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Air quality — Determination of performance characteristics of measurement methods

Qualité de l'air — Détermination des caractéristiques de performance des méthodes de mesurage

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Foreword

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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.

International Standard ISO 9169 was prepared by Technical Committee ISO/TC 146, *Air quality*, Subcommittee SC 4, *General aspects*.

Annexes A, B and C form an integral part of this International Standard. Annex D is for information only.

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Air quality — Determination of performance characteristics of measurement methods

1 Scope

This International Standard specifies procedures to quantify the following performance characteristics of air quality measurement methods defined in ISO 6879[1]: bias (in part only), calibration function and linearity, instability, lower detection limit, period of unattended operation, selectivity, sensitivity, upper limit of measurement.

The procedures given are applicable only to air quality measurement methods with linear[2] continuous calibration functions, the output variable of which is a defined time average. Additionally, replicate values belonging to the same input state are assumed to be normally distributed. Components needed to transform the primary measurement method output into the time averages desired are regarded as integral parts of this measurement method.

For measurement method stability surveillance under routine measurement conditions, it may suffice to check the essential performance characteristics using simplified tests, the degree of simplification acceptable being dependent on the knowledge of the invariance properties of the performance characteristics previously gained by the procedures presented here.

There is no fundamental difference between the instrumental (automatic) and the manual (e.g. wet-chemical) procedures as long as the measured value is an average representative for the predefined time interval. Therefore, the procedures given are applicable to both. Furthermore, they are applicable to measurement methods for ambient air, indoor air, workplace air, and emissions.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 3534-1:1993, *Statistics — Vocabulary and symbols — Part 1: Probability and general statistical terms.*

ISO 5725:1986, *Precision of test methods — Determination of repeatability and reproducibility for a standard test method by inter-laboratory tests.*

ISO 6879:—[3], *Air quality — Performance characteristics and related concepts for air quality measurement methods.*

1) The definition of method in ISO 6879:1983, 4.2.1.9 implies a specific instrumental setup.

2) This linearity may be enforced by a certain amount of postprocessing of the primary output variable.

3) To be published. (Revision of ISO 6879:1983)

3 Definitions

For the purposes of this International Standard the following definitions apply:

NOTE 1 The term *measuring system* used in the context of this International Standard does not constitute a new definition, as compared to the basic terms given in ISO 6879; it merely indicates a tangible realization of a measuring procedure.

3.1 averaging time, $\Delta\Theta$: Predefined time interval for which the air quality characteristic is made representative.

NOTE 2 Every measured value obtained is representative of a defined interval of time, τ, the value of which always lies above a certain minimum due to the intrinsic properties of the measuring procedure applied. In order to attain mutual comparability of data pertaining to comparable objects, a normalization to a common, predefined interval of time is necessary. By convention, this normalization is achieved by transformation by means of a simple, linear and unweighted averaging process.

Averaging of a series of discrete samples:

$$\hat{c}(\Theta|\Delta\Theta) = \frac{1}{K}\sum_{k=1}^{K}\hat{c}[\Theta_0 + (k-1)\tau|\tau] \qquad \ldots (1)$$

where

$$\Theta_0 = \Theta - \Delta\Theta$$

$$K\tau = \Delta\Theta, \quad \tau \ll \Delta\Theta$$

Averaging of a continuous time series:

$$\hat{c}(\Theta|\Delta\Theta) = \frac{1}{\Delta\Theta}\int_{\Theta_0}^{\Theta} \mathrm{d}\Theta\ \hat{c}(\Theta|\tau) \qquad \ldots (2)$$

In both cases, the original sample described by $\hat{c}(\tau)$ is linked to a representative interval of time τ, whereas $\hat{c}(\Delta\Theta)$, the result after application of the averaging process, is made representative for the interval of time $\Delta\Theta$ (just preceding Θ), the averaging time.

The averaging time, $\Delta\Theta$, is therefore the predefined and, by convention, common time interval for which the measured variable $\hat{c}$ is made representative in the sense that the square deviation of the original values, attributed to time intervals $\tau \ll \Delta\Theta$, from $\hat{c}$ over $\Delta\Theta$ is a minimum.

NOTE 3 The averaging process can alternatively be carried out by means of a special sampling technique (averaging by sampling).

3.2 continuously measuring system: System returning a continuous output signal upon continuous interaction with the air quality characteristic.

3.3 non-continuously measuring system: System returning a series of discrete output signals.

NOTE 4 The discretization of the output variable can be due to sampling in discrete portions or to inner function characteristics of the system components.

3.4 influence variable: Variable affecting the interrelationship between the (true) values of the air quality characteristic observed and the corresponding measured values, e.g. variable affecting the slope or the intercept of or the scatter around the calibration function.

3.5 reference conditions: Specified set of values (including tolerances) of influence variables delivering representative values of performance characteristics.

3.6 period of unattended operation: Maximum admissible interval of time for which the performance characteristics will remain within a predefined range without external servicing, e.g. refill, calibration, adjustment.

3.7 randomization: Drawing of numbers, from a population consisting of the natural numbers 1 to n, at random one by one successively without replacement until the population is exhausted, these numbers having been associated in advance with n distinct objects or n distinct operations which are then rearranged in the order in which the numbers are drawn.

The order of the objects or operations is then said to be randomized. (See ISO 3534-1.)

3.8 random variable: Variable which may take any of the values within a specified set of values and with which is associated a probability distribution. [ISO 3534-1]

3.9 variance function: Variance of the output variable as a function of the air quality characteristic observed.

3.10 warm-up time: Minimum waiting time for an instrument, after switching on, to meet predefined values of its performance characteristics stabilized in a non-operating condition.

NOTES

5 In practice, warm-up time can be determined by using the performance characteristic that is expected to need the longest time to stabilize.

6 In the case of manual procedures, the corresponding term is *run-up time*.

4 Symbols

a_0, a_1, a_2	Coefficients of the variance function model
b_0, b_1	Parameters of the estimate function for the calibration function
C	Air quality characteristic
c	Value of C
$\hat{c}$	Measured value at c
c_i	Value of C in the ith sample; this sample may be generated from reference material
c_0	Normalization factor for air quality characteristics; in this case $\|c_0\| = 1$
Δc_i	Inaccuracy of C at c_i
$\bar{c}_\omega$	Weighted mean, with set of weights ω_k
DEP$(\hat{c})_{IV_i}$	First-order dependence of the measured value on the ith influence variable at c
DEP$(b_0)_{IV_i}$	First-order dependence of the intercept on the ith influence variable
DEP$(b_1)_{IV_i}$	First-order dependence of the slope on the ith influence variable
DEP$(x)_{IV_i}$	First-order dependence of the output signal on the ith influence variable
$D(b_0)$	Drift (see ISO 6879) of the intercept of the linear calibration function
$D(b_1)$	Drift of the slope of the linear calibration function
$D(\hat{c})$	Drift of the measured value, $\hat{c}$, at c
F	Statistic (cf. F-test)
F_x	x-quantile of the F-distribution
I_{IV_i}	Selectivity with respect to the ith influence variable
IV_i	ith influence variable
iv_i	Value of IV_i
Δiv_i	Difference of values of IV_i
L	Total number of measurements of instability test
LDL	Lower detection limit
M	Total number of samples generated by reference material within one calibration experiment
N_i	Number of values of the output variable at c_i
p_l, p_u	Estimate of the slope of the regression function of the output variable with time at $c = c_l$, $c = c_u$ respectively
RES$_c$	Resolution at $C = c$
R, r	Reproducibility and repeatability, respectively
$\hat{s}$	Estimate of the smoothed standard deviation of X at c
$\hat{s}^2$	Smoothed estimate of the variance of X (repeated measurements) at c
s_0	Normalization factor for the standard deviation; in this International Standard the value of s_0 is assumed to be 1
s_{b_0}, s_{b_1}	Estimate of the standard deviation of instability (see ISO 6879) of the intercept, and of the slope of the linear calibration function, respectively
s_c	Estimate of the standard deviation of instability at c
$s_{\hat{c}x}$	Estimate of the standard deviation of the experimentally determined calibration function (in units of the air quality characteristic)
$s_{\hat{x}c}$	Estimate of the standard deviation of the experimentally determined calibration function (in units of the output variable)
s_i	Estimate of the standard deviation of repeated x_{ij} at c_i; j repetition index
$\hat{s}_i$	Smoothed estimate of the standard deviation of repeated x_{ij} at c_i; j repetition index
s_r	Estimate of the repeatability standard deviation

$t_{\nu;q}$	q-quantile of the t-distribution with ν degrees of freedom
TC	Test characteristic of Grubbs' outlier test
X	Output variable
x	Value of X
$\hat{x}$	Estimate of x
$\hat{x}_i$	Estimate of output signal at c_i
$\bar{x}_i$	Mean of the set of output signals at c_i
$x_{i,\text{extr}}$	Output signal at c_i with the highest absolute distance from $\bar{x}_i$
x_{ij}	jth output signal at c_i
$x_{\text{l};i}$, $x_{\text{u};i}$	Output signal after i time intervals at the lower and upper value of the air quality characteristic of the reference material
$\bar{x}_\omega$	Weighted mean of the whole set of output signals within the calibration experiment
β_0, β_1	Intercept and slope of the linear calibration function, respectively
Θ	Time
ν	Number of degrees of freedom in the calibration experiment
ν_1, ν_2	Number of degrees of freedom for the numerator of the F-distribution, respectively
$\omega = \omega(c)$	Continuous weighting factor gained by modelling s_i
ω_i	Weighting factor at c_i

5 Requirements

5.1 Description of the procedure

All steps of the measurement method such as sampling, analysis, postprocessing and calibration shall be described. Figure 1 illustrates schematically the steps to be followed in making a measurement or performing a series of calibration experiments in order to determine performance characteristics.

NOTE 7 Under certain conditions it may be suitable to test only one step or a selected group of steps of the measurement method. Under other conditions it may not be possible to include all steps of the measurement method. It is recommended to include as many steps as possible.

5.2 Specification of performance characteristics to be tested

The performance characteristics of the measurement method shall be specified in order of their relevance for the final assessment of accuracy. The descriptors of the calibration function, i.e. intercept, β_0, and slope, β_1, as well as their qualifying performance characteristics are vital. Those performance characteristics for which prior knowledge is available, and those pertaining influence variables covered by randomization, are of lesser importance and need not be determined.

5.3 Test conditions

Perform the tests under explicitly stated conditions which must be representative of the operational measurements. When testing for statistical performance characteristics, all specified influence variables shall remain constant. When testing for performance characteristics describing functional dependencies, all influence variables shall remain constant except the one under consideration.

By convention, the statistical performance characteristics used in this International Standard are estimated throughout at the confidence level $1 - \alpha = 0{,}95$.

6 Test procedures

6.1 Averaging time (see 3.1)

The range of allowable averaging times is constrained by the requirement that the differences among subsequent output signals be mutually statistically independent. The corresponding minimum of the averaging time is determined by a specific performance (time) characteristic:

a) for continuously measuring systems: the response time;

b) for non-continuously measuring systems: the sample time (filling time, accumulation time etc.).

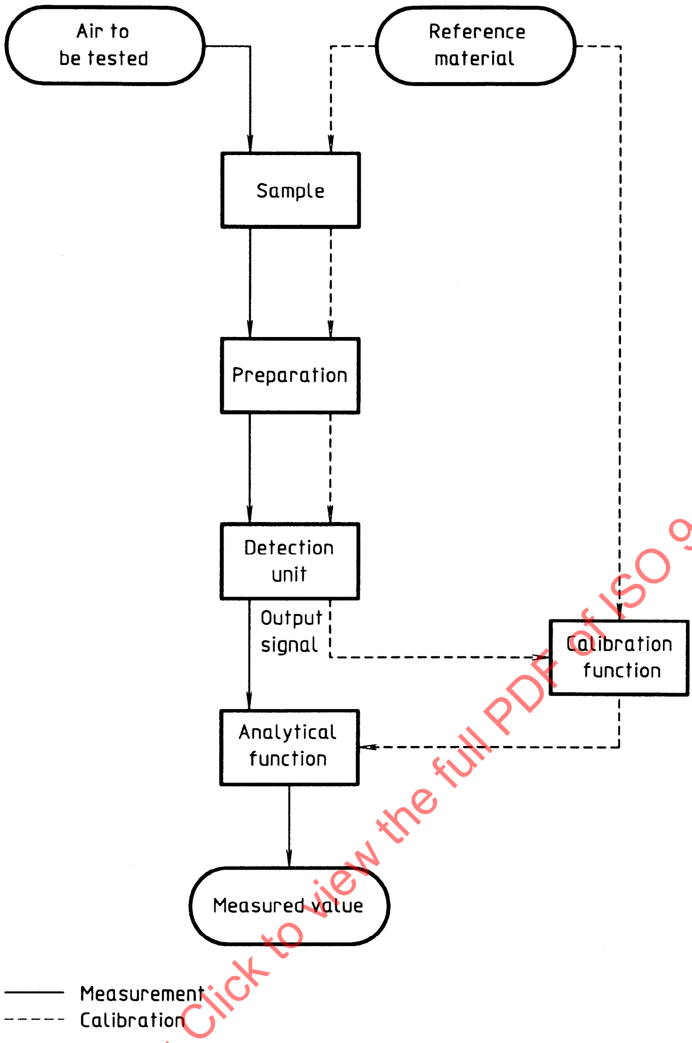


Figure 1 — Scheme of the measurement and evaluation of performance characteristics

6.1.1 Continuously measuring systems

In order to establish response time, lag time, rise time and fall time, a step function of the air quality characteristic is input to the continuously measuring system. This may be done by abruptly changing the value of the air quality characteristic from e.g. 20 % to 80 % of the upper limit of measurement (see figure 2). These performance characteristics should be confirmed by an appropriate number of repetitions. If rise time and fall time differ, the longer one is to be taken for the computation of the response time. By convention, the minimum averaging time equals four times the response time.

6.1.2 Non-continuously measuring systems

The minimum averaging time is determined by the maximum of the sampling time, filling time or accumulation time, depending on the measurement method.

6.2 Functional and statistical performance characteristics[4)]

The performance characteristics to be determined are

a) those related to the calibration function and its stability under reference conditions;

b) those related to the dependence of the calibration function on influence variables.

4) The functional and statistical performance characteristics may be calculated on a computer using the TurboPascal program adjunct to ASTM Standard D 5280, available from ASTM, 1916 Race St., Philadelphia PA 19103-1187, USA.

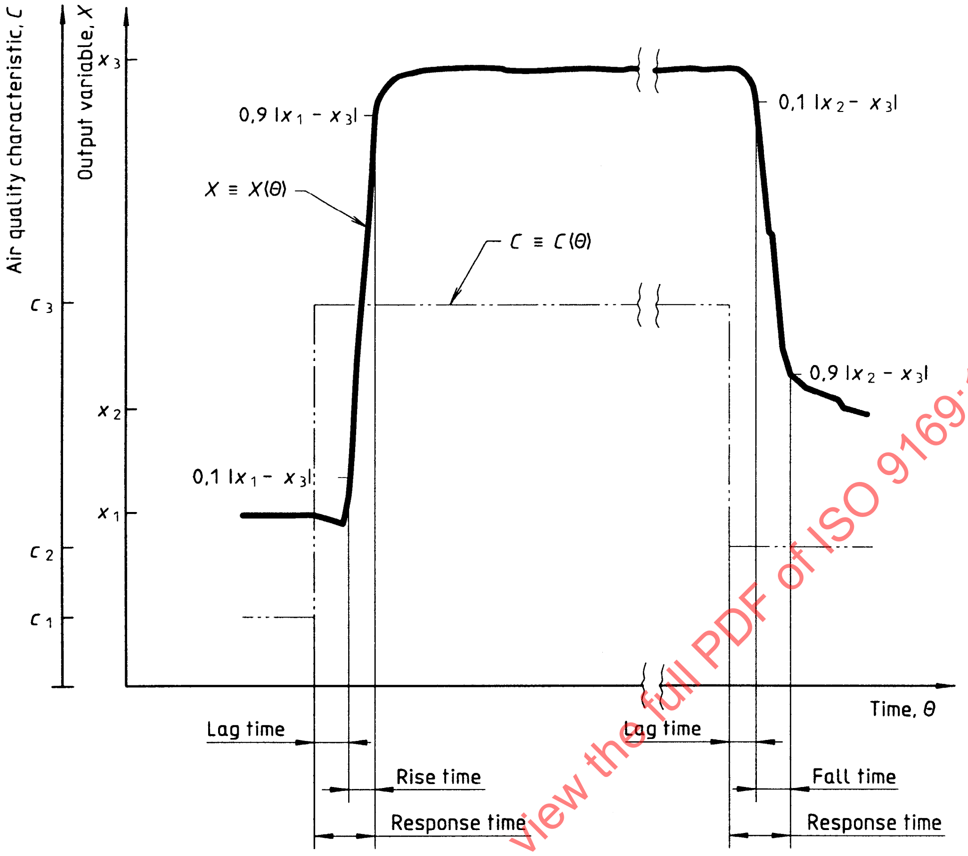


Figure 2 — Diagram illustrating the performance (time) characteristics of a continuously measuring system

A linear calibration function is determined by its slope (sensitivity) and its intercept. Instability and the effects of influence variables are described by their impacts on the slope (sensitivity) and intercept.

All ouput signals evaluated throughout these tests shall be obtained after the measuring system has reached stabilized conditions.

NOTE 8 Repetitions performed under reproducibility conditions (see ISO 5725) require a random sample of the population of the influence variables to be examined (randomization).

6.2.1 Calibration

A calibration experiment for the evaluation of performance characteristics consists of at least ten repeated measurements at a minimum of five different values of the air quality characteristic.

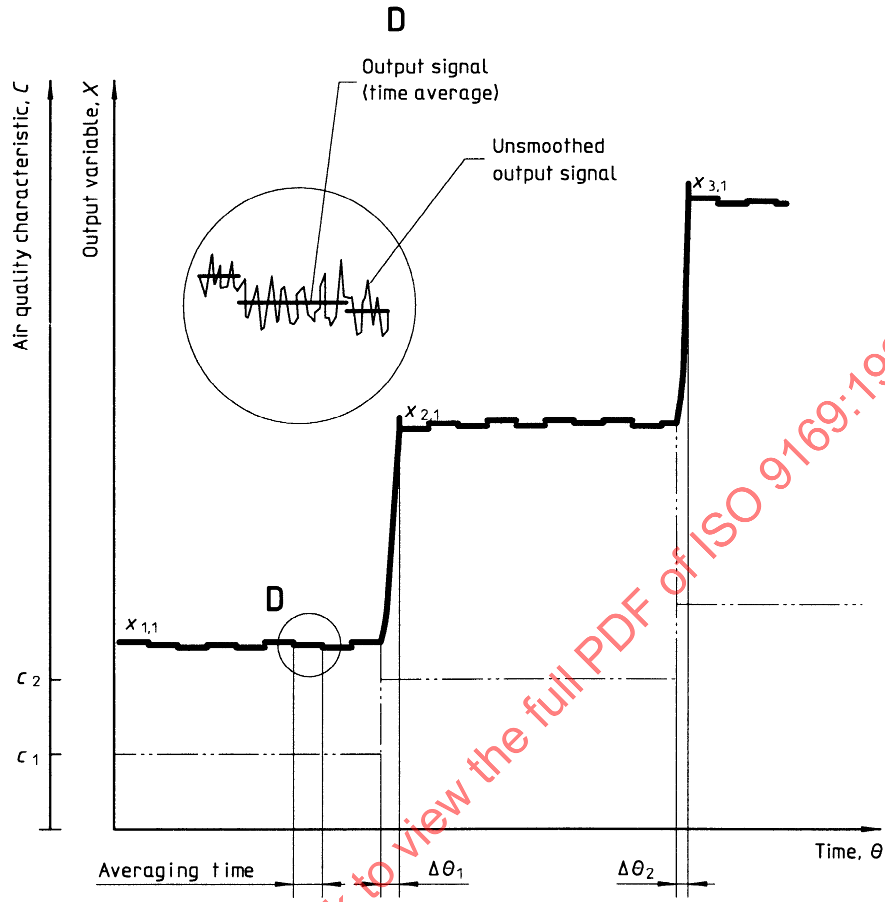
If drift occurs, the duration of the calibration experiment shall be kept as short as possible. This may be accomplished by consecutive instrument readings at a certain value of the air quality characteristic and after a change in that value and stabilization, again consecutive instrument readings at that value, etc. (see figure 3). This is only valid in the absence of hysteresis or if hysteresis is negligible.

6.2.1.1 Elimination of outliers

Usually, experience helps to identify potential outliers. A less arbitrary way of detection of such potential outliers is given by combination of this experience with, e.g., Grubbs' test [1]. However, it should be clear that such a test identifies *potential* outliers. The underlying reasons may be statistical or due to system operation interferences. The latter presents sufficient grounds for elimination of the respective output signal (confirmation as an outlier).

Estimate the standard deviation s_i at c_i by:

$$s_i = \sqrt{\left[\sum_j x_{ij}^2 - \left(\sum_j x_{ij}\right)^2 / N_i\right] / (N_i - 1)} \qquad \ldots (3)$$



x_{ij} jth time average over the interval of time $\Delta\Theta$ at the ith value of the air quality characteristic, generated by reference material

$\Delta\Theta_i$ Intervals of time during which unsmoothed output signals shall not be submitted to the averaging procedure and, thus, not be evaluated

Figure 3 — Example of a calibration experiment

At c_i, take the ouput signal $x_{i,\text{extr}}$ with the highest absolute distance from the mean output signal $\bar{x}_i$. Derive the test characteristic

$$\text{TC} = |x_{i,\text{extr}} - \bar{x}_i|/s_i \qquad \ldots (4)$$

where

$$\bar{x}_i = \left(\sum_j x_{ij}\right)/N_i \qquad \ldots (5)$$

and compare it with the tabulated value of Grubbs' two-sided outlier test (see annex A) to be taken as the critical value.

If TC exceeds the critical value, check if it is due to operational reasons, and if so, reject it. This procedure may be repeated; however, if more than 5 % of the number of output signals is rejected this way, this calibration experiment is not valid.

If operational reasons are not found for TC exceeding the critical value, the potential outlier may not be eliminated. In this case, verification of a basic test assumption or prerequisite is recommended.

6.2.1.2 Computation of the variance function

A central tool for the estimation of relevant performance characteristics is the variance function. Therefore, some guidelines for its computation, and the computation of related parameters are given.

Compute for each of the values c_i ($i = 1$ to M) of the air quality characteristic the variance s_i^2 of the output signals x_{ij} ($j = 1$ to N_i):

$$s_i^2 = \left[\sum_j x_{ij}^2 - \left(\sum_j x_{ij} \right)^2 / N_i \right] / (N_i - 1) \qquad \ldots (6)$$

Additionally, the dependence of s_i^2 on c is modelled [2] using

$$\log \frac{\hat{s}^2}{s_0^2} \approx a_0 + a_1 \sqrt{\frac{c}{c_0}} + a_2 \left(\sqrt{\frac{c}{c_0}} \right)^2 \qquad \ldots (7)$$

so the coefficients of this non-weighted second-order polynomial in $\sqrt{\frac{c}{c_0}}$ can be computed as:

$$a_2 = \frac{[Q_{(z^2, y)} \, Q_{(z, z)} - Q_{(z, y)} \, Q_{(z, z^2)}]}{\left[Q_{(z, z)} \, Q_{(z^2, z^2)} - (Q_{(z, z^2)})^2 \right]}$$

$$a_1 = \frac{[Q_{(z, y)} \, Q_{(z^2, z^2)} - Q_{(z^2, y)} \, Q_{(z, z^2)}]}{\left[Q_{(z, z)} \, Q_{(z^2, z^2)} - (Q_{(z, z^2)})^2 \right]} \qquad \ldots (8)$$

$$a_0 = \frac{\left(\sum_i y_i - a_1 \sum_i z_i - a_2 \sum_i z_i^2 \right)}{M}$$

with

$$Q_{(\zeta^m, \eta^n)} = \frac{\sum_i (\zeta_i^m \, \eta_i^n) - \left(\sum_i \zeta_i^m \right) \left(\sum_i \eta_i^n \right)}{M} \qquad \ldots (9)$$

Element $Q_{(\zeta^m, \eta^n)}$ is obtained by substituting ζ with z and η with z or y:

$$y_i = \log \frac{s_i^2}{s_0^2} \; ; \; z_i = \sqrt{\frac{c_i}{c_0}} \qquad \ldots (10)$$

An example of a variance function obtained this way is given in figure 4.

Consequently, the smoothed variance function $\hat{s}^2$ is obtained as:

$$\hat{s}^2 = \hat{s}^2(c) = s_0^2 \exp \left(a_0 + a_1 \sqrt{\frac{c}{c_0}} + a_2 \frac{c}{c_0} \right) \ldots (11)$$

The weighting factor, ω_i, at c_i ($i = 1$ to M), to be used later in the computation of the calibration function [1,2,3], is proportional to the inverse of the above variance,

$$\omega = \omega(c) = \frac{s_0^2}{\hat{s}^2} \qquad \ldots (12)$$

6.2.1.3 Computation of the calibration function

A linear calibration function [5]

$$x = \beta_0 + \beta_1 \, c \qquad \ldots (13)$$

may be estimated by

$$\hat{x} = b_0 + b_1 \, c \qquad \ldots (14)$$

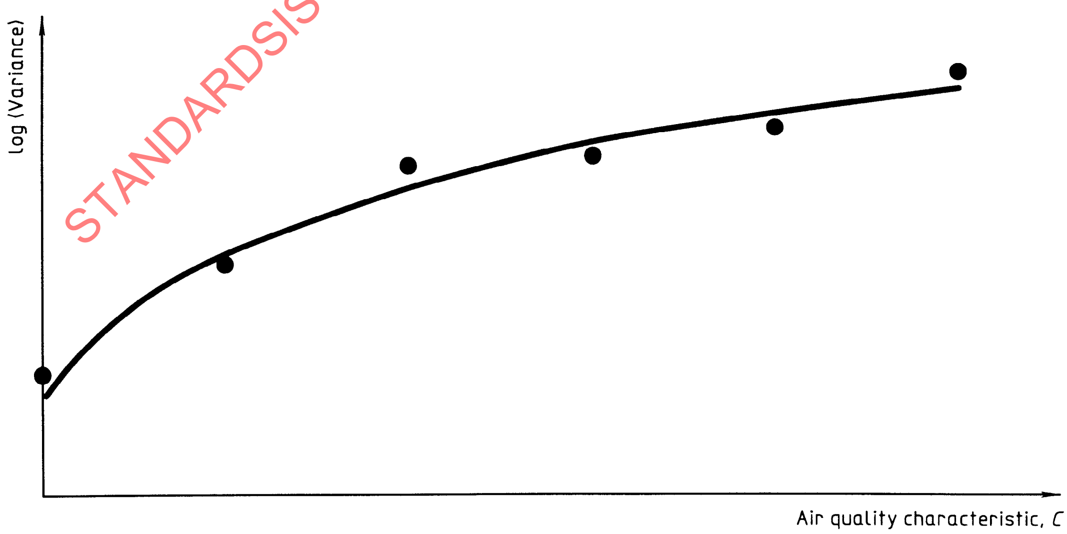


Figure 4 — Fit of the logarithm of the variance function

where

$$b_1 = \frac{\sum_i \sum_j \omega_i \, x_{ij} \, (c_i - \bar{c}_\omega)}{\sum_i N_i \, \omega_i \, (c_i - \bar{c}_\omega)^2}$$

$$b_0 = \bar{x}_\omega - b_1 \, \bar{c}_\omega \qquad \ldots (15)$$

and

$$\bar{c}_\omega = \sum_i N_i \, \omega_i \, c_i \, / \sum_k N_k \, \omega_k$$

$$\bar{x}_\omega = \sum_i \sum_j \omega_i \, x_{ij} \, / \sum_k N_k \, \omega_k \qquad \ldots (16)$$

In addition to the various standard deviations defined as descriptors for the mutual scattering of true values, measured values and output signals, there arises a special scatter to be attributed to the estimation process as a whole.

This scatter may be described by the following standard deviation [2]:

$$s_{\hat{x}c} = \sqrt{\frac{\sum_{i=1}^{M} \omega_i \sum_{k=1}^{N_i} (x_{ik} - \hat{x}_i)^2}{\left(\sum_{i=1}^{M} N_i\right) - 2}} \qquad \ldots (17)$$

Sometimes the output signal is obtained after correction for the blank. When the blanks correspond to genuine zero samples, the corrected calibration function must pass through the origin. In this case the coefficient, b_1, reduces to:

$$b_{1;\text{trf}} = \frac{\sum_i \sum_j \omega_i \, x_{ij} \, c_i}{\sum_k N_k \, \omega_k \, c_k^2} \qquad \ldots (18)$$

The standard deviation, $s_{\hat{x}c}$, is invariant to the transformation, but the number of degrees of freedom changes to:

$$\nu_{\text{trf}} = \left(\sum_{i=1}^{M} N_i\right) - 1 \qquad \ldots (19)$$

6.2.1.4 Computation of the analytical function

Compute the analytical function by inverting the calibration function:

$$\hat{c} = \frac{x - b_0}{b_1} \qquad \ldots (20)$$

6.2.1.5 Linearity

The hypothesis of linearity of the calibration function (see figure 5) is examined using the F-test [6]:

$$F = \frac{\left[\sum_i N_i \, \omega_i \, (\bar{x}_i - \hat{x}_i)^2\right] / \nu_1}{\left[\sum_i \sum_j \omega_i \, (x_{ij} - \bar{x}_i)^2\right] / \nu_2} \qquad \ldots (21)$$

where

$$\nu_1 = M - 2$$

$$\nu_2 = \sum_i (N_i - 1)$$

If F does not exceed the tabulated value $F_{\nu_1, \nu_2; 1-\alpha}$ of the F-distribution for the one-sided test for the significance level $\alpha = 0{,}05$ (see annex B) to be taken as critical value, non-linearity is negligible, and the subsequent performance characteristics can be determined.

If F does exceed the critical value, the hypothesis of linearity must be rejected. The question whether non-linearity is substantial as compared to other uncertainties may be tested by determining whether the following inequality criterion holds:

$$\operatorname{Max}_{i=1}^{M} \left\{ \frac{|\bar{x}_i - \hat{x}_i|}{2 \, s_i} \right\} < 1 \qquad \ldots (22)$$

If the inequality criterion is met (see figure 5), the subsequent performance characteristics can be calculated. If the inequality criterion is not met, the determination of performance characteristics must be terminated. For the latter situation, the following procedure is recommended:

a) Examine the quality of reference material samples as a potential cause for non-linearity.

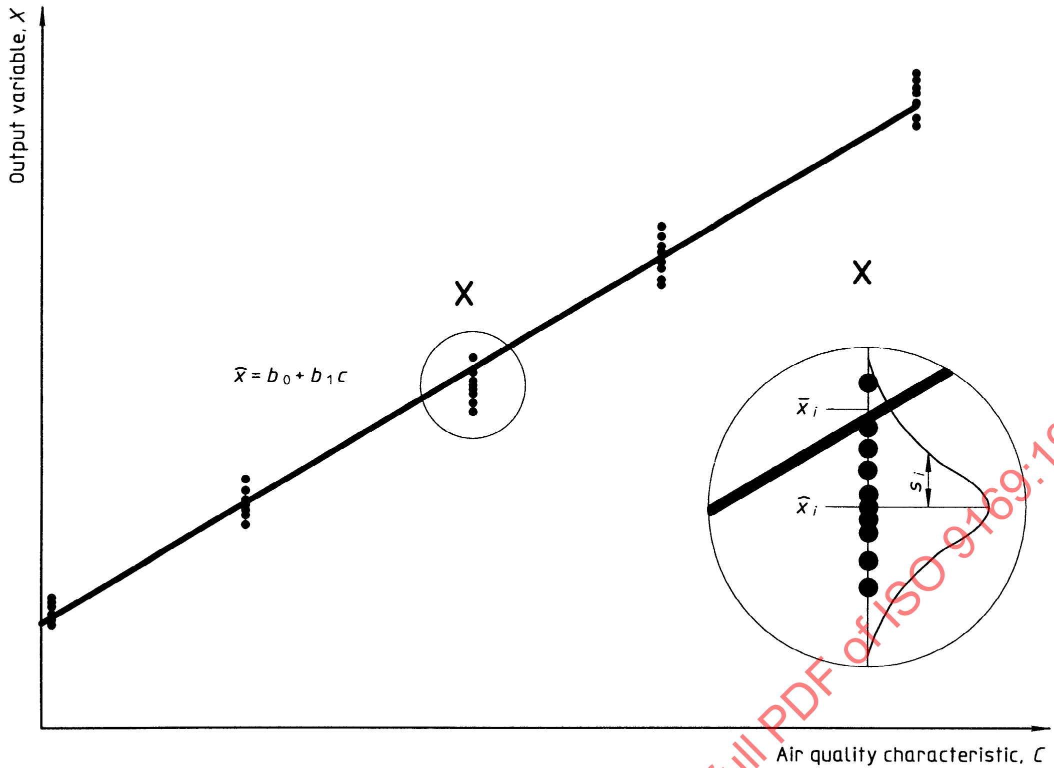


Figure 5 — Graph of a non-linear calibration function — Hypothesis of linearity rejected

b) If, based on the result of this examination, the problem cannot be solved, examine whether the subrange in which the inequality criterion is fulfilled contains the region of interest, or test for a monotonic transformation with a monotonic first derivative to reduce the deviation from linearity.

c) If the possibility of reducing the deviation from linearity is accepted, then a definition of a new measurement method requiring a new run for performance characteristics is required.

6.2.1.6 Uncertainty due to estimating the calibration function

The coefficients of the calibration function, b_0 and b_1, are estimates from a limited number of measurements. They will thus deviated from the true values which would be obtained with a complete set. Therefore any estimated value of measurement $\hat{c}$, obtained via the calibration function, will deviate from the true value. This deviation will change at random whenever the measuring system is calibrated.

The uncertainty of a measured value, $\hat{c}$, under the calibration experiment performed, may be described [3] by the estimate $s_{\hat{c}x}$ for the respective standard deviation (cf. 6.2.1.3)

$$s_{\hat{c}x} = \frac{s_{\hat{x}c}}{b_1}\left[\frac{1}{\sum_i N_i\,\omega_i} + \frac{(c-\bar{c}_\omega)^2}{\sum_i N_i\,\omega_i\,(c_i-\bar{c}_\omega)^2}\right]^{1/2} \qquad \ldots (23)$$

For a simplified two-point field calibration, assuming the performance characteristics evaluated remain stable, the following approximation formula may be used:

$$s_{\hat{c}x} \approx \frac{1}{b_1}\left[\left(1-\frac{c}{c_{sp}}\right)^2 \hat{s}^2(0) + \left(\frac{c}{c_{sp}}\right)^2 \hat{s}^2(c_{sp})\right]^{1/2} \qquad \ldots (24)$$

with the reference materials at

$C = 0$ (zero sample),

$C = c_{sp}$ (span sample).

6.2.1.7 Precision

6.2.1.7.1 Repeatability

Repeatability, r, is calculated using the variance function referring to the corresponding conditions (see ISO 5725).

Calculate the smoothed variance, $\hat{s}^2(c)$, (see 6.2.1.2) and hence estimate the repeatability standard deviation by:

$$s_r = \frac{\sqrt{\hat{s}^2(c)}}{b_1} \qquad \ldots (25)$$

Compute the repeatability, r, from:

$$r = t_{v;0,975}\, s_r \sqrt{2} \qquad \ldots (26)$$

where $t_{v;0,975}$ is the tabulated value $t_{v;1-\alpha/2}$ of the t-distribution for the two-sided test for the significance level $\alpha = 0,05$ (see annex C) and for v degrees of freedom ($v = \underset{i}{\mathrm{Min}}\,\{N_i - 1\}$).

NOTE 9 The presence of the factor $\sqrt{2}$ is due to the fact that r and R, by definition, refer to the difference between two single measurements.

6.2.1.7.2 Reproducibility

The performance test for reproducibility is described in ISO 5725.

6.2.1.8 Measurement resolution

Measurement resolution at $C = c$ may be estimated by:

$$\mathrm{RES}_c = \frac{t_{v;0,95}\, \hat{s}_c \sqrt{2}}{b_1} \qquad \ldots (27)$$

6.2.1.9 Lower limit of detection

Calculate the variance, $\hat{s}^2(0)$, at $C = 0$ from the variance function (6.2.1.2). The repeatability standard deviation is then, according to 6.2.1.7:

$$s_r = \frac{\sqrt{\hat{s}^2(0)}}{b_1} \qquad \ldots (28)$$

For reference conditions of operation, the lower detection limit (LDL) becomes:

$$\mathrm{LDL} = t_{v;0,95} \sqrt{s_r^2 + s_{\hat{c}x}^2} \quad (s_r \text{ and } s_{\hat{c}x} \text{ at } C = 0) \qquad \ldots (29)$$

6.2.1.10 Upper limit of measurement

The upper limit of measurement is approximated by the value of the air quality characteristic corresponding to the maximum measured value confirmed by the calibration process.

NOTE 10 For methods featuring signal averaging, the operational upper limit of measurement will be reduced by fluctuations of the value of the air quality characteristic within the averaging period.

6.2.2 Instability

Performance characteristics are assumed not to change with time. However, in practice they do. In particular, a change in the coefficients b_0 and b_1 of the calibration function may considerably influence the accuracy of the measured value. The change in the coefficients over a stated period of time (instability) may have a systematic part (drift) and a random part (dispersion). It is assumed that the value of drift is a constant. The value of the dispersion standard deviation is equal to or greater than the repeatability standard deviation.

Drift and dispersion are derived from the linear regression of the output variable with time, where the time interval between successive output signals is the time interval of interest (figure 6). Drift is equal to the slope of the regression function and dispersion is measured by the standard deviation of the residuals.

6.2.2.1 Test procedure

Select the interval of time, $\Delta\Theta$, over which the instability is to be tested, i.e. the interval of time between intended calibrations.

Use reference materials of $C = c_l$ and $C = c_u$ (c_l in the lower and c_u in the upper part of the range of measurement; $c_l \ll c_u$).

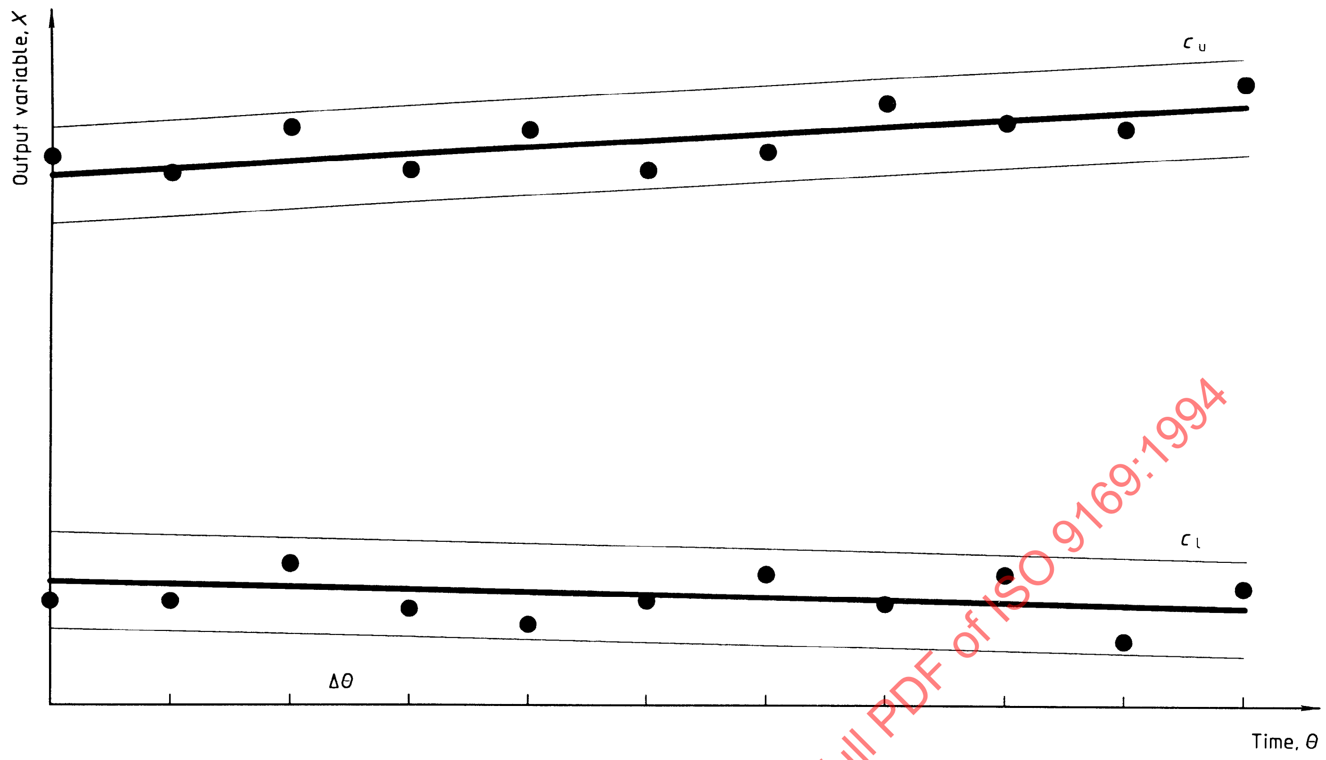


Figure 6 — Example of instability test results

At $\Theta = 0$, sample at $C = c_l$. Record the corresponding output signal $x_{l;0}$.

Sample at $C = c_u$. Record the corresponding output signal $x_{u;0}$.

Repeat this process at equal time intervals, $\Delta\Theta$. The total number of measurements, L, should be at least eight.

6.2.2.2 Calculation of limits

For $C = c_l$, compute the drift, p_l, and the dispersion standard deviation, s_l.

$$p_l = \frac{\sum_i \Theta_i \, x_{l;i} - \left(\sum_i \Theta_i\right)\left(\sum_i x_{l;i}\right)/L}{\sum_i \Theta_i^2 - \left(\sum_i \Theta_i\right)^2/L} \qquad \ldots (30)$$

$$s_l = \sqrt{\frac{1}{L-2} \sum_i \left[x_{l;i} - \bar{x}_l - p_l(\Theta_i - \bar{\Theta})\right]^2} \qquad \ldots (31)$$

For $C = c_u$, compute the corresponding values of p_u and s_u.

6.2.2.3 Calculation of drift

The drift is expressed as the change in b_0 and b_1 of the calibration curve with time:

$$D(b_0) = \frac{\Delta b_0}{\Delta\Theta} = \frac{c_l \, p_u - c_u \, p_l}{c_l - c_u} \qquad \ldots (32)$$

$$D(b_1) = \frac{\Delta b_1}{\Delta\Theta} = \frac{p_u - p_l}{c_u - c_l} \qquad \ldots (33)$$

It follows then, that for any value $C = c$ in the range considered, the estimated drift becomes:

$$D(\hat{c}) = \frac{\Delta c}{\Delta\Theta} = \frac{1}{b_1}\left[D(b_0) + c \, D(b_1)\right] \qquad \ldots (34)$$

6.2.2.4 Calculation of dispersion

The standard deviations of b_0 and b_1 are developed assuming $(c_u/c_l) > (s_u/s_l) \geqslant 1$:

$$s_{b_0} = \sqrt{\frac{c_u^2 \, s_l^2 - c_l^2 \, s_u^2}{c_u^2 - c_l^2}} \qquad \ldots (35)$$

$$s_{b_1} = \sqrt{\frac{s_u^2 - s_l^2}{c_u^2 - c_l^2}} \qquad \ldots (36)$$

Finally, the contribution of dispersion to instability is expected to be:

$$s_{\text{inst}} = \frac{1}{b_1} \sqrt{s_{b_0}^2 + c^2\, s_{b_1}^2} \qquad \ldots (37)$$

If the dispersion does not exceed the respective repeatability standard deviation, long-term fluctuations are negligible in the interval of time, $\Delta\Theta$, evaluated.

6.2.3 Dependence of the measured value on influence variables

This test is designed to estimate the performance obtained under field conditions[5]. It is assumed that the impact of the influence variable on the measured value can be adequately determined by tests at the extremes (see figure 7).

Divide the influence variables into classes of known and unknown effects on the measured value. Examples of the former are temperature and pressure as long as a classical gas state equation holds. Usually, however, the relationship is more complicated and unknown, e.g. the effects of temperature via electronics, those due to line voltage, and interferent concentrations.

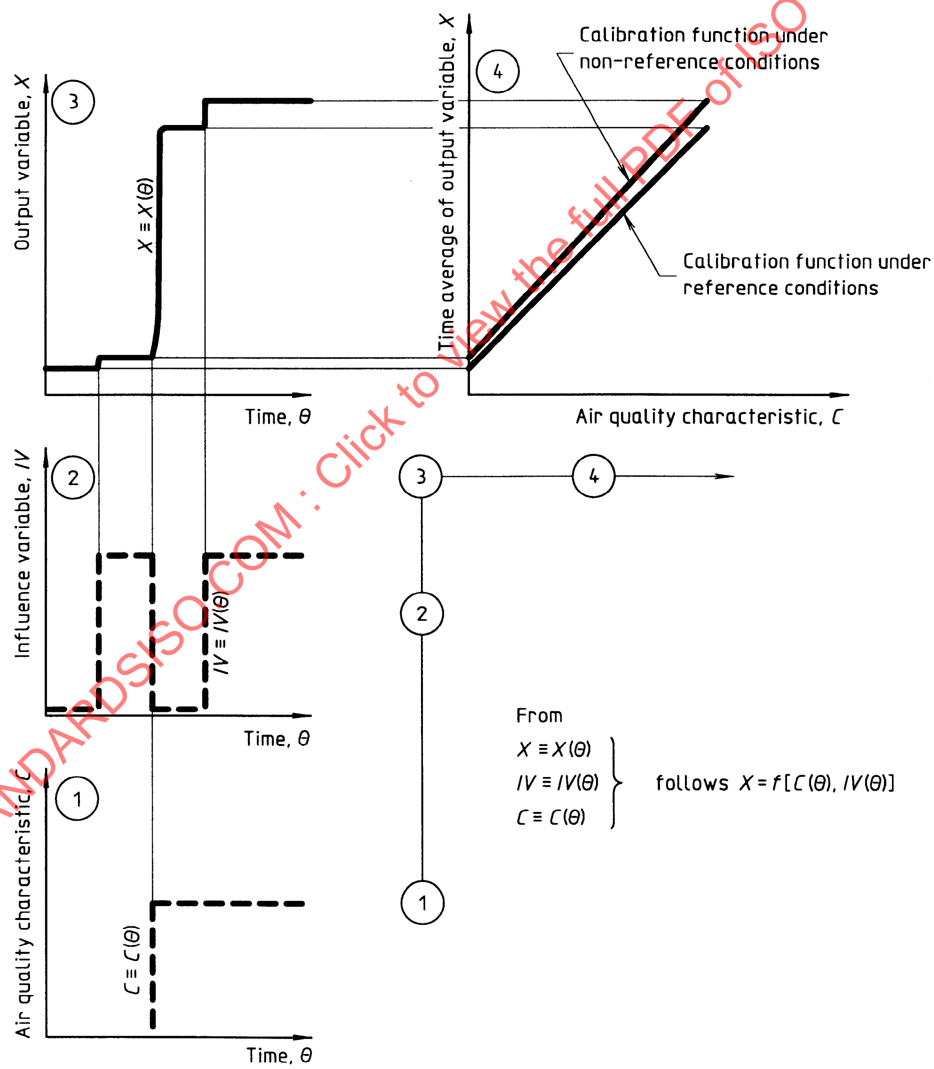


Figure 7 — Impact of an influence variable on a linear calibration function — Example of a two-point calibration

5) Accuracy itself will be dealt with in a separate standard.

6.2.3.1 Known dependence

Express the measured value, $\hat{c}$, as a function of the air quality characteristic and the ith influence variable, IV_i:

$$\hat{c} = g(C, \ IV_1, \ ..., \ IV_k)$$

The dependence, DEP, on IV_i at $C = c$ is approximated by the corresponding partial derivative:

$$\text{DEP}(\hat{c})_{IV_i} = \frac{\partial g}{\partial (IV_i)} \Big|_{c, iv_1, \ ..., \ iv_k} \qquad \text{. . . (38)}$$

6.2.3.2 Unknown dependence

Use reference material of $C = c_l$ and $C = c_u$ (c_l in the lower and c_u in the upper part of the measurement range; $c_l \ll c_u$).

In order to determine experimentally the dependence on the influence variable, perform tests at the operational extremes of the influence variable, and under reference conditions for the remaining influence variables as follows:

Record for each of the values of C the difference in output signal, Δx, on going from one extreme test value IV_i to the other.

Compute the dependence, DEP, on the influence variable, IV_i, at $C = c_k$, $k = $ l, u

$$\text{DEP}(x)_{IV_i} = \frac{\Delta x}{\Delta iv_i} \Big|_{C = c} \qquad \text{. . . (39)}$$

The dependence of b_0 and b_1 on the influence variable is shown by:

$$\text{DEP}(b_0)_{IV_i} = \frac{c_u \ \text{DEP}(x)_{IV_i}|_{c_l} - c_l \ \text{DEP}(x)_{IV_i}|_{c_u}}{c_u - c_l} \qquad \text{. . . (40)}$$

$$\text{DEP}(b_1)_{IV_i} = \frac{\text{DEP}(x)_{IV_i}|_{c_u} - \text{DEP}(x)_{IV_i}|_{c_l}}{c_u - c_l} \qquad \text{. . . (41)}$$

At any value $C = c$ in the range considered, the estimated dependence of the measured value on the influence variable, IV_i, becomes:

$$\text{DEP}(\hat{c})_{IV_i} = \frac{1}{b_1} \ [\text{DEP}(b_0)_{IV_i} + c \ \text{DEP}(b_1)_{IV_i}] \qquad \text{. . . (42)}$$

In accordance with ISO 6879, a first-order approximation for the selectivity, I, with respect to IV_i is shown by:

$$I_{IV_i} = b_1 \ \frac{\Delta iv_i}{\Delta x} \qquad \text{. . . (43)}$$

6.3 Operational performance characteristics

6.3.1 Warm-up time (run-up time)

Investigate the performance characteristic which is most likely to be the limiting factor in time.

Examples are

— lower detection limit;

— repeatability.

Investigate the most unfavourable operation conditions to be expected. Test at those conditions. If the measuring system was operating, return to a non-operating condition. Wait until the measuring system becomes stable. Initiate the measuring system. Determine the time elapsed to reach the given range of the chosen performance characteristic.

6.3.2 Period of unattended operation

Using the limiting value of the performance characteristics taken into account (see 6.3.1), investigate the critical performance characteristic limiting the period of unattended operation.

Investigate the most unfavourable operating conditions to be expected.

Perform the necessary maintenance operations.

Initiate the measuring system according to the operating instructions at the most unfavourable operating conditions with the measuring system warmed up or run up. Record the time elapsed until stabilization.

Run the measuring system without intervention.

Check the value of the limiting performance characteristic regularly until it is no longer within its limits.

Record the time elapsed since the last positive check and designate it as the period of unattended operation.

Repeat the test several times or test with various measuring systems. The minimum period in the set elapsed until the first negative check is taken as the general period of unattended operation.

Report the period together with the admissible ranges of the performance characteristics.

Annex A
(normative)

Grubbs' two-sided outlier test

Tabulated values of Grubbs' two-sided outlier test for the significance level $\alpha = 0{,}05$ are given in table A.1.

Table A.1

Number of replicates	Tabulated value (critical value)
3	1,155
4	1,481
5	1,715
6	1,887
7	2,020
8	2,126
9	2,215
10	2,290
11	2,355
12	2,412
13	2,462
14	2,507
15	2,549
16	2,585
17	2,620
18	2,651
19	2,681
20	2,709
25	2,822
30	2,908
40	3,036
50	3,128

Annex B
(normative)

F-distribution

Tabulated values $F_{\nu_1,\nu_2;\,1-\alpha}$ of the F-distribution for the one-sided test for the significance level $\alpha = 0{,}05$ are given in table B.1.

Table B.1

Denominator ν_2	**Number of degrees of freedom of variance in the numerator** ν_1											
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
40	4,08	3,23	2,84	2,61	2,45	2,34	2,25	2,18	2,12	2,08	2,04	2,00
50	4,03	3,18	2,79	2,56	2,40	2,29	2,20	2,13	2,07	2,03	1,99	1,95
60	4,00	3,15	2,76	2,53	2,37	2,25	2,17	2,10	2,04	1,99	1,95	1,92
100	3,94	3,09	2,70	2,46	2,31	2,19	2,10	2,03	1,97	1,93	1,89	1,85
120	3,92	3,07	2,68	2,45	2,29	2,18	2,09	2,02	1,96	1,91	1,87	1,83
∞	3,84	3,00	2,60	2,37	2,21	2,10	2,01	1,94	1,88	1,83	1,79	1,75

Values $F_{\nu_1,\nu_2;0{,}95}$ for $\nu_1 > 30$ can also be obtained from:

$$F_{\nu_1,\nu_2;0{,}95} = 10^A$$

where

$$A = \frac{1{,}4287}{\sqrt{2\,\nu_1\nu_2\,/\,(\nu_1+\nu_2)} - 0{,}95} - \frac{0{,}681\,(\nu_2-\nu_1)}{\nu_1\nu_2}$$

Annex C
(normative)

t-distribution

Tabulated values of the *t*-distribution for the significance level $\alpha = 0,05$ are given in table C.1.

Table C.1

Number of degrees of freedom ν	One-sided case $t_{\nu;1-\alpha} = t_{\nu;0,95}$	Two-sided case $t_{\nu;1-\alpha/2} = t_{\nu;0,975}$
1	6,314	12,706
2	2,920	4,303
3	2,353	3,182
4	2,132	2,776
5	2,015	2,751
6	1,943	2,447
7	1,895	2,365
8	1,860	2,306
9	1,833	2,262
10	1,812	2,228
11	1,796	2,201
12	1,782	2,179
13	1,771	2,160
14	1,761	2,145
15	1,753	2,131
16	1,746	2,120
17	1,740	2,110
18	1,734	2,101
19	1,729	2,093
20	1,725	2,086
30	1,697	2,042
40	1,684	2,021
60	1,671	2,000
∞	1,645	1,960

Values $t_{\nu;0,95}$ for $\nu > 3$ can also be obtained from:

$$t_{\nu;0,95} = \frac{1,6449\ \nu + 3,5283 + 0,85602\ /\ \nu}{\nu + 1,2209 - 1,5162\ /\ \nu}$$

Values $t_{\nu;0,975}$ for $\nu > 3$ are obtained from:

$$t_{\nu;0,975} = \frac{1,9600\ \nu + 0,60033 + 0,95910\ /\ \nu}{\nu - 0,90259 + 0,11588\ /\ \nu}$$