4	17,1	16,0	1,0	54	91,2	90,9	0,3
5	18,9	18,1	0,8	55	92,4	92,2	0,2
6	20,8	20,1	0,7	56	93,5	93,5	0,0
7	22,2	22,0	0,2	57	95,7	94,8	0,9
8	24,7	23,9	0,9	58	96,9	96,1	0,8
9	26,1	25,7	0,4	59	98,0	97,4	0,6
10	27,4	27,4	0,0	60	99,2	98,7	0,4
11	29,9	29,1	0,7	61	100,3	100,0	0,3
12	31,2	30,8	0,3	62	101,5	101,3	0,1
13	32,5	32,5	0,0	63	102,6	102,6	0,0
14	34,9	34,1	0,7	64	104,8	103,9	0,9
15	36,1	35,7	0,4	65	105,9	105,2	0,7
16	37,4	37,3	0,1	66	107,1	106,5	0,6
17	39,8	38,9	0,9	67	108,2	107,8	0,4
18	41,0	40,4	0,6	68	109,3	109,1	0,3
19	42,3	42,0	0,3	69	110,5	110,4	0,1
20	43,5	43,5	0,0	70	111,6	111,6	0,0
21	45,8	45,0	0,8	71	113,8	112,9	0,9
22	47,1	46,5	0,5	72	114,9	114,2	0,7
23	48,3	48,0	0,3	73	116,0	115,5	0,6
24	49,5	49,5	0,0	74	117,2	116,7	0,4
25	51,8	51,0	0,8	75	118,3	118,0	0,3

Table C.1 *(continued)*

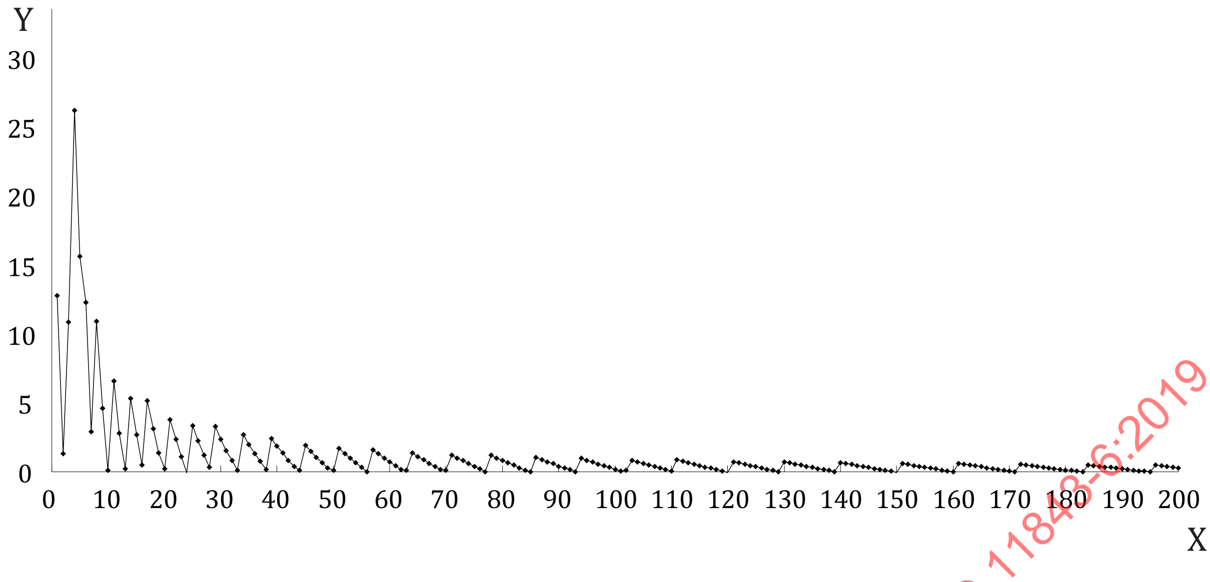
Background y_b	Poisson exact y_d	Normal approximation y_d	Difference	Background y_b	Poisson exact y_d	Normal approximation y_d	Difference
26	53,0	52,4	0,6	76	119,4	119,3	0,2
27	54,2	53,9	0,3	77	120,5	120,5	0,0
28	55,4	55,3	0,1	78	122,7	121,8	0,9
29	57,7	56,8	1,0	79	123,9	123,1	0,8
30	58,9	58,2	0,7	80	125,0	124,3	0,7
31	60,1	59,6	0,5	81	126,1	125,6	0,5
32	61,3	61,0	0,3	82	127,2	126,8	0,4
33	62,5	62,4	0,0	83	128,3	128,1	0,2
34	64,7	63,8	0,9	84	129,5	129,3	0,1
35	65,9	65,2	0,7	85	130,6	130,6	0,0
36	67,1	66,6	0,5	86	132,8	131,9	0,9
37	68,3	68,0	0,3	87	133,9	133,1	0,8
38	69,5	69,4	0,1	88	135,0	134,3	0,6
39	71,7	70,8	1,0	89	136,1	135,6	0,5
40	72,9	72,1	0,8	90	137,2	136,8	0,4
41	74,1	73,5	0,6	91	138,3	138,1	0,3
42	75,2	74,9	0,4	92	139,5	139,3	0,1
43	76,4	76,2	0,2	93	140,6	140,6	0,0
44	77,5	77,6	0,0	94	142,7	141,8	0,9
45	79,8	78,9	0,9	95	143,9	143,1	0,8
46	80,9	80,3	0,7	96	145,0	144,3	0,7
47	82,1	81,6	0,5	97	146,1	145,5	0,6
48	83,3	82,9	0,3	98	147,2	146,8	0,4
49	84,4	84,3	0,1	99	148,3	148,0	0,3
50	85,6	85,6	0,0	100	149,4	149,2	0,2

Table C.1 *(continued)*

Background y_b	Poisson exact y_d	Normal approximation y_d	Difference	Background y_b	Poisson exact y_d	Normal approximation y_d	Difference
101	150,5	150,5	0,1	151	211,8	210,9	0,9
102	151,6	151,7	−0,1	152	212,9	212,1	0,8
103	153,8	152,9	0,9	153	214,0	213,3	0,7
104	154,9	154,2	0,7	154	215,0	214,4	0,6
105	156,0	155,4	0,6	155	216,1	215,6	0,5
106	157,1	156,6	0,5	156	217,2	216,8	0,4
107	158,2	157,8	0,4	157	218,3	218,0	0,3
108	159,3	159,1	0,3	158	219,4	219,2	0,2
109	160,4	160,3	0,2	159	220,5	220,4	0,1
110	161,5	161,5	0,0	160	221,6	221,6	0,0
111	163,7	162,7	1,0	161	223,7	222,7	1,0
112	164,8	163,9	0,9	162	224,8	223,9	0,9
113	165,9	165,2	0,7	163	225,9	225,1	0,8
114	167,0	166,4	0,6	164	227,0	226,3	0,7
115	168,1	167,6	0,5	165	228,1	227,5	0,6
116	169,2	168,8	0,4	166	229,1	228,6	0,5
117	170,3	170,0	0,3	167	230,2	229,8	0,4
118	171,4	171,2	0,2	168	231,3	231,0	0,3
119	172,5	172,5	0,1	169	232,4	232,2	0,2
120	173,6	173,7	0,0	170	233,5	233,4	0,1
121	175,8	174,9	0,9	171	234,6	234,5	0,0
122	176,9	176,1	0,8	172	236,7	235,7	1,0
123	178,0	177,3	0,7	173	237,8	236,9	0,9
124	179,1	178,5	0,6	174	238,9	238,1	0,8
125	180,2	179,7	0,4	175	240,0	239,3	0,7

Table C.1 *(continued)*

Background y_b	Poisson exact y_d	Normal approximation y_d	Difference	Background y_b	Poisson exact y_d	Normal approximation y_d	Difference
126	181,3	180,9	0,3	176	241,0	240,4	0,6
127	182,4	182,1	0,2	177	242,1	241,6	0,5
128	183,5	183,3	0,1	178	243,2	242,8	0,4
129	184,6	184,5	0,0	179	244,3	244,0	0,3
130	186,7	185,8	1,0	180	245,4	245,1	0,2
131	187,8	187,0	0,9	181	246,5	246,3	0,2
132	188,9	188,2	0,8	182	247,5	247,5	0,1
133	190,0	189,4	0,6	183	248,6	248,6	0,0
134	191,1	190,6	0,5	184	250,7	249,8	0,9
135	192,2	191,8	0,4	185	251,8	251,0	0,8
136	193,3	193,0	0,3	186	252,9	252,2	0,8
137	194,4	194,2	0,2	187	254,0	253,3	0,7
138	195,5	195,4	0,1	188	255,1	254,5	0,6
139	196,6	196,6	0,0	189	256,2	255,7	0,5
140	198,7	197,8	1,0	190	257,2	256,8	0,4
141	199,8	198,9	0,9	191	258,3	258,0	0,3
142	200,9	200,1	0,8	192	259,4	259,2	0,2
143	202,0	201,3	0,6	193	260,5	260,3	0,1
144	203,1	202,5	0,6	194	261,6	261,5	0,1
145	204,2	203,7	0,5	195	262,6	262,7	0,0
146	205,3	204,9	0,3	196	264,8	263,8	0,9
147	206,4	206,1	0,2	197	265,8	265,0	0,8
148	207,5	207,3	0,1	198	266,9	266,2	0,7
149	208,6	208,5	0,1	199	268,0	267,3	0,7
150	209,6	209,7	0,0	200	269,1	268,5	0,6



Key

X background counts

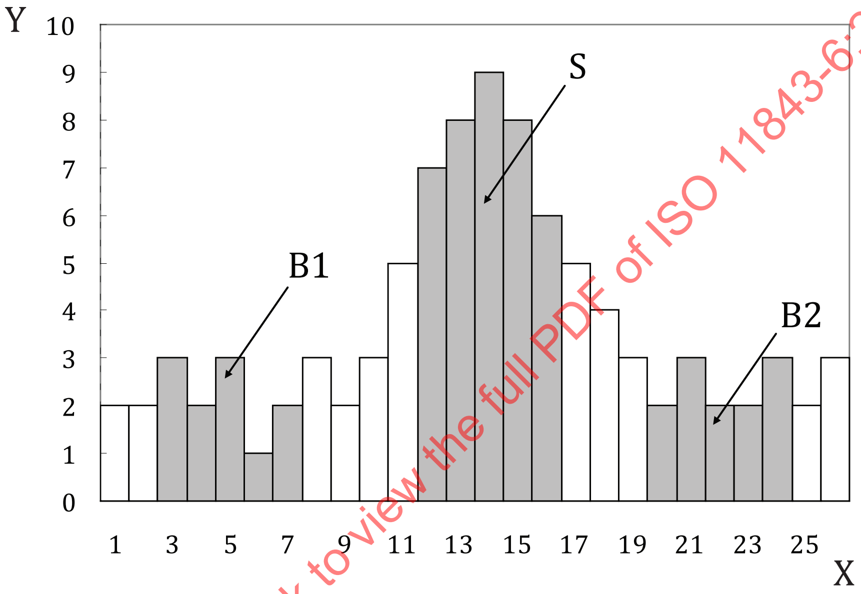
Y difference by percentage (%)

Figure C.1 — The variation in the percent difference between the Poisson distribution and the normal approximation with the background value

Annex D
(informative)

Selecting the number of channels for the detector

The number of detector channels selected for the measurement determines the range that can be covered. It is important to ensure that there is no overlap between neighbouring peaks and that the number of channels is the same for measuring the background noise and for the sample.



Key

X channels

Y relative intensity (counts)

S signal region

B1 left background region

B2 right background region

Figure D.1 — Specification of signal regions

Annex E
(informative)

Examples of calculations

E.1 Example 1: Measurement of hazardous substances by X-ray diffractometry (XRD)

The hazardous substance chrysotile asbestos can be detected using an X-ray diffractometer. 0,10 mg of chrysotile asbestos were weighed accurately, dispersed in pure water, trapped on filter paper and analysed. The quantity analysed was equivalent to 0,10 %, 0,10 mg/100 mg, the maximum regulated value allowed in building materials. Five repeated measurements of the concentration in the blank, x_b $x_b = 0$, and in the unknown, x_g, were conducted. A powder XRD scan of chrysotile asbestos, presented as a plot of relative intensity against the Bragg angle, 2θ, is given in Figure E.1. Using five repetitions, the capability of detection was calculated for $K = J = 1$ and $\alpha = \beta = 0,05$.

Conditions of measurements:

Instrument: X-ray diffractometer

X-ray source: Cu, providing a 0,154 nm K-alpha monochromatic X-ray

Output power: 40 kV, 40 mA

Channel width: 0,02 degrees of the Bragg angle, 2θ

Total number of channels: 23 (for both background noise and peak area)

Number of measurements: 5

Accumulation time of each channel: 0,2 s

Full width at half maximum (FWHM): 0,46 degrees of the Bragg angle, 2θ