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Gas analysis — Comparison methods for determining and checking the composition of calibration gas mixtures

Analyse des gaz — Méthodes comparatives pour la détermination et la vérification de la composition des mélanges de gaz pour 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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

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.

International Standard ISO 6143 was prepared by Technical Committee ISO/TC 158, *Analysis of gases*, to cancel and replace the first edition (ISO 6143:1981), of which the methods for the design and evaluation of calibrations of analytical systems have been updated and a method for estimating the uncertainty of the composition of calibration gas mixtures has been added. It also cancels and replaces ISO 6711:1981, of which entirely new methods for checking the composition of calibration gases have been specified, thus replacing the method which is no longer in use.

Annex A forms a normative part of ISO 6143. Annexes B and C are for information only.

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Introduction

In gas analysis, calibration of analytical systems, as specified in the first edition of ISO 6143, has largely been confined to the determination of a straight line through the origin, or of a straight-line segment, using only the minimum number of calibration standards (one for a straight line through the origin, two for a line segment). The approach adopted in the revision, relating to calibration as well as to uncertainty evaluation, goes far beyond this simple scheme by

— including non-linear response curves and/or functions,

— replacing interpolation by regression,

— taking into account the uncertainty on the calibration standards,

— including validation of calculated response curves and/or functions,

— calculating uncertainties by uncertainty propagation.

As a consequence of adopting non-linear response models, advanced regression techniques (errors in both variables) and uncertainty propagation, the main calculation procedures can only be performed on a computer, using a specific program. Such a program is available (see annex C). As an alternative, sufficient information is given in the document to enable the user to develop a program on his own.

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Gas analysis — Comparison methods for determining and checking the composition of calibration gas mixtures

1 Scope

This International Standard provides methods for

- determining the composition of a calibration gas mixture by comparison with appropriate reference gas mixtures,
- calculating the uncertainty of the composition of a calibration gas mixture in relation to the known uncertainty of the composition of the reference gas mixtures with which it was compared,
- checking the composition attributed to a calibration gas mixture by comparison with appropriate reference gas mixtures,
- comparing the composition of several calibration gas mixtures, e.g. for the purpose of comparing different methods of gas mixture preparation, or for testing consistency among gas mixtures of closely related composition.

NOTE In principle, the method described in this document is also applicable to the analysis of (largely) unknown samples instead of prospective calibration gas mixtures (i.e. gas mixtures which are intended for use as calibration gas mixtures). Such applications, however, require appropriate care and consideration of additional uncertainty components, for example concerning the effect of matrix differences between the reference gases used for calibration and the analysed sample.

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2 Terms and definitions

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

2.1
composition

characteristic of a gas mixture given by the kind and content of each specified mixture component (analyte) and the composition of the complementary gas (matrix)

NOTE In this International Standard, the analyte content is specified as a mole fraction, exclusively. Mole fractions have the advantage of being perfectly independent of the pressure and the temperature of the gas mixture. Therefore their use is recommended. However, for specific measuring systems, other composition measures (e.g. mass concentrations) may be more appropriate. Their use then requires due care concerning the dependence on pressure and temperature.

2.2
comparison method

method for determining the content of a specified gas mixture component (analyte) by measuring an instrumental response

NOTE Comparison of measuring systems requires calibration, in which the relationship between response and analyte content is established. This is achieved by measuring the response to known values of analyte content provided by reference gas mixtures.

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2.3
calibration

set of operations that establish, under specified conditions, the relationship between values of quantities indicated by a measuring instrument or measuring system, or values represented by a material measure or reference material, and the corresponding values realized by standards

[VIM]

2.4
response function

functional relationship between instrumental response and analyte content

NOTE 1 The response function can be expressed in two different ways as a calibration function or an analysis function, depending on the choice of the dependent and the independent variable.

NOTE 2 The response function is conceptual and cannot be determined exactly. It is determined approximately through calibration.

2.4.1
calibration function

instrumental response expressed as a function of analyte content

2.4.2
analysis function

analyte content expressed as a function of instrumental response

2.5
uncertainty of measurement

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

[GUM]

NOTE In keeping with the GUM, in this International Standard the uncertainty of the composition of a gas mixture is expressed as a standard uncertainty, i.e. as a single standard deviation.

2.6
traceability

property of the result of a measurement or the value attributed to a standard whereby it can be related to stated references, usually national or international standards, through an unbroken chain of comparisons all having stated uncertainties

[VIM]

2.7
measurement 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]

2.8
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]

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2.9

working standard

standard that is used routinely to calibrate or check material measures, measuring instruments or reference materials

[VIM]

NOTE A working standard is usually calibrated against a reference standard.

2.10

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 measuring method, or for assigning values to materials

[ISO Guide 30]

2.11

calibration gas mixture

gas mixture whose composition is sufficiently well established and stable to be used as a working standard of composition

2.12

reference gas mixture

gas mixture whose composition is sufficiently well established and stable to be used as a reference standard of composition

3 Symbols and abbreviated terms

a_j	parameters of the calibration function F ($j = 0, 1, ..., N$)
b_j	parameters of the analysis function G ($j = 0, 1, ..., N$)
$\boldsymbol{D}$	sensitivity matrix
F	calibration function, $y = F(x)$, for the specified analyte
G	analysis function, $x = G(y)$, for the specified analyte
k	coverage factor
L	limit of detection
M_{cal}	(sample of) calibration gas mixture
M_{ref}	(sample of) reference gas mixture
$\boldsymbol{Q}$	transform matrix
S	sum of weighted squared deviations
S_{res}	residual sum of weighted squared deviations
t	Student's t-factor
$U(q)$	expanded uncertainty of an estimated quantity q, $U(q) = ku(q)$

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$u(q)$	uncertainty of an estimated quantity q, expressed as a standard deviation (standard uncertainty)
$u(p,q)$	covariance of two estimated quantities p and q
$u^2(q)$	variance of an estimated quantity q
$\boldsymbol{V}$	variance/covariance matrix
W	half-width of a confidence range
x	mole fraction of the specified analyte
(x_i, y_i)	calibration points (i = 1, 2, ..., n)
$\left(\hat{x}_i, \hat{y}_i\right)$	adjusted calibration points (i = 1, 2, ..., n)
y	instrumental response of the specified analyte
Z	normal distribution percentage point
δ	relative analytical accuracy
γ	dilution factor
Γ	measure of goodness-of-fit

4 Principle

The composition of a gas mixture is determined by separate determination of the mole fraction of every specified analyte. Therefore the procedure for determining the mole fraction of only one specified analyte is described. Possible interferences of other components on the measurement of the analyte under consideration should be considered by the user and taken into account. However, this subject is not addressed in this International Standard.

This International Standard is also applicable if other composition quantities than mole fraction are used. However it is recommended that the final result be expressed as a mole fraction.

The general procedure for determining the mole fraction x of a specified analyte in a sample of a calibration gas mixture, or in a series of such samples, is performed in a sequence of steps summarized below.

a) Specify the analytical range of interest, i.e. the range of the mole fractions x to be determined, and the acceptable uncertainty level (see 5.1, step A).

b) Specify the analytical method and the measuring system to be used (see 5.1, step B).

c) Examine the available information on the relevant response characteristics of the measuring system (e.g. linearity and sensitivity), paying attention to possible interferences. If necessary, carry out a performance evaluation to check the suitability of the system. Specify the type of mathematical function to be considered for description of the response in the specified range (see 5.1, step C).

d) Design a calibration experiment in which the relevant experimental parameters are specified. Examples are:

- calibration range (to include the analytical range),
- composition, including uncertainty, of the reference gas mixtures for calibration,

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- parameters of the analytical method,
- conditions of measurement, if relevant,
- number and sequence of calibration measurements (see 5.1, steps D, E, F).

e) Perform the calibration experiment, i.e. measure the response, y, for samples of the chosen reference gas mixtures, and estimate the uncertainty $u(y)$ of these response values (see 5.1, step G).

f) Calculate the analysis function, $x = G(y)$, from the calibration data, using regression analysis (see 5.1, step H).

g) Examine whether the calculated analysis function is consistent with the calibration data within the relevant uncertainties. If the result is acceptable, proceed to h). If not, revise the calibration design (see 5.2.1).

h) Determine the uncertainty level of the prospective results based on the analysis function for the relevant ranges of responses and analyte contents. If the result is acceptable, proceed to i). If not, revise the calibration design (see 5.2.2).

i) Prior to analysing a prospective calibration gas sample, test for instrument drift to ensure that the analysis function is still valid for the specified analytical task (see 5.2.3). If the result is acceptable, proceed to j). If not, recalibrate the measuring system.

If the prospective calibration gas contains other components than the reference gas mixtures used for calibration, validate the applicability of the analysis function using at least one additional reference gas mixture of appropriate composition (see 5.2.4).

NOTE It is not necessary to test for drift in conjunction with every analysis of a calibration gas sample. The frequency should be based on experience concerning the stability of the measuring system.

Similarly, the composition of additional reference gas mixtures used for validation should be based on experience concerning the cross-sensitivities of the measuring system.

j) Determine the composition of the prospective calibration gas as follows:

- measure the response y,
- determine the uncertainty $u(y)$ of the response y,
- calculate the mole fraction $x = G(y)$ using the analysis function determined in f),
- calculate the uncertainty $u(x)$ of the mole fraction x using the results obtained in h) (see 5.3).

k) State the result of the entire analysis (see clause 7).

In addition to determining the composition of a (prospective) calibration gas mixture, the general procedure may be used to check a pre-established composition. To this end, the mixture under consideration is analysed using the procedure outlined above, and the composition obtained is compared with the pre-established composition. Clause 6 specifies a procedure where, for each analyte concerned, the difference between the content obtained by the confirmation analysis and the pre-established content is examined against the uncertainty on this difference for significant departure from zero.

The general procedure may also be used to examine the mutual consistency of pre-established composition data for a series of calibration gas mixtures or reference gas mixtures. Clause 6 specifies a procedure where, for each analyte concerned, the measured responses and the pre-established analyte contents of all calibration gases under consideration are tested for compatibility with the known response behaviour of the measuring system.

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5 General procedure

5.1 Determination of the analysis function

For a specified analyte and a specified measuring system, including relevant operating conditions, the calibration function, $y = F(x)$, is a mathematical function approximately expressing measured responses $y_1, y_2, ..., y_n$ in relation to known analyte contents $x_1, x_2, ..., x_n$ of appropriate reference gas mixtures. Inversely, the analysis function, $x = G(y)$, approximately expresses known analyte contents $x_1, x_2, .., x_n$ in relation to corresponding measured responses $y_1, y_2, ..., y_n$. The analysis function is required for calculating unknown analyte contents x of calibration gas mixtures from measured responses y.

The analysis function can be determined either directly, or indirectly by determination of the calibration function and subsequent inversion. It is recommended to make a direct determination of the analysis function. Therefore only this procedure is specified in the body of this International Standard. In particular applications, however, indirect determination using the calibration function may be preferable. For such applications, a brief description of this procedure is given in A.5.

The following description, in terms of a series of steps, of the calibration experiment and its evaluation resumes and elaborates the principles outlined in clause 4.

a) **Step A**: Specify the analytical range, i.e. the range of the analyte contents x in the calibration gas mixtures considered, and the acceptable uncertainty level of analytical results.

b) **Step B**: Specify the measuring system to be used and its operating conditions, e.g. sample pressure, sample temperature and sample flow.

c) **Step C**: Specify the type of mathematical function to be considered for the analysis function, $x = G(y)$. Select the function from the following:

— linear functions	$x = b_0 + b_1 y$
— second-order polynomials	$x = b_0 + b_1 y + b_2 y^2$
— third-order polynomials	$x = b_0 + b_1 y + b_2 y^2 + b_3 y^3$
— power functions	$x = b_0 + b_1 y^{b_2}$
— exponential functions	$x = b_0 + b_1 \mathrm{e}^{b_2 y}$

The parameters b_i of the analysis function are determined by regression analysis using the values from the calibration data set, i.e. the response data collected in the calibration experiment and the composition data taken from the specification of the reference gases used for calibration.

The type of mathematical function is chosen according to the response characteristics of the measuring system, which may be linear or non-linear. Although the method described in this International Standard is, in principle, completely general, it is recommended to restrict its use to linear response curves and to non-linear response curves which only moderately deviate from a straight line.

NOTE In this International Standard, only a limited number of types of functions are explicitly considered. However, the procedures equally apply to other types of functions, e.g. the algebraic inverses of the types of functions specified above, as far as feasible.

d) **Step D**: Specify the number n of calibration points (x_i, y_i) required, depending on the type of mathematical function to be used for the analysis function.

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The minimum number of calibration points recommended for the different types of functions considered is:

- 3 for a linear function,
- 5 for a second-order polynomial,
- 7 for a third-order polynomial,
- 5 for a power function,
- 5 for an exponential function.

The recommended number of calibration points is greater than the number of indeterminate parameters of the analysis function because it is also necessary to validate the function chosen. If calibration experiments were only based on the minimum number of calibration points, it would be necessary to validate the analysis function using additional reference gas mixtures. It is better, instead, to incorporate these additional “reference points” into the set of calibration points so as to reduce the calibration uncertainty of the estimated parameters.

For the majority of comparison methods, an appropriate “zero gas” will provide a valid calibration point.

e) **Step E**: Select reference gas mixtures $M_{\mathrm{ref},1}$, $M_{\mathrm{ref},2}$, ..., $M_{\mathrm{ref},n}$ such that their analyte contents x_1, x_2, ..., x_n span an appropriate calibration range, i.e. approximately equally spaced, with one value below the lower limit and one value above the upper limit of the analytical range.

The analyte contents shall be determined independently to the greatest possible extent. Dilution series may only be used under the conditions specified in 5.4.2.

If interferences between mixture components cannot be safely excluded, it may be necessary to use reference gases of similar composition to those of the calibration gases considered, for the critical components. In any case, it is recommended to use reference gas mixtures with the same complementary gas.

Calibration designs using equally spaced values for analyte contents are not the optimum choice for cases of strongly non-linear response. They are, however, well suited for linear and moderately non-linear responses, as considered in this International Standard [see c), step C].

f) **Step F**: Establish the standard uncertainties $u(x_1)$, $u(x_2)$, ..., $u(x_n)$ of the analyte contents x_1, x_2, ..., x_n.

For reference gas mixtures prepared or analysed by recently standardized methods, the standard uncertainty for the content of each specified component should be contained in the certificate of mixture composition.

For reference gas mixtures with other specifications of uncertainty, e.g. in terms of tolerance limits, these data have to be converted into standard uncertainties. If x_{min} and x_{max} are the lower and upper tolerance limit of the analyte content, and if all the values within this interval are equally likely as potentially true values, the data recommended for use as the analyte content and its standard uncertainty are the mean and the standard deviation of a rectangular distribution between the tolerance limits as follows:

$$x = \frac{x_{\mathrm{max}} + x_{\mathrm{min}}}{2} \quad , \qquad u(x) = \frac{x_{\mathrm{max}} - x_{\mathrm{min}}}{\sqrt{12}}$$

The conversion of other uncertainty specifications is treated in A.1.

If the complementary gas is taken as a reference gas for zero analyte content, $x_{\mathrm{min}} = 0$, and $x_{\mathrm{max}} = L_x$. Here L_x denotes the limit of detection (see reference [6]) of the analytical method used for determining the potential impurity, i.e. the maximum content of the analyte in the complementary gas that the analytical method fails to detect.

g) **Step G**: Determine the responses y_1, y_2, ..., y_n to the analyte contents x_1, x_2, ..., x_n, together with their standard uncertainties $u(y_1)$, $u(y_2)$, ..., $u(y_n)$.

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So as to establish the response data y_i and $u(y_i)$ for a given x_i, it is recommended to use the mean value of ten individual responses, y_{i1}, y_{i2}, ..., y_{i10}, measured independently under appropriate reproducibility conditions and to take the standard deviation of this mean value.

$$y_i = \frac{1}{10}\sum_{j=1}^{10} y_{ij}$$

$$u(y_i) = \frac{1}{\sqrt{90}}\sqrt{\sum_{j=1}^{10}(y_{ij} - y_i)^2}$$

The purpose in requiring ten independent measurements for each reference gas is to ensure that the response data, y_i and $u(y_i)$, are determined with acceptable precision. If the analytical system is under statistical control, the mean value y_i may be determined from a smaller number of independent measurements and the standard uncertainty $u(y_i)$ may be calculated from the known method standard deviation.

The requirement of appropriate reproducibility conditions means that the variability of the conditions of measurement in the calibration experiment should be about the same as those in the applications.

If the complementary gas is taken as a reference gas for zero analyte content and if the response to zero content is known to be zero response (and positive to non-zero contents), the values of y and $u(y)$ can be calculated from the response limit of detection, L_y, as follows:

$$y = \frac{L_y}{2} \quad , \qquad u(y) = \frac{L_y}{\sqrt{12}}$$

Here the response limit of detection is the upper limit of fluctuations at zero response.

To secure the independence of the individual responses, and to randomize sample interaction effects, e.g. memory effects, it is recommended to measure the responses for the reference gas mixtures $M_{\mathrm{ref},1}$, $M_{\mathrm{ref},2}$, ..., $M_{\mathrm{ref},n}$ in an irregular sequence.

Depending on the number of repeated measurements, the “uncertainty of the uncertainty” of a mean value (i.e. the relative standard deviation of the standard deviation of a mean value) can be surprisingly large, for example for ten measurements, it is 24 % (see reference [2] of the Bibliography). Therefore a smaller number of repeated measurements should not be used when determining the standard deviation of a mean value.

h) **Step H**: Calculate the parameters b_j of the mathematical function to be used for the analysis function.

The set of input data for this calculation consists of:

- the analyte contents (expressed as mole fractions), x_1, x_2, ..., x_n,
- the standard uncertainties of the analyte contents, $u(x_1)$, $u(x_2)$, ..., $u(x_n)$,
- the responses to the analyte contents, y_1, y_2, ..., y_n,
- the standard uncertainties of the responses, $u(y_1)$, $u(y_2)$, ..., $u(y_n)$.

These parameters are calculated by regression analysis, according to the method described in A.2.

In contrast with ordinary least squares regression, the regression technique used in this International Standard equally takes into account the uncertainties of the composition of the reference gas mixtures and the uncertainties of the measured responses.

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5.2 Validation of the analysis function

5.2.1 Purpose

Before using the analysis function determined according to 5.1, it is necessary to perform validations. These validations serve a number of different purposes:

- to validate the response model,
- to examine compliance with uncertainty requirements,
- to control drift of the measuring system,
- to validate the applicability to mismatching calibration gases.

5.2.2 Validation of the response model

The response model shall be validated by testing whether the selected type of analysis function is compatible with the calibration data set:

- the analyte contents (mole fractions), $x_1, x_2, ..., x_n$,
- the standard uncertainties of the analyte contents, $u(x_1), u(x_2), ..., u(x_n)$,
- the responses to the analyte contents, $y_1, y_2, ..., y_n$,
- the standard uncertainties of the responses, $u(y_1), u(y_2), ... u(y_n)$.

To assess the overall fit of a calculated response curve to the calibration data, the residual sum of weighted squared deviations, S_{res}, is compared with the relevant degrees of freedom (equal to the number of calibration points less the number of response curve parameters), as given in A.2. For the purpose of this International Standard, however, satisfactory fit is required for each individual calibration point by using the following test procedure. For each experimental calibration point (x_i, y_i), an adjusted calibration point $(\hat{x}_i, \hat{y}_i)$ is calculated, as a by-product of the regression analysis used to determine the analysis function (see A.2). The coordinates $\hat{x}_i$ and $\hat{y}_i$ of the adjusted calibration point are estimates of the true analyte content and of the true response, respectively, for the reference gas $M_{\text{ref},i}$ $(i = 1, 2, ..., n)$. By construction the calculated response curve passes through the adjusted calibration points. The selected response model is considered compatible with the calibration data set if the following conditions are fulfilled for every calibration point $(i = 1, 2,…, n)$:

$$\left|\hat{x}_i - x_i\right| \leqslant 2u\left(x_i\right) \quad \text{and} \quad \left|\hat{y}_i - y_i\right| \leqslant 2u\left(y_i\right)$$

NOTE 1 In almost all cases, this condition is equivalent to requiring that the calculated response curve pass through every experimental "calibration rectangle" $[x_i \pm 2u(x_i),\ y_i \pm 2u(y_i)]$, based on the expanded uncertainty $U = ku$ with the standard coverage factor $k = 2$.

If the model validation test fails, one possibility is to examine other response models until a model is found that is compatible with the calibration data set. Another possibility is to examine, and possibly revise, the calibration data.

To effectively test the compatibility of a prospective analysis function, calculate the measure of goodness-of-fit, Γ, defined as the maximum value of the weighted differences, $\left|\hat{x}_i - x_i\right| / u\left(x_i\right)$ and $\left|\hat{y}_i - y_i\right| / u\left(y_i\right)$, between the coordinates of measured and adjusted calibration points $(i = 1, 2, ..., n)$. A function is admissible if $\Gamma \leqslant 2$.

If several functions are considered and found to be admissible, take the final choice as follows:

a) If a physical model of the response behaviour of the analytical system is available, and if the function corresponding to this model is admissible, use this function.

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b) If no such physical model is available, and if several functions give about the same fit, i.e. similar values of the goodness-of-fit parameter Γ, use the simplest function, i.e. the one with the lowest number of parameters.

c) If no physical model is available and admissible functions differ considerably with respect to their fit, use the function which gives the best fit, i.e. the lowest value of Γ.

NOTE 2 The individual weighted differences can be used as a diagnostic tool for identifying potential outliers among the calibration data.

In addition to the procedures described above, every calculated response curve has to be inspected visually. This visual inspection is necessary to reveal “nonsense correlations” which can occur without being detected by local examination of the curve fit to the calibration points. Such nonsense correlations are liable to occur in the case of polynomial response functions, which can exhibit non-monotonic behaviour with excellent local fit. Another case of nonsense correlations can occur if, by mistake, one of the calibration data uncertainties is very small. Then this calibration point is given erroneously a very high weight. Consequently, the response curve is forced through this point with little importance given to the other calibration points.

5.2.3 Examining compliance with uncertainty requirements

For the specified analytical range, an upper bound is determined for the uncertainty of the prospective results based on the analysis function. This upper bound is compared with the acceptable uncertainty.

For determining this upper bound, the calculation described in 5.3 is performed, using simulated extreme response data y_{lo}, $u(y_{\mathrm{lo}})$ and y_{hi}, $u(y_{\mathrm{hi}})$, respectively. The data y_{lo} and $u(y_{\mathrm{lo}})$ are given by the response of the reference gas with the lowest analyte content, and by the standard uncertainty of that response, as determined in the calibration experiment. Analogously, y_{hi} and $u(y_{\mathrm{hi}})$ are given by the calibration data determined on the reference gas with the highest analyte content. From these response data, the values of $u(x_{\mathrm{lo}})$ and $u(x_{\mathrm{hi}})$ can be calculated. The larger of these two values, $\max[u(x_{\mathrm{lo}}), u(x_{\mathrm{hi}})]$, constitutes an upper bound of the uncertainty of the prospective results based on the analysis function.

NOTE The calculated uncertainty takes its highest values at the limits of the calibration range, as given by x_{lo} and x_{hi}. This calibration range includes the specified analytical range.

5.2.4 Drift control of the measuring system

If significant changes of the response of the analytical system cannot be safely excluded, it is necessary to perform a drift test. A simple one-point validation procedure is described below, aimed at providing the minimum required 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 to test whether a previously determined analysis function is still valid or whether the response of the analytical system has changed significantly.

Perform drift control in a problem-specific mode, i.e. tailored for the prospective calibration gas mixture M_{cal} under investigation, by measuring the response of one of those two reference gas mixtures among $M_{\mathrm{ref},1}$, $M_{\mathrm{ref},2}$, ..., $M_{\mathrm{ref},n}$ which bracket the analyte content of the calibration gas mixture M_{cal}.

Before and after measuring the response of the calibration gas mixture M_{cal}, make ten independent measurements of the selected reference gas mixture, $M_{\mathrm{ref},i}$. These data are used to derive mean responses, y_i(before) and y_i(after), which are to be compared with the mean response, y_i(calib), obtained on $M_{\mathrm{ref},i}$ at the time of calibration, and with each other. The drift test is passed if none of the three differences, $|y_i(\text{before}) - y_i(\text{calib})|$, $|y_i(\text{calib}) - y_i(\text{after})|$ and $|y_i(\text{before}) - y_i(\text{after})|$ exceeds the critical value for these differences. This critical value is given by $2{,}83u[y_i(\text{calib})]$, where $u[y_i(\text{calib})]$ is the standard deviation of the mean response obtained at calibration (see 5.1, step G). Should any of these differences be greater than the critical value, then the drift control test has failed, and the analytical system has to be recalibrated.

NOTE The drift control test assumes that for each of the series of measurements performed on the drift control mixture $M_{\mathrm{ref},i}$ before and after measuring the calibration gas mixture M_{cal}, the standard deviation is about the same as that for the series of calibration measurements performed on $M_{\mathrm{ref},i}$. Based on this assumption and a significance level of 95 %, the critical

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value for any of the three differences is given by $2\sqrt{2}$ times the standard deviation of the mean response obtained in calibration.

If it is impractical to make ten measurements ($n = 10$) on the drift control gas before and after measuring a prospective calibration gas, fewer measurements ($n < 10$) may be made but will result in a lower drift-detection capability. If fewer measurements are made, the critical values for the differences have to be changed accordingly. The conditions for passing the drift control test then are given by

$$\left| y_i(\text{before}) - y_i(\text{calib}) \right| \leqslant 2\sqrt{1+\frac{10}{n}} \times u[y_i(\text{calib})]$$

$$\left| y_i(\text{calib}) - y_i(\text{after}) \right| \leqslant 2\sqrt{1+\frac{10}{n}} \times u[y_i(\text{calib})]$$

$$\left| y_i(\text{before}) - y_i(\text{after}) \right| \leqslant 2\sqrt{\frac{20}{n}} \times u[y_i(\text{calib})]$$

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

If the drift control test fails, recalibrate the analytical system.

5.2.5 Validation of applicability to mismatching calibration gases

If the calibration gas mixture under investigation contains other components than the reference gas mixtures used for determining the analysis function, it is necessary to validate the applicability of the analysis function. This validation requires at least one additional reference gas mixture whose composition is sufficiently similar to that of the prospective calibration gas mixture so as to ensure that the uncertainty due to matrix mismatch is kept under adequate control.

Perform the validation as follows. First, identify the critical analytes, whose determination is likely to be sensitive to matrix mismatch. Second, for each critical analyte, measure the response for the reference gas mixture. Thirdly, using the response data, calculate the analyte content, x_{obs}, and its standard uncertainty, $u(x_{\text{obs}})$, using the analysis function. Finally, compare the observed value, x_{obs}, with the established reference value, x_{ref}, of the analyte content of the reference gas mixture, taking into account the uncertainty of these values. If the following condition holds true for each critical analyte:

$$\left| x_{\text{obs}} - x_{\text{ref}} \right| \leqslant 2\sqrt{u^2(x_{\text{obs}}) + u^2(x_{\text{ref}})}$$

the analysis function can be used for determining the composition of the mismatching gas mixture.

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5.3 Determination of the composition of a calibration gas mixture

Determination of the composition of a (prospective) calibration gas mixture, M_{cal}, consists in determining the content (mole fraction), x, and its standard uncertainty, $u(x)$, of each specified analyte. For any specified analyte, these data are determined in a series of three steps as follows.

a) **Step I:** Determine the response y for the analyte content together with its standard uncertainty $u(y)$. For establishing these data, it is recommended to use the mean value of ten individual responses, $y_1, y_2, \ldots, y_{10}$, measured independently, and the standard deviation of this mean value.

$$y = \frac{1}{10}\sum_{j=1}^{10} y_j$$

$$u(y) = \frac{1}{\sqrt{90}} \sqrt{\sum_{j=1}^{10} (y_j - y)^2}$$

The purpose in requiring ten independent measurements to be made is to ensure that the response data, y and $u(y)$, are determined with acceptable precision. If the analytical system is under statistical control, the mean value y may be determined from a smaller number of independent measurements, and the standard uncertainty $u(y)$ may be calculated from the known method standard deviation.

The conditions of measurement shall be the same as those of the calibration experiment. Otherwise, it is necessary to correct the results for the differences in the measuring conditions and to incorporate the uncertainty relating to these corrections into the calculation of uncertainty.

The response y shall be located well within the calibration range of responses to ensure that the analyte content x is included in the specified analytical range.

b) **Step J:** Calculate the analyte content, $x = G(y)$, using the analysis function determined according to the procedure described in 5.1. The input value for this calculation is the response y determined in a) step I.

c) **Step K:** Calculate the standard uncertainty of the analyte content, $u(x)$, using the propagation of uncertainty on the measured response and on the parameters of the analysis function, as follows.

$$u^2(x) = \left(\frac{\partial G}{\partial y}\right)^2 u^2(y) + \sum_{j=0}^{N} \left(\frac{\partial G}{\partial b_j}\right)^2 u^2(b_j) + 2\sum_{j=0}^{N-1} \sum_{l=j+1}^{N} \left(\frac{\partial G}{\partial b_j}\right)\left(\frac{\partial G}{\partial b_l}\right) u(b_j, b_l)$$

where

$u(x)$ is the standard uncertainty of the analyte content x, calculated using $x = G(y)$;

$u(y)$ is the standard uncertainty of the response y, determined in a) step I.

$u^2(b_j)$ is the variance of the parameter b_j of the analysis function;

$u(b_j,b_l)$ is the covariance of the parameters b_j, b_l of the analysis function.

The input data required for calculating the standard uncertainty $u(x)$ according to this equation are determined as follows.

The partial derivatives $(\partial G/\partial y)$ and $(\partial G/\partial b_j)$ are derived by formal differentiation from the mathematical expression for the analysis function.

The standard uncertainty of the response, $u(y)$, is determined according to a) step I.

The variances $u^2(b_j)$ are calculated by propagation of uncertainty on the calibration data according to the procedure described in A.3.

The covariances $u(b_j,b_l)$ are calculated by propagation of uncertainty on the calibration data according to the procedure described in A.3.

NOTE In general, the parameters of the analysis function are independent physical quantities. However, as a rule, the estimators of these quantities are dependent, since they are based on the same set of calibration data. Therefore the parameter covariances $u(b_j, b_l)$ have to be included in the uncertainty calculation. The algebraic sign of the covariance terms can be positive or negative (positive or negative correlation). Hence their contribution can be additive or subtractive.

If several prospective calibration gases are analysed using the same analysis function, the results are correlated. This correlation shall be taken into account if these gases are used jointly in the same application. For this purpose, in addition to the standard uncertainty of the analyte content, the covariance of the analyte

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contents for every pair of gases has to be known. This covariance can be calculated by propagation of the uncertainty on the measured responses, and on the parameters of the analysis function, using a similar equation as the one for calculating the standard uncertainty. An analogous equation is given in A.3, where the covariance between analysis function parameters is calculated by uncertainty propagation.

5.4 Supplementary instructions

5.4.1 Exceptional uncertainties

In exceptional cases it may happen that the uncertainty calculated for the analyte content in a calibration gas mixture M_{cal} is lower than the uncertainty of the analyte content in some or even all of the reference gas mixtures $M_{\mathrm{ref},1}$, $M_{\mathrm{ref},2}$, ..., $M_{\mathrm{ref},n}$. This effect may occur when using a large number of reference gas mixtures whose analyte contents have been established independently, and a high-precision comparison method yielding response data with a relative uncertainty below that of the analyte contents in the reference gas mixtures. However, failing to account for correlations, as for example present in dilution series, or underestimating the uncertainty of response data would completely invalidate any such uncertainty statement. Claiming an exceptional uncertainty in the sense specified above therefore requires positive proof that

a) there is no major correlation between analyte contents of different reference gas mixtures,

b) the uncertainty of response measurements has not been underestimated,

c) the analysis function has been rigorously validated.

Major correlation between analyte contents in different reference gas mixtures will occur if they have a major uncertainty component in common. This is most often the case in dilution series, see 5.4.2.

The uncertainty of response measurements will be grossly underestimated if based on a series of measurements obtained under repeatability conditions instead of appropriate reproducibility conditions, see 5.1, step G.

Rigorous validation implies demonstration that

— the analysis function is compatible with the calibration data, and

— there are no significant uncertainty contributions from other sources such as instrumental drift or matrix mismatch.

5.4.2 Correlation between reference gas mixtures

NOTE 1 In this clause, ponderous verbal constructions such as “correlation between the contents of the analyte under consideration in different gas mixtures” have been simplified to “correlation between different mixtures” and similar.

The procedure for determining the analysis function is restricted to uncorrelated or at most weakly correlated reference gas mixtures, i.e. there shall be no correlations or at most weak correlations between analyte contents of different reference gas mixtures. Therefore the analyte contents shall, to the greatest possible extent, be determined independently for all reference gas mixtures used. This is, however, not the case for dilution series which are often used in multi-level calibration. Mixtures prepared by dilution from the same parent mixture are always correlated. Therefore measures have to be taken to limit the extent (number and strength) of such correlations to an acceptable level as follows.

— In minimum sets of reference gases, i.e. sets containing only the minimum number required for the type of analysis function (see 5.1, step D), all mixtures shall be totally independent. In extended sets of reference gases, i.e. sets containing more than this minimum number, mixtures beyond a minimum set may be related by dilution.

— Subsets of mixtures related by dilution shall either be two independent dilutions of the same parent gas or a single dilution and the parent gas. Successive dilutions and larger subsets of dilution series than pairs shall not

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be used. For either case of pairs, the relative uncertainty of the parent mixture shall be much lower (factor of 1/3 or less) than the relative uncertainty of dilution factors.

NOTE 2 In the case of correlated reference gas mixtures, the data evaluation procedure has to be modified by including covariances in the weighted regression and in the uncertainty propagation. As shown in a recent publication [15], the main impact of correlations is on the uncertainty of the parameters, while the parameters themselves are much less affected. For weak correlations, the parameters may be estimated using the regression procedure without correlations, while correlations have to be included in estimating the uncertainty of the parameters. This is covered by this International Standard. Strong correlations have to be included in the regression procedure too. Such a procedure has been developed at the BAM (see reference [15]), but is beyond the scope of this International Standard.

6 Special procedures

6.1 Checking of a pre-assigned composition

For every analyte considered, determine:

- the content;
- the uncertainty of the content.

Then check whether the determined content and the pre-assigned content agree within their uncertainty limits.

For this purpose the following compatibility criterion, based on a coverage factor of $k = 2$, may be used (see 5.2.5).

$$\left|x_{\mathrm{det}} - x_{\mathrm{pas}}\right| \leqslant 2\sqrt{u^2\left(x_{\mathrm{det}}\right) + u^2\left(x_{\mathrm{pas}}\right)}$$

In this inequality x_{det} and x_{pas} denote the determined content and the pre-assigned content, respectively, and $u(x_{\mathrm{det}})$, $u(x_{\mathrm{pas}})$ denote the standard uncertainties of these quantities.

If the determined content and the pre-assigned content agree within uncertainty limits, this provides an independent confirmation of the pre-assigned content. The level of added confidence depends on the ratio of uncertainties. If $u(x_{\mathrm{det}})$ and $u(x_{\mathrm{pas}})$ are about the same, then agreement with $x_{\mathrm{det}} \pm u(x_{\mathrm{det}})$ adds significant confidence in $x_{\mathrm{pas}} \pm u(x_{\mathrm{pas}})$. This can be expressed by using a mean value and the standard uncertainty of that mean value, resulting in a reduction of uncertainty by a factor of $1/\sqrt{2}$. If $u(x_{\mathrm{det}})$ is much larger than $u(x_{\mathrm{pas}})$, then agreement with $x_{\mathrm{det}} \pm u(x_{\mathrm{det}})$ does not provide much added confidence in $x_{\mathrm{pas}} \pm u(x_{\mathrm{pas}})$.

6.2 Comparison of several calibration gas mixtures

The method requires an analytical system with known type of response, preferably linear. Given this, for every analyte considered, determine the responses and their uncertainties for every calibration gas mixture.

Then check whether the pre-assigned contents and uncertainties together with the measured responses and uncertainties are compatible with the known response type, that is, whether there is a straight line passing through all the uncertainty rectangles (see 5.2.1).

7 Test report

Report the results in accordance with the requirements of ISO 17025. Prepare certificates for calibration gas mixtures in accordance with the requirements of ISO 6141.

The test report shall contain the following information:

a) a description of the analytical system used;

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b) the composition, including uncertainty, of the reference gas mixtures used for calibration;

c) the mathematical function type used for the analysis function;

d) a reference to this International Standard, i.e. ISO 6143:2001.

In stating the results of analysis, the analyte contents, x, shall preferably be expressed as a mole fraction. The uncertainty of the analyte contents shall be expressed as standard uncertainties, $u(x)$, i.e. as one standard deviation. In addition, an expanded uncertainty, $U(x) = ku(x)$, may be given. 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 followed in accordance with clause 6, the report of results has to be designed accordingly.

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Annex A
(normative)

Procedures for data evaluation

A.1 Uncertainty specifications for reference gas mixtures

A.1.1 Conversion to standard uncertainties

This International Standard requires that for the analyte under consideration, the uncertainties, $u(x_1)$, $u(x_2)$, ..., $u(x_n)$, ascribed to the analyte contents, x_1, x_2, ..., x_n in the reference gas mixtures $M_{\text{ref},1}$, $M_{\text{ref},2}$, ..., $M_{\text{ref},n}$ used for calibration, be expressed as standard uncertainties.

Producers and manufacturers of reference gas mixtures usually express uncertainties for analyte contents using specifications other than standard uncertainties.

This annex gives guidance on the conversion of frequently used specifications to standard uncertainties.

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A.1.2 Expanded uncertainty

Should the uncertainty be expressed as an expanded uncertainty, $U(x_i) = ku(x_i)$, then the producer should indicate on the certificate the coverage factor, k, used to determine the quoted value.

In this case the standard uncertainty is given by:

$$u(x_i) = \frac{U(x_i)}{k}$$

If the certificate does not indicate the coverage factor used to determine the quoted uncertainty, then it is reasonable to assume a coverage factor of 2.

A.1.3 Confidence limits

The uncertainty for the analyte content may be expressed using confidence limits of the form $x_i \pm W(x_i)$ with a stated confidence probability, i.e. the true value of x_i is expected to lie within the range $x_i - W(x_i)$ to $x_i + W(x_i)$ with a stated probability. In this case, it is reasonable to assume that the estimate of the true value is distributed normally about the certified value. The standard uncertainty can be determined by dividing half the width of the confidence range, $W(x_i)$, by a factor Z, corresponding to the tabulated value for the stated probability in two-sided normal distribution tables as follows:

$$u(x_i) = \frac{W(x_i)}{Z}$$

The most widely used confidence probability is the 95 % level for which the tabulated value of Z is 1,96.

NOTE As a first approximation, this is equivalent to an expanded uncertainty using a coverage factor of 2.

Occasionally a Student's t-factor t, relating to a specified number of degrees of freedom, is used instead of Z. Then $W(x_i)$ has to be divided by the appropriate t value.

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A.1.4 Analytical accuracy

Analyte contents are regularly quoted with a given analytical accuracy, e.g. x_i (1 ± 10 %). In this case, it has to be assumed that the true value has a uniform probability of lying within the range x_i (1 – 10 %) to x_i (1 + 10 %).

In the general case of x_i ($1 \pm \delta$ %), the true value of x_i is expected to lie within a rectangular distribution with mean x_i and half range $\delta x_i/100$. Since the variance of a rectangular distribution of width 2a is given by $a^2/3$ (see 4.3.7 in reference [2]), the standard uncertainty is given by

$$u(x_i) = \frac{\delta x_i}{100\sqrt{3}}$$

A.1.5 Range or tolerance

If the analyte concentration is defined by a range or tolerance, e.g. $x_{\text{max}} - x_{\text{min}}$, then it is necessary to assume that the true value for x_i has a uniform probability of lying within this range.

In this case, the true value of x_i is expected to lie within a rectangular distribution with mean $(x_{\text{max}} + x_{\text{min}})/2$, taken as the certified value for the analyte concentration, and half range $(x_{\text{max}} - x_{\text{min}})/2$. Since the variance of a rectangular distribution of width 2a is given by $a^2/3$ (see 4.3.7 in reference [2]), the standard uncertainty is given by

$$u(x_i) = \frac{x_{\text{max}} - x_{\text{min}}}{2\sqrt{3}} = \frac{x_{\text{max}} - x_{\text{min}}}{\sqrt{12}}$$

A.2 Calculation of the parameters of the analysis function

The parameters of the analysis function are calculated according to the Deming's generalized least-squares method (see reference [8]). Recent implementations and applications of this method are given in references [9] to [14].

The principle of this method is the following. For each calibration point (x_i, y_i), an adjusted point ($\hat{x}_i$, $\hat{y}_i$) is determined such that the corresponding sum of squared deviations, weighted by the inverse squares of the associated uncertainties, is a minimum.

$$S = \sum_{i=1}^{n} \left[\frac{\left|\hat{x}_i - x_i\right|^2}{u^2(x_i)} + \frac{\left|\hat{y}_i - y_i\right|^2}{u^2(y_i)} \right] = \text{minimum}$$

Here the condition is that the coordinates ($\hat{x}_i$, $\hat{y}_i$) of the adjusted points satisfy the equation anticipated for the analysis function.

$$\hat{x}_i = G(\hat{y}_i) \text{ for } i = 1, 2, \ldots, n$$

In the case of a linear analysis function, this condition means that the adjusted points are subject to lie on a straight line. For a non-linear model function, the adjusted points are subject to lie on a corresponding response curve.

By insertion of the condition $\hat{x}_i = G(\hat{y}_i)$ into the expression for the sum S, the generalized least-squares problem takes the form

$$S = \sum_{i=1}^{n} \left[\frac{\left|G(\hat{y}_i) - x_i\right|^2}{u^2(x_i)} + \frac{\left|\hat{y}_i - y_i\right|^2}{u^2(y_i)} \right] = \text{minimum}$$

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where the analysis function G depends on a specified number of indeterminate parameters, b_0, b_1, ..., b_N. Thus the problem is to simultaneously determine the optimum values of the parameters b_j and of the y-coordinates, $\hat{y}_i$, of the adjusted points, which make the sum S a minimum. For this purpose, the condition S = minimum is converted into a system of equations for the unknown parameters b_j and the y-coordinates $\hat{y}_i$ (the so-called normal equations) as follows.

The minimum of a function of several variables or parameters is specified when the partial derivatives of the function with respect to each variable or parameter are zero. That is, the optimum values of the parameters b_j and the y-coordinates $\hat{y}_i$ are given by the solution of the following system of $(N + 1) + n$ equations.

$$\frac{\partial S}{\partial b_j} = 0 \qquad (j = 0, 1, ..., N)$$

$$\frac{\partial S}{\partial \hat{y}_i} = 0 \qquad (i = 1, 2, ..., n)$$

These equations are solved by numerical methods, as indicated below. The missing x-coordinates, $\hat{x}_i$, are calculated from the y-coordinates, $\hat{y}_i$, using the analysis function determined before.

NOTE In the generalized least-squares method, the normal equations are always non-linear, even for a linear analysis function. Therefore no closed-form analytical solution is available, and numerical methods have to be used. This, however, is not a problem if the computations are performed using a personal computer.

The recommended numerical procedure is a two-step iteration where in the first step the estimates of the analysis function parameters are re-calculated while in the second step the estimates of the coordinates are adjusted. These two steps are repeated alternately until convergence is achieved.

The method described above provides unbiased estimates for the parameters b_j (j = 0, 1, ..., N) of the analysis function. In addition, for each reference gas mixture $M_{\mathrm{ref},i}$ (i = 1, 2, ..., n), the method provides an estimate $\hat{x}_i$ of the true value of the analyte content and an estimate $\hat{y}_i$ of the true value of the response.

The residual sum of squared weighted deviations, S_{res}, i.e. the minimum value of S obtained after convergence, provides an overall measure of fit. The expected value of this minimum is $n - N$, and this value should not be exceeded by more than a factor of two. For the purpose of this International Standard, however, the definitive acceptance test is the goodness-of-fit test specified in 5.2.2. In this procedure, the fit is examined at each individual calibration point.

A.3 Calculation of the parameter variances and covariances

A.3.1 General

The variances, $u^2(b_j)$, and the covariances, $u(b_j,b_l)$, of the parameters of the analysis function are calculated from the calibration data as follows:

$$u^2(b_j) = \sum_{i=1}^{n}\left(\frac{\partial b_j}{\partial x_i}\right)^2 u^2(x_i) + \sum_{i=1}^{n}\left(\frac{\partial b_j}{\partial y_i}\right)^2 u^2(y_i) + 2\sum_{i=1}^{n-1}\sum_{h=i+1}^{n}\left(\frac{\partial b_j}{\partial x_i}\right)\left(\frac{\partial b_j}{\partial x_h}\right)u(x_i,x_h)$$

$$u(b_j,b_l) = \sum_{i=1}^{n}\left(\frac{\partial b_j}{\partial x_i}\right)\left(\frac{\partial b_l}{\partial x_i}\right)u^2(x_i) + \sum_{i=1}^{n}\left(\frac{\partial b_j}{\partial y_i}\right)\left(\frac{\partial b_l}{\partial y_i}\right)u^2(y_i) + \sum_{i=1}^{n-1}\sum_{h=i+1}^{n}\left[\left(\frac{\partial b_j}{\partial x_i}\right)\left(\frac{\partial b_l}{\partial x_h}\right) + \left(\frac{\partial b_l}{\partial x_i}\right)\left(\frac{\partial b_j}{\partial x_h}\right)\right]u(x_i,x_h)$$

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where

$u^2(x_i)$ is the variance of the analyte content x_i of the reference gas mixture $M_{\text{ref},i}$;

$u^2(y_i)$ is the variance of the corresponding response y_i;

$u(x_i,x_h)$ is the covariance of the analyte contents x_i and x_h of the reference gas mixtures $M_{\text{ref},i}$ and $M_{\text{ref},h}$.

In most cases, in both these equations the third term can be considered equal to zero, because in general the analyte contents of different reference gas mixtures are determined independently. However, there are also other cases such as dilution series. If two daughter gases, $M_{\text{ref},i}$ and $M_{\text{ref},h}$ are derived from the same parent gas, then the uncertainty of the analyte content of the parent gas propagates to the daughter gases in a (positively) correlated fashion. As a consequence, the corresponding covariance, $u(x_i,x_h)$, is different from zero, and has to be included in the calculation.

The input data required for calculating the parameter variances and the covariances according to these equations are determined as follows:

The derivatives $(\partial b_j/\partial x_i)$, $(\partial b_j/\partial y_i)$ are calculated by numerical differentiation from the function $b_j = f_j(x_1,\ldots,x_N, y_1,\ldots, y_N)$ which is implicitly given by the regression algorithm described in A.2.

The variances $u^2(x_i)$ and $u^2(y_i)$ are given by the squared standard uncertainties, i.e. $u^2(x_i) = [u(x_i)]^2$ and $u^2(y_i) = [u(y_i)]^2$.

If relevant, the covariances $u(x_i,x_h)$ are calculated by propagation of uncertainty for those variables, on which both analyte contents depend. The procedure for this calculation is described in A.4.

So as to implement the procedure described above practically, the following methods are recommended.

A.3.2 Transform matrix approach

In this approach, the variance/covariance matrix $\boldsymbol{V}_{\text{out}}$ relating to the output variables of the regression calculation is calculated from the variance/covariance matrix $\boldsymbol{V}_{\text{in}}$ relating to the input variables of the regression calculation by means of a transform matrix $\boldsymbol{Q}$ according to the following equation:

$$\boldsymbol{V}_{\text{out}} = \boldsymbol{Q} \cdot \boldsymbol{V}_{\text{in}} \cdot \boldsymbol{Q}^{\text{T}}$$

Here the output variables are the analysis function parameters b_j and the y-coordinates $\hat{y}_i$ of the adjusted calibration points. The input variables are the analyte contents, x_i, of the reference gases used for calibration, and the corresponding responses, y_i.

The transform matrix $\boldsymbol{Q}$ is calculated from the sensitivity matrices $\boldsymbol{D}_{\text{in}}$ and $\boldsymbol{D}_{\text{out}}$, relating to the normal equations (see A.2). These are matrices consisting of second-order derivatives $\partial^2 S/\partial p \partial q$ where S is the objective function to be minimized, p is one of the output variables and q is again one of the output variables in the case of $\boldsymbol{D}_{\text{out}}$, whereas in the case of $\boldsymbol{D}_{\text{in}}$, q is one of the input variables. In terms of these sensitivity matrices, the transform matrix is given by

$$\boldsymbol{Q} = \boldsymbol{D}_{\text{out}}^{-1} \cdot \boldsymbol{D}_{\text{in}}$$

A major problem in this procedure is the inversion of the matrix $\boldsymbol{D}_{\text{out}}$.

The parameter variances and covariances, $u^2(b_j)$ and $u(b_j,b_l)$, constitute a diagonal block of the output variance/covariance matrix $\boldsymbol{V}_{\text{out}}$.

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A.3.3 Numerical differentiation

This approach is based on the observation that any product $(\partial F/\partial z)u(z)$ consisting of a derivative $(\partial F/\partial z)$ and the standard uncertainty $u(z)$ of the variable concerned can be calculated approximately as follows:

$$(\partial F/\partial z)u(z) \approx \Delta_z = F\left[z + u(z)/2\right] - F\left[z - u(z)/2\right]$$

Due to the fact that a variance is the square of a standard uncertainty according to $u^2(z) = [u(z)]^2$, and that a covariance can be expressed as the product of two standard uncertainties and the correlation coefficient according to $u(z,z') = r(z,z')u(z)u(z')$, the expressions for the variances, $u^2(b_j)$, and the covariances, $u(b_j,b_l)$, of the analysis function parameters are sums of products of two such compound terms, with an additional factor r in the case of terms involving reference gas correlations (covariances).

Using this approach the parameter variances and covariances, $u^2(b_j)$ and $u(b_j,b_l)$, are calculated as follows.

One after the other, the calibration data x_i and y_i are changed, first by adding the respective $u/2$, second by subtracting $u/2$, while the other calibration data keep their original value. For each of these locally changed calibration data sets, the analysis function parameters are calculated. From the resulting data set, i.e. $4n$ sets of analysis function parameter values in the case of n calibration points, the approximate values of the parameter variances and covariances are calculated.

For these calculations the use of a spreadsheet computer program is recommended.

A.4 Correlations between reference gases

In general, the analyte contents of different reference gas mixtures are determined independently. However, there are also other cases such as dilution series. If two daughter gases, $M_{\text{ref},i}$ and $M_{\text{ref},h}$, are derived from the same parent gas, then an error in the analyte content of the parent gas propagates to the daughter gases in a (positively) correlated fashion. As a consequence, there is a non-zero covariance, $u(x_i,x_h)$, which has to be included in the uncertainty calculation, in addition to the standard uncertainties $u(x_i)$ and $u(x_h)$. Specifically, these covariances are required for the calculation according to A.3.

The general procedures for deciding whether correlations between reference gases are relevant and calculating the associated covariances may be summarized as follows.

a) Correlations are relevant if the analyte contents of different reference gases depend on the same quantity, or on a common set of quantities, and if the uncertainty on these quantities is significant.

b) Covariances are calculated by propagation of uncertainties on the common variables, as follows. If the analyte contents x_i and x_h depend on common quantities p, q, ... , then the covariance $u(x_i,x_h)$ is given by

$$u(x_i,x_h) = \left(\frac{\partial x_i}{\partial p}\right)\left(\frac{\partial x_h}{\partial p}\right)u^2(p) + \left(\frac{\partial x_i}{\partial q}\right)\left(\frac{\partial x_h}{\partial q}\right)u^2(q) + \ldots$$

where $u^2(p)$, $u^2(q)$, ... are the variances of the quantities p, q, ...

EXAMPLE If a reference gas mixture $M_{\text{ref},2}$ is derived from another reference gas mixture $M_{\text{ref},1}$ by dilution, the analyte contents x_1 and x_2 are correlated, since an error in x_1 will propagate to x_2. If x_2 is expressed as $x_2 = \gamma x_1$ with a dilution factor γ, the variances $u^2(x_1)$ and $u^2(x_2)$ result as follows

$$u^2(x_1) = \left[u(x_1)\right]^2$$

$$u^2(x_2) = \gamma^2\left[u(x_1)\right]^2 + x_1^2\left[u(\gamma)\right]^2$$

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where

$u(x_1)$ is the standard uncertainty of the analyte content x_1;

$u(\gamma)$ is the standard uncertainty of the dilution factor γ.

In addition to these terms, there is a non-zero covariance term as follows.

$$u(x_1, x_2) = \gamma \left[u(x_1) \right]^2$$

If another reference gas mixture $M_{\text{ref},3}$ is derived from $M_{\text{ref},1}$ using a different dilution factor γ', then the covariance between the analyte contents of $M_{\text{ref},2}$ and $M_{\text{ref},3}$ is given by

$$u(x_2, x_3) = \gamma \gamma' \left[u(x_1) \right]^2$$

Multiple-step dilution series can be treated analogously but are not relevant for this International Standard.

A.5 Indirect determination of the analysis function

Indirect determination of the analysis function proceeds in two steps. In the first step, an estimate of the calibration function, $y = F(x)$, is determined from the calibration data, using regression analysis. In the second step, the estimate of the calibration function is inverted to yield an estimate of the analysis function, $x = G(y)$. This procedure has two major disadvantages:

- indirect determination of the analysis function most often results in larger uncertainties of the analytical results;
- the inversion of the calibration function may cause problems, e.g. in the case of polynomials.

For these reasons, this International Standard recommends direct determination of the analysis function.

In particular cases, however, indirect determination of the analysis function may be preferable, for example if there are good reasons to assume that the response behaviour of an analytical system is very accurately described by a specific type of non-linear calibration function. If this model function can be inverted algebraically, the inverse should be used as a prospective analysis function. However, if algebraic inversion is not possible, the model function can only be used as a prospective calibration function. Then the parameters, a_j, are determined by regression, using the method described in A.2 with a slight adaptation, as follows:

The parameters a_j of the calibration function are determined by minimizing the expression of S obtained by elimination of the coordinates $\hat{y}_i$.

$$S = \sum_{i=1}^{n} \left[\frac{\left| \hat{x}_i - x_i \right|^2}{u^2(x_i)} + \frac{\left| F(\hat{x}_i) - y_i \right|^2}{u^2(y_i)} \right] = \text{minimum}$$

Here the calibration function, F, depends on a specified number of indeterminate parameters, $a_0, a_1, \ldots, a_N$. The problem then is to determine, simultaneously, the optimum values for these parameters and for the x-coordinates, $\hat{x}_i$, of the adjusted points. The y-coordinates, $\hat{y}_i$, are calculated from the $\hat{x}_i$, using the calibration function determined before.

After determination of the parameters the (estimated) calibration function, $y = F(x)$, has to be inverted to yield the (estimated) analysis function, $x = G(y)$. This inversion, however, can only be done numerically, solving the equation $y = F(x)$ point-by-point, that is, for individual input values y, yielding the corresponding output values $x = G(y)$. For this purpose, any equation solver, as contained in general purpose mathematical software program, can be used.

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For an indirectly determined analysis function, the uncertainty calculation described in 5.3 has to be modified accordingly.

$$u^2(x) = \left(\frac{\partial G}{\partial y}\right)^2 u^2(y) + \sum_{j=0}^{N}\left(\frac{\partial G}{\partial a_j}\right)^2 u^2(a_j) + 2\sum_{j=0}^{N-1}\sum_{l=j+1}^{N}\left(\frac{\partial G}{\partial a_j}\right)\left(\frac{\partial G}{\partial a_l}\right)u(a_j, a_l)$$

In this equation, G is the inverted calibration function, calculated numerically, and the a_j are the parameters of the calibration function.

Due to the fact that G was obtained from F by numerical inversion, the partial derivatives ($\partial G/\partial y$) and ($\partial G/\partial a_j$) have to be calculated by numerical methods, too.

The variances $u^2(a_j)$ and the covariances $u(a_j,a_l)$ of the parameters of the calibration function are calculated by propagation of uncertainty on the calibration data, analogously to the procedure described in A.3.

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Annex B
(informative)

Examples

B.1 General considerations

The following practical examples illustrate the application of the method recommended in this International Standard. Furthermore, they may serve as a reference for checking the performance of tailored software. These practical examples have been taken from different laboratories using different analytical methods.

All calculations have been made using B_LEAST, a computer program implementing the methodology of this International Standard (see annex C for program description). The program has extensively been tested and validated. It is made available in good faith and does not contain known errors. **However, this does not imply any warranty for any contractual or commercial situations nor a guarantee of warranted properties of the software, in particular no guarantee that it is error-free.**

Moreover, users of B_LEAST or any other tailored software implementing the methodology of this International Standard should be aware of the following considerations.

— The process of solving generalized least-squares problems is iterative even for linear model functions. Consequently, the results obtained may differ slightly in dependence on the numerical algorithms used and the truncation criterion applied.

— B_LEAST is not intended for use to solve least-squares problems in general. If used as such (in particular for problems beyond the scope of this International Standard), the user should do this with due care, and all the responsibility lies with him for carrying out appropriate checks regarding the truncation criterion and (possible) dependencies of the results on the initial guesses.

— B_LEAST is a compromise between robustness, short processing times and result accuracy. When special applications are concerned, the user should adjust accuracy (by altering the truncation criterion) at the expense of longer data processing times. Stiff data sets may even require an alteration of the initial guesses (set by default), and ill-posed problems may cause unexpected program termination.

NOTE Standard uncertainties can hardly be estimated with a relative precision better than 10 %. Therefore, standard uncertainties $u(x)$ should not be specified with more than two digits and for the corresponding data x, the decimal presentation should be matched to that for $u(x)$. However, for comparison purposes, in the examples input and output of the computer program B_LEAST, the decimal presentation is given with a higher number of digits.

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B.2 Examples

B.2.1 Example 1

In this example, the application of the main procedure as described in clause 5 has been followed so as to determine the content of NO in N_2. Therefore, it is subdivided into steps A to H of 5.1, the validation procedure of 5.2.1, and steps I to K of 5.3. Actions and results are summarized and briefly commented under the corresponding step.

a) **Step A:** The content of NO in N_2 is determined as a mole fraction in the range of 10^{-6} (approximately 5 µmol/mol to 50 µmol/mol).

b) **Step B:** Measurements are carried out using UV absorption at a wavelength of 190,5 nm with a spectral bandwidth of the analyser of 2 nm.

c) **Step C:** UV absorption intensity is known to be a linear function of analyte content over a wide range. Therefore a linear model function is considered.

d) **Step D:** For a straight line, the minimum number of calibration points is three. A minimum calibration design with three reference gas mixtures (no blank) is used.

e) **Steps E + F:** For the selected reference gas mixtures, the analyte contents and their standard uncertainties are given in Table B.1.

Table B.1

Reference gas No.	x_i	$u(x_i)$
1	4,5	0,045
2	18,75	0,187 5
3	50	0,5

f) **Step G:** The responses to the analyte contents (as the mean of ten individual measurements) and response uncertainties (as the corresponding standard deviation) are determined and yield the values given in Table B.2.

Table B.2

Reference gas No.	y_i	$u(y_i)$
1	0,196 9	0,003 938
2	0,787 4	0,015 748
3	2,022 8	0,040 456

g) **Step H:** The complete data set for the determination of the parameters of the analysis function and their uncertainties is given in Table B.3.

Table B.3

x_i	$u(x_i)$	y_i	$u(y_i)$
4,5	0,045	0,196 9	0,003 938
18,75	0,187 5	0,787 4	0,015 748
50	0,5	2,022 8	0,040 456

The parameters are calculated by regression analysis (see A.2). Using B_LEAST for calculations, the following function parameters and their uncertainties are obtained.

intercept b_0:	$-3{,}574\,7 \times 10^{-1}$
slope b_1:	$2{,}461\,2 \times 10$
standard uncertainty of the intercept:	$1{,}571\,6 \times 10^{-1}$
standard uncertainty of the slope:	$4{,}804\,8 \times 10^{-1}$
covariance between intercept and slope:	$-5{,}692\,1 \times 10^{-2}$

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h) **Validation step (see 5.2.1):** For the calculated regression line, the residual sum of squared (weighted) deviations, S_{res}, is 0,674 3, a value small enough for a good fit. The uncertainty-weighted deviations of adjusted points from corresponding calibration points with respect to analyte content and response are given in Table B.4.

Table B.4

Reference gas No.	Weighted deviation with respect to analyte content (x_i)	Weighted deviation with respect to response (y_i)
1	$4{,}52 \times 10^{-2}$	$-9{,}73 \times 10^{-2}$
2	$-2{,}75 \times 10^{-1}$	$5{,}68 \times 10^{-1}$
3	$2{,}31 \times 10^{-1}$	$-4{,}60 \times 10^{-1}$

The measure of goodness-of-fit, Γ, (maximum absolute value of the six values listed above) is 0,568, far below the critical value of 2, indicating excellent compatibility of the regression line with the calibration data. Therefore, the linear model function may be used for determining the analyte content of prospective calibration gas mixtures.

i) **Step I:** The prospective calibration gas mixtures are selected and their responses and the corresponding uncertainties (mean and standard deviation of ten individual measurements) are determined. For the three mixtures selected here, the results are given in Table B.5.

Table B.5

Mixture No.	Analyser response y	Uncertainty $u(y)$
1	$2{,}580\,0 \times 10^{-1}$	$5{,}160\,0 \times 10^{-3}$
2	$6{,}000\,0 \times 10^{-1}$	$1{,}200\,0 \times 10^{-2}$
3	$1{,}800\,0$	$3{,}600\,0 \times 10^{-2}$

j) **Steps J + K:** For the selected mixtures, the analyte contents and their uncertainties are calculated using the analysis function determined in step H as described in 5.3. Using B_LEAST for calculations, the values given in Table B.6 are obtained.

Table B.6

Mixture No.	Assigned value of x	Uncertainty $u(x)$
1	$5{,}992\,3$	$1{,}637\,7 \times 10^{-1}$
2	$1{,}440\,9 \times 10$	$3{,}559\,9 \times 10^{-1}$
3	$4{,}394\,3 \times 10$	$1{,}163\,1$

Due to the fact that the same calibration was used for determining the NO content in all three mixtures, the assigned values have covariances. Covariances are as follows:

— between values for mixtures 1 and 2: $1{,}16 \times 10^{-2}$

— between values for mixtures 1 and 3: $1{,}48 \times 10^{-2}$

— between values for mixtures 2 and 3: $1{,}37 \times 10^{-1}$

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If the mixtures are to be used together within a set of standards for further calibration, covariances between them should be taken into account properly.

B.2.2 Example 2

In this example, nitrogen N_2 in a synthetic natural gas is determined by gas chromatography (GC) as the analytical method. A GC equipped with a thermal conductivity detector is used. The calibration data set consists of seven data points derived from measurement of reference gas mixtures (standards) and a blank measurement as given in Table B.7.

Table B.7

x_i	$u(x_i)$	y_i	$u(y_i)$
$1{,}500 \times 10^{-3}$	$9{,}000 \times 10^{-4}$	$6{,}000 \times 10$	$3{,}500 \times 10$
$1{,}888 \times 10^{-1}$	$4{,}500 \times 10^{-4}$	$7{,}786 \times 10^{3}$	$1{,}357 \times 10^{2}$
$1{,}990$	$4{,}000 \times 10^{-3}$	$8{,}170 \times 10^{4}$	$3{,}670 \times 10$
$3{,}796$	$3{,}900 \times 10^{-2}$	$1{,}562 \times 10^{5}$	$2{,}232 \times 10^{2}$
$5{,}677$	$1{,}250 \times 10^{-2}$	$2{,}333 \times 10^{5}$	$1{,}372 \times 10^{2}$
$7{,}118$	$1{,}250 \times 10^{-2}$	$2{,}930 \times 10^{5}$	$2{,}455 \times 10^{2}$
$9{,}210$	$2{,}000 \times 10^{-2}$	$3{,}806 \times 10^{5}$	$1{,}251 \times 10^{2}$
$1{,}090 \times 10$	$2{,}500 \times 10^{-2}$	$4{,}497 \times 10^{5}$	$3{,}218 \times 10^{2}$

The number of data points allows all four types of model functions to be fit to this data. Determining a linear analysis function using the method recommended in this International Standard, the following parameters are obtained:

intercept b_0: $3{,}918\,9 \times 10^{-4}$

slope b_1: $2{,}428\,6 \times 10^{-5}$

standard uncertainty of the intercept: $1{,}145\,8 \times 10^{-3}$

standard uncertainty of the slope: $2{,}416\,1 \times 10^{-8}$

covariance between intercept and slope: $-7{,}274\,7 \times 10^{-12}$

The residual sum of squared deviations, S_{res}, is 6,169 7, indicating an acceptable fit. Accordingly, the measure of goodness-of-fit, Γ, is 1,632 2, still below the critical value of 2. Therefore, compatibility is acceptable, and the linear model function may be used for determining the analyte content of the prospective calibration gas mixtures. For the two mixtures selected here, results are given in Table B.8.

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