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**Gas analysis — Comparison methods  
for the determination of the  
composition of gas mixtures based on  
one- and two-point calibration**

*Analyse des gaz — Méthodes de comparaison pour la détermination  
de la composition des mélanges de gaz basées sur un ou deux points  
d'étalonnage*





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## Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see [www.iso.org/directives](http://www.iso.org/directives)).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see [www.iso.org/patents](http://www.iso.org/patents)).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation on the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: [www.iso.org/iso/foreword.html](http://www.iso.org/iso/foreword.html).

This document was prepared by Technical Committee ISO/TC 158, *Analysis of gases*.

## Introduction

Whereas the comparison methods described in ISO 6143 based on multipoint calibration are in principle suited for all applications in gas analysis for determining the composition of calibration gas mixtures, in many cases, simpler calibration methods can be used. These methods typically require a smaller number of calibration gas mixtures with a traceable composition.

One- and two-point calibration of instruments is widely used in the gas industry and in national metrology institutes. They often constitute fair compromise between costs and efforts on one hand, and accuracy on the other. These simpler methods require validation to confirm that the conditions of use are appropriate.

It is the intention of this document to set up and describe comparison methods and data evaluation techniques based on one- and two-point calibration. The applicable conditions and limitations of the methods are derived from the analytical requirements and are clearly specified.

This document describes the assessment, calculation and expression of measurement uncertainty arising from significant contributors in the different comparison methods.



# Gas analysis — Comparison methods for the determination of the composition of gas mixtures based on one- and two-point calibration

## 1 Scope

This document provides methods for

- calibrating an instrument with one or two calibration gas mixtures,
- determining the composition of a gas sample, and
- evaluating the uncertainty of the composition of the gas sample in relation to the uncertainty of the composition of the calibration gases used and the contribution of the measurement process.

This document sets requirements to, and acceptance criteria for, the utilization of different measurement calibration designs with a limited (i.e. minimum) number of calibration gas mixtures used in calibration.

The methods in this document are described for amount-of-substance fractions, but are also applicable for other composition quantities (such as mass fractions, volume fractions or concentrations).

## 2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 6141, *Gas analysis — Contents of certificates for calibration gas mixtures*

ISO 6143, *Gas analysis — Comparison methods for determining and checking the composition of calibration gas mixtures*

ISO 7504, *Gas analysis — Vocabulary*

ISO/IEC Guide 98-3:2008, *Uncertainty of measurement — Part 3: Guide to the expression of uncertainty in measurement (GUM:1995)*

ISO/IEC Guide 99, *International vocabulary of metrology — Basic and general concepts and associated terms (VIM)*

## 3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 7504, ISO/IEC Guide 98-3 and ISO/IEC Guide 99 apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- IEC Electropedia: available at <http://www.electropedia.org/>
- ISO Online browsing platform: available at <http://www.iso.org/obp>

## 4 Symbols

$\alpha_j$	coefficients of the best available calibration function $f$ ( $j = 0, 1, \dots, N$ ) with $N \leq 3$ as determined in the performance evaluation procedure, with $N$ being the order of the polynomial
$b_j$	parameters of the simplified analysis function $g$ ( $j = 0, 1$ )
$\beta_j$	parameters of the best-available analysis function $g$ ( $j = 0, 1, \dots, N$ ) with $N \leq 3$ as determined in the performance evaluation procedure, with $N$ being the order of the polynomial
$f$	calibration function, $y = f(x)$
$g$	analysis function, $x = g(y)$
$k$	coverage factor
$m$	number of replicate measurements taken
$N$	order of the polynomial
$R$	range of amount-of-substance fractions within which the selected method of calibration is applied to samples of unknown composition (hereinafter: unknown samples)
$U(q)$	expanded uncertainty associated with the quantity, $q$ , $U(q) = k \times u(q)$
$u(q)$	standard uncertainty associated with the quantity, $q$
$u(\Delta)$	uncertainty contribution due to zero-deviations and analyser nonlinearity
$u^2(q)$	variance associated with the quantity, $q$
$x$	amount fraction
$(x_i, y_i)$	calibration point(s) ( $i = 1, 2, \dots, n$ ), with $n$ being its number
$y(l)$	instrumental response, with $l$ indicating the replicate number
$\bar{y}$	mean replicated instrumental responses
$\Gamma$	goodness of fit; a measure of local compatibility of a calibration point with the calculated calibration or analysis function
$\Delta$	bias due to zero-deviation and analyser nonlinearity
$\delta$	bias
$\bar{\delta}$	average bias

## 5 Abbreviated terms

b	blank
GLS	generalized least squares
MPC	multipoint calibration



Re	measurement of the matching reference
r	subscript denoting a calibration gas mixture
r1, r2	calibration gas mixtures bracketing the composition of the unknown sample
S	unknown gas sample
s	subscript denoting an unknown gas sample
SSD	sum of weighted squared deviations
SPEM	single-point exact-match calibration
SPO	single-point through origin calibration
TPB	two-point calibration using a single point and a blank
TPC	two-point calibration

## 6 Principle

### 6.1 General requirements

The composition of a gas mixture is determined by separate measurement of the amount fraction of every specified component. “Separate” implies that the response obtained for the component of interest is treated independently of any other response obtained for any other component. It does not impede obtaining several responses for several components in the same instrument run. Therefore, the procedure for determining the amount fraction of only one specified component is described. Possible interferences of other components on the measurement of the component of interest shall be avoided or corrected for separately. This subject is not further addressed in this document.

The procedure for determining the amount fraction  $x$  of a specified component  $X$  in a sample of a gas mixture, or in a series of such samples, is performed in a sequence of steps as summarized below.

- a) Specify the analytical range of interest,  $R$ , i.e. the range of the amount fraction  $x$  to be determined, and the acceptable or required (if applicable) uncertainty level.
- b) Specify the analytical method and the measuring system to be used:
  - 1) calibration range (to encompass the analytical range);
  - 2) composition, including uncertainty, of the calibration gas mixtures;
  - 3) parameters of the analytical method;
  - 4) measuring conditions;
  - 5) number and sequence of calibration measurements (see [8.1](#)).
- c) Select, from the list given in [6.2](#), an approach for calibration and determining the amount fractions of components in unknown samples in the regular, i.e. daily mode when one- and two-point based analysis functions are used.
- d) For the relevant ranges of responses and component amount fractions, determine the uncertainty level of the prospective results based on the analysis function. If the result is acceptable, performance evaluation was successful.

For the calculation of the measurement uncertainty of results obtained in the regular calibration mode, an estimate  $u(\Delta)$  for the contribution of possible nonlinearity of the system is needed. This estimate is calculated in a performance evaluation of the system according to [Clause 8](#) and [Annex C](#).

The evaluation is best done after the specifications according to a) to c) are set. The estimate is used in all subsequent regular calibrations until there is reason to assume significant changes in the instrument performance. The main reasons for such changes are given in [9.1](#).

- e) Perform calibration and measurement according to the steps given in [Clause 7](#).

### 6.2 Calibration methods

The following calibration methods for determining the amount fraction of a specified component in an unknown gas sample may apply:

- a) single-point exact-match calibration (SPEM) and direct transfer of value and uncertainty of the matching calibration gas mixture;
- b) single-point through origin calibration (SPO) and transfer of the value assuming a straight-line calibration function through the origin;
- c) two-point calibration using a single-point and a blank (TPB) calculation of the value from a straight-line analysis function;
- d) two-point calibration: bracketing using two calibration gas mixtures (TPC).

NOTE Multipoint calibration (MPC) uses at least three calibration points.

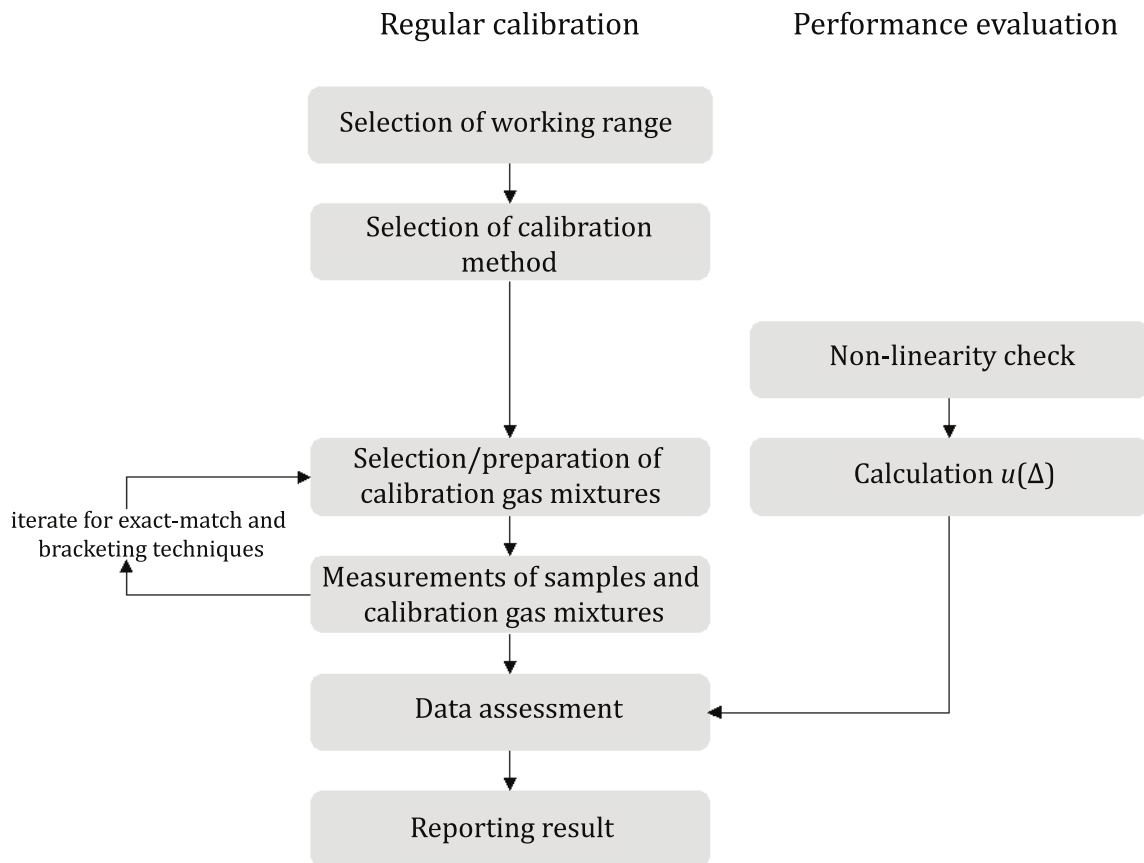
## 7 Main procedure

### 7.1 Pre-requisites

Stability of the system within the period of time equal to a normal calibration interval shall be demonstrated during method validation. The use of unstable systems is strongly discouraged in general, in particular for designs SPO and TPB in [6.2](#). For use of designs SPEM and TPC with not sufficiently stable systems, see [Annex A](#).

### 7.2 Sequence of operations (overview)

[Figure 1](#) illustrates the basic steps of carrying out measurements according to the calibration methods described in this document. Aims, steps and frequency of the performance evaluation are described in [Clause 8](#).



**Figure 1 — Sequence of operations**

## 7.3 Calibration and measurement designs

### 7.3.1 General

All designs as specified in 6.2 consist of four basic steps, namely

- step A: calibration of the instrument;
- step B: measurement of the sample;
- step C: calculation of the unknown amount fraction of the component in the sample;
- step D: calculation of the uncertainty of the amount fraction of the component.

In practice, steps A and B apply in order to adjust the calibration gas mixture to the unknown sample, in particular for SPEM and SPO. For SPEM, the calibration gas mixture shall resemble the unknown (see 7.3.2); for SPO, the measured response of the sample shall be in the predefined range in the vicinity of the response of the calibration gas mixture.

For all designs, at least three replicates should be taken for any unknown or calibration gas mixture, whenever practicable. Such a number should be sufficient to confirm adequate repeatability of the responses. If three replicates are not feasible, the user shall have a reliable estimate of the standard uncertainty of the sample measurement.

Expressions for the mean and the standard deviations of replicate signal measurements used throughout this document are given in Annex B.

### 7.3.2 Single-point exact-match calibration (SPEM)

**Step A:** Select a calibration gas mixture such that the measuring system produces, on this mixture, responses which are statistically indistinguishable from those obtained on the unknown sample.

Take at least three replicate measurements of the calibration gas mixture and calculate the mean response value of these replicates,  $y_r$ , and the standard uncertainty,  $u(y_r)$ , of the mean response value (see [Annex B](#)).

**Step B:** Take at least three replicate measurements of the sample and calculate the mean response value of these replicates,  $y_s$ , and the standard uncertainty,  $u(y_s)$ , of the mean response value (see [Annex B](#)).

Calibration gas and sample are indistinguishable if it holds

$$\frac{|y_r - y_s|}{2 \times \sqrt{u^2(y_r) + u^2(y_s)}} \leq 1 \quad (1)$$

**Step C:** If the condition according to [Formula \(1\)](#) is fulfilled, the value of the unknown is estimated by direct transfer of the value of the calibration gas mixture, i.e. it holds

$$x_s = x_r \cdot \frac{y_s}{y_r} \quad (2)$$

In an exact-match situation, the signal ratio for the measurements of the unknown and the reference should ideally be unity, yielding the “exact” match,  $x_s = x_r$ . [Formula \(2\)](#) thus accounts for situations rather at the edges of the condition according to [Formula \(1\)](#).

**Step D:** Repeat the measurements with the calibration gas mixture in order to check system stability in accordance with [Annex A](#).

**Step E:** The uncertainty of the value of the unknown is derived from the uncertainty of the calibration gas mixture by direct transfer, taking into account that measurements are carried out on both the calibration and the unknown gas sample; see [Formula \(3\)](#):

$$u^2(x_s) = u^2(x_r) + \frac{x_r^2}{y_r^2} \cdot [u^2(y_s) + u^2(y_r)] \quad (3)$$

### 7.3.3 Single-point through origin calibration (SPO)

**Step A:** Select a calibration gas mixture such that the measuring system produces, on this mixture, responses which are sufficiently close to those obtained on the unknown sample. Closeness is characterized by the pre-selected range,  $R$ . A calibration gas may be considered sufficiently close to the unknown sample if the amount fraction of the component of interest does not differ by more than +50 % or -10 % from the unknown sample.

Take at least three replicate measurements of the calibration gas mixture and calculate the mean response value of these replicates,  $y_r$ , and the standard uncertainty,  $u(y_r)$ , of the mean response value (see [Annex B](#)).

**Step B:** Take at least three replicate measurements of the sample and calculate the mean response value of these replicates,  $y_s$ , and the standard uncertainty,  $u(y_s)$ , of the mean response value (see [Annex B](#)).

**Step C:** The value of the unknown is calculated by assuming a straight-line analysis function through the origin and calculated from the value of the calibration gas mixture according to [Formula \(4\)](#):

$$x_s = b_1 \times y_s \quad (4)$$

where  $b_1$  denotes the slope of the analysis function, i.e. the ratio  $x_r/y_r$ .

**Step D:** The uncertainty associated with the value of the unknown is evaluated from the uncertainty of the calibration gas mixture, the uncertainty of the response measurements and the contributions of the prediction errors according to [Formula \(5\)](#):

$$u^2(x_s) = \left(\frac{y_s}{y_r}\right)^2 \times u^2(x_r) + \left(\frac{x_r}{y_r}\right)^2 \times u^2(y_s) + \left(\frac{y_s \times x_r}{y_r}\right)^2 \times u^2(y_r) + u^2(\Delta) \quad (5)$$

The estimation of the term  $u(\Delta)$  is described in [Clause 8](#) and [Annex C](#).

### 7.3.4 Two-point calibration with a blank (TPB)

**Step A:** Select a calibration gas mixture such that the measuring system produces, on this mixture, responses which are sufficiently close to those obtained on the unknown sample. Closeness is characterized by the pre-selected range,  $R$ . Here, the same considerations to sufficient closeness apply as given under [7.3.3](#). Select a fit-for-purpose (i.e. sufficiently pure and free of interferences) blank matrix gas.

Take at least three replicate measurements of the calibration gas mixture and the blank gas, and calculate the mean response values of these replicates,  $y_r$  and  $y_b$ , respectively, and the standard uncertainties,  $u(y_r)$  and  $u(y_b)$ , of the mean response values for both the reference and the blank gases, respectively (see [Annex B](#)).

**Step B:** Take at least three replicate measurements of the sample and calculate the mean response value of these replicates,  $y_s$ , and the standard uncertainty,  $u(y_s)$ , of the mean response value (see [Annex B](#)).

**Step C:** The value of the unknown is estimated using a straight-line function with a non-zero intercept given by the blank measurement and calculated from the value of the calibration gas mixture according to [Formula \(6\)](#):

$$x_s = b_0 + b_1 \cdot y_s = \frac{y_r \cdot x_b - y_b \cdot x_r}{y_r - y_b} + \frac{x_r - x_b}{y_r - y_b} \cdot y_s \quad (6)$$

with  $b_1$  being the slope and  $b_0$  the intercept of the analysis function, on the right-hand side expressed in terms of the responses and the amount fractions of the reference and the blank gases.

**Step D:** The uncertainty associated with the amount fraction of the unknown is evaluated from the uncertainty of the calibration gas mixture, the uncertainty of the response measurements and the contributions of the prediction errors according to [Formula \(7\)](#):

$$u^2(x_s) = \left(\frac{\partial x_s}{\partial y_s}\right)^2 \cdot u^2(y_s) + \left(\frac{\partial x_s}{\partial y_r}\right)^2 \cdot u^2(y_r) + \left(\frac{\partial x_s}{\partial y_b}\right)^2 \cdot u^2(y_b) + \left(\frac{\partial x_s}{\partial x_r}\right)^2 \cdot u^2(x_r) + \left(\frac{\partial x_s}{\partial x_b}\right)^2 \cdot u^2(x_b) + u^2(\Delta) \quad (7)$$

The analytical expressions for the sensitivity coefficients  $\partial x_s / \partial y_s$ ,  $\partial x_s / \partial y_r$ ,  $\partial x_s / \partial y_b$ ,  $\partial x_s / \partial x_r$  and  $\partial x_s / \partial x_b$  are given in [Annex B](#).

The estimation of the term  $u(\Delta)$  is described in [Clause 8](#) and [Annex C](#).

NOTE It is assumed in general that the responses to the reference and the blank gas are uncorrelated. It is also assumed that the reference and the blank gas are independent; therefore, the values  $x_r$  and  $x_b$  are uncorrelated.

### 7.3.5 Two-point calibration with bracketing (TPC)

**Step A:** Select two calibration gas mixtures such that the measuring system produces, on these mixtures, responses which bracket, within a specified range,  $R$ , those obtained on the unknown sample.

Take at least three replicate measurements of the two calibration gas mixture, and calculate the mean response values of these replicates,  $y_{r1}$  and  $y_{r2}$ , respectively, and the standard uncertainties,  $u(y_{r1})$  and  $u(y_{r2})$ , of the respective mean response values for both calibration gases (see [Annex B](#)).

**Step B:** Take at least three replicate measurements of the sample and calculate the mean response value of these replicates,  $y_s$ , and the standard uncertainty,  $u(y_s)$ , of the mean response value (see [Annex B](#)).

**Step C:** The value of the unknown is estimated by assuming a straight-line analysis function with a non-zero intercept approximating the true calibration function within a specified range and calculated from the values of the calibration gas mixtures according to [Formula \(8\)](#):

$$x_s = b_0 + b_1 \cdot y_s = \frac{y_{r2} \cdot x_{r1} - y_{r1} \cdot x_{r2}}{y_{r2} - y_{r1}} + \frac{x_{r2} - x_{r1}}{y_{r2} - y_{r1}} \cdot y_s \quad (8)$$

with  $b_1$  being the slope and  $b_0$  the intercept of the calibration function determined using the bracketing calibration gas mixtures.

**Step D:** Repeat the measurements with the mixtures in order to check system stability in accordance with [Annex A](#).

**Step E:** The uncertainty of the value of the unknown is derived from the uncertainty of the calibration gas mixtures, the uncertainty of the response measurements and the contributions of the prediction errors according to [Formula \(9\)](#):

$$u^2(x_s) = \left(\frac{\partial x_s}{\partial y_s}\right)^2 \cdot u^2(y_s) + \left(\frac{\partial x_s}{\partial y_{r2}}\right)^2 \cdot u^2(y_{r2}) + \left(\frac{\partial x_s}{\partial y_{r1}}\right)^2 \cdot u^2(y_{r1}) + \left(\frac{\partial x_s}{\partial x_{r2}}\right)^2 \cdot u^2(x_{r2}) + \left(\frac{\partial x_s}{\partial x_{r1}}\right)^2 \cdot u^2(x_{r1}) + u^2(\Delta) \quad (9)$$

The analytical expressions for the sensitivity coefficients  $\partial x_s / \partial y_s$ ,  $\partial x_s / \partial y_{r2}$ ,  $\partial x_s / \partial y_{r1}$ ,  $\partial x_s / \partial x_{r2}$  and  $\partial x_s / \partial x_{r1}$  are given in [Annex B](#). A worked example is given in [Annex D](#).

The estimation of the term  $u(\Delta)$  is described in [Clause 8](#) and [Annex C](#).

NOTE It is assumed in general that the responses to the two bracketing gases are uncorrelated. It is also assumed that the two bracketing gases are independent, i.e. not derived from a common source by, for example, dilution. Therefore, the values  $x_{r1}$  and  $x_{r2}$  are uncorrelated.

### 7.3.6 Multipoint calibration (MPC)

Procedures and designs are comprehensively described in ISO 6143.

## 8 Performance evaluation of the measuring system

### 8.1 General

The performance evaluation aims at quantifying the effects of nonlinearity of the analyser system on its performance when using SPO, TPB and TPC (see [6.2](#) for a description of these designs). It shall be carried out before using the system in regular mode and repeated only in cases mentioned in [9.1](#). The SPEM approach does not require performance evaluation of the response function.

Performance evaluation of the system used shall be performed:

- a) at the time of implementing and validating the method (initial performance evaluation);
- b) each time after the system or one of the components of the system have been altered, maintained or replaced.

Nonlinearity of the measuring system would require a content-dependent correction throughout the analytical range. To avoid such a correction, there are several alternatives. In this document, a possible nonlinearity is treated according to ISO 15796:2005, 5.3.4, by including the maximum possible deviation in the uncertainty budget of the reported value. Alternatively, the approach described in ISO/IEC Guide 98-3:2008, F.2.4.5 can be used, involving the calculation of the average bias correction and its associated standard uncertainty. This approach is explained in [Annex C](#). For a detailed description of the GLS regression approach, see ISO 6143.

**Step A:** Select a minimum of seven different calibration gas mixtures covering the analytical range within which it is intended to use the one- or two-point based regular calibration. Measure the response,  $y$ , for samples of the chosen calibration gas mixtures.

If reliable documented information on the kind-of-analysis-function of the analyser under performance evaluation exists (as e.g. from sources mentioned in [8.2](#)), and only the actual analysis function parameter are to be determined in the performance evaluation, the number of different calibration gases may be reduced to five for analysers with known quadratic and three for analysers with known linear response.

The composition range of calibration gas mixtures chosen for performance evaluation shall cover but not grossly exceed the specified analytical range for the specific component.

**Step B:** On the given calibration data, test a best-available analysis function according to the approach chosen, according to [Formula \(10\)](#) and [Formula \(11\)](#), namely for

SPO

$$x = \beta_1 \times y \quad (10)$$

TPB and TPC

$$x = \beta_0 + \beta_1 \times y \quad (11)$$

using GLS regression. Calculate the residual SSD and the goodness-of-fit measure,  $\Gamma$ . If the SSD is less than two times the number of calibration data points, and  $\Gamma < 2$ , the system is linear. Under these conditions, the parameters of the best-available analysis function are equally the parameters of the simplified regular analysis function according to the approach selected, i.e. set  $b_0 = \beta_0$  and  $b_1 = \beta_1$ . Set  $u(\Delta) = 0$ . End performance evaluation.

**Step C:** If under step B linearity of the system could not be confirmed, fit a second-order polynomial analysis function to the given calibration data. Use GLS regression. Calculate the residual SSD and the goodness-of-fit measure,  $\Gamma$ . If the SSD is less than two times the number of calibration data points, and  $\Gamma < 2$ , the system is slightly nonlinear. Go to step E and assess the uncertainty contribution,  $u(\Delta)$ .

**Step D:** If under step C the performance criteria were not met, fit a third-order polynomial analysis function to the given calibration data. Use GLS regression. Calculate the residual SSD and the goodness-of-fit measure,  $\Gamma$ . The residual SSD shall be less than two times the number of calibration data points and the  $\Gamma < 2$ . Furthermore, the analysis function shall not have an inflexion point in the analytical range.

The system is nonlinear. Go to step E and assess the uncertainty contribution,  $u(\Delta)$ .

**Step E:** Let  $g(y)$  be the best-available analysis function describing the system according to steps C or D of the performance evaluation. Calculate, within the analytical range,  $R$ , the deviation of the real analysis function and the simplified regular function as given under step B; see [Formula \(12\)](#):

$$\Delta = g(y) - b_0 - b_1 \cdot y = \sum_{i=0}^N \beta_i \cdot y^i - b_0 - b_1 \cdot y \quad (12)$$

with  $b_0 = 0$  for the SPO case. Assess  $u(\Delta)$  as the maximum of  $|\Delta|$  within the range considered.

$$u(\Delta) = \max(|\Delta|)_R \quad (13)$$

The analytical range,  $R$ , within which simplified calibration approaches are to be used is normally defined in terms of the (assumed) composition of the potential sample gases to be determined. For the three SPO, SPB and TPC approaches, these ranges, which may be different from time to time, may well lay within the range span of the performance evaluation or (at least) reach the borders of the latter. For defining the range,  $R$ , in the signal (or response) domain, the best-available analysis function should be used. For quadratic and cubic polynomials, this leads to root-finding according to, e.g. for the lower bound  $x_{lb} = \sum \beta_i \cdot y_{lb}^i$ . If, additionally, a calibration function is determined, the method described in [C.2](#) can be used.

As the analysis function shall not have an inflection point in the analytical range, the maximum deviation according to [Formula \(13\)](#) is either located at the lower or upper edge of the range,  $R$ , or at the local maximum or minimum within the range if such exists.

An inflection (sometimes also written as inflexion) point of a function,  $f$ , describes the point where the curvature of the function graph changes. The necessary condition for an inflexion point at  $x_0$  is the second derivative of the function to be zero,  $f''(x_0) = 0$ , the sufficient existence condition requires  $f''(x_0 + \varepsilon)$  and  $f''(x_0 - \varepsilon)$  to have opposite signs in the neighbourhood of  $x_0$ . A useful analytical function shall not have an inflection point. This document does not require proof of inflection-point absence for the best-available analysis function; however, at least a visual inspection of the function graph is recommended.

The local maximum or minimum has the property of a first derivative equal to zero,  $d\Delta/dy = 0$  and can be found using [Formula \(14\)](#) and [Formula \(15\)](#):

for quadratic functions:

$$(\beta_1 - b_1) + 2 \cdot \beta_2 \cdot y = 0 \quad (14)$$

for cubic functions:

$$(\beta_1 - b_1) + 2 \cdot \beta_2 \cdot y + 3 \cdot \beta_3 \cdot y^2 = 0 \quad (15)$$

NOTE For truly linear systems, the maximum deviation point is always at one of the edges of the range,  $R$ .

Use the maximum of the absolute of the three values as the assessment of the nonlinearity uncertainty contribution,  $u(\Delta)$ .

For enhanced and value-dependent accuracy of determination, an alternative approach using an average correction,  $\bar{\delta}$ , and uncertainties on these corrections may be used. The approach is described in [Annex C](#). The average correction,  $\bar{\delta}$  [see [Formula \(C.4\)](#)], shall be applied to each value determined from regular calibration and an individual uncertainty of the correction,  $u(x_{reg})$  [see [Formula \(C.5\)](#)], applies replacing the worst-case estimate,  $u(\Delta)$ .



## 8.2 Sources of performance evaluation data and alternative approach

### 8.2.1 Performance evaluation other than in-house

Beside in-house performance evaluation, the following sources of validation data are accepted provided they can deliver the information necessary to calculate the estimate according to [Formula \(13\)](#):

- validation of the instrument(s) by the manufacturer, for the components and matrices of interest, with data enabling the assessment of possible nonlinearity;
- validation of the instrument(s) by a third party, as e.g. a consultant firm or a calibration laboratory, for the components and matrices of interest, with data enabling the assessment of possible nonlinearity.

### 8.2.2 Alternative for performance evaluation

For screening and exploratory analyses, the approach described in [Annex E](#) may be used. It omits the performance evaluation but replaces it by a (in most cases large) worst-case estimate for a possible nonlinearity between the fixed sampling points. It might be useful for the TPC and, if uncertainties arising from the worst-case estimate are not considered to be too large to be feasible, also for the TPB design. The approach may also be used in research into new fields where (certified) calibration gases are not available or do not exist in a sufficient number. Note that this is not covered by this document and [Annex E](#) has an informative character only.

## 9 Quality assurance measures

### 9.1 Validation of the assumptions made

From the results of the performance evaluation, estimates according to [Formula \(13\)](#) shall be derived which remain valid until the next instance of the abovementioned case in [8.1 b](#)).

The time of validity of a working calibration according to the approaches of [6.2](#) shall be determined in a drift/stability control experiment according to [9.2](#). This will normally be done within the framework of the initial performance evaluation. In this initial performance evaluation phase, independent calibration gases can be used for obtaining a number of control-chart data sufficient for assessing the stability of the system and the period of validity of the working calibration. It is recommended to re-calibrate the system (working calibration) not later than at an instance in time when half of the determined period-of-stability has elapsed.

The above does not apply to exact-match calibration (SPEM) and bracketing using two reference standards (TPC). For these techniques, the exact-match calibration gas or the bracketing calibration gases are to be measured at the time and each time an unknown sample is determined.

### 9.2 Drift/stability control of the measuring system

If significant changes of the response of the analytical system cannot be excluded, it is necessary to perform a drift test. In this subclause, a simple one-point validation procedure is described, aimed at providing a minimum protection against systematic errors due to drift. If more information on the performance of the analytical system is available, e.g. due to extensive monitoring, drift tests of better performance should be used.

Drift control means testing whether a previously determined analysis function is still valid or whether the response of the analytical system has changed significantly.

Drift control is performed in a problem-specific mode, i.e. tailored for the calibration gas mixture,  $M$ , under investigation, by measuring the response of one of those two calibration gas mixtures among  $Re_1, Re_2, \dots, Re_n$  which bracket the component amount fraction of the calibration gas mixture,  $M$ .

Before and after measuring the response of the calibration gas mixture,  $M$ , 10 independent measurements of the selected calibration gas mixture,  $R_i$ , are made. These data are used to derive mean responses,  $y_{i,before}$  and  $y_{i,after}$ , which are compared with the mean response,  $(y_{i,calib})$ , obtained on  $R_i$  at the time of calibration and with each other. The drift test is passed if none of the three differences,  $|y_{i,before} - y_{i,calib}|$ ,  $|y_{i,calib} - y_{i,after}|$  and  $|y_{i,before} - y_{i,after}|$ , exceeds the critical value for these differences. This critical value is given by  $2,83 \times u(y_{i,calib})$ , where  $u(y_{i,calib})$  is the standard uncertainty of the mean response obtained at calibration (see 8.2). Should any of these differences be greater than the critical value, then the drift control test has failed and the analytical system shall be recalibrated.

NOTE The drift control test assumes that for each of the series of measurements performed on the drift control mixture,  $R_i$ , before and after measuring the calibration gas mixture,  $M$ , the standard uncertainty is about the same as that for the series of calibration measurements on  $R_i$ . Based on this assumption and a significance level of 95 %, the critical value for any of the three differences is given by 2,8 times the standard uncertainty of the mean response obtained in calibration.

If  $n = 10$  measurements, each, on the drift control gas before and after measuring a candidate calibration gas should be impractical, a lower number  $n$  may be used, at the expense of a lower drift-detection capability. Then the critical values for the differences shall be changed accordingly. The conditions for passing the drift control test then are given by Formulae (16), (17) and (18):

$$|y_{i,before} - y_{i,calib}| \leq 2 \times \sqrt{1 + \frac{10}{n}} \times u(y_{i,calib}) \quad (16)$$

$$|y_{i,calib} - y_{i,after}| \leq 2 \times \sqrt{1 + \frac{10}{n}} \times u(y_{i,calib}) \quad (17)$$

$$|y_{i,before} - y_{i,after}| \leq 2 \times \sqrt{\frac{20}{n}} \times u(y_{i,calib}) \quad (18)$$

The period bracketed by the two sets of measurements on the drift control gas may be extended to include measurements of several candidate calibration gases of similar composition at the risk of having to discard a larger set of measurements.

If the drift control test has failed, the analytical system shall be recalibrated.

## 10 Report of results

### 10.1 Calibration gas certificates

Prepare certificates for calibration gas mixtures in accordance with the requirements of ISO 6141.

### 10.2 Report of analysis

The report of analysis shall contain the following:

- a) a description of the analytical system used;
- b) the composition, including uncertainty, of the calibration gas mixtures used for calibration;
- c) the mathematical function type used for the analysis function;
- d) a reference to this document, i.e. ISO 12963.

In stating the results of analysis, the contents should preferably be expressed as amount fractions. The uncertainty of the component amount fractions shall be expressed as expanded uncertainties,  $U(x) = k \times u(x)$ . The recommended coverage factor is  $k = 2$ . The coverage factor used shall be specified. Uncertainties can be expressed as an absolute value or as a relative value.

For the special procedures according to [Clause 7](#), the report of results shall be designed accordingly.

## Annex A (normative)

### System-stability check required when using exact-match and bracketing designs

#### A.1 General

In general, the use of an insufficiently stable system (within time periods required for carrying out a certain measurement campaign) is strongly discouraged. Method validation and performance evaluation of the system should reveal any possible instability over short intervals of time exceeding the reproducibility estimates derived. For the single-point exact-match and bracketing technique designs, checks of stability of the system are mandatory at the time of analysis of the sample. This check is accomplished by following the measurement sequence and the data assessment as described below.

#### A.2 Layout of the measurement sequence

The basic time sequence for measuring an unknown sample in the single-point exact-match technique is

Re(1) - Re(2) - Re(3) - S(1) - S(2) - S(3) - Re(4) - Re(5) - Re(6)

where Re stands for the measurement of the matching reference and S for the unknown sample, the number in brackets for the replicate required by the design. Other sequences are suitable as long as they do not fall below the minimum number of measurements required above.

When using the bracketing-technique design, measure the three required replicates for calibration gas R1, calibration gas R2 and the unknown sample S in the following sequence

Re1(1) - Re1(2) - Re1(3) - Re2(1) - Re2(2) - Re2(3) - S(1) - S(2) - S(3) - Re2(4) - Re2(5) - Re2(6) - Re1(4) - Re1(5) - Re1(6)

where again the number in brackets stands for the replicate. Other sequences are suitable given the limitation above.

**NOTE** From a statistical point of view, it might be sensible to randomize the sequences as given above. The intention of the check-for-stability test is, however, to cover the largest possible interval in time for the measurement of the same gas sample, such that measurements of calibration gas samples are foreseen at the beginning and in the end.

It might be necessary to carry out more than the necessary three replicate measurements both for the sample and the references. Additional replicates may be distributed randomly over the (minimum) sequences as given above, however, they should start and end with three measurements of the references.

#### A.3 Data assessment and decision

When using the exact-match design, check whether the criterion of [Formula \(1\)](#) is fulfilled separately when using the series of measurements on the matching reference taken in the beginning [Re(1) to Re(3)] and at the end [Re(4) to Re(6)]. If this is the case, state the value and the uncertainty of the value of the unknown sample according to [Formulae \(2\)](#) and [\(3\)](#), respectively.

If the criterion is not fulfilled for any of the two combinations between reference and sample measurements, a potential drift shall be suspected. Repeat the measurement sequence in order to

exclude random effects. If non-compliance with the criterion of [7.3.2](#) continues, check and improve the stability of the system.

When using the bracketing technique design, calculate the value and the uncertainty of the value of the unknown sample according to [Formulae \(8\)](#) and [\(9\)](#) separately, using the series of measurements on the bracketing reference taken in the beginning [Re1(1) to Re2(3)] and at the end [Re1(4) to Re2(6)].

Check whether the criterion

$$\frac{|x_{s,b} - x_{s,e}|}{2 \times \sqrt{u^2(x_{s,b}) + u^2(x_{s,e})}} \leq 1 \tag{A.1}$$

is fulfilled, where the subscripts *b* and *e* denote the result for the unknown sample calculated using the reference measurements taken in the beginning and at the end.

If the criterion is fulfilled, state  $x_{s,b}$  as the value and  $u(x_{s,b})$  as the uncertainty of the composition of the unknown.

NOTE Given compliance of the data according to [Formula \(A.1\)](#), a statement of the weighted mean of the two results, accompanied by the average uncertainty of these, would also be acceptable.

If the criterion is not fulfilled, a potential drift shall be suspected. Repeat the measurement sequence in order to exclude random effects. If non-compliance with the criterion of [Formula \(A.1\)](#) continues, check and improve the stability of the system.

## Annex B (normative)

### Statistics and sensitivity coefficients used in [Clause 7](#)

Throughout this document, means and standard deviations of (replicate) signal measurements,  $y_i$ , are calculated according to [Formula \(B.1\)](#)

$$\bar{y} = \frac{\sum_{l=1}^m y_l}{m} \quad (\text{B.1})$$

for the mean and [Formula \(B.2\)](#)

$$u^2(\bar{y}) = \frac{\sum_{l=1}^m (y_l - \bar{y})^2}{m \cdot (m-1)} \quad (\text{B.2})$$

for the standard deviation as an estimate for the analytical uncertainty.

The expressions for the sensitivity coefficients in [Formula \(7\)](#) are as follows:

$$\frac{\partial x_s}{\partial y_s} = \frac{x_r - x_b}{y_r - y_b} \quad (\text{B.3})$$

$$\frac{\partial x_s}{\partial y_r} = \frac{x_r - x_b}{(y_r - y_b)^2} \cdot (y_b - y_s) \quad (\text{B.4})$$

$$\frac{\partial x_s}{\partial y_b} = \frac{x_r - x_b}{(y_r - y_b)^2} \cdot (y_s - y_r) \quad (\text{B.5})$$

$$\frac{\partial x_s}{\partial x_r} = \frac{y_s - y_b}{y_r - y_b} \quad (\text{B.6})$$

$$\frac{\partial x_s}{\partial x_b} = \frac{y_r - y_s}{y_r - y_b} \quad (\text{B.7})$$

The expressions for sensitivity coefficients in [Formula \(9\)](#) are as follows:

$$\frac{\partial x_s}{\partial y_s} = \frac{x_{r2} - x_{r1}}{y_{r2} - y_{r1}} \quad (\text{B.8})$$

$$\frac{\partial x_s}{\partial y_{r2}} = \frac{x_{r2} - x_{r1}}{(y_{r2} - y_{r1})^2} \cdot (y_{r1} - y_s) \quad (\text{B.9})$$

$$\frac{\partial x_s}{\partial y_{r1}} = \frac{x_{r2} - x_{r1}}{(y_{r2} - y_{r1})^2} \cdot (y_s - y_{r2}) \quad (\text{B.10})$$

$$\frac{\partial x_s}{\partial x_{r2}} = \frac{y_s - y_{r1}}{y_{r2} - y_{r1}} \quad (\text{B.11})$$

$$\frac{\partial x_s}{\partial x_{r1}} = \frac{y_{r2} - y_s}{y_{r2} - y_{r1}} \quad (\text{B.12})$$

## Annex C (normative)

### Alternative approach to assessing the nonlinearity contribution

#### C.1 General

This annex describes the processing of the analyser nonlinearity based on ISO/IEC Guide 98-3:2008, F.2.4.5. This approach provides an estimate of the average bias and the associated standard uncertainty. This average bias can be used to correct the measured values obtained with the simplified calibration approach (see [6.2](#) and [7.3](#)) or in the uncertainty budget as part of  $u(\Delta)$ .

#### C.2 Procedure

Step 1: Calculation of the end points of the analytical range.

Calculate the true calibration function for the analyser in accordance with ISO 6143. Let the analytical range of interest,  $R$ , be specified by a lower amount-of-substance fraction,  $x_1$ , and an upper fraction,  $x_2$ . Then, compute the lower response using [Formula \(C.1\)](#)

$$y_1 = f(x_1; \alpha) = \alpha_0 + \alpha_1 x_1 + \alpha_2 x_1^2 + \alpha_3 x_1^3 \quad (\text{C.1})$$

where  $f$  denotes the true calibration function and  $\alpha$  the coefficients obtained from the procedure of ISO 6143.

NOTE 1 In this annex, it is assumed that the true calibration function and true analysis function can be represented as third-order polynomials. For lower degree-polynomials, the coefficients of the highest-order terms are set to zero, so for example for a straight line,  $\alpha_2 = 0$  and  $\alpha_3 = 0$  (the same applies to the corresponding analysis function).

Calculate the upper using [Formula \(C.2\)](#):

$$y_2 = f(x_2; \alpha) = \alpha_0 + \alpha_1 x_2 + \alpha_2 x_2^2 + \alpha_3 x_2^3 \quad (\text{C.2})$$

Step 2: Calculate the coefficients of the true analysis function.

Calculate, using the procedure of ISO 6143, the coefficients  $\beta_0, \dots, \beta_N$  of the true analysis function.

Step 3: Calculate the coefficients of the simplified analysis function.

Obtain  $b_0$  and  $b_1$  for the appropriate method (see [7.3.3](#) to [7.3.5](#)).

Step 4: Calculate the average bias.

Calculate the average bias using [Formula \(C.3\)](#)

$$\bar{\delta} = \frac{F(y_2) - F(y_1)}{y_2 - y_1} \quad (\text{C.3})$$

where

$$F(y) = (\beta_0 - b_0)y + \frac{1}{2}(\beta_1 - b_1)y^2 + \frac{1}{3}\beta_2 y^3 + \frac{1}{4}\beta_3 y^4$$

The variance (squared standard uncertainty) of the average bias is calculated using [Formula \(C.4\)](#)

$$u^2(\bar{\delta}) = \frac{G(y_2) - G(y_1)}{y_2 - y_1} + \frac{H(y_2) - H(y_1)}{y_2 - y_1} \quad (\text{C.4})$$

where

$$\begin{aligned} G(y) = & \frac{1}{7}\beta_3^2 y^7 + \frac{1}{6}\beta_2\beta_3 y^6 + \frac{1}{5}(2(\beta_1 - b_1)\beta_3 + \beta_2^2)y^5 + \\ & \frac{1}{4}(2(\beta_0 - b_0 - \bar{\delta})\beta_3 + 2(\beta_1 - b_1)\beta_2)y^4 + \\ & \frac{1}{3}(2(\beta_0 - b_0 - \bar{\delta})\beta_2 + (\beta_1 - b_1)^2)y^3 + \\ & (\beta_0 - b_0 - \bar{\delta})(\beta_1 - b_1)y^2 + (\beta_0 - b_0 - \bar{\delta})^2 y \end{aligned}$$

and

$$\begin{aligned} H(y) = & yu^2(b_0) + \frac{1}{3}y^3u^2(b_1) + y^2u(b_0, b_1) + \\ & yu^2(\beta_0) + \frac{1}{3}y^3u^2(\beta_1) + \frac{1}{5}y^5u^2(\beta_2) + \frac{1}{7}y^7u^2(\beta_3) + \\ & y^2u(\beta_0, \beta_1) + \frac{2}{3}y^3u(\beta_0, \beta_2) + \frac{1}{4}y^4u(\beta_0, \beta_3) + \\ & \frac{1}{2}y^4u(\beta_1, \beta_2) + \frac{2}{5}y^5u(\beta_1, \beta_3) + \frac{1}{3}y^6u(\beta_2, \beta_3) \end{aligned}$$

NOTE 2 In case of a lower-order polynomial (than 3) for the true analysis function, the corresponding variances and covariances involving  $\beta_3$  (second-order polynomial) or  $\beta_3$  and  $\beta_2$  (straight line) are zero.

Step 5a: Calculate  $u(\Delta)$ .

Calculate  $u(\Delta)$  using [Formula \(C.5\)](#):

$$u(\Delta) = \sqrt{\bar{\delta}^2 + u^2(\bar{\delta})} \quad (\text{C.5})$$

Step 5b: Correct measured value (alternative to step 5a).

Correct the measured value by adding  $\bar{\delta}$  to it. The calculated standard uncertainty associated with the measured value should be combined with  $u(\bar{\delta})$ , the standard uncertainty associated with the correction  $\bar{\delta}$ .

NOTE 3 The approach described in this annex is usually more accurate than the one described in [Clause 8](#). The procedure including step 5b is usually more accurate than the one involving step 5a. Practical deliberations dictate which the preferred approach is.



## Annex D (informative)

### Worked-out example

#### D.1 General

The worked-out example is intended to:

- exemplify the procedures described;
- show some typical results;
- provide benchmark data for the calculation procedure and possible implementations in tailored software codes.

The example refers to the determination of carbon dioxide in a natural gas by gas chromatography. Given the specific conditions at the site of exploration, the amount of carbon dioxide is expected to be in the range between 2 cmol/mol and 5 cmol/mol (analytical range for the working calibration). The performance evaluation of the GC system is extended to both sides and covers carbon dioxide amount fractions between 0,2 cmol/mol and 10 cmol/mol.

#### D.2 Calibration set

According to the specifications set, the analytical range and the seven calibration gas mixtures containing carbon dioxide in a natural gas matrix covering the analytical between 0,2 cmol/mol and 10 cmol/mol were selected, and measured in triplicate, with the results as shown in [Table D.1](#).

**Table D.1 — Measurement results for CO<sub>2</sub> in a natural gas**

Content	cmol/mol		
Amount fraction	U amount fraction	Mean signal	U (mean)
0,225	0,001 1	835,61	0,69
0,967	0,004 8	3 515,24	0,79
1,883	0,009 5	6 833,68	2,51
4,595	0,023	16 646,19	6,87
5,791	0,029	20 932,59	6,59
7,558	0,038	26 935,06	8,79
9,317	0,047	32 891,19	3,88

All calibration gases come with a relative uncertainty of the content of 0,5 %. Instrument responses are represented by the means of three replicates taken, with uncertainties estimated as standard uncertainties of these means.

#### D.3 Regular calibration

For the simplified working calibration, the TPC approach (bracketing) was selected.

**Step A:** Preparation of two calibration gas mixtures such that the measuring system obtains, on this mixture, responses which bracket, within a specified range *R*, those obtained on the unknown sample. From the seven gases used in the performance evaluation, gas 3 and 5 were selected to bracket the

expected carbon dioxide amount fraction in the unknowns under investigation. Gases were analysed in triplicate, the mean values and standard uncertainties are shown in [Table D.2](#) (based on the measurements reported in [Table D.1](#)).

**Table D.2 — Mean values and standard uncertainties in step A**

Amount fraction	U (amount fraction)	Mean response	U (response)
1,883	0,009	6 833,7	2,5
5,791	0,029	20 932,6	6,6

As mentioned above, uncertainties of the measurements are standard uncertainties of the means calculated from the replicates taken, and the uncertainties of the calibration gases from the documentation accompanying the calibration gas mixtures, stating that the calibration gases provide a relative standard uncertainty of 0,5 %.

**Step B:** Three replicate measurements of the sample have been taken, and the mean response value of the three replicates  $y_s$  and the standard uncertainty  $u(y_s)$  of the mean response value calculated as shown in [Table D.3](#).

**Table D.3 — Mean value and standard uncertainty in step B**

Amount fraction	U (amount fraction)	Mean response	U (response)
		13 510,0	4,7

**Step C:** The value of the unknown was estimated using [Formula \(8\)](#), resulting in a value of 3,734 cmol/mol. The governing parameters of the straight-line calibration function are -0,011 19 (intercept, expressed in the unit of the signal) and 0,000 277 (slope).

**Step D:** The uncertainty of the value of the unknown was derived from the uncertainty of the calibration gas mixtures, the uncertainty of the response measurements and the contributions of the prediction error according to [Formula \(9\)](#), i.e. the contribution  $u(\Delta)$  determined under [D.4](#), using the sensitivity coefficients listed in [Annex B](#). The corresponding uncertainty contributions are shown in [Table D.4](#).

**Table D.4 — Corresponding uncertainty contributions in step D**

Source	Contribution cmol/mol
amount fraction r1	0,004 96
response r1	0,000 37
amount fraction r2	0,013 71
response r2	0,000 87
response sample	0,001 30
$u(\Delta)$	0,050 80
combined $u$	0,052 87

This yields a total uncertainty of the value of 0,053 cmol/mol and completes the data for the unknown as shown in [Table D.5](#).

**Table D.5 — Final results of mean value and uncertainty in step D**

Amount fraction	Amount fraction	Mean response	U(response)
3,734	0,053	13 510	4,70

The largest contributions in the uncertainty budget of the measurement result are the nonlinearity estimate,  $u(\Delta)$ , and the uncertainty of the calibration gas forming the upper bracket.

#### D.4 Performance evaluation

Performance evaluation for deriving the  $u(\Delta)$  estimate assesses the results obtained on the seven calibration gases as given in [Table D.1](#). From the replicates, an analytical uncertainty is calculated as the standard uncertainty of the replicates. A first-order polynomial with intercept is fitted to the data using GLS as the regression technique. The performance characteristics obtained are as follows:

```
Linear case
b0          b1          u(b0)        u(b1)        covariance:
-8,3766E-03  2,7875E-04    1,3211E-03   6,2981E-07   -4,6035E-10

Residual SSD is:          20,8221
Goodness-of-fit measure:  3,3648
```

The system is slightly nonlinear. A second-order polynomial function is fitted using the same regression technique, yielding acceptable performance parameters:

```
Linear case/Quadratic model function
b0          b1          b2
-3,7660E-03  2,7387E-04  2,4027E-10

Parameter standard uncertainties/covariances:
u(b0)  u(b1)  u(b2)  : 1,790E-03  1,427E-06  6,298E-11
cov(b0,b1)  cov(b0,b2)  : -2,007E-09  7,611E-14
cov(b1,b2)  : -8,064E-17

Residual SSD is:          6,2702
Goodness-of-fit measure:  1,4897
```

For the intended range of application of the TPC design, the deviation of the identified as fully describing the system analysis function from the regular (linear) function is assessed according to [Formula \(13\)](#) between the selected brackets. The maximum of the deviation is at the upper end of the range with  $\Delta = 0,051$  mmol/mol. The estimate of  $u(\Delta)$  is set to this value. Then go to [D.3](#).

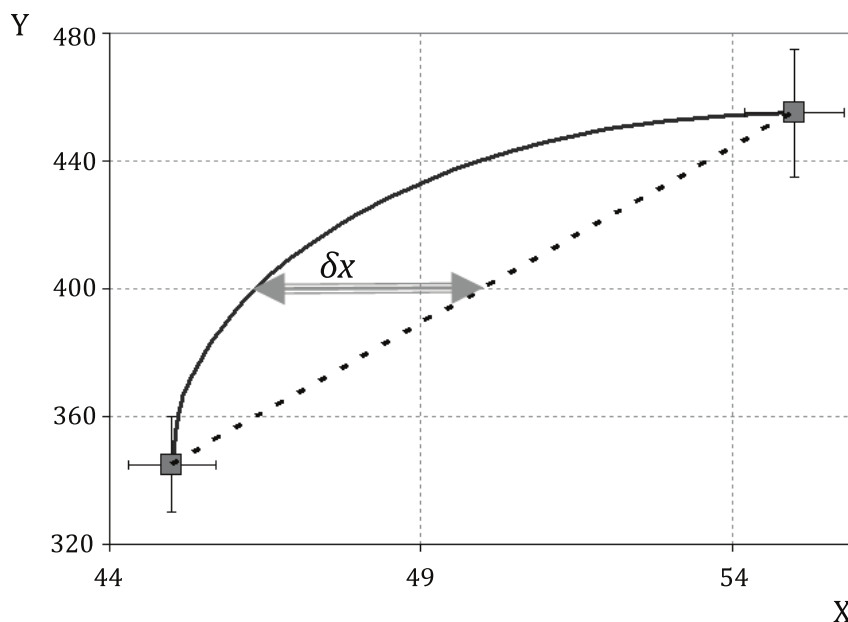
## Annex E (informative)

### Using the designs without preceding system performance evaluation

For this annex, the general requirements and limitations of [7.3](#) apply. For a TPC design, the possible contribution of a nonlinearity can be assessed in a worst-case scenario. If the measurement result uncertainty turns out to be (still) fit for the intended purpose, a performance evaluation may be omitted.

Starting point of the worst-case scenario is the fact that for any component/matrix combination, any kind of equipment, and any separation column and detector it should be assumed that the calibration function is continuous (within the range considered) and has a positive, non-zero and non-infinite first derivative. This equally excludes local minima and maxima which would make the calibration curve ambiguous. Given a certain nonlinearity of the system, the first derivative of the calibration function may be either increasing or decreasing. An increasing first derivative can most likely be expected close to the limit of detection, a case not considered here. In the range well above the limit of quantification, a (at least slightly) decreasing first derivative of the calibration function shall be expected due to saturation effects. However, even a first derivative changing between increase and decrease does not alter the below worst-case scenario considerations as long as it does not change sign (which would make the calibration curve useless).

With this, a limiting, worst-case nonlinear behaviour in the bracketing approach would be a calibration having an infinite first derivative at the lower bracket  $(x_l, y_l)$  and a zero derivative at the upper bracket  $(x_u, y_u)$ . A functional relationship corresponding to this limiting case is an ellipse, namely the upper left quarter of an ellipse passing through  $(x_l, y_l)$  and  $(x_u, y_u)$  as the extremes. [Figure E.1](#) displays the bracketing points, the assumed linear relationship, the worst-case estimation and the uncertainty contribution from the worst-case estimation.

**Key**

X amount-of-substance (arbitrary units)

Y signal (arbitrary units)

**Figure E.1 — Worst-case estimation for the bracketing approach**

Let  $\Delta x = (x_u - x_l)$  be the width of the bracket in the  $x$  direction (amount-of-substance space) and  $\Delta y = (y_u - y_l)$  the width of the bracket in the  $y$  direction (signal space). The limiting calibration function is calculated using [Formula \(E.1\)](#):

$$\frac{(x - x_l)^2}{\Delta x^2} + \frac{(y - y_u)^2}{\Delta y^2} = 1 \quad (\text{E.1})$$

while the determination is carried out using the linear approximation; see [Formula \(E.2\)](#):

$$y = \frac{\Delta y}{\Delta x} \cdot x^* + \frac{y_l \cdot x_u - y_u \cdot x_l}{\Delta x} = \frac{\Delta y}{\Delta x} \cdot x^* + \beta \quad (\text{E.2})$$

For a given signal  $y$ , a difference  $\delta x$  occurs between the determination on the basis of the worst-case limiting and the assumed linear calibration function between the bracketing points. This difference for a given signal  $y$  is calculated using [Formula \(E.3\)](#):

$$\delta x = x - x^* = \Delta x \cdot \sqrt{1 - \frac{(y - y_u)^2}{\Delta y^2}} + x_l - \frac{\Delta x}{\Delta y} \cdot (y - \beta) \quad (\text{E.3})$$

The  $\delta x/2$  contribution from the worst-case scenario is included in the uncertainty budget of the measurement instead of the contributions  $u(\Delta)$ . It depends on the width of the bracket applied and may, in certain cases, be reduced to an acceptable extent. The above worst-case estimation may, in principle, also be applied to the TPB design. Since this design normally spans wider component amount-of-substance ranges, the uncertainty contribution from such worst-case estimation will, in most of the cases, be unacceptable large, making the performance evaluation mandatory, at least highly recommended.

## Bibliography

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