
**Air quality — Evaluation of the suitability of
a measurement procedure by comparison
with a required measurement uncertainty**

*Qualité de l'air — Évaluation de l'aptitude à l'emploi d'une procédure de
mesurage par comparaison avec une incertitude de mesure requise*



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ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.ch
Web www.iso.ch

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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 3.

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 International Standard may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 14956 was prepared by Technical Committee ISO/TC 146, *Air quality*, Subcommittee SC 4, *General aspects*.

Annex B forms a normative part of this International Standard. Annexes A, C and D are for information only.

Introduction

A measuring task generally includes information on the required quality of the measurement result, which may be quantified by the measurement uncertainty. The required quality may be specified, e.g. by legislation, by authorities or the parties involved.

The quality of a measurement result strongly depends on the performance of the measuring method used. This International Standard specifies the procedures to determine the measurement uncertainty of an individual measurement result, using relevant performance characteristics of the measuring method, and to verify compliance with the requirements of the measuring task.

A procedure for establishing the uncertainty of the time average of a series of single measurements will be given in a separate International Standard [3].

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Air quality — Evaluation of the suitability of a measurement procedure by comparison with a required measurement uncertainty

1 Scope

This International Standard specifies, for the field of air quality measurement procedures, the:

- estimation of measurement uncertainty from actual or claimed values of all important performance characteristics of a method under stationary conditions;
- assessment of whether or not specified values for these performance characteristics comply with the required quality of a measured value at a stated measurand value;
- evaluation of the applicability of the measurement method based on laboratory performance and confirmatory field test;
- establishment of requirements on dynamic behaviour of instruments.

This International Standard is applicable to measurement procedures whose output is a defined time average.

2 Normative reference

The following normative document contains provisions which, through reference in this text, constitute provisions of this International Standard. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent edition of the normative document indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 6879:1995, *Air quality — Performance characteristics and related concepts for air quality measuring methods*

3 Terms and definitions

For the purposes of this International Standard, the terms and definitions given in ISO 6879 and the following apply.

3.1

dynamic condition

(of operation) condition where the measurand value or/and the value of an influence quantity is time-dependent

3.2

performance requirement

requirement of the measurement, in terms of standard uncertainty and dynamic behaviour, against which the suitability of the measurement system is being assessed

3.3

standard uncertainty

uncertainty of the result of a measurement expressed as a standard deviation.

[GUM:1993, 2.3.1]

3.4

stationary condition

(of operation) condition where the measurand value and the values of all influence quantities are constant.

3.5

uncertainty

parameter, associated with the result of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the measurand.

[VIM:1993, C.2.11]

4 Symbols and abbreviated terms

b_j	sensitivity coefficient of c for influence quantity x_j at $C = c_{\text{test}}$
$b_{j, \text{max}}$	maximum value of b_j
C	measurand
c	measured value of the measurand
c_{test}	value of the measurand at which the required measurement uncertainty is given
$D(y_i)$	drift of measured value on input quantity Y_i at $C = c_{\text{test}}$
$f(y_i)_{\text{cal}}$	analytical function; function of input quantities where the impact of influence quantities is excluded
I_j	ratio of the change in measured value and the corresponding change of the interferent value x_i at $C = c_{\text{test}}$
i	index of input quantities Y
j	index of influence quantities X
k	coverage factor
n	total number of input quantities; last number
m	total number of influence quantities
P	percentage value
p	index of the performance characteristic
p_{max}	maximum number of performance characteristics considered
$s[c(x_j)]$	standard deviation of c caused by x_j at $C = c_{\text{test}}$
$s(x_j)$	standard deviation of x_j at $C = c_{\text{test}}$

$s_{\text{inst}}(y_i)$	standard deviation of y_i due to the random part of instability
$s_r(y_i)$	repeatability standard deviation of input quantity Y_i at y_i
$s_R(y_i)$	reproducibility standard deviation of input quantity Y_i at y_i
$s(\hat{y}_i)$	standard deviation of experimentally determined calibration functions (bias due to calibration) of input quantity Y_i
$t_{0,975}$	97,5 percentile of the t -distribution
U_c	combined expanded uncertainty of c at $C = c_{\text{test}}$ expressed as a 95 % confidence interval
U_{req}	required expanded uncertainty of c at $C = c_{\text{test}}$ expressed as a 95 % confidence interval
u_c	combined standard uncertainty of c at $C = c_{\text{test}}$
$u(b_j)$	standard uncertainty of b_j at $C = c_{\text{test}}$
$u[c(x_j)]$	partial standard uncertainty of c due to the value x_j of influence quantity j at $C = c_{\text{test}}$
$u(x_j), u(\Delta x_j)$	standard uncertainty of the difference of x_j between measurement and corresponding calibration
u_p	partial standard uncertainty of uncertainty source or group of sources of uncertainty represented by performance characteristic p at $C = c_{\text{test}}$
$u[\hat{c}(\hat{y}_i)]$	partial standard uncertainty of c due to uncertainty of the experimentally determined calibration functions of input quantity Y_i at y_i corresponding to $C = c_{\text{test}}$
$u_{\text{fit}}[c(y_i)]$	partial standard uncertainty of c due to lack of fit of the calibration function of input quantity Y_i at y_i corresponding to $C = c_{\text{test}}$
$u_{\text{inst}}[c_i(y_i)]$	partial standard uncertainty of c due to the random part of instability of input quantity Y_i at y_i corresponding to $C = c_{\text{test}}$
$u_r[c(y_i)]$	partial standard uncertainty of c due to repeatability of input quantity Y_i at y_i corresponding to $C = c_{\text{test}}$
$u_R[c(y_i)]$	partial standard uncertainty of c due to reproducibility of input quantity Y_i at y_i corresponding to $C = c_{\text{test}}$
u_{req}	maximum allowable standard uncertainty of the measured value at $C = c_{\text{test}}$
$u(y_i)$	standard uncertainty of input quantity Y_i
w_i	weighting factor of input quantity Y_i ; first derivative $\frac{\partial f(y_1, \dots, y_n)}{\partial y_i}$
X	influence quantity

X_j	j th influence quantity
x_j	value of X_j
$x_{j, \text{cal}}$	value of influence quantity X_j during calibration
$x_{j, \text{max}}$	maximum value of influence quantity X_j
$x_{j, \text{min}}$	minimum value of influence quantity X_j
Y	input quantity
Y_i	i th input quantity
y_i	value of Y_i
$y_{i, \text{fit}}$	lack of fit of input quantity Y_i at y_i corresponding to $C = c_{\text{test}}$
$\Delta c(x_j)$	systematic deviation of c due to x_j
$\Delta c(x_{j, \text{p}})$	change in c caused by the maximum positive change of influence quantity X_j after calibration; take care to include the sign of the value
$\Delta c(x_{j, \text{n}})$	change in c caused by the maximum negative change of influence quantity X_j after calibration; take care to include the sign of the value
Δx_j	difference of x_j between measurement and corresponding calibration
$\Delta x_{j, \text{p}}$	maximum positive difference of x_j between measurement and corresponding calibration
$\Delta x_{j, \text{n}}$	maximum negative difference of x_j between measurement and corresponding calibration

5 Principle

Performance characteristics indicate the deviation from a perfect measurement and therefore contribute to the uncertainty of the measurement result. The combined impact of the performance characteristics on the measurement result quantified by measurement uncertainty is taken as the criterion of suitability of a measurement method rather than each of the performance characteristics.

The procedure for calculating measurement uncertainty as follows is based on the law on propagation of uncertainty laid down in the GUM.

- Define the measurand and determine the analytical function relating the measured value to the input quantities. Take the quantity representing that part of the measurement system covered by calibration as a single input quantity.
- Identify all (major) sources of uncertainty (influence quantities) contributing to any of the input quantities or to the measurand directly.
- Determine the model function and the variance function. Retain major sources of uncertainty.
- Use available performance characteristics of the measurement system.

- e) Assign all (major) sources of uncertainty uniquely to performance characteristics. One performance characteristic may cover several sources of uncertainty (e.g. reproducibility). Each major uncertainty source shall not be assigned to more than one performance characteristic. If major sources of uncertainty are not covered by available performance characteristics, their uncertainty shall be quantified separately.
- f) Convert all uncertainty components (performance characteristics) to standard uncertainties of input and influence quantities. Apply the weighting factor w_i derived from the analytical function or the sensitivity coefficient b_j and the difference Δx_j between measurement and corresponding calibration for influence quantity x_j to calculate the corresponding standard uncertainty of the measured value.
- g) Calculate the combined standard uncertainty and the expanded uncertainty taking correlation into account.
- h) Judge the suitability of the measurement procedure by comparing the expanded uncertainty with the required value.
- i) Verify the expanded uncertainty in a field test.
- j) Accept or reject fitness for use of the measurement procedure.

A flowchart for assessing fitness for use of the measurement procedure regarding the performance under stationary conditions is given in Figure 1.

The dynamic response may contribute to measurement uncertainty. Performance requirements related to dynamic conditions of operation are excluded from the uncertainty criterion. For the purpose of this International Standard, it shall be demonstrated that the impact of the dynamic response on measurement uncertainty is negligible.

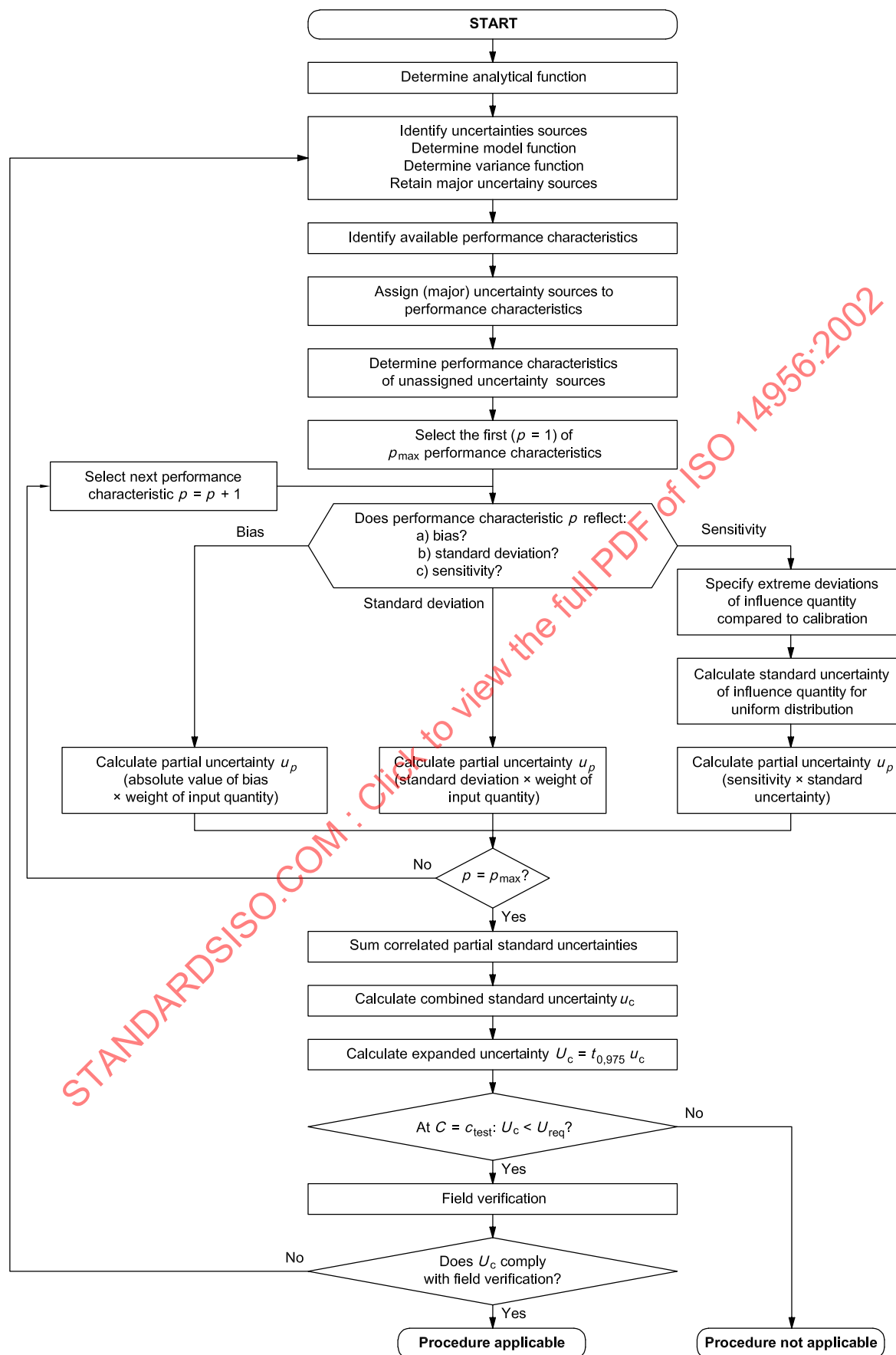


Figure 1 — Flowchart for assessing fitness for use of the measurement procedure

6 Requirements

6.1 Methods and materials

Ensure that the measurand is unambiguously defined.

Describe which steps of the measurement procedure (such as sampling, analysis, postprocessing and calibration) and which materials (such as reference materials) are included in the procedure to estimate measurement uncertainty.

If the output is continuous and the additional equipment to obtain a time-averaged value is not covered in the evaluation, it shall not significantly contribute to measurement uncertainty.

6.2 Performance characteristics

Performance characteristics of the measurement system shall be available.

6.3 Required measurement quality

In order to apply this International Standard, the following information is required:

- the required expanded uncertainty U_{req} , expressed as a 95 % confidence interval;
- the test value c_{test} at which U_{req} is defined;
- the averaging time at which U_{req} is defined.

If the required measurement quality is given as a standard uncertainty, derive the expanded uncertainty by multiplying by a coverage factor $k = 2$.

7 Required performance related to dynamic conditions

7.1 General

Dynamic performance characteristics are treated separately from those related to stationary conditions. It shall be demonstrated that the impact of the dynamic response on measurement uncertainty is negligible.

7.2 Response time

Since the response time is finite, the measured value will be influenced by previous air samples, either by the sampling process (e.g. residence, mixing, reversible adsorption) or by the measurement process (e.g. electronic time constant, residence in detection cell). The actual impact depends on the time pattern of the measurand (frequency and amplitude).

The following requirements apply:

- response time shall be less than 25 % of the averaging time, since the impact is generally negligible if the response time is less than 25 % of the averaging time;
- under highly dynamic conditions, where measurand fluctuations higher than the test value, c_{test} , occur within 5 % of the averaging time, the response time shall be less than 10 % of the averaging time.

The response time applies to continuously measuring systems. For non-continuously measuring systems a similar characteristic shall be considered, e.g. the residence time in the sampling train.

If the requirement is not met, the performance of the measurement procedure shall not be accepted.

8 Required performance related to stationary conditions

8.1 Analytical function, model function and variance function

The value c of a measurand is obtained from input quantities y_i applying a mathematical relationship called the *analytical function* f [see Equation (1)]:

$$c = f(y_1, \dots, y_n) \quad (1)$$

Input quantities are variables and constants. The values of the variables are obtained from (imperfectly) calibrated systems. As long as actual measurements resemble calibration in every respect, the measurand is solely a function of the input quantities. The impact of influence quantities, e.g. temperature and sample matrix, is calibrated out.

Usually, actual measurement does not match calibration completely. If the measurement gives rise to additional terms for influence quantities x_j , the general model function for the measured value c of the measurand shall be applied [see Equation (2)].

$$c = f(y_1, \dots, y_n)_{\text{cal}} + \sum_{j=1}^m b_j (x_j - x_{j, \text{cal}}) \quad (2)$$

The size of the influence depends on the sensitivity b_j and the mismatch $(x_j - x_{j, \text{cal}})$. As influence quantities are not input quantities of the analytical function, their impact shall not be corrected for in the experiment.

The variance function is derived from the general model function by application of the law of propagation of uncertainty in accordance with the GUM. Provided the input and influence quantities are uncorrelated, the variance of c is given by Equation (3):

$$\text{var}(c) = \sum_i \left(\frac{\partial f}{\partial y_i} \right)^2 \text{var}(y_i) + \sum_j b_j^2 \text{var}(x_j - x_{j, \text{cal}}) + \sum_j (x_j - x_{j, \text{cal}})^2 \text{var}(b_j) \quad (3)$$

The squared combined standard uncertainty u_c derived from Equation (3) is a weighted sum of squared uncertainties of input quantities and influence quantities [see Equation (4)]:

$$u_c^2 = \sum_i w_i^2 u^2(y_i) + \sum_j b_j^2 u^2(\Delta x_j) \quad (4)$$

If the uncertainty in the experimentally determined sensitivity coefficients is not negligible, the term $\sum \Delta x_j^2 u^2(b_j)$ shall be included in Equation (4).

NOTE 1 The intrinsic uncertainty $u(y_i)$ of a measured input quantity originate from “natural” fluctuations of the signal (“noise”) and calibration. Sources of calibration uncertainty are lack of fit, uncertainty of reference materials and the uncertainty of the calibration function due to a limited number of calibration points.

NOTE 2 Automated measuring systems (AMS) determine the measurand directly. Ideally, the measurand is the only input quantity. However, the transmission efficiency of the sampling line is an extra input quantity, if transmission is not covered by calibration. Several manual procedures consist of absorbing the analyte in a liquid followed by analysis of the solution in the laboratory. As the chemical calibration is performed on solutions, the concentration of the analyte in the solution c' is an input quantity. The other input quantities are the volume of solution V_{sol} , the collection efficiency f_{col} and the volume of air V_{air} . Each of the weighting factors w_i is directly obtained as a first derivative of the analytical function $c = c' V_{\text{sol}} / (V_{\text{air}} f_{\text{col}})$.

Experimentally determined contributions to measurement uncertainty are given by, or are derived from, performance characteristics. Performance characteristics express directly or indirectly an effect on measurement uncertainty.

- Bias characteristics (e.g. lack of fit and trueness) and dispersion characteristics (e.g. repeatability and reproducibility) are direct measures of uncertainty of an input quantity or the measurand.
- Sensitivity coefficients of influence quantities (e.g. selectivity and temperature dependence) indicate the tendency of an influence quantity to affect measurement uncertainty of an input quantity or the measurand. The uncertainty contribution itself equals the product of the sensitivity coefficient and the uncertainty of the influence quantity.

Definitions of performance characteristics are given in ISO 6879 and the corresponding test procedures in ISO 9169.

8.2 Identification of sources of uncertainty

Not all sources of uncertainty need to be included in the calculation scheme. Any performance characteristic that is not able to create a standard uncertainty of more than 20 % of the highest standard uncertainty of the others may be excluded from the selection.

Identify all potentially important sources of uncertainty related to calibration of the input quantities (variables). Consider

- deviation of the experimental calibration function (deviation from linearity, lack of fit),
- uncertainty of the calibration function due to limited number of calibration points (bias due to calibration),
- uncertainty of reference materials or reference method,
- (instrumental) drift/instability.

Identify all potentially important influence quantities of the input quantities. Consider

- all constituents in air that may change the measured value (lack of selectivity),
- all physical quantities that change the measured value, like temperature, pressure, radiation, mains voltage and frequency,
- operator influence, chemicals.

Identify all potentially important uncertainties of implicit and explicit constants:

- collection efficiency;
- desorption efficiency;
- recovery and transmission efficiency of the sample line.

Identify potentially important residual sources of uncertainty:

- noise.

8.3 Assignment of sources of uncertainty to performance characteristics

Take the list of potentially important sources of uncertainty, which is the result of 8.2, and the list of all available performance characteristics.

Assign every potentially important uncertainty source uniquely to a performance characteristic. Avoid assignment of one source to more than one performance characteristic.

NOTE A performance characteristic may cover more than one uncertainty source. Repeatability comprises all uncontrolled, residual internal sources but no external influences. Reproducibility includes all sources of uncertainty of repeatability and may include the uncertainty of the calibration function, influences induced by operators, chemicals, environmental conditions and instrumental drift. However, reproducibility does not provide information on bias, if one or more of these sources of uncertainty give rise to it.

If a potentially important uncertainty source is not covered by one of the available performance characteristics, its contribution to measurement uncertainty shall be quantified experimentally or estimated.

Retain all performance characteristics uniquely linked to all potentially important sources of uncertainty. For those characteristics that quantify the sensitivity for the uncertainty source, the conditions of operating the measurement system shall first be investigated before the effect on the measured value can be estimated.

8.4 Definition and quantification of conditions of operation of the measurement system

8.4.1 General

Determine, for each important influence quantity, the maximum positive and negative changes from the value during calibration in order to quantify the mismatch between calibration and measurement. Details are given in 8.4.2 to 8.4.4.

NOTE Calibration conditions play an important role in establishing the impact of influence quantities on the measured value. Every time an input quantity is calibrated, the new calibration refers to environmental conditions at that time. Any change in (interfering) environmental conditions during subsequent measurements will cause a deviation until a new calibration is performed (mismatch).

If calibration is performed at regular intervals during the measuring period, the variation of the influence quantity between successive calibrations should be determined, rather than the variation over the whole measurement period.

8.4.2 Chemical influence quantities

Assign to $x_{j, \max}$ the maximum value x_j of chemical interferent X_j that may be obtained in the field. If there is no solid information on that value, use the maximum value given in annex A.

Assign the minimum value that may occur to $x_{j, \min}$. Usually, this value equals zero.

Assign the given value of the calibration material to $x_{j, \text{cal}}$

If calibration is performed by comparing measurement data with those obtained in parallel with a reference method, in order to exclude the overall systematic impact of chemical influence quantities, use as a reference value for $x_{j, \text{cal}}$ the average of the expected minimum and maximum values ($x_{j, \min}$ and $x_{j, \max}$, respectively) of j th influence quantity. The use of a reference method may introduce an additional uncertainty source. It may be minimized by repeated measurements.

In order to reproduce the sample matrix as closely as possible, sometimes calibration material is introduced instantly in the sample stream by spiking known amounts of measurement component. In such a case, the value of the chemical influence quantity during subsequent calibrations is not constant. Estimate directly the maximum positive and negative deviations of the value of the chemical interferent that may occur between successive calibrations from the process dynamics.

8.4.3 Physical influence quantities

If the value x_j of the physical influence quantity X_j (e.g. temperature and pressure) is the same every time calibration is performed, take this value as $x_{j, \text{cal}}$ and use for $x_{j, \text{max}}$ and $x_{j, \text{min}}$ the maximum and minimum values of the influence quantity during measurement.

If the value during calibration is not the same estimate, the maximum positive and negative changes that may occur during measurement until the next calibration is performed shall directly be taken, i.e. $x_{j, \text{max}} - x_{j, \text{cal}}$ and $x_{j, \text{min}} - x_{j, \text{cal}}$ respectively (take care to include the sign of the value).

Use values representative for the application as the extreme changes of physical influence quantities.

8.5 Quantification of the impact of selected performance characteristics as partial standard uncertainties

8.5.1 General

The value of the performance characteristic may either be a claim (manufacturer's specification) or the actual determined value (see ISO 9169). Either can be used to determine compliance with the required measurement quality. Values used in this procedure shall be representative for the measurement procedure.

For any value of the performance characteristics that may contribute to measurement uncertainty, the impact shall be quantified only at the test level $C = c_{\text{test}}$.

The effect of a performance characteristic (e.g. influence quantity x_j) can be quantified as a systematic deviation $\Delta c(x_j)$ and a standard deviation $s[c(x_j)]$. The GUM recommends always correcting for systematic deviations. Usually, the standardized measurement method does not require to do so, e.g. in the case of interfering substances. The square root of the Mean Squared Error (MSE) is taken as a measure of standard uncertainty. This measure is equivalent to the relationship presented by Equation (5):

$$u[c(x_j)] = \sqrt{\Delta c^2(x_j) + s^2[c(x_j)]} \quad (5)$$

The equation for the uncertainty of an influence quantity is similarly described by Equation (6):

$$u(x_j) = \sqrt{\Delta x_j^2 + s^2(x_j)} \quad (6)$$

If the upper and lower bounds of deviations of an influence quantity are known, obtain the standard uncertainty $u(x_j)$ by Equation (7):

$$u(x_j) = \sqrt{\frac{\Delta x_{j,p}^2 + (\Delta x_{j,p}) (\Delta x_{j,n}) + \Delta x_{j,n}^2}{3}} \quad (7)$$

Here, it is assumed that the probability distribution of the quantity, e.g. temperature, is uniform (rectangular); take care to include the sign of $\Delta x_{j,p}$ and $\Delta x_{j,n}$.

If the extremes are symmetric about zero, Equation (7) can be transformed to Equation (8):

$$u(x_j) = \frac{\Delta x_{j,p}}{\sqrt{3}} \quad (8)$$

Usually, the value of a performance characteristic is the result of experimental tests. The uncertainty associated with this determination should be considered as an additional contribution in the procedure, unless the contribution is rated minor.

8.5.2 Repeatability and reproducibility

Reproducibility of an input quantity may cover several sources of uncertainty such as noise, calibration uncertainty, instability/drift, operator effects and environmental influence quantities.

Reproducibility only covers the random portion of the effects of sources of uncertainty. Systematic influences of the same source shall be treated separately.

Make sure that the contribution of an uncertainty source to the reproducibility is representative of that source in the field, e.g. temperature fluctuations during the reproducibility experiment shall be similar to fluctuations in the field. If the contribution is likely to be much less, treat that source of uncertainty separately.

Calculate at $C = c_{\text{test}}$ the reproducibility standard uncertainty $u_R[c(y_i)]$ from the reproducibility standard deviation $s_R(y_i)$ of input quantity y_i according to Equation (9):

$$u_R[c(y_i)] = w_i \cdot s_R(y_i) \quad (9)$$

If repeatability is selected as a performance characteristic, all sources of uncertainty that may be covered by reproducibility, apart from noise, shall be introduced separately in the procedure.

Calculate at $C = c_{\text{test}}$ the repeatability standard uncertainty $u_r(c)$ from the repeatability standard deviation $s_r(y_i)$ of input quantity i according to Equation (10):

$$u_r[c(y_i)] = w_i \cdot s_r(y_i) \quad (10)$$

Because reproducibility covers repeatability, never select both.

8.5.3 Lack of fit

If the applied calibration function, e.g. a straight line, does not comply with the actual calibration function, there is lack of fit, e.g. non-linearity. A measure of lack of fit for the measurement of input quantity Y_i at $Y_i = y_{i, \text{test}}$ corresponding to $C = c_{\text{test}}$ is the difference $\Delta y_{i, \text{fit}}$ between the measured value of Y_i using the calibration function and $y_{i, \text{test}}$.

The corresponding partial standard uncertainty of the measured value c is given by Equation (11):

$$u_{\text{fit}}[c(y_i)] = w_i \cdot \Delta y_{i, \text{fit}} \quad (11)$$

If lack of fit is specified as a symmetrical upper and lower bound, e.g. as a percentage value $\pm P$, apply the equivalent of Equation (8).

8.5.4 Uncertainty of calibration function (bias due to calibration)

The experimental calibration function is obtained from measurements. Due to the limited number of measurements (averaging effect), there will always be a residual uncertainty in the applied function.

Determine the uncertainty of the calibration function of input quantity Y_i at $Y_i = y_{i, \text{test}}$ corresponding to $C = c_{\text{test}}$ as a standard deviation $s(\hat{y}_i)$. Calculate the corresponding partial standard uncertainty for the measured value c according to Equation (12)

$$u[c(\hat{y}_i)] = w_i \cdot s(\hat{y}_i) \quad (12)$$

8.5.5 Instability/drift

In accordance with ISO 9169, the change in time of the measured value of input quantity Y_i at $Y_i = y_{i, \text{test}}$ corresponding to $C = c_{\text{test}}$ is expressed by instability, consisting of a systematic term called drift $D(y_i)$ and a random term given by $s_{\text{inst}}(y_i)$. The partial standard uncertainty of measured value c is given by Equation (13):

$$u_{\text{inst}}[c(y_i)] = w_i \sqrt{\frac{D^2(y_i) + s_{\text{inst}}^2(y_i)}{3}} \quad (13)$$

NOTE Drift is specified as the change in measured value after a specified time interval. As indicated in ISO 9169, the interval should be the time interval between successive operational calibrations. If so, the distribution of the deviation of all measured values between successive calibrations is a uniform distribution with extreme values of 0 and D . Using Equation (7), the corresponding standard uncertainty is given as the first term in Equation (13). The quantity $s_{\text{inst}}(y_i)$ is treated similarly.

If instability (drift) is specified as a symmetrical upper and lower bound, e.g. as a percentage value $\pm P$ per q days, apply the equivalent of Equation (8) to obtain the standard uncertainty.

8.5.6 Selectivity

Selectivity I_j indicates the change in measured value c due to a change of the interferent value x_j (see ISO 9169). It is equivalent to the sensitivity coefficient b_j .

Calculate, at $C = c_{\text{test}}$ for each j of the selected chemical and physical influence quantities, the maximum positive and negative deviations caused by lack of selectivity: $x_{j, \text{p}} = x_{j, \text{max}} - x_{j, \text{cal}}$ and $x_{j, \text{n}} = x_{j, \text{min}} - x_{j, \text{cal}}$ respectively; take care to include the sign of the value. The range of chemical interferents of annex B shall be used unless otherwise specified.

Obtain the sensitivity coefficients (selectivities) b_j of all influence quantities X_j at $C = c_{\text{test}}$.

Calculate the partial standard uncertainty $u[c(x_j)]$ by Equation (14):

$$u[c(x_j)] = |b_j| \cdot u(x_j) \quad (14)$$

where $u(x_j)$ is obtained by Equation (7) or (8).

In the case where selectivity is not specified as a constant but as a (symmetrical) range of values or as a value less than a maximum value, take the maximum value $b_{j, \text{max}}$ and calculate the partial standard uncertainty $u[c(x_j)]$ by Equation (15):

$$u[c(x_j)] = \frac{|b_{j, \text{max}}|}{\sqrt{3}} \cdot u(x_j) \quad (15)$$

The approach should be followed for physical influence quantities as well.

Particularly with chemical pollutants, deviations created by different interferents occur at the same time in the same proportion, i.e. the standard uncertainties of those substances are correlated. To avoid underestimation of additive effects and overestimation of effects by compensation, perform the following:

- calculate standard uncertainties of all correlated interferents;
- sum all standard uncertainties of interferents with a positive impact on the measured value;
- sum all standard uncertainties of interferents with a negative impact on the measured value;
- retain the highest sum as the representative value for all interferents.

Treat uncorrelated interferents individually.

8.6 Estimation of the combined standard uncertainty

Calculate at $C = c_{\text{test}}$ the combined standard uncertainty $u_c(c)$ from all partial standard uncertainties u_p by Equation (16):

$$u_c = \sqrt{\sum_p u_p^2} \quad (16)$$

8.7 Estimation of the expanded uncertainty

Calculate the expanded uncertainty $U_c(c)$ corresponding to a coverage probability of approximately 95 % by Equation (17):

$$U_c = k \cdot u_c \quad (17)$$

where $k = 2$ is used if the standard uncertainty has sufficient reliability, i.e. if none of the major uncertainty contributions is obtained from experimental investigation based on less than ten observations. Otherwise, see annex B.

8.8 Evaluation of compliance with the required measurement quality

Compare the calculated expanded uncertainty with the required value. Accept the values of the set of performance characteristics preliminarily, if Equation (18) is fulfilled:

$$U_c < U_{\text{req}} \quad (18)$$

If Equation (18) is not fulfilled, fitness for use of the measurement procedure has not been demonstrated. In this case, the field verification shall not be performed. After modification, the method may be evaluated as a new method.

An example of an evaluation of compliance with the required quality is given in annex C.

9 Field verification

Before finally accepting the set of performance characteristics that successfully pass the requirement of Equation (1), the method shall be tested under field conditions in order to verify that its performance data and its calculated measurement uncertainty comply with results obtained under field conditions. The design of such a field test may depend on operational conditions, availability of testing equipment and field experience with similar measurement techniques. Field verification may include:

- using the same method in parallel to verify reproducibility and (differences in) drift;
- comparison with an accepted reference method to verify measurement uncertainty and various other related performance characteristics;
- periodic checks using control samples to verify reproducibility;
- additional measurements of influence quantities, e.g. temperature, to investigate their impact.

NOTE An example of an operational procedure to verify instrumental methods in the field is given in annex D.

Evaluate the field data.

Accept the performance of the measurement procedure, if the expanded measurement uncertainty from the field verification is lower than the value calculated using Equation (17).

If disagreement is caused by a selected performance characteristic, adapt its value and finally re-evaluate the uncertainty assessment. If disagreement is not caused by a selected performance characteristic, identify the uncertainty source, quantify it and finally re-evaluate the uncertainty assessment.

If the identity of the uncertainty source is not found, the method may be accepted, if the impact of the unknown uncertainty source does not lead to exceeding the required expanded uncertainty U_{req} .

10 Report

The report shall include at least the following information:

- full description of the evaluated measurement procedure. If only part of the whole procedure is evaluated, mention this explicitly;
- test value and required quality at that value;
- analytical function and list of the input quantities;
- model and variance function and list of the influence quantities, including those disregarded according to 8.2;
- list of assignment of the sources of uncertainty to performance characteristics;
- values of performance characteristics used and reference to their origins;
- field conditions of operation used in the uncertainty assessment;
- determination and assessment of expanded uncertainty;
- applied field verification and its results;
- reference to this International Standard.

Annex A

(informative)

Default ranges of chemical interferents

Table A.1 — Default ranges and minimum values to be applied for calculating the impact of chemical interferents in ambient and indoor air

Component	Unit	Amount in ambient air	Amount in domestic indoor air
H ₂ O	%	30 to 90	30 to 90
O ₃	µg/m ³	0 to 250	0 to 200
CO	mg/m ³	0 to 30	0 to 50
CO ₂	mg/m ³	600 to 1 000	600
CH ₄	mg/m ³	1,2 to 2,0	1,2
C ₂ H ₄	µg/m ³	0 to 200	
C ₆ H ₆	µg/m ³	0 to 30	0 to 60
NO	µg/m ³	0 to 100 ^a	
NO ₂	µg/m ³	0 to 200	
NH ₃	µg/m ³	0 to 20	
H ₂ S	µg/m ³	0 to 30	
SO ₂	µg/m ³	0 to 400	
^a In traffic area, 0 µg/m ³ to 1 000 µg/m ³ .			

Table A.2 — Default ranges to be applied for calculating the impact of chemical interferents in the waste gas of stationary sources (combustion processes)

Component	Unit	Amount in waste gas
O ₂	%	3 to 21
H ₂ O	%	1 to 30
CO	mg/m ³	0 to 300
CO ₂	%	0 to 15
CH ₄	mg/m ³	0 to 50
N ₂ O	mg/m ³	0 to 20
N ₂ O fluidized-bed combustion	mg/m ³	0 to 100
NO	mg/m ³	0 to 300
NO ₂	mg/m ³	0 to 30
NH ₃	mg/m ³	0 to 20
SO ₂	mg/m ³	0 to 200
SO ₂ from coal-fired power plants (without desulfurization)	mg/m ³	0 to 1000
HCl	mg/m ³	0 to 50
HCl from coal-fired power plants	mg/m ³	0 to 200

Annex B (normative)

Coverage factors derived from effective degrees of freedom

The coverage factor corresponding to a 95 % coverage probability requires that the reliability of the standard uncertainty be taken into account. This is the case, if a major uncertainty contribution is obtained from an experimental investigation based on less than ten observations.

A suitable measure of the reliability of the combined standard uncertainty is its effective number of degrees of freedom ν_{eff} estimated from the Welch-Satterthwaite Equation (B.1):

$$\nu_{\text{eff}} = \frac{u_c^4}{\sum_p \frac{u_p^4}{\nu_p}} \quad (\text{B.1})$$

where

u_c is the combined standard uncertainty;

u_p is the partial standard uncertainty; standard uncertainty of the measured value caused by performance characteristic p ;

ν_p is the number of degrees of freedom of the partial standard uncertainty contribution u_p .

The number of degrees of freedom of a partial standard uncertainty obtained from n repetitive observations is given by $\nu_p = n - 1$.

Under the assumption that the distribution of the influence quantity is uniform, the number of degrees of freedom is infinite. Here, it is assumed that the uncertainty of the experimentally determined sensitivity coefficient is negligible.

For a 95 % confidence interval, the coverage factor k given by Equation (B.2) shall be used:

$$k = t_{0,975}(\nu_{\text{eff}}) \quad (\text{B.2})$$

where $t_{0,975}(\nu_{\text{eff}})$ is the 97,5 percentile of the t distribution for ν_{eff} degrees of freedom.

Annex C

(informative)

Example of an assessment of compliance of UV fluorescence method for SO₂ with requirements on ambient air quality

Subclause 6.1 Methods and materials (definition of measurand and measurement system)

To be measured: concentration of SO₂ in air, expressed in micrograms per cubic metre at standard temperature and pressure.

Measurement system: UV fluorescence. Measurement procedure is given in a Standard Operating Procedure (SOP). Operation is in conformity with the SOP. All steps of the procedure, including sampling, analysis, half-hourly averaging of data and calibration, are subject to the uncertainty investigation.

Subclause 6.2 Performance characteristics

Selected performance characteristics for UV fluorescence method	Obtained value for performance characteristic
Response time:	2,0 min
Non-linearity at 400 µg/m ³ :	< 0,5 %
Reproducibility standard deviation at 400 µg/m ³ (n = 15):	12 µg/m ³
Instability at 400 µg/m ³ :	< 8 µg/m ³ per 14 days
Pressure dependence at 400 µg/m ³ :	+ 0,7 % per kPa
Temperature dependence at 400 µg/m ³ :	– 0,4 µg/m ³ per K
Selectivity: addition of component at 400 µg/m ³ SO ₂	Change in measured SO ₂ concentration:
30 mg/m ³ CO	– 0,8 µg/m ³ SO ₂
30 µg/m ³ H ₂ S	+ 1,4 µg/m ³ SO ₂
20 µg/m ³ NH ₃	< 0,4 µg/m ³ SO ₂
30 µg/m ³ C ₆ H ₆	< 0,4 µg/m ³ SO ₂
200 µg/m ³ C ₂ H ₄	< 0,4 µg/m ³ SO ₂
100 µg/m ³ NO	< 0,4 µg/m ³ SO ₂
200 µg/m ³ NO ₂	+ 4,6 µg/m ³ SO ₂
2,0 mg/m ³ CH ₄	< 1,0 µg/m ³ SO ₂
1 000 mg/m ³ CO ₂	– 2,3 µg/m ³ SO ₂
Moisture 90 % (relative humidity)	– 14 µg/m ³ SO ₂
Loss of SO ₂ in sampling line at 400 µg/m ³ :	< 1,0 %

Subclause 6.3 Required measurement quality	
Regulation	Requirement
Test value of SO ₂ concentration:	400 µg/m ³
Averaging time of measured values:	30 min
95 % confidence interval of measured values:	15 % (equivalent to standard uncertainty of 7,5 %)

Clause 7 Required performance related to dynamic conditions	
Requirement for response time in moderate dynamic conditions:	25 % of 30 min, equal to 7,5 min
Measured response time:	2,0 min
Conclusion:	Requirement met

Subclause 8.1 Analytical function, model function and variance function	
The whole measurement system is covered by calibration, except the first part of the sampling line. The quantity covered by calibration is c'. The concentration c at the entrance of the sampling line is to be measured. The number of influence quantities is m. The analytical function is given by: $c = c'$ The model function is given by: $c = c' + \sum_{j=1}^m b_j (x_j - x_{j, \text{cal}})$ The variance function is given by: $\text{var}(c) = \text{var}(c') + \sum_{j=1}^m b_j^2 \text{var}(x_j - x_{j, \text{cal}})$	

Subclause 8.2 Identification of sources of uncertainty	
Number	Uncertainty source
1	Non-linearity
2	Bias due to calibration
3	Drift/instability
4	Interfering components: CO, H ₂ S, NO ₂ , CH ₄ , CO ₂ (NH ₃ , C ₂ H ₄ , C ₆ H ₆ and NO are negligible)
5	Interfering component: Moisture
6	Ambient temperature
7	Ambient pressure
8	SO ₂ loss in first part of sampling line
9	Uncontrolled residual sources
10	Uncertainty of calibration gas

Subclause 8.3 Assignment of sources of uncertainty to performance characteristics	
Performance characteristic	Uncertainty source
Non-linearity	Non-linearity
Instability/drift	Instability/drift of calibration (already covered by reproducibility)
Pressure dependence	Ambient pressure (already covered by reproducibility)
Temperature dependence	Ambient temperature
Selectivity of CO, H ₂ S, NO ₂ , CH ₄ , CO ₂ , moisture	Interferent CO, H ₂ S, NO ₂ , CH ₄ , CO ₂ , moisture
Transmission efficiency	SO ₂ loss in first part sample line
Reproducibility under laboratory conditions (test air at almost constant temperature) ^a	Uncontrolled residual sources: Repeatability of the measured value Bias due to calibration Instability/drift of calibration Ambient pressure
Uncertainty of calibration gas ^{a, b}	Calibration gas (certificate: ± 3 %)
^a The reproducibility under laboratory conditions and the uncertainty of the calibration gas contribute to the variance of the calibrated measured value c' given by: $\text{var}(c') = u_R^2 + u_{\text{cal}}^2$ ^b The uncertainty of the calibration gas is an "external" performance characteristic of the measurement procedure.	

Subclause 8.4 Definition and quantification of conditions of operation of the measurement procedure
Measurements are performed in an ambient industrial environment where fluctuations of temperature inside the enclosure are within 15 °C compared to calibration temperature, where barometric fluctuations are within 5 kPa and where maintenance (calibration) is performed every 14 days. Calibration gas is dry and does not contain any interferents except 700 mg/m ³ CO ₂ . Its certified SO ₂ concentration has an uncertainty of 3 %. Continuous measurement output is processed as half-hourly averages. Concentration ranges of interferents are taken from annex A.