
**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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Printed in Switzerland

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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.

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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.

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.

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

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[GUM]

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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]

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

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3 Symbols and abbreviated terms

a_j	parameters of the calibration function F ($j = 0, 1, \dots, N$)
b_j	parameters of the analysis function G ($j = 0, 1, \dots, N$)
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
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
V	variance/covariance matrix
W	half-width of a confidence range
x	mole fraction of the specified analyte
(x_i, y_i)	calibration points ($i = 1, 2, \dots, n$)
(\hat{x}_i, \hat{y}_i)	adjusted calibration points ($i = 1, 2, \dots, n$)
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

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4 Principle

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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,

- 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.

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, \dots, y_n in relation to known analyte contents x_1, x_2, \dots, x_n of appropriate reference gas mixtures. Inversely, the analysis function, $x = G(y)$, approximately expresses known analyte contents x_1, x_2, \dots, x_n in relation to corresponding measured responses y_1, y_2, \dots, 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:

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- linear functions $x = b_0 + b_1y$
- second-order polynomials $x = b_0 + b_1y + b_2y^2$
- third-order polynomials $x = b_0 + b_1y + b_2y^2 + b_3y^3$
- power functions $x = b_0 + b_1y^{b_2}$
- exponential functions $x = b_0 + b_1e^{b_2y}$

The parameters b_j 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.

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 $M_{\text{ref},1}$, $M_{\text{ref},2}$, ..., $M_{\text{ref},n}$ 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:

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

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, $x_{\text{min}} = 0$, and $x_{\text{max}} = L_x$. 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 $u(y_1)$, $u(y_2)$, ..., $u(y_n)$.