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

Analyse des gaz — Méthodes de comparaison pour la détermination et la vérification de la composition des mélanges de gaz d'étalonnage

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Foreword

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

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

This document was prepared by Technical Committee ISO/TC 158, *Analysis of gases*, in collaboration with the European Committee for Standardization (CEN) Technical Committee CEN/TC 238, *Test gases, test pressures and categories of appliances*, in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

This third edition cancels and replaces the second edition (ISO 6143:2001), which has been technically revised.

The main changes ~~compared to the previous edition~~ are as follows:

— ~~—~~update of definitions, in particular those taken from the VIM;

— ~~—~~update of the bibliography and the corresponding references in the text;

— ~~—~~update of the information in ~~Annex C~~Annex C on the computer programme B_LEAST; information on alternative software ~~(Annex D);~~(Annex D);

— ~~—~~amendment of ~~6.2~~6.2 (now ~~7.2~~)7.2) “Comparison of several calibration gas mixtures” and related statements in other parts of the document

— ~~—~~amendment of the recommendations concerning the number of replicate measurements per sample;

— ~~—~~revision of the requirements for the report of results (“Test report”);

— ~~—~~new ~~Annex D~~Annex D (informative) “Additional information on data evaluation”;

— ~~—~~deletion of ~~A.1~~A.1 “Uncertainty specifications for reference gas mixtures”;

— ~~—~~additional references to relevant ISO standards (ISO 12963, ISO 14912, ISO 15796);

— ~~—~~correction of ~~formula~~ Formula (4) for the power functions.

~~Recently, independent calculations of the examples in Annex B at METAS (Switzerland) have shown that B_LEAST provides incorrect values for the parameter uncertainties of the exponential function (Example 3) while the parameter values themselves were confirmed. For all other function types, the results of the example calculations by B_LEAST were confirmed. It is therefore recommended not to use B_LEAST for evaluations using the exponential function or to calculate the parameter uncertainties (standard uncertainties and covariances) separately.~~

— recommendation added to Annexes to not to use B_LEAST for evaluations using the exponential function (due to recently demonstrated errors) or to calculate the parameter uncertainties (standard uncertainties and covariances) separately.

Any feedback or questions on this document should be directed to the user’s national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Field Code Changed

Introduction

In gas analysis, calibration of analytical systems is most often 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). This approach was also adopted in the first edition (1981) of ISO 6143:1981). However, ISO 6143this document is devoted tointended for a very specialspecific task: the derivation of calibration gases from appropriate reference gases. Consequently, the multiplier effect of errors in calibration gases – an error in a calibration gas can cause errors in thousands of analytical results – implies high demands on the metrological quality of the analysis of calibration gases. In the development of the second edition (ISO 6143:2001), it was therefore decided to use the best available measurement strategy and data evaluation method. The main changes in the revision of the (ISO 6143:1981) edition related to calibration as well as to uncertainty evaluation:

— —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.

After twenty years, the principles and procedures specified in the second edition of this document are still fit for purpose. The current revision therefore mainly concerns additional supporting information.

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. A dedicated program (B_LEAST) is available and will be provided without cost as a part of this document (see Annex CAnnex C)[1]. Information on other publicly available software that can be used for at least the vast majority of the calculations required by ISO 6143this document is given in Annex D.Annex D. As an alternative, sufficient information is given in thethis document to enable the user to develop a program on their own.

[1] The software "B_LEAST" can be obtained via the following link: https://standards.iso.org/iso/6143/ed-3/en.

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

1 Scope

This document providesspecifies 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;

— consistency testing and outlier search in suites of calibration gas mixtures of closely related composition.

NOTE 1 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, requireneed 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.

NOTE 2 Comparison methods based on one- and two-point calibration are described in ISO 12963[5].

2 Normative references

There are no normative references in this document.

3 Terms and definitions

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

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

— ISO Online browsing platform: available at https://www.iso.org/obphttps://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/https://www.electropedia.org/

3.1 3.1
composition
characteristic of a gas mixture given by the kind and content of each specified mixture component (analyte) and a specification of the complementary gas (matrix)

Note 1 to entry: In this document, the analyte content is specified as an amount of substance fraction, exclusively. Amount 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) can be more appropriate. Their use then requires due care concerning the

dependence on pressure and temperature. Methods for conversion between different quantities of composition are specified in ISO 14912.

3.2 ~~**3.2**~~
comparison method
method for determining the content of a specified gas mixture component (analyte) by measuring an instrumental response

Note 1 to entry: ~~———~~ 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.

3.3 ~~**3.3**~~
calibration
operation that, under specified conditions, in a first step, establishes a relation between the quantity values with measurement uncertainties provided by measurement standards and corresponding indications with associated measurement uncertainties and, in a second step, uses this information to establish a relation for obtaining a measurement result from an indication

[SOURCE: ISO/IEC Guide 99:2007, 2.39]

3.4 ~~**3.4**~~
response function
functional relationship between instrumental response and analyte content

Note 1 to entry: ~~———~~ The response function can be expressed in two different ways as a *calibration function* (3.4.1) or an *analysis function*, (3.4.2), depending on the choice of the dependent and the independent variable.

3.4.1 ~~**3.4.1**~~
calibration function
instrument response expressed as a function of analyte content

3.4.2 ~~**3.4.2**~~
analysis function
analyte content expressed as a function of instrument response

3.5 ~~**3.5**~~
measurement uncertainty
uncertainty of measurement
uncertainty
non-negative parameter characterizing the dispersion of the quantity values being attributed to a measurand, based on the information used

[SOURCE: ISO/IEC Guide 99:2007, 2.26]

~~**3.6**~~
~~**metrological traceability**~~
~~traceability~~
~~property of a measurement result whereby the result can be related to a reference through a documented unbroken chain of calibrations, each contributing to the measurement uncertainty~~

~~[ISO/IEC Guide 99:2007, 2.41]~~

3.6 ~~3.7~~
measurement standard
realization of the definition of a given quantity, with stated quantity value and associated measurement uncertainty, used as a reference

[SOURCE: ISO/IEC Guide 99:2007, 5,1]

3.7 ~~3.8~~
reference standard
reference measurement standard
measurement standard (3.6) designated for the calibration of other measurement standards for quantities of a given kind in a given organization or at a given location

[SOURCE: ISO/IEC Guide 99:2007, 5.6]

3.8 ~~3.9~~
calibration gas mixture
gas mixture of known stability and homogeneity whose composition is well established for use in the calibration or verification of a measuring instrument or for the validation of a measurement

[SOURCE: ISO 7504:2015, 5.1, modified — Note 1 to entry has been removed]

3.9 ~~3.10~~
reference gas mixture
calibration gas mixture whose composition is well established and stable to be used as a reference standard (3.7) of composition from which other composition data measurements are derived

[SOURCE: ISO 7504:2015, 5.2, modified — Note 1 to entry has been removed]

4 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
n	number of data points
$\boldsymbol{Q}$	transform matrix
s	standard deviation of a data set (sample standard deviation)
S	sum of weighted squared deviations
S_{res}	residual sum of weighted squared deviations

$t_{\nu;(1-\alpha)}$	quantile of the t-distribution (ν degrees of freedom, confidence level (1-α))
$U(q)$	expanded uncertainty of an estimated quantity q, $U(q) = ku(q)$
$u(q)$	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
x	amount fraction of the specified analyte
(x_i, y_i)	calibration points (i = 1, 2, ..., n)
~~$(\hat{x}_i, \hat{y}_i$~~ ~~$)$~~ ~~$(\hat{x}_i, \hat{y}_i)$~~	adjusted calibration points (i = 1, 2, ..., n)
y	instrument response of the specified analyte
$\chi^2_{\nu;(1-\alpha)}$	quantile of the Chi²-distribution (ν degrees of freedom, confidence level (1-α))
~~γ~~	dilution factor
σ	standard deviation of a probability distribution
Γ	measure of goodness-of-fit

5 Principle

The composition of a gas mixture is determined by separate determination of the amount fraction of every specified analyte. Therefore, the procedure for determining the amount fraction of only one specified analyte is described. Possible interferences due to the presence 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 document.

This document is also applicable if other composition quantities than amount fraction are used. However, it is recommended that the final result be expressed as an amount fraction. Methods for conversion between different quantities of composition are specified in ISO 14912[~~6~~].[6].

The general procedure for determining the amount 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) ~~a)~~ Specify the analytical range of interest, i.e., the range of the amount fractions x to be determined, and the acceptable uncertainty level (see ~~6.1,~~6.1, step A).

b) ~~b)~~ Specify the analytical method and the measuring system to be used (see ~~6.1,~~6.1, step B).

c) ~~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 an evaluation of the system characteristics 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 ~~6.1,~~6.1, step C).

d) ~~d)~~ Set up a design for the calibration experiment in which the relevant experimental parameters are specified, such as:

- ~~—~~ 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 ~~6.1,~~6.1, steps D, E, F).

e) ~~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 ~~6.1,~~6.1, step G).

f) ~~f)~~ Calculate the analysis function, $x = G(y)$, from the calibration data, using regression analysis (see ~~6.1,~~6.1, step H).

g) ~~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 ~~6.2.2).~~6.2.2).

h) ~~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 ~~6.2.3).~~6.2.3).

i) ~~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 ~~6.2.4).~~6.2.4). 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 ~~6.2.5).~~6.2.5).

~~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) ~~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 amount fraction $x = G(y)$ using the analysis function determined in f),
- ~~—~~ calculate the uncertainty $u(x)$ of the amount fraction x by propagation of uncertainty on the measured response and on the parameters of the analysis function (see ~~6.3).~~6.3).

k) ~~k)~~ State the result of the entire analysis (see ~~clause 8).~~clause 8).

Essentially the same steps apply if, instead of the analysis function, $x = G(y)$, the calibration function, $y = F(x)$, is determined from the calibration data. Given the calibration function, the analyte content x for response y is obtained by solving the ~~equation~~formula $y = F(x)$ for x, given y. To this end, if possible, the calibration function is inverted algebraically, yielding the corresponding analysis function, $x = F^{-1}(y)$. As an example, a linear calibration function $y = a_0 + a_1x$ can be inverted yielding $x = (y - a_0)/a_1$. If algebraic inversion is not possible, the corresponding analysis function is obtained by "numerical inversion", i.e., the ~~equation~~formula $y = F(x)$ is solved pointwise, using an appropriate numerical method. The approach using the calibration function is described in ~~A.4.~~A.4.

In addition to determining the composition of a (prospective) calibration gas mixture, the general procedure can 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 7~~Clause 7 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 can also be used for consistency testing and outlier search in suites of calibration gas mixtures of closely related composition. ~~Clause 7~~Clause 7 specifies a procedure where entire suites of calibration gases are measured in a calibration experiment, using an analyser with linear response. For each analyte concerned the calibration data are examined for compatibility with a straight-line response curve. A positive test result provides confirmation that the assigned contents and their uncertainties are mutually consistent. Restriction to subsets provides a tool for outlier search in cases of a negative test result.

Numerical examples for applying the methodology are given in ~~Annex B.~~Annex B.

6 General procedure

6.1 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 (i.e., solving the ~~equation~~formula $y = F(x)$ for x, given y). It is recommended to make a direct determination of the analysis function. Therefore, only this procedure is specified in the body of this document. In particular applications, however, indirect determination using the calibration function can be preferable. For such applications, a brief description of this procedure is given in ~~A.4.~~A.4.

The following description of the calibration experiment and its evaluation, in terms of a series of steps, ~~resumes~~summarizes and elaborates the principles outlined in ~~clause 5.~~clause 5.

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.