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Air quality — Determination of the uncertainty of the time average of air quality measurements

Qualité de l'air — Détermination de l'incertitude de mesure de la moyenne temporelle de mesurages de la qualité de l'air



Reference number ISO 11222:2002(E)

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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.

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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 11222 was prepared by Technical Committee ISO/TC 146, Air quality, Subcommittee SC 4, General aspects.

Annex A of this International Standard is for information only.

Introduction

Measurands in the field of air quality monitoring can be highly varying functions of time. Special considerations are-required when estimating measurement uncertainties of time averages of air quality monitoring data. The approach [3], using the standard deviation of the recorded measurement results divided by the square root of the number of measurement, is applicable only to measurands that do not change with time and to measuring systems that do not exhibit systematic uncertainties.

The statistical treatment of random and systematic deviations of measurement results has been harmonized by the concept of measurement uncertainty introduced by the *Guide to the expression of uncertainty in measurement* in 1993 (GUM). This approach is based on the general application of the rule of uncertainty propagation. Although not addressed explicitly by the GUM, the concept of uncertainty propagation and measurement uncertainty can also be applied to measurands exhibiting distinct time structure.

Standard uncertainty may be required as a measure of data quality to be provided when reporting a time average of air quality monitoring data. If appropriate, data quality objectives can be defined separately for:

- a) the uncertainty of the time average induced by the measuring system,
- b) the uncertainty of the time average induced by incomplete time coverage of the monitoring data,
- c) the uncertainty of the time average due to limited spatial coverage of monitoring data.

These influences make up independent contributions to the mean square uncertainty of a time average. In this International Standard, a time average of measured air quality data is intended to describe the air quality at a specified location or within a specified stack within a given time period. The uncertainty of the time average due to spatial coverage of monitoring data is not considered.

Air quality — Determination of the uncertainty of the time average of air quality measurements

1 Scope

This International Standard provides a method for the quantification of the uncertainty of a time average of a set of air quality data obtained at a specified location over a defined averaging time period. The method is applicable to air quality data obtained by continuous or intermittent monitoring by means of a specified measuring system. The uncertainty of the time average depends on both the uncertainty of the measurement results and the uncertainty due to incomplete time coverage of the data set.

This International Standard is only applicable if:

- a) the set of air quality data used to calculate the time average is representative of the temporal structure of the measurand over the defined time period,
- b) appropriate information on the uncertainty of the measurement results is available, and
- c) the measurement results have all been obtained at the same location.

This International Standard implements recommendations of the *Guide to the expression of uncertainty in measurement* (GUM).

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.

GUM:1995, Guide to the expression of uncertainty in measurement, First edition, BIPM/IEC/IFCC/ISO/IUPAC/IUPAP/OIML

3 Terms and definitions

For the purposes of this International Standard, the following terms and definitions apply.

3.1
arithmetic mean
average
sum of values divided by the number of values

[ISO 3534-1:1993, 2.26]

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3.2

combined standard uncertainty

standard uncertainty of the result of a measurement when that result is obtained from the values of a number of other quantities, equal to the positive square root of a sum of terms, the terms being the variances and covariances of these quantities weighted according to how the measurement result varies with changes in these quantities

[GUM:1995, 2.3.4]

NOTE The (combined) standard uncertainty of the result of a measurement is the positive square root of its mean square uncertainty

3.3

covariance

measure of the statistical dependence of two observable quantities which may be considered as random variables

Two observable quantities have a non-zero covariance if they are correlated, i.e. a change in one quantity results in a change in the other quantity.

3.4

coverage factor

numerical factor used as a multiplier of the combined standard uncertainty in order to obtain an expanded uncertainty

[GUM:1995, 2.3.6]

expanded uncertainty

quantity defining an interval about the result of a measurement that may be expected to encompass a large fraction of the distribution of values that could reasonably be attributed to the measurand

[GUM:1995, 2.3.5]

If the expanded uncertainty of a result X of measurement on the level of confidence p is given by $U_n(X)$, the unknown true value of X is expected with probability p to be located within the interval $[X - U_n(X); X + U_n(X)]$.

3.6

influence quantity

quantity that is not the measurand but that affects the result of the measurement

[GUM:1995, B.2.10]

mean square uncertainty

(of a result of measurement) square of the combined standard uncertainty of a measurement result

The mean square uncertainty of a measurement result may also be estimated by the mean square deviation of the NOTE measurement result from material measures of the "true" value.

3.8

measurand

particular quantity subject to measurement

[VIM:1993, 2.6]

In the field of air quality monitoring, the measurand can be a highly varying function of time. NOTE

3.9

measuring system

complete set of measuring instruments and other equipment with operating procedures for carrying out specified air quality measurements

NOTE The operating procedure includes or refers to a specification of the calibration routine, if calibration of the measuring system is needed for its proper operation.

3.10

model equation

mathematical model of the measurement that transforms the set of (repeated) observations performed into the measurement result

3.11

number of degrees of freedom

in general, the number of terms in a sum minus the number of constraints on the terms of the sum

[GUM:1995, C.2.31]

3.12

random variable

a variable that may take any of the values of a specified set of values and with which is associated a probability distribution

[GUM:1995, C.2.2]

3.13

reference material

material or substance one or more of whose property values are sufficiently homogeneous and well established to be used for the calibration of an apparatus, the assessment of a measurement method, or for assigning values to materials

[VIM:1993, 6.13]

3.14

reference standard

standard, generally having the highest metrological quality available at a given location or in a given organization, from which measurements made there are derived

[VIM:1993, 6.6]

3.15

result of a measurement

value attributed to a measurand, obtained by measurement

[VIM:1993, 3.1]

3.16

standard

material measure, measuring instrument, reference material or measuring system intended to define, realize, conserve or reproduce a unit or one or more values of a quantity to serve as a reference

[VIM:1993, 6.1]

3.17

standard deviation

positive square root of the variance of the random variable considered

NOTE Adapted from the GUM:1993, C.2.12.

3.18

standard uncertainty

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

[GUM:1995, 2.3.1]

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3.19

time average

mean value of a set of measurement results (air quality data) recorded within a defined time period

3.20

uncertainty

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

[VIM:1993, 3.9]

The uncertainty of a result of a measurement may be described by the (combined) standard uncertainty or by an expanded uncertainty on a stated level of confidence.

3.21

variance

(of a random variable or of a probability distribution) central moment of order 2

The variance of a random variable may be defined equivalently as the expected value of the quadratic deviation of NOTE the random variable about its expected value.

Symbols and abbreviated terms

| C_i | individual measurement result recorded in the time period ${\it T}$ |
|------------------|--|
| \overline{C}_T | time average of air quality monitoring data C_i |
| f | number of degrees of freedom |
| f_{eff} | effective number of degrees of freedom |
| f_{M} | number of degrees of freedom assigned to the standard uncertainty $u_{\rm M}(\bar{C}_T)$ induced by the measuring system applied |
| <i>f</i> s | number of degrees of freedom assigned to the standard uncertainty $u_{S}(\bar{C}_{T})$ due to incomplete time coverage |
| f(u(j)) | number of degrees of freedom when assessing the standard uncertainty $u(j)$ |
| $f(u_{r}(j))$ | number of degrees of freedom when assessing the standard uncertainty $u_{\rm r}(j)$ |
| $f(u_{nr}(j))$ | number of degrees of freedom when assessing the standard uncertainty $u_{\mathrm{nr}}(j)$ |
| $f(u_{nr})$ | number of of degrees of freedom when assessing the standard uncertainty $\boldsymbol{u}_{\text{nr}}$ |
| $f(u_{r}(C_i))$ | number of of degrees of freedom when assessing the standard uncertainty $u_{\rm r}(C_{\it i})$ |
| $k_p(f)$ | coverage factor for confidence level \boldsymbol{p} and number of degrees of freedom \boldsymbol{f} |
| M | number of time intervals $T(j)$ covering the time period T |
| Max | maximum of set of values |
| N | number of measurement results C_i recorded in the time period T |
| $N_{\sf max}$ | number of measurement results \mathcal{C}_i necessary for complete coverage of the time period \mathcal{T} |
| n(j) | number of observed measurement results in time interval $T(j)$ |

| $s(C_i)$ | standard deviation of the set of N individual measurement results C_i used to calculate the time average \overline{C}_T |
|---------------------------|---|
| T | time period allocated to the time average \overline{C}_{T} |
| T_{S} | time period allocated to an individual measurement result \mathcal{C}_i |
| T(j) | sub-interval of time period T |
| $u(C_i)$ | standard uncertainty of C_i |
| $u_{r}(C_i)$ | random part of the standard uncertainty of C_i |
| u_{r} | constant random part of the standard uncertainty of C_i |
| $u_{\sf nr}$ | non-random part of the standard uncertainty of C_i |
| u(j) | standard uncertainty of C_i in time interval $T(j)$ |
| $u_{r}(j)$ | random part of the standard uncertainty of C_i in time interval $T(j)$ |
| $u_{nr}(j)$ | non-random part of the standard uncertainty of C_i in time interval $T(j)$ |
| $u(\overline{C}_T)$ | (combined) standard uncertainty of the time average $\overline{\!C}_T$ |
| $u_{M}(\overline{C}_T)$ | standard uncertainty of the time average $\bar{\mathcal{C}}_T$ induced by the measuring system |
| $u_{S}(\overline{C}_{T})$ | standard uncertainty of the time average \bar{C}_T due to incomplete coverage of the time period T by the data set used to calculate the time average |
| $u_{r}(\overline{C}_T)$ | random part of $u_{M}(\overline{C}_T)$ |
| $u_{\sf nr}(\bar{C}_T)$ | non-random part of $u_{M}(\bar{C}_T)$ |
| $U_p(\overline{C}_T)$ | expanded uncertainty of $\overline{\!C}_T$ on the stated level of confidence p |
| v_{r} | constant relative standard uncertainty of C_i |

5 Requirements on the input data

5.1 General

This International Standard provides methods to estimate the uncertainty of the time average of a set of scalar measurement results quantifying a time series of an air quality measurand within a defined time period. The measurand may exhibit significant time structure. The approach [3], using the standard deviation of the measurement results divided by the square root of the number of available measurement results, is applicable only to measurands not exhibiting significant temporal structure and to measuring systems that are only influenced by random uncertainties. In the field of air quality monitoring, measurands often exhibit significant temporal structure and distinct non-random uncertainties. Therefore, a different approach is needed to quantify the uncertainty of time averages in the field of air quality monitoring.

The set of N measurement results C_i of air quality recorded within a defined averaging time period T used to calculate the time average \overline{C}_T is given by formula (1):

$$\{C_i: i=1 \text{ to } N\}$$

The index i indicates sequential time intervals of equal length T_{S} , which may be interspersed with intervals not monitored (missing values). The measurement results C_i may have been recorded by continuous monitoring or intermittent sampling by means of a specified air quality measuring system with sampling time T_{S} .

The measurement results C_i shall have been measured at the same location. The sampling time T_S of the individual measurement result C_i is generally shorter than the averaging time period T. The coverage of the averaging time period T by N measurement results C_i is given by $N/N_{\text{max}} \le 1$ with $N_{\text{max}} = T/T_{\text{S}}$. The N measurement results C_i are used to calculate the time average \overline{C}_T (see 6.1).

In order to quantify the uncertainty of the time average \overline{C}_T , information is required on the uncertainty of the measurement results C_i and on the coverage of the averaging time period T by the data set. Appropriate information on the measurement uncertainty may be provided in accordance with the recommendations of the GUM.

For the purposes of this International Standard, the mean square uncertainty of a measurement result C_i is described by equation (2):

$$u^{2}(C_{i}) = u_{r}^{2}(C_{i}) + u_{nr}^{2}(C_{i})$$
(2)

The term $u_{\Gamma}^2(C_i)$ designates the random and $u_{\Gamma\Gamma}^2(C_i)$ the non-random part of the mean square uncertainty of the measurement result C_i . The non-random part $u_{\Gamma\Gamma}^2(C_i)$ describes uncorrected systematic deviation. In the field of air quality monitoring, the non-random part often exceeds the random part of the mean square uncertainty of the measurement result C_i .

Splitting the mean square uncertainty into a random and a non-random part simplifies the quantification of uncertainties of the resulting time average as described in clause 6. For identification of random and non-random parts of the mean square uncertainty of the measurement result C_i , the following rule applies.

The random part $u_r^2(C_i)$ is due to random changes in the measuring process and to random variations of influence quantities of the measuring process, which take place under monitoring conditions. It may be assessed by the variance of the response of the measuring system to repeated application of check standards under monitoring conditions, e.g. by zero and span checks. The random part $u_r^2(C_i)$ is not influenced by the temporal structure of the measurand, but it may be a function of the measurement result C_i .

Furthermore, the mean square uncertainty $u^2(C_i)$ may exhibit a non-random part $u_{nr}^2(C_i)$. A non-random part may be induced by uncertainties of fixed influence quantities of the measuring process or by uncorrected systematic deviations within the measuring process.

5.2 Specific requirements on input data

The available set of measurement results C_i used to calculate the time average \bar{C}_T shall be representative of the temporal structure of the measurand over the averaging time period T.

NOTE 1 In order to meet this requirement it is necessary to have knowledge of the expected temporal structure of the measurand.

Missing values shall not have been replaced, e.g. by using interpolation technique. The individual measurement results C_i shall have been generated independently.

It is usually assumed that the measurement results are generated independently, if the sampling time is at least four times the response time T_{R} of the measuring system.

Information on the uncertainty of the measurement results C_i used to calculate the time average \bar{C}_T shall be provided in line with the recommendations of the GUM.

Concerning the uncertainty of the measurement results C_i , the following three cases shall be distinguished.

The whole data set has a single associated uncertainty statement, which separates random and non-random uncertainty parts.

In this case, the following information shall be available:

- 1) variances $u_r^2(C_i)$, u_{nr}^2
- 2) number of degrees of freedom $f(u_r(C_i))$, $f(u_{nr})$

Both the random part $u_{\Gamma}^2(C_i)$ and the non-random part u_{Γ}^2 of the standard uncertainty shall be applicable over the averaging time period T. The random part $u_{\Gamma}^2(C_i)$ may depend on the measurement result C_i . The non-random part u_{Γ}^2 is considered to be the same for all measurement results C_i recorded in the averaging time period. The number of degrees of freedom assigned to $u_{\Gamma}^2(C_i)$ is $f(u_{\Gamma}(C_i))$. The number of degrees of freedom assigned to u_{Γ}^2 is $f(u_{\Gamma}(C_i))$ and u_{Γ}^2 were assessed from the same set of data, then $f(u_{\Gamma}(C_i))$ is equal to $f(u_{\Gamma}(C_i))$.

b) The set of data is split into a number M (M > 1) of sub-sets, each of which has an accociated uncertainty statement, that separates random and non-random uncertainty parts.

In this case, the following information shall be available for the blocks of measurement j = 1 to M:

- 1) variances $u_r^2(j)$, $u_{nr}^2(j)$
- 2) number of measurements n(j) and time period T(j)
- 3) number of degrees of freedom $f(u_r(j))$, $f(u_{nr}(j))$

where
$$T = \sum_{j=1}^{M} T(j)$$
 and $N = \sum_{j=1}^{M} n(j)$

The standard uncertainty of the measurement results C_i shall have been assessed independently for each time interval T(j). The sum of the time intervals T(j) shall completely cover the averaging time period T. The random part $u_\Gamma^2(j)$ and the non-random part $u_{\Gamma\Gamma}^2(j)$ of the standard uncertainty shall be applicable over the time interval T(j). The uncertainty statements provided for the time intervals T(j) shall not be based on the same set of reference standards. The number of degrees of freedom assigned to $u_\Gamma^2(j)$ is $f(u_\Gamma(j))$. The number of degrees of freedom assigned to $u_{\Gamma\Gamma}^2(j)$ is $f(u_\Gamma(j))$. If $u_\Gamma(j)$ and $u_{\Gamma\Gamma}^2(j)$ were assessed from the same set of data, then $f(u_\Gamma(j))$ is equal to $f(u_{\Gamma\Gamma}^2(j))$.

c) The data set has one or more associated uncertainty statement $(M \ge 1)$, that does not separate random and non-random uncertainty parts.

In this case, the following information shall be available for i = 1 to M:

- 1) uncertainty u(j)
- 2) number of measurements n(j) and time period T(j)
- 3) number of degrees of freedom f(j)

where
$$T = \sum_{j=1}^{M} T(j)$$
 and $N = \sum_{j=1}^{M} n(j)$

The standard uncertainty of the measurement results C_i shall have been assessed independently for each time interval T(j). The sum of the time intervals T(j) shall completely cover the time period T_i . The standard uncertainty u(j) shall be applicable to the time interval T(j). The standard uncertainty u(j) is considered to be constant within the time interval T(j). The uncertainty statements provided for the time intervals T(j) shall not be based on the same set of reference standards. The number of degrees of freedom assigned to u(j) is f(j).

If the available uncertainty statements do not allow separation of random and non-random parts of the mean square uncertainty $u^2(C_i)$, the provided standard uncertainty $u(C_i)$ shall be considered as non-random.

Procedure 6

General 6.1

Based on the set of measurement results C_i (i = 1 to N) provided in accordance with clause 5, the time average \overline{C}_T shall be calculated by means of equation (3):

$$\overline{C}_T = \frac{1}{N} \sum_{i=1}^{N} C_i \tag{3}$$

This International Standard takes into account the following contributions to the uncertainty of a time average \bar{C}_T :

- the uncertainty of the individual measurement results C_i of sampling time T_S used to calculate the time average
- the uncertainty due to incomplete coverage of the time period T by the measurement results C_i used to calculate the time average \bar{C}_T , if $N \cdot T_S < T$.

Since both contributions are not correlated, the mean square uncertainty $u^2(\bar{C}_T)$ of the time average \bar{C}_T is given by equation (4):

$$u^{2}(\bar{C}_{T}) = u_{M}^{2}(\bar{C}_{T}) + u_{S}^{2}(\bar{C}_{T}) \tag{4}$$

where

- $u_{\rm M}^2(\bar{C}_T)$ is the mean square uncertainty of the time average \bar{C}_T due to the measuring system used to record the set of measurement results C_i ;
- $u_S^2(\overline{C}_T)$ is the mean square uncertainty of the time average \overline{C}_T due to incomplete coverage of the time period T by the set of measurement results C_i .

In case of complete coverage of the averaging time period by measurement results C_i , the uncertainty of the time average is completely determined by the measuring system.

The uncertainty of the time average due to the measuring system is quantified in 6.2 in line with the recommendations of the GUM, based on information to be provided on the uncertainty of the measurement results used to calculate the time average. The uncertainty of the time average due to incomplete coverage of the time period T by measurement results is not addressed explicitly by the GUM. The solution of this problem is described in 6.3.

Standard uncertainty induced by the measuring system

The mean square uncertainty of the time average \bar{C}_T due to the measuring system used to record the measurement results C_i is given by equation (5):

$$u_{\mathsf{M}}^{2}(\bar{C}_{T}) = u_{\mathsf{r}}^{2}(\bar{C}_{T}) + u_{\mathsf{nr}}^{2}(\bar{C}_{T}) \tag{5}$$

where

- $u_{\rm f}^2(\overline{C}_T)$ is the random part of the mean square uncertainty of the time average \overline{C}_T due to the measuring system;
- $u_{nr}^2(\bar{C}_T)$ is the non-random part of the mean square uncertainty of the time average \bar{C}_T due to the measuring system.

The random part $u_{\rm r}^2(\bar{C}_T)$ is quantified based on the random parts $u_{\rm r}^2(C_i)$ of the mean square uncertainty of the measurement result C_i . The non-random part $u_{\rm nr}^2(\bar{C}_T)$ is calculated based on the non-random parts $u_{\rm nr}^2(C_i)$ of the mean square uncertainty of the measurement results C_i .

Based on uncertainty statements provided in accordance with 5.2, the standard uncertainty $u_{\rm M}^2(\bar{C}_T)$ of the time average \bar{C}_T induced by the measuring system and the corresponding number of degrees of freedom $f_{\rm M}$ shall be estimated as follows for the cases described in 5.2.

a) The whole data set has a single associated uncertainty statement, that separates random and non-random uncertainty parts.

$$u_{\mathsf{M}}^{2}(\overline{C}_{T}) = \frac{1}{N^{2}} \sum_{i=1}^{N} u_{\mathsf{r}}^{2}(C_{i}) + u_{\mathsf{nr}}^{2} \tag{6}$$

In equation (6), the random part $u_r^2(C_i)$ may be a function of the measurement result C_i .

If $u_{\Gamma}(C_i) = u_{\Gamma}$ is constant, equation (6) may be transformed to equation (7):

$$u_{\mathsf{M}}^{2}(\overline{C}_{T}) = \frac{u_{\mathsf{r}}^{2}}{N} + u_{\mathsf{nr}}^{2} \tag{7}$$

In case of $u_r(C_i) = C_i v_r$ and constant relative standard uncertainty v_r , equation (6) may be transformed to equation (8):

$$u_{\mathsf{M}}^{2}(\bar{C}_{T}) = \frac{v_{\mathsf{r}}^{2}}{N} \frac{1}{N} \sum_{i=1}^{N} C_{i}^{2} + u_{\mathsf{nr}}^{2}$$
(8)

The number of degrees of freedom $f_{\rm M}$ of the standard uncertainty $u_{\rm M}(\overline{C}_T)$ is calculated from the Welch-Satterthwaite solution specified in the GUM [see equation (9)].

$$\frac{u_{\mathsf{M}}^{4}(\bar{C}_{T})}{f_{\mathsf{M}}} = \sum_{i=1}^{N} \frac{u_{\mathsf{r}}^{4}(C_{i})}{f(u_{\mathsf{r}}(C_{i}))} + \frac{u_{\mathsf{nr}}^{4}}{f(u_{\mathsf{nr}})}$$
(9)

If $f(u_r(C_i)) > 29$ and $f(u_{nr}) > 29$, then the number of degrees of freedom may be set to $f_{\rm M} = 30$.

b) The set of data is split into a number M (M > 1) of sub-sets, each of which has an associated uncertainty statement, that separates random and non-random uncertainty parts.

$$u_{\mathsf{M}}^{2}(\overline{C}_{T}) = \frac{1}{N^{2}} \left[\sum_{j=1}^{M} u_{\mathsf{r}}^{2}(j) \ n(j) + \sum_{j=1}^{M} u_{\mathsf{nr}}^{2}(j) \ n^{2}(j) \right]$$
 (10)

Equation (10) demonstrates that random and non-random parts of the mean square uncertainty of the measurement results C_i are to be weighted differently in the mean square uncertainty of the time average \overline{C}_T .

The number of degrees of freedom $f_{\rm M}$ of the standard uncertainty $u_{\rm M}(\bar{C}_T)$ is calculated from the Welch-Satterthwaite solution specified in the GUM [see equation (11)].

$$\frac{u_{\mathsf{M}}^{4}(\overline{C}_{T})}{f_{\mathsf{M}}} = \sum_{j=1}^{M} \left[\frac{u_{\mathsf{r}}^{4}(j)}{f(u_{\mathsf{r}}(j))} + \frac{u_{\mathsf{nr}}^{4}(j)}{f(u_{\mathsf{nr}}(j))} \right] \tag{11}$$

If $f(u_r(j)) > 29$ and $f(u_{nr}(j)) > 29$ for j = 1 to M, then the number of degrees of freedom may be set to

The data set has one or more associated uncertainty statement $(M \ge 1)$ that does not separate random and C) non-random uncertainty parts.

$$u_{\mathsf{M}}^{2}(\bar{C}_{T}) = \frac{1}{N^{2}} \sum_{j=1}^{M} u^{2}(j) \ n^{2}(j)$$
 (12)

Due to the provisions specified in case c) of 5.2, the standard uncertainties u(i) are to be treated as non-random.

The number of degrees of freedom f_{M} of the standard uncertainty $u_{\mathsf{M}}(\overline{C}_T)$ is calculated from the Welch-Satterthwaite solution specified in the GUM [see equation (13)].

$$\frac{u_{\mathsf{M}}^{4}(\bar{C}_{T})}{f_{\mathsf{M}}} = \sum_{j=1}^{M} \frac{u^{4}(j)}{f(u(j))} \tag{13}$$

If f(u(j)) > 29 for j = 1 to M, then the number of degrees of freedom may be set to $f_M = 30$.

Standard uncertainty due to incomplete time coverage

Incomplete coverage of the time period T by the measurement results C_i results in an additional source of uncertainty of the time average \vec{C}_T not covered by measurement uncertainty described in 6.2. According to statistical theory [3], the standard uncertainty $u_S(\overline{C}_T)$ of the time average \overline{C}_T due to incomplete time coverage of the measurement results C_i used to calculate the time average shall be determined by means of equation (14):

$$u_{S}^{2}(\overline{C}_{T}) = \left(1 - \frac{N}{N_{\text{max}}}\right) \frac{1}{N} s^{2}(C_{i})$$

$$\tag{14}$$

Here, $s^2(C_i)$ designates the variance of the measured values as determined by equation (15):

$$s^{2}(C_{i}) = \frac{1}{N-1} \sum_{i=1}^{N} (C_{i} - \overline{C}_{T})^{2}$$
(15)

The number of degrees of freedom f_S associated with the variance $u_S^2(\overline{C}_T)$ is given by equation (16):

$$f_{S} = N - 1 \tag{16}$$

NOTE 1 In the case of complete time coverage of the measurement results C_i , i.e. $N=N_{\rm max}$, equation (14) leads to $u_{\rm S}^2(\vec{C}_T)=0$. Then the uncertainty of the time average \vec{C}_T is completely determined by the measurement uncertainty.

NOTE 2 In the case of a small sample size $N << N_{\rm max}$, equation (14) is approximated by the standard deviation of a mean value of a sample from an infinite population $u_{\rm S}^2(\bar{C}_T) = s^2/N$.

Correlation of observed time series of results of measurement induced by the time structure of the measurand is not taken into account, as it does not influence measurement uncertainty.

6.4 Combined standard uncertainty

The combined standard uncertainty $u(\overline{C}_T)$ of the time average \overline{C}_T shall be determined by equation (17):

$$u(\overline{C}_T) = \sqrt{u_{\mathsf{M}}^2(\overline{C}_T) + u_{\mathsf{S}}^2(\overline{C}_T)} \tag{17}$$

The number of degrees of freedom $f_{\rm eff}$ of the standard uncertainty $u(\bar{C}_T)$ is calculated from the Welch-Satterthwaite solution specified in the GUM [see equation (18)].

$$\frac{u^4(\overline{C}_T)}{f_{\text{eff}}} = \frac{u_{\text{M}}^4(\overline{C}_T)}{f_{\text{M}}} + \frac{u_{\text{S}}^4(\overline{C}_T)}{f_{\text{S}}} \tag{18}$$

If $f_{\rm M}$ > 29 and $f_{\rm S}$ > 29, then the number of degrees of freedom may be set to $f_{\rm eff}$ = 30.

6.5 Expanded uncertainty

The expanded uncertainty $U_p(\bar{C}_T)$ of the time average \bar{C}_T on a stated level of confidence p shall be estimated by means of equation (19):

$$U_p(\overline{C}_T) = k_p(f_{\text{eff}}) \ u(\overline{C}_T) \tag{19}$$

The coverage factor $k_p(f_{\text{eff}})$ is determined by a percentage point of the *t*-distribution with the number of degrees of freedom f_{eff} , describing a two-sided confidence interval [1]. Table 1 provides values for the coverage factor $k_p(f_{\text{eff}})$.

The expanded uncertainty $U_{0,95}(\overline{C}_T)$ of the mean value \overline{C}_T on a level of confidence of 95 % may be calculated by equation (20), if the effective number of degrees of freedom f_{eff} exceeds 29:

$$U_{0.95}(\overline{C}_T) = 2 \ u(\overline{C}_T) \quad \text{if } f_{\text{eff}} > 29$$
 (20)

Table 1 — Coverage factor $k_p(f)$ as a function of the level of confidence p and the number of degrees of freedom f as specified in the GUM

| f | k_p | k_p | k_p |
|-----|----------|----------|----------|
| | p = 0,90 | p = 0.95 | p = 0.99 |
| 1 | 6,31 | 12,71 | 63,66 |
| 2 | 2,92 | 4,30 | 9,92 |
| 3 | 2,35 | 3,18 | 5,84 |
| 4 | 2,13 | 2,78 | 4,60 |
| 5 | 2,01 | 2,57 | 4,03 |
| 6 | 1,94 | 2,45 | 3,71 |
| 7 | 1,90 | 2,36 | 3,50 |
| 8 | 1,86 | 2,31 | 3,36 |
| 9 | 1,83 | 2,26 | 3,25 |
| 10 | 1,81 | 2,23 | 3,17 |
| 20 | 1,72 | 2,09 | 2,85 |
| 30 | 1,70 | 2,04 | 2,75 |
| 100 | 1,66 | 2,025 | 2,626 |

Reporting uncertainty

The report on the determination of the uncertainty of a time average \bar{C}_T of air quality measurement results in accordance with this International Standard shall include the following information:

- averaging time period T;
- time average \bar{C}_T ;
- statement on the uncertainty of the time average;
- procedure used to determine the uncertainty of the individual measurement results C₁.

The statement on the uncertainty shall be provided in one of the following forms.

- If the combined standard uncertainty $u(\overline{C}_T)$ is chosen as measure of uncertainty of the time average \overline{C}_T , it shall be reported in units of \overline{C}_T or as relative combined standard uncertainty $u(\overline{C}_T)/\overline{C}_T$. This information shall be accompanied by the number of degrees of freedom $f_{\rm eff}$.
- If the expanded uncertainty $U_p(\overline{C}_T)$ on the level of confidence p is chosen as measure of uncertainty of the time average \overline{C}_T , it shall be reported in units of \overline{C}_T or as relative expanded uncertainty $U_p(\overline{C}_T)/\overline{C}_T$. This information shall be accompanied by the coverage factor $k_p(f_{\text{eff}})$ applied and the number of degrees of freedom f_{eff}
- If the standard uncertainty induced by the measuring system, $u_{\mathsf{M}}(\overline{C}_T)$, is chosen as measure of uncertainty of the time average \overline{C}_T , it shall be reported in units of \overline{C}_T or as relative standard uncertainty $u_{\mathsf{M}}(\overline{C}_T)/\overline{C}_T$. This information shall be accompanied by the number of degrees of freedom $f_{\rm M}$.
- If the standard uncertainty due to incomplete time coverage of the monitoring data, $u_S(\overline{C}_T)$, is chosen as measure of uncertainty of the time average \bar{C}_T , it shall be reported in units of \bar{C}_T or as relative standard uncertainty $u_S(\bar{C}_T)/\bar{C}_T$. This information shall be accompanied by the number of degrees of freedom f_S .

The documentation of the procedure used to determine the uncertainty of the individual measurement results C_i shall comprise information on

- assessment of the random variance contributions of the measurement results C_i used to calculate the time average \overline{C}_T ,
- assessment of the non-random variance contributions of the measurement results C, used to calculate the time average \bar{C}_T ,
- the basis on which the above variance contributions were determined to be applicable to the measurement results C_i .

The report shall also include the basis on which the set of measurement results used to calculate the time average C_T was determined to be representative of the temporal structure of the measurand over the averaging time period T.

Annex A

(informative)

Example — Quantification of the uncertainty of a monthly average of nitrogen dioxide in ambient air

A.1 Input

A.1.1 Measuring system

A nitrogen dioxide monitor (chemiluminescence) is used for continuous monitoring of ambient air. It has been shown that the monitor used exhibits a straight-line calibration function.

A.1.2 Control procedure

The control procedure consists of two levels.

- a) Every 25 h, zero and span gases were applied to the measuring system. The zero gas results were used to correct for zero-drift. Span gas results were used to detect changes in the slope of the model equation.
- b) Every three months, the slope of the model equation is adjusted by comparison to a reference standard of gas concentration C_R and standard uncertainty $u(C_R) = 4 \mu g/m^3$ (one-point calibration).

The data set has one or more associated uncertainty statements ($M \ge 1$) that does not separate random and non-random uncertainty parts. The uncertainty of the monthly average \overline{C}_{month} of nitrogen dioxide in ambient air for January 2000 recorded at a monitoring site in Bottrop, Germany, was calculated from N = 692 hourly mean values C_i in accordance with equation (3):

$$\bar{C}_{\text{month}} = 38 \, \mu \text{g/m}^3$$

A.1.3 Uncertainty estimation for hourly mean values

Input data for the calculation of the monthly average \overline{C}_{month} were hourly mean values C_i recorded within the month considered. In January 2000, N=692 of possible $N_{max}=744$ hourly mean values of nitrogen dioxide were recorded at the monitoring site considered. This set of measurement results was judged as representative of the month considered, because

- 30 of the 52 missing hourly values were found isolated and randomly distributed throughout this month,
- the remaining missing values covered a coherent interval of 22 h.

The input data for uncertainty estimation of the hourly mean values C_i are given in Table A.1 for 30 of 31 days of the month considered, where $Y_0(d)$ is the response of the measuring system on application of zero gas and B(d) the slope of the model equation observed on application of span gas on day d.

Table A.1 — Set of control data of NO₂-monitor (January 2000)

| Date Y₀(d) µg/m³ B(d) µg/m³ (dC)² (µg/m³)² (dB)² 2000-01-01 −4,3 1,04 18,5 0,001 6 2000-01-02 −1,9 1,03 3,6 0,000 9 2000-01-03 −4,0 1,04 16,0 0,001 6 2000-01-04 −3,4 1,05 11,6 0,002 5 2000-01-05 −3,3 1,06 10,9 0,003 6 2000-01-06 −3,3 1,06 10,9 0,003 6 2000-01-07 −1,5 1,06 2,3 0,003 6 2000-01-08 −4,3 1,06 18,5 0,003 6 2000-01-09 −2,4 1,07 5,8 0,004 9 2000-01-10 1,6 1,06 2,6 0,003 6 2000-01-11 −5,4 1,02 29,2 0,000 4 2000-01-12 −0,4 1,02 29,2 0,000 4 2000-01-13 −0,8 1,07 0,6 0,004 9 2000-01-14 2,3 1,04 5,3 | | Oct of contro | 2 | | · · · · · · · · · · · · · · · · · · · |
|--|------------|-------------------|-----------------------|-----------------|---------------------------------------|
| μg/m³ (μg/m³)² (μg/m³)² | Date | $Y_0(d)$ | <i>B</i> (<i>d</i>) | $(dC)^{2}$ | $(dB)^2$ |
| 2000-01-02 | Date | μg/m ³ | | $(\mu g/m^3)^2$ | |
| 2000-01-03 | 2000-01-01 | - 4,3 | 1,04 | 18,5 | 0,001 6 |
| 2000-01-04 - 3,4 1,05 11,6 0,002 5 2000-01-05 - 3,3 1,06 10,9 0,003 6 2000-01-06 - 3,3 1,06 10,9 0,003 6 2000-01-07 - 1,5 1,06 2,3 0,003 6 2000-01-08 - 4,3 1,06 18,5 0,003 6 2000-01-09 - 2,4 1,07 5,8 0,004 9 2000-01-10 1,6 1,06 2,6 0,003 6 2000-01-11 - 5,4 1,02 29,2 0,000 4 2000-01-12 - 0,4 1,02 29,2 0,000 4 2000-01-13 - 0,8 1,07 0,6 0,004 9 2000-01-14 2,3 1,04 5,3 0,001 6 2000-01-15 1,4 1,01 2,0 0,000 1 2000-01-16 2,5 1,02 6,3 0,000 1 2000-01-18 0,0 0,97 0,0 0,000 9 2000-01-18 0,0 0,97 0,0 0,0 | 2000-01-02 | - 1,9 | 1,03 | 3,6 | 0,000 9 |
| 2000-01-05 - 3,3 1,06 10,9 0,003 6 2000-01-06 - 3,3 1,06 10,9 0,003 6 2000-01-07 - 1,5 1,06 2,3 0,003 6 2000-01-08 - 4,3 1,06 18,5 0,003 6 2000-01-09 - 2,4 1,07 5,8 0,004 9 2000-01-10 1,6 1,06 2,6 0,003 6 2000-01-11 - 5,4 1,02 29,2 0,000 4 2000-01-12 - 0,4 1,02 29,2 0,000 4 2000-01-13 - 0,8 1,07 0,6 0,004 9 2000-01-14 2,3 1,04 5,3 0,001 6 2000-01-15 1,4 1,01 2,0 0,000 1 2000-01-16 2,5 1,02 6,3 0,000 1 2000-01-18 0,0 0,97 0,0 0,000 9 2000-01-19 - 1,3 0,95 1,7 0,002 5 2000-01-20 0,2 0,96 0,0 0,00 | 2000-01-03 | - 4,0 | 1,04 | 16,0 | 0,001 6 |
| 2000-01-06 - 3,3 1,06 10,9 0,003 6 2000-01-07 - 1,5 1,06 2,3 0,003 6 2000-01-08 - 4,3 1,06 18,5 0,003 6 2000-01-09 - 2,4 1,07 5,8 0,004 9 2000-01-10 1,6 1,06 2,6 0,003 6 2000-01-11 - 5,4 1,02 29,2 0,000 4 2000-01-12 - 0,4 1,02 0,2 0,000 4 2000-01-13 - 0,8 1,07 0,6 0,004 9 2000-01-14 2,3 1,04 5,3 0,001 6 2000-01-15 1,4 1,01 2,0 0,000 1 2000-01-16 2,5 1,02 6,3 0,000 4 2000-01-17 - 0,9 1,01 0,8 0,000 1 2000-01-18 0,0 0,97 0,0 0,000 9 2000-01-20 0,2 0,96 0,0 0,001 6 2000-01-21 - 0,7 0,96 0,5 0,001 | 2000-01-04 | - 3,4 | 1,05 | 11,6 | 0,002 5 |
| 2000-01-07 - 1,5 1,06 2,3 0,003 6 2000-01-08 - 4,3 1,06 18,5 0,003 6 2000-01-09 - 2,4 1,07 5,8 0,004 9 2000-01-10 1,6 1,06 2,6 0,003 6 2000-01-11 - 5,4 1,02 29,2 0,000 4 2000-01-12 - 0,4 1,02 0,2 0,000 4 2000-01-13 - 0,8 1,07 0,6 0,004 9 2000-01-14 2,3 1,04 5,3 0,001 6 2000-01-15 1,4 1,01 2,0 0,000 1 2000-01-16 2,5 1,02 6,3 0,000 1 2000-01-17 - 0,9 1,01 0,8 0,000 1 2000-01-18 0,0 0,97 0,0 0,000 9 2000-01-20 0,2 0,96 0,0 0,001 6 2000-01-21 - 0,7 0,96 0,5 0,001 6 2000-01-22 0,0 0,99 0,0 0,000 1 </td <td>2000-01-05</td> <td>- 3,3</td> <td>1,06</td> <td>10,9</td> <td>0,003 6</td> | 2000-01-05 | - 3,3 | 1,06 | 10,9 | 0,003 6 |
| 2000-01-08 - 4,3 1,06 18,5 0,003 6 2000-01-09 - 2,4 1,07 5,8 0,004 9 2000-01-10 1,6 1,06 2,6 0,003 6 2000-01-11 - 5,4 1,02 29,2 0,000 4 2000-01-12 - 0,4 1,02 0,2 0,000 4 2000-01-13 - 0,8 1,07 0,6 0,004 9 2000-01-14 2,3 1,04 5,3 0,001 6 2000-01-15 1,4 1,01 2,0 0,000 1 2000-01-16 2,5 1,02 6,3 0,000 4 2000-01-17 - 0,9 1,01 0,8 0,000 1 2000-01-18 0,0 0,97 0,0 0,000 9 2000-01-20 0,2 0,96 0,0 0,001 6 2000-01-21 - 0,7 0,96 0,5 0,001 6 2000-01-22 0,0 0,99 0,0 0,000 1 2000-01-23 3,5 0,98 12,3 0,000 4 <td>2000-01-06</td> <td>- 3,3</td> <td>1,06</td> <td>10,9</td> <td>0,003 6</td> | 2000-01-06 | - 3,3 | 1,06 | 10,9 | 0,003 6 |
| 2000-01-09 -2,4 1,07 5,8 0,004 9 2000-01-10 1,6 1,06 2,6 0,003 6 2000-01-11 -5,4 1,02 29,2 0,000 4 2000-01-12 -0,4 1,02 0,2 0,000 4 2000-01-13 -0,8 1,07 0,6 0,004 9 2000-01-14 2,3 1,04 5,3 0,001 6 2000-01-15 1,4 1,01 2,0 0,000 1 2000-01-16 2,5 1,02 6,3 0,000 4 2000-01-17 -0,9 1,01 0,8 0,000 1 2000-01-18 0,0 0,97 0,0 0,000 9 2000-01-19 -1,3 0,95 1,7 0,002 5 2000-01-20 0,2 0,96 0,0 0,001 6 2000-01-21 -0,7 0,96 0,5 0,001 6 2000-01-22 0,0 0,99 0,0 0,000 1 2000-01-23 3,5 0,98 12,3 0,000 4 < | 2000-01-07 | - 1,5 | 1,06 | 2,3 | 0,003 6 |
| 2000-01-10 1,6 1,06 2,6 0,003 6 2000-01-11 -5,4 1,02 29,2 0,000 4 2000-01-12 -0,4 1,02 0,2 0,000 4 2000-01-13 -0,8 1,07 0,6 0,004 9 2000-01-14 2,3 1,04 5,3 0,001 6 2000-01-15 1,4 1,01 2,0 0,000 1 2000-01-16 2,5 1,02 6,3 0,000 4 2000-01-17 -0,9 1,01 0,8 0,000 1 2000-01-18 0,0 0,97 0,0 0,000 9 2000-01-19 -1,3 0,95 1,7 0,002 5 2000-01-20 0,2 0,96 0,0 0,001 6 2000-01-21 -0,7 0,96 0,5 0,001 6 2000-01-22 0,0 0,99 0,0 0,001 6 2000-01-23 3,5 0,98 12,3 0,000 4 2000-01-24 3,6 0,96 13,0 0,001 6 < | 2000-01-08 | - 4,3 | 1,06 | 18,5 | 0,003 6 |
| 2000-01-11 -5,4 1,02 29,2 0,000 4 2000-01-12 -0,4 1,02 0,2 0,000 4 2000-01-13 -0,8 1,07 0,6 0,004 9 2000-01-14 2,3 1,04 5,3 0,001 6 2000-01-15 1,4 1,01 2,0 0,000 1 2000-01-16 2,5 1,02 6,3 0,000 4 2000-01-17 -0,9 1,01 0,8 0,000 1 2000-01-18 0,0 0,97 0,0 0,000 9 2000-01-19 -1,3 0,95 1,7 0,002 5 2000-01-20 0,2 0,96 0,0 0,001 6 2000-01-21 -0,7 0,96 0,5 0,001 6 2000-01-22 0,0 0,99 0,0 0,000 1 2000-01-23 3,5 0,98 12,3 0,000 4 2000-01-24 3,6 0,96 13,0 0,001 6 2000-01-25 9,2 0,96 84,6 0,001 6 | 2000-01-09 | - 2,4 | 1,07 | 5,8 | 0,004 9 |
| 2000-01-12 - 0,4 1,02 0,2 0,000 4 2000-01-13 - 0,8 1,07 0,6 0,004 9 2000-01-14 2,3 1,04 5,3 0,001 6 2000-01-15 1,4 1,01 2,0 0,000 1 2000-01-16 2,5 1,02 6,3 0,000 4 2000-01-17 - 0,9 1,01 0,8 0,000 1 2000-01-18 0,0 0,97 0,0 0,000 9 2000-01-19 - 1,3 0,95 1,7 0,002 5 2000-01-20 0,2 0,96 0,0 0,001 6 2000-01-21 - 0,7 0,96 0,5 0,001 6 2000-01-22 0,0 0,99 0,0 0,000 1 2000-01-23 3,5 0,98 12,3 0,000 4 2000-01-24 3,6 0,96 13,0 0,001 6 2000-01-25 9,2 0,96 27,0 0,001 6 2000-01-26 5,2 0,96 27,0 0,001 6 | 2000-01-10 | 1,6 | 1,06 | 2,6 | 0,003 6 |
| 2000-01-13 - 0,8 1,07 0,6 0,004 9 2000-01-14 2,3 1,04 5,3 0,001 6 2000-01-15 1,4 1,01 2,0 0,000 1 2000-01-16 2,5 1,02 6,3 0,000 4 2000-01-17 - 0,9 1,01 0,8 0,000 1 2000-01-18 0,0 0,97 0,0 0,000 9 2000-01-19 - 1,3 0,95 1,7 0,002 5 2000-01-20 0,2 0,96 0,0 0,001 6 2000-01-21 - 0,7 0,96 0,5 0,001 6 2000-01-22 0,0 0,99 0,0 0,000 1 2000-01-23 3,5 0,98 12,3 0,000 4 2000-01-24 3,6 0,96 13,0 0,001 6 2000-01-25 9,2 0,96 27,0 0,001 6 2000-01-26 5,2 0,96 27,0 0,001 6 2000-01-28 3,7 0,99 13,7 0,000 1 | 2000-01-11 | - 5,4 | 1,02 | 29,2 | 0,000 4 |
| 2000-01-14 2,3 1,04 5,3 0,001 6 2000-01-15 1,4 1,01 2,0 0,000 1 2000-01-16 2,5 1,02 6,3 0,000 4 2000-01-17 -0,9 1,01 0,8 0,000 1 2000-01-18 0,0 0,97 0,0 0,000 9 2000-01-19 -1,3 0,95 1,7 0,002 5 2000-01-20 0,2 0,96 0,0 0,001 6 2000-01-21 -0,7 0,96 0,5 0,001 6 2000-01-22 0,0 0,99 0,0 0,000 1 2000-01-23 3,5 0,98 12,3 0,000 4 2000-01-24 3,6 0,96 13,0 0,001 6 2000-01-25 9,2 0,96 84,6 0,001 6 2000-01-25 9,2 0,96 27,0 0,001 6 2000-01-27 3,3 0,96 10,9 0,001 6 2000-01-28 3,7 0,99 13,7 0,000 1 < | 2000-01-12 | - 0,4 | 1,02 | 0,2 | 0,000 4 |
| 2000-01-15 1,4 1,01 2,0 0,000 1 2000-01-16 2,5 1,02 6,3 0,000 4 2000-01-17 -0,9 1,01 0,8 0,000 1 2000-01-18 0,0 0,97 0,0 0,000 9 2000-01-19 -1,3 0,95 1,7 0,002 5 2000-01-20 0,2 0,96 0,0 0,001 6 2000-01-21 -0,7 0,96 0,5 0,001 6 2000-01-22 0,0 0,99 0,0 0,000 1 2000-01-23 3,5 0,98 12,3 0,000 4 2000-01-24 3,6 0,96 13,0 0,001 6 2000-01-25 9,2 0,96 84,6 0,001 6 2000-01-26 5,2 0,96 27,0 0,001 6 2000-01-28 3,7 0,99 13,7 0,000 1 2000-01-28 3,7 0,99 13,7 0,000 1 2000-01-29 3,6 1,01 13,0 0,000 1 | 2000-01-13 | - 0,8 | 1,07 | 0,6 | 0,004 9 |
| 2000-01-16 2,5 1,02 6,3 0,000 4 2000-01-17 -0,9 1,01 0,8 0,000 1 2000-01-18 0,0 0,97 0,0 0,000 9 2000-01-19 -1,3 0,95 1,7 0,002 5 2000-01-20 0,2 0,96 0,0 0,001 6 2000-01-21 -0,7 0,96 0,5 0,001 6 2000-01-22 0,0 0,99 0,0 0,000 1 2000-01-23 3,5 0,98 12,3 0,000 4 2000-01-24 3,6 0,96 13,0 0,001 6 2000-01-25 9,2 0,96 84,6 0,001 6 2000-01-26 5,2 0,96 27,0 0,001 6 2000-01-27 3,3 0,96 10,9 0,001 6 2000-01-28 3,7 0,99 13,7 0,000 1 2000-01-31 1,8 1,01 13,0 0,000 1 2000-01-31 1,8 1,01 10,82 0,001 7 | 2000-01-14 | 2,3 | 1,04 | 5,3 | 0,001 6 |
| 2000-01-17 - 0,9 1,01 0,8 0,000 1 2000-01-18 0,0 0,97 0,0 0,000 9 2000-01-19 - 1,3 0,95 1,7 0,002 5 2000-01-20 0,2 0,96 0,0 0,001 6 2000-01-21 - 0,7 0,96 0,5 0,001 6 2000-01-22 0,0 0,99 0,0 0,000 1 2000-01-23 3,5 0,98 12,3 0,000 4 2000-01-24 3,6 0,96 13,0 0,001 6 2000-01-25 9,2 0,96 84,6 0,001 6 2000-01-26 5,2 0,96 27,0 0,001 6 2000-01-27 3,3 0,96 10,9 0,001 6 2000-01-28 3,7 0,99 13,7 0,000 1 2000-01-29 3,6 1,01 13,0 0,000 1 2000-01-31 1,8 1,01 3,2 0,000 1 std 0,04 0,04 0,041 | 2000-01-15 | 1,4 | 1,01 | 2,0 | 0,000 1 |
| 2000-01-18 0,0 0,97 0,0 0,000 9 2000-01-19 - 1,3 0,95 1,7 0,002 5 2000-01-20 0,2 0,96 0,0 0,001 6 2000-01-21 - 0,7 0,96 0,5 0,001 6 2000-01-22 0,0 0,99 0,0 0,000 1 2000-01-23 3,5 0,98 12,3 0,000 4 2000-01-24 3,6 0,96 13,0 0,001 6 2000-01-25 9,2 0,96 84,6 0,001 6 2000-01-26 5,2 0,96 27,0 0,001 6 2000-01-27 3,3 0,96 10,9 0,001 6 2000-01-28 3,7 0,99 13,7 0,000 1 2000-01-29 3,6 1,01 13,0 0,000 1 2000-01-31 1,8 1,01 3,2 0,000 1 std 0,04 0,04 0,041 | 2000-01-16 | 2,5 | 1,02 | 6,3 | 0,000 4 |
| 2000-01-19 - 1,3 0,95 1,7 0,002 5 2000-01-20 0,2 0,96 0,0 0,001 6 2000-01-21 - 0,7 0,96 0,5 0,001 6 2000-01-22 0,0 0,99 0,0 0,000 1 2000-01-23 3,5 0,98 12,3 0,000 4 2000-01-24 3,6 0,96 13,0 0,001 6 2000-01-25 9,2 0,96 27,0 0,001 6 2000-01-26 5,2 0,96 27,0 0,001 6 2000-01-27 3,3 0,96 10,9 0,001 6 2000-01-28 3,7 0,99 13,7 0,000 1 2000-01-29 3,6 1,01 13,0 0,000 1 2000-01-31 1,8 1,01 3,2 0,000 1 mean 1,01 10,82 0,001 7 std 0,04 3,3 0,041 | 2000-01-17 | - 0,9 | 1,01 | 0,8 | 0,000 1 |
| 2000-01-20 0,2 0,96 0,0 0,001 6 2000-01-21 -0,7 0,96 0,5 0,001 6 2000-01-22 0,0 0,99 0,0 0,000 1 2000-01-23 3,5 0,98 12,3 0,000 4 2000-01-24 3,6 0,96 13,0 0,001 6 2000-01-25 9,2 0,96 84,6 0,001 6 2000-01-26 5,2 0,96 27,0 0,001 6 2000-01-27 3,3 0,96 10,9 0,001 6 2000-01-28 3,7 0,99 13,7 0,000 1 2000-01-29 3,6 1,01 13,0 0,000 1 2000-01-31 1,8 1,01 3,2 0,000 1 mean 1,01 10,82 0,001 7 std 0,04 3,3 0,041 | 2000-01-18 | 0,0 | 0,97 | 0,0 | 0,000 9 |
| 2000-01-21 - 0,7 0,96 0,5 0,001 6 2000-01-22 0,0 0,99 0,0 0,000 1 2000-01-23 3,5 0,98 12,3 0,000 4 2000-01-24 3,6 0,96 13,0 0,001 6 2000-01-25 9,2 0,96 84,6 0,001 6 2000-01-26 5,2 0,96 27,0 0,001 6 2000-01-27 3,3 0,96 10,9 0,001 6 2000-01-28 3,7 0,99 13,7 0,000 1 2000-01-29 3,6 1,01 13,0 0,000 1 2000-01-31 1,8 1,01 3,2 0,000 1 mean 1,01 10,82 0,001 7 std 0,04 3,3 0,041 | 2000-01-19 | - 1,3 | 0,95 | 1,7 | 0,002 5 |
| 2000-01-22 0,0 0,99 0,0 0,000 1 2000-01-23 3,5 0,98 12,3 0,000 4 2000-01-24 3,6 0,96 13,0 0,001 6 2000-01-25 9,2 0,96 84,6 0,001 6 2000-01-26 5,2 0,96 27,0 0,001 6 2000-01-27 3,3 0,96 10,9 0,001 6 2000-01-28 3,7 0,99 13,7 0,000 1 2000-01-29 3,6 1,01 13,0 0,000 1 2000-01-31 1,8 1,01 3,2 0,000 1 mean 1,01 10,82 0,001 7 std 0,04 3,3 0,041 | 2000-01-20 | 0,2 | 0,96 | 0,0 | 0,001 6 |
| 2000-01-23 3,5 0,98 12,3 0,000 4 2000-01-24 3,6 0,96 13,0 0,001 6 2000-01-25 9,2 0,96 84,6 0,001 6 2000-01-26 5,2 0,96 27,0 0,001 6 2000-01-27 3,3 0,96 10,9 0,001 6 2000-01-28 3,7 0,99 13,7 0,000 1 2000-01-29 3,6 1,01 13,0 0,000 1 2000-01-31 1,8 1,01 3,2 0,000 1 mean 1,01 10,82 0,001 7 std 0,04 square root of mean 3,3 0,041 | 2000-01-21 | - 0,7 | 0,96 | 0,5 | 0,001 6 |
| 2000-01-24 3,6 0,96 13,0 0,001 6 2000-01-25 9,2 0,96 84,6 0,001 6 2000-01-26 5,2 0,96 27,0 0,001 6 2000-01-27 3,3 0,96 10,9 0,001 6 2000-01-28 3,7 0,99 13,7 0,000 1 2000-01-29 3,6 1,01 13,0 0,000 1 2000-01-31 1,8 1,01 3,2 0,000 1 mean 1,01 10,82 0,001 7 std 0,04 square root of mean 3,3 0,041 | 2000-01-22 | 0,0 | 0,99 | 0,0 | 0,000 1 |
| 2000-01-25 9,2 0,96 84,6 0,001 6 2000-01-26 5,2 0,96 27,0 0,001 6 2000-01-27 3,3 0,96 10,9 0,001 6 2000-01-28 3,7 0,99 13,7 0,000 1 2000-01-29 3,6 1,01 13,0 0,000 1 2000-01-31 1,8 1,01 3,2 0,000 1 mean 1,01 10,82 0,001 7 std 0,04 3,3 0,041 | 2000-01-23 | 3,5 | 0,98 | 12,3 | 0,000 4 |
| 2000-01-26 5,2 0,96 27,0 0,001 6 2000-01-27 3,3 0,96 10,9 0,001 6 2000-01-28 3,7 0,99 13,7 0,000 1 2000-01-29 3,6 1,01 13,0 0,000 1 2000-01-31 1,8 1,01 3,2 0,000 1 mean 1,01 10,82 0,001 7 std 0,04 3,3 0,041 | 2000-01-24 | 3,6 | 0,96 | 13,0 | 0,001 6 |
| 2000-01-27 3,3 0,96 10,9 0,001 6 2000-01-28 3,7 0,99 13,7 0,000 1 2000-01-29 3,6 1,01 13,0 0,000 1 2000-01-31 1,8 1,01 3,2 0,000 1 mean 1,01 10,82 0,001 7 std 0,04 square root of mean 3,3 0,041 | 2000-01-25 | 9,2 | 0,96 | 84,6 | 0,001 6 |
| 2000-01-28 3,7 0,99 13,7 0,000 1 2000-01-29 3,6 1,01 13,0 0,000 1 2000-01-31 1,8 1,01 3,2 0,000 1 mean 1,01 10,82 0,001 7 std 0,04 square root of mean 3,3 0,041 | 2000-01-26 | 5,2 | 0,96 | 27,0 | 0,001 6 |
| 2000-01-29 3,6 1,01 13,0 0,000 1 2000-01-31 1,8 1,01 3,2 0,000 1 mean 1,01 10,82 0,001 7 std 0,04 square root of mean 3,3 0,041 | 2000-01-27 | 3,3 | 0,96 | 10,9 | 0,001 6 |
| 2000-01-31 1,8 1,01 3,2 0,000 1 mean 1,01 10,82 0,001 7 std 0,04 square root of mean 3,3 0,041 | 2000-01-28 | 3,7 | 0,99 | 13,7 | 0,000 1 |
| mean 1,01 10,82 0,001 7 std 0,04 square root of mean 3,3 0,041 | 2000-01-29 | 3,6 | 1,01 | 13,0 | 0,000 1 |
| std 0,04 square root of mean 3,3 0,041 | 2000-01-31 | 1,8 | 1,01 | 3,2 | 0,000 1 |
| square root of mean 3,3 0,041 | mean | | 1,01 | 10,82 | 0,001 7 |
| mean 3,3 0,041 | std | | 0,04 | | |
| f 30 30 | • | | | 3,3 | 0,041 |
| | f | | | 30 | 30 |

According to the control procedure applied, the control data, provided every 25 h, cover all days of the month as well as all hours of the day. The uncertainty data presented in Table A.1 cover a period of unattended operation not interrupted by maintenance or calibration. Therefore, the available control data were judged as applicable to the time period of interest.

The model equation used for uncertainty analysis of the hourly mean values C_i is given by equation (A.1):

$$C_i = (Y_i + \mathsf{d}C) \ (1 + \mathsf{d}B) \tag{A.1}$$

where

 C_i is the measurement result (hourly mean value of nitrogen dioxide);

 Y_i is the response of the measuring system;

dC is the zero-point drift (corrected daily);

dB is the deviation about the slope B equal to one (not corrected for).

Taking into account first-order deviations only, equation (A.1) may be transformed to equation (A.2):

$$C_i = Y_i + \mathsf{d}C + Y_i \, \mathsf{d}B \tag{A.2}$$

The value of the daily drift correction dC is determined by application of zero gas to the measuring system, as described by equations (A.3) and (A4):

$$0 = Y_0 + dC \tag{A.3}$$

$$dC = -Y_0 \tag{A.4}$$

where Y_0 is the response of the measuring system on application of zero gas (see Table A.1).

After daily determination of the drift correction dC, span-gas of known concentration C_1 is applied to the measuring system in order to determine the deviation dB of the slope from the value 1 established within the calibration routine as described by equations (A.5) and (A.6):

$$C_1 = (Y_1 - Y_0)(1 + dB)$$
 (A.5)

$$dB = C_1/(Y_1 - Y_0) - 1 (A.6)$$

In equations (A.5) and (A.6), the term $(Y_1 - Y_0)$ represents the response of the measuring system on application of the span gas after correction for zero-point drift.

Based on model equation (A.1), the variance of the hourly mean value C_i is given by equation (A.7):

$$u^{2}(C_{i}) = u^{2}(Y_{i}) + u^{2}(dC) + Y_{i}^{2}u^{2}(dB)$$
(A.7)

where

- $u(C_i)$ is the standard uncertainty of the hourly mean value C_i ;
- $u(Y_i)$: is the standard uncertainty of the response Y_i (in unit of the measurand C) of the measuring system under calibration conditions;
- u(dC) is the standard uncertainty of the measuring system due to zero-point drift;
- u(dB) is the standard uncertainty of the measuring system due to slope drift.

The measuring system was calibrated by a one-point calibration routine applying a transfer standard of concentration C_R one time to the measuring system. Accordingly, the standard uncertainty u(Y) of the response Y_i of the measuring system under calibration conditions is given by the known standard uncertainty of the transfer standard $u(C_R)$ as described by equation (A.8):

$$u(Y_i) = u(C_{\mathsf{R}}) \tag{A.8}$$

The corresponding number of degrees of freedom is f = 5.

The variance of the drift dC is estimated by the mean square of the observed values $dC = -Y_0$ as described by equation (A.9):

$$u^2(\mathsf{d}C) = \overline{Y_0^2} \tag{A.9}$$

The variance of the drift dB is given by the mean square deviations of the observed values B from the value 1 as described by equation (A.10):

$$u^{2}(dB) = \overline{(dB)^{2}}$$
(A.10)

Since the mean value of B is very close to 1 (see Table A.1), $u^2(dB)$ is considered as a (mainly) random contribution to the uncertainty budget of the hourly mean value C_i .

Table A.2 summarizes the assessment of the variance contributions of the hourly mean values used to calculate the monthly average. The corresponding number of degrees of freedom as well as the type of the uncertainty contributions are also indicated. Table A.3 summarizes the random and non-random uncertainty contributions of the hourly mean values.

Table A.2 — Summary of variance contributions of the hourly mean values C_i for $Y \le 100 \,\mu\text{g/m}^3$

| Input quantity | Variance contribution | Quantification of variance contribution | Value of variance contribution (μg/m³) ² | Number of degrees of freedom | Type of variance contribution |
|-------------------|--------------------------|---|--|------------------------------------|-------------------------------|
| Y | $u^2(Y)$ | $u^2(C_{R})$ | 16 | 5 | non-random |
| d C | $u^2(dC)$ | $\overline{Y_0^2}$ | 10,82 | 30 | random |
| d <i>B</i> | $Y^2 u^2(dB)$ | $10\ 000\ \overline{\left(dB\right)^2}$ | ≤ 17,0 | 30 | random (mainly) |

Table A.3 — Random and non-random uncertainty contributions of the hourly mean values C_i for $Y \le 100 \ \mu g/m^3$

| Uncertainty contribution | Equation | Number of degrees of freedom |
|-----------------------------|------------------------|------------------------------|
| $u_{r}^{2}(C_{i})$ | $u^2(dC) + Y^2u^2(dB)$ | 30 |
| $u_{nr}^{2}(C_{i})$ | $u^2(C_{R})$ | 5 |

The assumption of $Y \le 100 \,\mu\text{g/m}^3$ was justified for the set of measurement results used to calculate the monthly average of interest. This assumption leads to an overestimation of the variance contribution of the deviation d*B*.

The input data on the uncertainty of the measurement results C_i used to calculate the monthly average are suitable for application of case 5.2 a).

A.2 Uncertainty estimation of the monthly average

A.2.1 Measurement uncertainty

According to 6.2 a), the mean square uncertainty of the time average \bar{C}_{month} due to the measuring system is given by equation (A.11):

$$u_{\mathsf{M}}^{2}(\overline{C}_{\mathsf{month}}) = \frac{1}{N^{2}} \sum_{i=1}^{N} u_{\mathsf{r}}^{2}(C_{i}) + u_{\mathsf{nr}}^{2} \tag{A.11}$$

where N is the number of hourly mean values used to calculate the average.

Table A.4 summarizes the assessment of the mean square uncertainty of the time average \bar{C}_{month} due to the measuring system as described by equation (A.11). The corresponding number of degrees of freedom as well as the type of the variance contributions are also indicated.

Table A.4 — Assessment of variance contributions of the monthly average \bar{C}_{month} due to the measuring system for $Y \le 100 \ \mu g/m^3$

| Variance | Variance contribution | Quantification of variance contribution | Value of variance contribution (µg/m³)² | Number of degrees of freedom | Type of variance contribution |
|------------------------------------|---|---|--|------------------------------------|-------------------------------|
| u 2 nr | | $u^2(C_{R})$ | 16,00 | 5 | non-random |
| $\sum u_{\rm r}^2(C_i)/N^2$ | $\sum u^2 (dC) / N^2 +$ $\sum Y_i^2 u^2 (dB) / N^2$ | | | | |
| | $\sum u^2(dC)/N^2$ | $\overline{Y_0^2} / N$ | 0,016 | 30 | random |
| | $\sum Y_i^2 u^2 (dB) / N^2$ | 10 000 (dB) ² / N | ≤ 0,025 | 30 | random (mainly) |
| $u_{\rm M}^2(\bar{C}_{\rm month})$ | | | 16,041 | 5 | |
| $u_{M}(\bar{C}_{month})$ | | | 4,01 | 5 | |

Table A.4 shows that the measurement uncertainty of the average \overline{C}_{month} is dominated by the non-random contribution of the reference standard used for calibration of the measuring system. The number of degrees of freedom of \overline{C}_{month} , determined according to 6.2, is also dominated by the small number of degrees of freedom of the non-random contribution to the measurement uncertainty. The assumption of $Y \leqslant 100~\mu g/m^3$ leads to an overestimation of the variance contribution of the deviation dB.

A.2.2 Uncertainty due to missing values

The standard deviation of the hourly mean values C_i used to calculate the monthly average \overline{C}_{month} are determined according to equation (15). The standard uncertainty $u_S^2(\overline{C}_{month})$ of the average \overline{C}_{month} due to the missing values is determined by application of equation (14). The corresponding number of degrees of freedom is N-1. Table A.5 summarizes the results.

Table A.5 — Assessment of the standard uncertainty of the monthly average $\overline{C}_{\mathrm{month}}$ due to missing values

| Quantity | Value |
|-------------------------------|------------------------|
| $N_{\sf max}$ | 744 |
| N | 692 |
| $s(C_i)$ | 18,7 μg/m ³ |
| \overline{C}_{month} | 38,0 μg/m ³ |
| $u_{S}(\overline{C}_{month})$ | 0,2 μg/m ³ |
| f | 691 |

A.2.3 Statements on the uncertainty of the time average

The uncertainty of the time average is calculated from the values $u_{\rm M}(\overline{C}_{\rm month}) = 4,01~\mu {\rm g/m^3}$ and $u_{\rm S}(\overline{C}_{\rm month}) = 0,2~\mu {\rm g/m^3}$ by means of equation (17). The number of degrees of freedom is calculated by means of equation (18).

Table A.6 summarizes results of the uncertainty analysis performed, where

Tis the averaging time period;

 \bar{C}_{month} the time average considered;

 $u(\overline{C}_{month})$ is the combined standard uncertainty of \bar{C}_{month} ;

is the expanded uncertainty of \overline{C}_{month} on the level of confidence p; $U_p(\overline{C}_{month})$

is the effective number of degrees of freedom; f_{eff}

is the level of confidence p;

 $k_p(f_{\mathsf{eff}})$ is the coverage factor for number of degrees of freedom f_{eff} and the level of confidence p.

Table A.6 — Statements on uncertainty of the time average \bar{c}_{month}

| Quantity | Value |
|------------------------|------------------------|
| T | 1 month |
| $ar{C}_{month}$ | 38,0 μg/m ³ |
| $u(\bar{C}_{month})$ | 4,0 μg/m ³ |
| $U_p(\bar{C}_{month})$ | 10,4 μg/m ³ |
| f_{eff} | 5 |
| p | 0,95 |
| $k_p(f_{eff})$ | 2,6 |

A.3 Discussion

The example considered is a large-sample application from the field of ambient air monitoring. The time coverage of the averaging time period of one month by the data set used to calculate the monthly average is, with 93 %, reasonably high. Accordingly, the contribution of the 7 % missing values to the uncertainty of the monthly average is negligible. The procedures described within this International Standard are applicable in the same way, if averages are calculated from data sets exhibiting a small coverage of the averaging time period considered, as long as the small data sets are representative of the averaging time period.

If the number of available hourly mean values of nitrogen dioxide within the example considered were reduced to N = 31 (one hourly mean value per day of the month), then the standard uncertainty of the monthly average due to missing values is given by equation (A.12):

$$u_{S}(\overline{C}_{month}) = 18,7 \ \mu g/m^{3} \sqrt{1 - \frac{31}{744}/31}$$

$$= 3,3 \ \mu g/m^{3}$$
(A.12)

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