TECHNICAL
SPECIFICATION

ISO/TS
14167

First edition
2003-04-15

Gas analysis — General quality assurance aspects in the use of calibration gas mixtures — Guidelines

Analyse des gaz — Aspects généraux de l'assurance qualité dans l'utilisation de mélanges de gaz pour étalonnage — Lignes directrices

Reference number
ISO/TS 14167:2003(E)

PDF disclaimer

This PDF file may contain embedded typefaces. In accordance with Adobe's licensing policy, this file may be printed or viewed but shall not be edited unless the typefaces which are embedded are licensed to and installed on the computer performing the editing. In downloading this file, parties accept therein the responsibility of not infringing Adobe's licensing policy. The ISO Central Secretariat accepts no liability in this area.

Adobe is a trademark of Adobe Systems Incorporated.

Details of the software products used to create this PDF file can be found in the General Info relative to the file; the PDF-creation parameters were optimized for printing. Every care has been taken to ensure that the file is suitable for use by ISO member bodies. In the unlikely event that a problem relating to it is found, please inform the Central Secretariat at the address given below.

STANDARDSISO.COM : Click to view the full PDF of ISO/TS 14167:2003

© ISO 2003

All rights reserved. Unless otherwise specified, no part of this publication may be reproduced or utilized in any form or by any means, electronic or mechanical, including photocopying and microfilm, without permission in writing from either ISO at the address below or ISO's member body in the country of the requester.

ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

Published in Switzerland

Contents

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 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

In other circumstances, particularly when there is an urgent market requirement for such documents, a technical committee may decide to publish other types of normative document:

— an ISO Publicly Available Specification (ISO/PAS) represents an agreement between technical experts in an ISO working group and is accepted for publication if it is approved by more than 50 % of the members of the parent committee casting a vote;

— an ISO Technical Specification (ISO/TS) represents an agreement between the members of a technical committee and is accepted for publication if it is approved by 2/3 of the members of the committee casting a vote.

An ISO/PAS or ISO/TS is reviewed after three years in order to decide whether it will be confirmed for a further three years, revised to become an International Standard, or withdrawn. If the ISO/PAS or ISO/TS is confirmed, it is reviewed again after a further three years, at which time it must either be transformed into an International Standard or be withdrawn.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO/TS 14167 was prepared by Technical Committee ISO/TC 158, *Analysis of gases*.

Introduction

Gas analyses are performed on samples covering a wide range of compositions.

All gas analyses fall into one of two categories:

- those for which calibration gas mixtures exist with compositions that are traceable to reference gas mixtures (e.g. primary or national standards);
- those for which the above do not exist.

In both cases, this Technical Specification provides the overall guidance on quality assurance aspects required to achieve a result with a valid measurement uncertainty.

It is applicable only to calibration gas mixtures of gaseous, or totally vaporized, components which do not react with each other or with the cylinder walls.

The user of this Technical Specification chooses, prior to any analyses, an appropriate measurement procedure depending on the application of the final results of the analyses and the requirements for a particular measurement uncertainty. This use may vary considerably, ranging from qualitative analysis to accurate quantitative analysis for which evidence has to be provided that claimed measurement uncertainty levels are met. Each type of measurement procedure involves a number of issues, which are considered beforehand. Typically, for gas analysis these include:

a) sampling;

b) selection and use of calibration gas mixtures;

c) selection and validation of measurement method;

d) identification of uncertainty sources;

e) quantification of uncertainty contributions;

f) documentation.

For a given measurement procedure, the effect of the above issues, influencing the uncertainty of the final measurement result, is calculated approximately. This may imply that several calculations have to be made in advance, with different sets of values for the parameters involved, before the required level of uncertainty is achieved. In practice, this calculation process is repeated until the desired target uncertainty is reached. This process of defining target uncertainties is an effective way of finding correct solutions for specific measurement procedures. The final analysis is then performed using this evaluated procedure.

To illustrate the use of this Technical Specification, two practical examples are given in Annex A.

Annex B gives information on the validation of reference gas mixtures in those cases where calibration gases of widely acknowledged composition do not exist.

Annex C describes the traditional hierarchy of reference gas mixtures.

The references are given in the Bibliography.

Gas analysis — General quality assurance aspects in the use of calibration gas mixtures — Guidelines

1 Scope

This Technical Specification provides guidance on the quality aspects in the field of gas analysis that are implemented in order to achieve a result with a valid measurement uncertainty.

It provides guidelines on quality aspects to be employed in gas analysis using calibration gas mixtures and their subsequent validation and/or verification, and the testing of the analytical performance of gas analysis instruments. These guidelines have the overall objective of defining procedures which will ensure that measurements of gas composition are reliable, comparable and consistent between different organizations and countries.

This Technical Specification explains, in particular, the concepts of measurement uncertainty and of traceability as effective quality assurance tools for defining the measurement uncertainty of particular measurement results. It also gives guidance on how to identify and estimate measurement uncertainty components of the result, and how to combine these uncertainty components in order to obtain the overall uncertainty.

2 Terms and definitions

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

2.1
traceability

property of a result of a measurement or the value of 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

NOTE 1 The unbroken chain of comparisons is called a “traceability chain”.

NOTE 2 A calibration gas mixture is traceable at best to a primary reference gas mixture.

[VIM [1]]

2.2
uncertainty (of measurement)

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

NOTE 1 The parameter may be, for example, a standard deviation or a given multiple of it, or the half-width of an interval having a stated level of confidence.

NOTE 2 Uncertainty of measurement comprises, in general, many components. Some of these components may be evaluated from the statistical distribution of the results of series of measurements and can be characterized by experimental standard deviations. The other components, which can also be characterized by standard deviations, are evaluated from assumed probability distributions based on experience or other information.

NOTE 3 It is understood that the result of the measurement is the best estimate of the value of the measurand, and that all components of uncertainty, including those arising from systematic effects, such as components associated with corrections and reference standards, contribute to the dispersion.

NOTE 4 Uncertainty can be expressed as a standard uncertainty or, when multiplied by a coverage factor, as an expanded uncertainty.

[Adapted from GUM [2]]

2.3
uncertainty of a certified value

estimate attached to a certified value of a quantity which characterizes the range of values within which the "true value" is asserted to lie with a stated level of confidence

[ISO Guide 30:1992 [3]]

2.4
calibration gas mixture

gas mixture of sufficient stability and homogeneity whose composition is properly established for use in the calibration of a measuring instrument or for the validation of a measurement or gas analytical method

NOTE Calibration gas mixtures are the analogues of measurement standards in physical metrology

[ISO 7504:2001 [4]]

2.5
reference gas mixture

calibration gas mixture whose composition is sufficiently well established and stable to be used as a reference standard of composition from which other composition data are derived

NOTE Reference gas mixtures are the analogues of reference standards.

[ISO 7504:2001 [4]]

2.6
primary reference gas mixture

reference gas mixture which is designated, or generally accepted, as realizing a specific composition of the highest metrological quality

NOTE 1 Primary reference gas mixtures are the analogues of primary standards.

NOTE 2 Normally the use of primary reference gas mixtures is confined to comparisons with other primary reference gas mixtures of similar compositions and to secure secondary reference gas mixtures by comparison.

NOTE 3 Primary reference gas mixtures are sometimes designated as measurement standards by national metrology institutes, and may then be known as primary standard gas mixtures

[ISO 7504:2001 [4]]

2.7
secondary reference gas mixture

reference gas mixture whose composition is assigned by comparison with a primary reference gas mixture of similar composition, or with several such primary reference gas mixtures

NOTE 1 Secondary reference gas mixtures are the analogues of secondary standards.

NOTE 2 A secondary reference gas mixture may be used as a calibration gas mixture then having traceability to a primary reference gas mixture.

[ISO 7504:2001 [4]]

2.8

stability

attribute of a gas mixture, stored or used under specified conditions, to maintain its composition within its specified uncertainty limits for a specified period of time (maximum storage life) and over a specified range of pressure and of temperature

NOTE It is appropriate to specify the uncertainty limits for each component of interest.

[ISO 7504:2001 [4]]

2.9

homogeneity

state of a gas mixture wherein all of its components are distributed uniformly throughout the volume occupied by the gas mixture

NOTE Unless any other indication is given, it is normally to be assumed that the gas mixture is homogeneous in composition in time and space within the gas mixture.

[ISO 7504:2001 [4]]

2.10

validation

confirmation, through the provision of objective evidence, that the requirements for a specific intended use or application have been fulfilled

NOTE 1 In design and development, validation concerns the process of examining a product to determine conformity with user requirements.

NOTE 2 Validation is normally performed on the final product under defined operating conditions. It may be necessary in earlier stages.

NOTE 3 The term “validated” is used to designate the corresponding status.

NOTE 4 Multiple validations may be carried out if there are different intended uses.

NOTE 5 In gas composition analysis, validation refers to the confirmation that the method, as applied, is fit for the intended purpose.

[Adapted from ISO 7504:2001 [4]]

2.11

verification

Confirmation, through the provision of objective evidence, that the specified requirements have been fulfilled

NOTE 1 In design and development, verification concerns the process of examining the result of a given activity to determine the conformity with the stated requirements for that activity.

NOTE 2 The term “verified” is used to designate the corresponding status.

NOTE 3 In gas composition analysis, verification refers to an individual result that agrees with the result of an independent method.

[ISO 7504:2001 [4]]

3 Gas analysis using a comparison method

The acceptability of individual measurement results is improved when rigorous quality control provides evidence that the results are in agreement with results from:

a) measurements on similar samples by other laboratories;

b) previous measurements on similar samples by the same laboratory;

c) previous measurements on other samples.

Whenever links are made between measurement systems, these links have to be identified (traceability chain) and its strength quantified (uncertainty). In the following clauses, these concepts are elaborated as well as the quality control aspects of the steps in the measurement procedure.

Calibration gas mixtures should be prepared using either static or dynamic methods:

— Gravimetric preparation of fully gaseous gas mixtures is described in ISO 6142 [5].

— Static volumetric methods are described in ISO 6144 [6].

— The various parts of ISO 6145 [7] to [15] deal with a great number of dynamic methods for preparing gas mixtures. Mixtures prepared in accordance with any of these parts will have stated compositions and uncertainty evaluations.

Mixtures prepared by the methods given should first be verified before they can actually be used as calibration gas mixtures. ISO 6143 [16] gives a comparison method that is in most cases suited for verification purposes.

ISO 6141 [17] describes the contents of a certificate of a calibration gas mixture.

Figure 1 gives a scheme explaining gas analysis using a comparison method. The numbers in the boxes refer to references in the Bibliography.

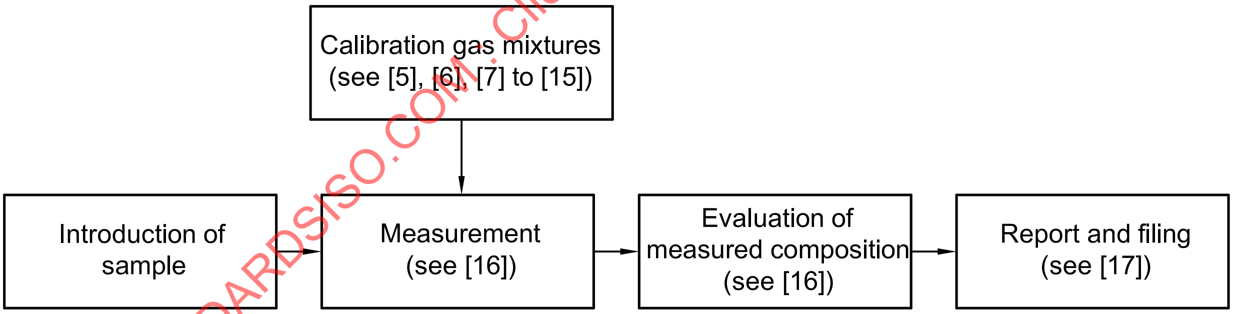

Figure 1 — Gas analysis scheme using a comparison method

4 Uncertainty

4.1 General

The main task of gas analysis is to determine the composition of gases, i.e. to measure the content of one or several specified target components (analytes) in a matrix gas. This clause mainly gives guidance on how to evaluate and express the uncertainty of results in gas composition analysis. However, the same principles and analogous procedures may be used to evaluate and express the uncertainty of results in the preparation of calibration gas mixtures or in other fields of gas analysis such as the direct measurement of physico-chemical properties of gases.

The uncertainty of an analytical procedure is determined in accordance with two fundamentally different strategies:

- the **step-by-step** approach (also called the bottom-up approach), where the uncertainty is calculated as a combination of various components, relating to building blocks of the overall procedure or to significant error sources;
- the **direct** approach (also called the top-down approach), where the uncertainty is determined directly by investigating the spread of results obtained on gases of known composition.

The step-by-step approach (see 4.2) requires a thorough investigation of the analytical procedure and proper assessment of component uncertainties. Its main tools are uncertainty budgets and uncertainty propagation, based on an appropriate mathematical model of the measurement process or the preparation process.

The direct approach (see 4.3) requires appropriate reference gases or reference analytical methods. In addition, the comparison measurements have to be performed under appropriate reproducibility conditions.

4.2 Step-by-step approach

This approach attempts to evaluate the uncertainty of the result of an analytical procedure by identifying the uncertainty components of that procedure. Each of the uncertainty components are evaluated to determine their contribution and are combined mathematically using the principles described in GUM [2]. This approach requires the user to produce a detailed uncertainty budget in a series of steps as follows:

a) Separate the analytical procedure into a series of well-designed steps, e.g. sample pre-treatment, measurement, data evaluation.

b) For each step, identify and list all factors that may influence the performance of this step and consequently give rise to uncertainty.

NOTE 1 It is understood that a correction is applied to every identified source of systematic error, leaving as a contribution to the overall uncertainty budget the uncertainty of the correction.

NOTE 2 In a number of International Standards produced by ISO/TC 158, comprehensive lists of uncertainty sources and assessments of their relevance are given. [5], [6], [7], [16]

NOTE 3 To prove the validity of the results, traceability to acknowledged measurement standards should be demonstrated where available.

c) Some of the identified uncertainties will have a large influence on the uncertainty of the method, and others only a small influence. To determine this influence, an estimate is now made of the contribution of each of the uncertainty sources to the final combined standard uncertainty. Each of the identified uncertainties should now be classed as being either significant or insignificant when compared to the combined standard uncertainty. Uncertainty sources classed as insignificant should be neglected. (Insignificant uncertainties may be classed as those which contribute less than 10 % to the combined standard uncertainty.)

d) For the uncertainty sources classed as significant, design a mathematical model describing the final result of the procedure, y, as a function of the input parameters (significant contributors) x_i (i = 1, 2, …, N), e.g. sample flow, pressure and temperature, recovery rates, measured instrument response, response function parameters, conversion factors and corrections:

$$y = f(x_1, x_2, \ldots, x_N) \tag{1}$$

e) For each significant uncertainty source, evaluate the contribution $u_i(y)$ to the uncertainty of the final result y as a **standard uncertainty**, that is as a standard deviation, either of a series of repeated measurement results (Type A evaluation) or of a hypothetical distribution expressing the available information about the respective quantity (Type B evaluation). The contribution to the total uncertainty due to x_i is $u_i(y)$, and is determined as a product of a sensitivity coefficient c_i taken from the model in accordance with step d) and the standard uncertainty $u(x_i)$ of the respective input quantity:

$$u_i(y) \equiv \left| c_i \right| u(x_i) \tag{2}$$

where $c_i = \dfrac{\partial f}{\partial x_i}$

f) Consider possible correlations between different uncertainty contributions $u_i(y)$ and $u_j(y)$, determined in step e), e.g. due to use of the same measurement standard. If the correlation is determined as being significant, estimate the corresponding **covariance** $u_{ij}(y)$:

$$u_{ij}(y) = c_i c_j \, u(x_i, x_j) \tag{3}$$

g) Calculate the **combined standard uncertainty** $u(y)$ of the final result y as the root of the sum of squares of the component standard uncertainties and their possible covariances:

$$u_c{}^2(y) = \sum_{i=1}^{N} c_i{}^2 u^2(x_i) + 2 \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} c_i c_j \, u(x_i, x_j) \tag{4}$$

4.3 Direct approach

In this approach, the analytical procedure is applied to appropriate reference samples, and the results are compared with the reference values attributed to the reference samples. Alternatively, the procedure under investigation and an established reference method are applied in parallel to appropriate samples, and the results are compared. This comparison serves a double purpose:

a) By comparing the mean of repeated measurements with the corresponding reference value, any significant analytical bias is detected. In addition, an appropriate bias correction should be derived.

b) From the spread of results of repeated measurements and the uncertainty of the reference values, the uncertainty of the results of the analytical procedure, including a bias correction, is calculated. It is emphasized that a proper evaluation of the variability is necessary.

A more detailed description of this comparison and its evaluation are given in 5.2.

This approach is applied either by an individual laboratory or in an interlaboratory study. In the first case, it is essentially a calibration study. Then it is important to ensure that:

- the reference values and their uncertainties are well established;
- the calibration samples are representative of the range of samples to be analysed;
- the variability of the measurement conditions in the calibration study covers the variability in the intended applications.

In the second case of an interlaboratory study, the procedures described in the ISO 5725 series of International Standards [18] to [23] should be followed.

If neither suitable reference samples nor suitable reference methods are available, the comparison may be based on consensus values instead of reference values, as a substitute but by no means as an equivalent.

5 Traceability

5.1 General

Traceability is universally recognized as one of the basic prerequisites for comparability of the results of measurements made in different laboratories and in different countries, and of the conclusions drawn from these results. When comparing different measurement results for the same quantity, three basic requirements have to be fulfilled:

a) the uncertainties of the measurement results have to be known;

b) the units used to express the measurement results (including the uncertainties) have to be the same, or at least convertible;

c) the measures used to express the uncertainties have to be the same, or at least convertible.

Evidently, requirements b) and c) call for standardization. For the units of physical quantities, the standardization problem was solved by establishing the International System of Units (SI System). Concerning the standardization of uncertainty measures, the "standard uncertainty" proposed by the *Guide to the expression of uncertainty in measurement (GUM)* [2] has the potential of worldwide acceptance.

The remaining requirement a) is the most demanding one. In short, known uncertainty means that in the uncertainty budget of the measurement no major contribution has been overlooked, and that the quantification and combination of uncertainty contributions has been done correctly. Traceability, where applicable, simultaneously solves all these problems by comparison between measured values and corresponding reference values. Thus, where appropriate reference standards are available, traceability is a direct and effective way of demonstrating accuracy.

A traceability chain is established by comparison between measured values and corresponding reference values. In practice, there are different strategies for making use of such comparisons: **calibration** and **verification**. In short, in calibration the comparison results are used to derive measurement results from raw data, while in verification measurement results are tested for agreement with the results of an independent reference method.

In calibration, different methods are used depending on the type of task. For example, calibration may refer to a measuring system or to a measurement standard. The main case considered in this document is calibration of an analytical system. Here, the purpose of calibration can either be determination and correction of bias or determination of the relationship between measured response and analyte contents.

The traceability strategies considered in this document fall into three main categories:

— detection and correction of analytical bias;

— determination of response characteristics;

— examining agreement with the results of an independent method.

For each of these strategies, different procedures are available and the following options are available:

— single-level or multi-level comparison;

— interpolation or regression;

— uncertainty propagation or statistical analysis of residual scattering.

5.2 Calibration for response function determination

When determining the relationship between instrumental response and the target quantity — typically the content of a specified analyte in a specified matrix gas — the response is measured using standards of known analyte content, covering the measurement range. From the comparison between the measured responses and the reference values, parameters of the response curve (e.g. slope and intercept of a straight line) are derived, including the uncertainties of these parameters. Using this data, the analyte content of an unknown sample is estimated from its measured response. In addition, the uncertainty of the estimated analyte content is calculated from the uncertainty of the measured response and the uncertainties of the response curve parameters.

The main requirements for this procedure are as follows:

- the calibration samples have to be representative of the range of samples to be analysed;
- the variability in the measurement conditions in the calibration study has to cover the variability in the intended applications;
- the response curve has to be compatible with the calibration data, including their uncertainties.

By using this procedure, the uncertainty of the analytical method is traceable to reference values and includes the uncertainties attributed to the calibration standards.

ISO 6143 [16] specifies a method for deriving the composition, including uncertainty, of calibration gases from a set of reference gases, using the approach outlined in this clause.

5.3 Calibration for bias detection and correction

To determine the uncertainty of the results of a selected analytical method, the method is applied to appropriate calibration samples. The results are compared with the reference values attributed to the calibration samples. Alternatively, the method selected and a reference method, i.e. a method whose uncertainty is known, are applied in parallel to appropriate samples. The results of the method selected are compared with those of the reference method. This comparison is performed and evaluated in a series of three steps as follows:

a) The measurement results and the corresponding reference values are compared, and the differences between corresponding values are tested for significance against the expanded uncertainty using an appropriate coverage factor, e.g. Student's t for 95 % confidence, and the relevant number of degrees of freedom.

b) If significant bias was found in step a), a bias correction for the specified measurement range is derived. For a restricted measurement range, this is a bias factor or an additive correction term based on a single-level comparison. For extended measurement ranges, correction curves or correction functions are required based on multi-level comparisons.

c) The uncertainty of the results of future measurements, including bias correction, is calculated by the combination of two contributions: the uncertainty of the uncorrected measurement result and the uncertainty of the correction. The uncertainty of the correction is estimated from the calibration data, either by uncertainty propagation or by statistical analysis of the residual scattering.

The main requirements for this type of calibration are described in 4.3.

5.4 Verification of individual results

For the purpose of this Technical Specification, an individual result is the value of a specified measurand obtained using a specified gas, e.g. the content of a specified analyte in a gas sample, determined either by gravimetry or analysis, or the value of a physico-chemical property determined by direct measurement.

Verification of an individual result means examination whether, and confirmation that, the result agrees with the result from an independent method (see Clause 6). Verification can provide traceability if the independent method used is a reference method, that is if its uncertainty is known.

5.5 Traceability of reference values

For the purpose of this Technical Specification, reference values are values of gas mixture composition or physico-chemical gas properties provided by reference standards. Reference standards have to be prepared by a method with an established uncertainty, and verified by independent analysis where possible. Reference standards meeting these requirements are called reference gas mixtures (see 2.5, 2.6 and 2.7). Other calibration gas mixtures have to be made traceable to appropriate reference gas mixtures using the protocol specified in ISO 6143 [16].

Annex C shows a hierarchy of calibration gas mixtures, based on ISO 14111 [24].

As part of the criteria for calibration gas mixtures being acceptable as reference standards, the methods of analysis have to be thoroughly understood. A thoroughly understood method means that the analysis methodology has a fully established and robust uncertainty budget and, in addition, the user has to supply adequate evidence showing implementation of the uncertainty budget.

6 Validation and verification

6.1 Validation of methods

Method validation, as defined in this Technical Specification, consists of four steps:

a) specification of the analytical task;

b) determination of the method's performance characteristics;

c) comparing specifications against characteristics;

d) confirming fitness, or stating lack of fitness, for the intended use.

The main task in method validation is determining the method's performance characteristics. The requirement is to specify a given analytical method with an application range with defined uncertainty, for example:

— Specificity and selectivity are intended to specify the range of matrix gases for which the uncertainty budget is valid. For other matrix gases, a correction and/or an additional uncertainty component is necessary.

— Robustness and ruggedness are intended to specify a range of operating conditions for which the uncertainty budget is valid. For other operating conditions, a correction and/or an additional uncertainty component are necessary.

— Linearity is intended to specify that range of analyte content for which a linear response function applies. Beyond this range, a correction and/or an additional uncertainty component are necessary.

— Reproducibility aims at establishing a “top-down” estimate of the uncertainty of an analytical method, including interlaboratory bias as an uncertainty component.

Validation may also include other issues such as sample size, time and costs. These items are not addressed in this Technical Specification.

Method validation has to be distinguished from instrument qualification because the latter refers to proper functioning rather than fitness for a specified purpose.

6.2 Verification of individual results

Verification of an individual result, as defined in this Technical Specification, consists of four steps. In this clause, a general procedure for verification of an assigned analyte content is specified. The verification of other results follows the same principles:

a) Establish the assigned analyte content x_1 and its standard uncertainty u_1.

b) Establish the result of the independent analysis x_2 and its standard uncertainty u_2.

c) Examine the agreement between these results in accordance with an appropriate statistical criterion, e.g. by comparing $x_1 - x_2$ against the expanded uncertainty U for this difference, given by:

$$U = k\sqrt{{u_1}^2 + {u_2}^2} \quad (5)$$

using a suitable coverage factor k. This test is most conclusive when u_1 and u_2 are of the same order of magnitude.

d) Confirm agreement or state disagreement.

In principle, the result of a verification step is a yes/no decision. However, it may be profitable to combine agreeing results because the mean of a set of independent measurements can lead to a lower uncertainty.

In the case of a positive test result, the assigned analyte content of the calibration gas, including its uncertainty, is confirmed by comparison with an independent analysis. If this analysis was made using an established reference method, this amounts to establishing a link to a reference value (see 5.4).

Using appropriate statistics, the procedure outlined above may be extended to a multi-level comparison.

Results of determination of gas composition may also be verified by comparing physical-property values calculated from an assigned composition (e.g. density) with the results of direct measurements. In this case, the sensitivity, i.e. the degree of correlation between variations in composition and variations in property values, has to be taken into account.

7 Documentation

For each analytical task, a uniquely identified report should be made and filed in a retrievable way. This report should contain fully documented data on the following items:

a) specifications of the analytical assignment;

b) identification of the sample;

c) the method of sampling used;

d) the analytical method used;

e) the analytical procedure, including data on the calibration gases;

f) an assessment of all possible contributions to the uncertainty;

g) the calibration model used;

h) the calculation of the final analytical result, including the uncertainty.

Detailed information on documentation can be found in a number of standards, e.g. ISO/IEC 17025 [25] and ISO 6141 [17].

Annex A
(informative)

Examples where traceable standards are available

A.1 Assuring the quality of gas analysis where traceable standards are available

This example seeks to use the information given in this Technical Specification to help the user have a clearer understanding of the steps involved in formulating a valid quality assurance method for gas analysis. This example shows how the whole quality assurance process is iterative until the method is shown to be “fit for purpose”.

In this example, the steps involved in producing a valid quality assurance procedure for the determination of carbon monoxide in nitrogen over the range from 1×10^{-3} mol/mol to 5×10^{-3} mol/mol are covered.

Requirements:

- the analysis is to be traceable to internationally accepted standards of gas composition;
- a target expanded relative measurement uncertainty of 5 % ($k = 2$);
- a report at an appropriate level is to be provided.

The initial step is to confirm that traceable standards are available for the analysis and the uncertainty of the standard is appropriate for the analysis. In this case, the measurement uncertainty requirement is 5 %. This allows procurement of a traceable reference gas mixture from an accredited commercial supplier. If for example the uncertainty requirement was more stringent, then a reference gas mixture with a lower uncertainty would be required, and as a consequence the procurement would have to be made from higher in the hierarchical chain (see Annex C).

The laboratory charged to perform this analysis has two instruments which are capable of performing the analysis. The first uses non-dispersive infrared (NDIR), and the second involves a gas-chromatographic method using a thermal-conductivity detector. A comparison of instrument performance is required to ensure the most appropriate instrument is used for the analysis.

The next step involves sampling considerations. The laboratory's past experience has shown that the materials used for construction of its sampling equipment is suitable for this analyte over the range 1×10^{-3} mol/mol to 5×10^{-3} mol/mol. The sampling systems of the analytical instruments have been tested for both vacuum and pressure integrity, and the cleanliness of the system has been maintained through regular heated purging and evacuation. Carbon monoxide is not considered as a reactive gas and, as a consequence, purge times will not have to be excessive. However, in the case of more reactive gases such as HCl, much longer purge and evacuation times will be required to ensure the sampling system has been sufficiently conditioned prior to analysis.

The laboratory has chosen to use the NDIR instrument rather than the GC method after considering the following performance aspects:

a) **Sensitivity and stability:** Both instruments were shown to have comparable sensitivities and stabilities.

b) **Instrument response function:** The linearity of both instruments was assessed and it was concluded that the GC response function was more linear than that of the NDIR.

c) **Repeatability:** Repeat analyses of the sample showed the standard deviation of the NDIR to be smaller than of the GC by a factor of 6. The standard deviation of the GC represented a standard uncertainty of 3 %, which alone is unacceptable considering the pre-set expanded-uncertainty requirement of 5 %.

d) **Selectivity:** The selectivity of the NDIR was confirmed through comparative analysis with the GC. This comparison was necessary as the NDIR is sensitive to other infrared active species which may be present in the sample.

Although the instrument linearity for the GC was better than that of the NDIR, the instrument repeatability was the overriding factor in the selection of the analytical instrument. The calibration protocol was established for the NDIR instrument and consisted of a multi-point calibration over the range of interest. The analysis function and the uncertainty of the analysis function was determined using ISO 6143 software [16]. The ISO 6143 software incorporates both the reference gas uncertainty as outlined in ISO 6142 [5], and the instrument performance uncertainty.

In this case, the standard uncertainty arising from the method validation amounts to 2 %. In principle, this method would be “fit for purpose” since the basic requirement is 5 % in terms of expanded uncertainty

A.2 Uncertainty evaluation for a dynamic blending system

A.2.1 General

The aim of such a system is to prepare gas mixtures using a dynamic gravimetric method (ISO 6145-7 [12]). In this particular example, the gas mass flow is important rather than the gas mass. The example describes the preparation of a four-component mixture consisting of:

$0{,}2 \times 10^{-2}$ mol/mol propane;

$3{,}5 \times 10^{-2}$ mol/mol carbon monoxide;

$14{,}0 \times 10^{-2}$ mol/mol carbon dioxide;

the balance being nitrogen.

The system used for the preparation consists mainly of:

- Thermal mass-flow controllers (MFCs), one for each gas channel, which are used as “intelligent” valves.
- Thermal mass-flow meters (MFMs), one for each gas channel, for the measurement of the resulting mass flow. The mass-flow meters are calibrated using a primary method.
- Gas analysers that are sensitive to at least three of the four components. In this case, NDIR systems for CO, CO_2 and propane are used. The gas analyser allows the homogeneity of the resulting gas mixture to be checked and shows the comparability with other static gravimetric mixtures, for example from a cylinder. The NDIR systems are only used as monitors.

The resulting gas mixtures are used for the analysis of other gas mixtures or for the immediate calibration of analysers. The mole fractions of the components can be varied easily and quickly within certain limits. The resulting mixtures are only transient, and it is not usually the purpose of such a system to fill gas cylinders.

A.2.2 Calculation of composition

The composition of the resulting gas mixture is determined by the use of the molar masses of the components and the mass flows calculated from the MFM readings using the calibration curve. The impurities of the components are taken into account by a correction factor representing the purity of the gas as a fraction (e.g. $f = 0{,}999\,95$):

$$x(l) = \frac{Q_{m_i} \times f_l / M_l}{\sum_{j=1}^{n} \left(Q_{m_j} \times f_j / M_j \right)} \qquad \text{(A.1)}$$

where

$x(l)$ is the amount-of-substance mole fraction of component l;

Q_m is the mass flow, expressed in grams per second;

M is the molar mass, expressed in grams per mole;

f is the impurity correction factor;

j is the index of all components (here $1 < j < 4$);

l is the index of the target component ($l \in j$);

n is the number of components (here $n = 4$).

The results for the example are given in Table A.1.

Table A.1 — Mixing parameters of the example

Component	**MFM value** ml/min	Q_m g/s	M g/mol	$x(l)$
CO_2	73,175	$2{,}422 \times 10^{-3}$	44,009 6	$13{,}523 \times 10^{-2}$
CO	17,732	$3{,}642 \times 10^{-4}$	28,010 3	$3{,}196 \times 10^{-2}$
C_3H_8	1,0984	$3{,}696 \times 10^{-5}$	44,096 8	$0{,}2060 \times 10^{-2}$
N_2	449,216	$9{,}469 \times 10^{-3}$	28,013 4	$83{,}075 \times 10^{-2}$
NOTE The MFM values are the averages of 411 readings of the MFM at 1 s intervals.				

If a purity analysis of the gases is carried out, the resulting mole fraction of the pure component is used as the correction factor. If no purity analysis is carried out, the impurity correction factor is set at 1 and the impurity value given by the manufacturer is used as an upper limit of its uncertainty. The uncertainty of the impurity factor has to be taken into account in the uncertainty budget.

In the example the latter case applies, i.e. no purity analysis and therefore no purity correction ($f = 1$).

A.2.3 Calculation of the uncertainties

For the determination of the standard uncertainties of the mole fractions calculated using Equation (A.1), the rules given in GUM [2] are used.

$$u^2[x(l)] = \sum_{j=1}^{4}\left(\frac{\partial x(l)}{\partial Q_{m\,j}}\right)^2 \times u^2(Q_{m\,j}) + \sum_{j=1}^{4}\left(\frac{\partial x(l)}{\partial f_j}\right)^2 \times u^2(f_j) + \sum_{j=1}^{4}\left(\frac{\partial x(l)}{\partial M_j}\right)^2 \times u^2(M_j) \quad \text{(A.2)}$$

Carrying out the partial differentiations in Equation (A.2) and simplifying gives Equation (A.3) which has the same indices as Equation (A.1):

$$\begin{aligned} u^2[x(l)]_{\text{rel}} = {} & [1-2x(l)]\left[u^2(Q_{m\,l})_{\text{rel}} + u^2(f_l)_{\text{rel}} + u^2(M_l)_{\text{rel}}\right] + \\ & + \sum_{i=1}^{4} x(i)^2 \times \left[u^2(Q_{m\,i})_{\text{rel}} + u^2(f_i)_{\text{rel}} + u^2(M_i)_{\text{rel}}\right] \end{aligned} \quad \text{(A.3)}$$

In order to use this equation, the uncertainties of the mass flows, purities and molar masses have to be determined. The uncertainty of a mass-flow measured with a calibrated MFM consists of two components — the uncertainty of the calibration of the MFM, $u(Q_m)_{\text{cal}}$, and the uncertainty of measurement with the MFM, $u(\text{MFM})$.

$$u_{\text{rel}}(Q_m) = \sqrt{u_{\text{rel}}{}^2(Q_m)_{\text{cal}} + u_{\text{rel}}{}^2(\text{MFM})} \quad \text{(A.4)}$$

The uncertainty of the calibration of the MFM is a result of the estimation of the calibration curve. The calibration curve was estimated by linear regression of pairs of values consisting of the average values of the MFM readings and reference mass flows measured simultaneously.

The uncertainty of measurement with the MFM consists of the standard uncertainty of the MFM mean value, $u(\text{MFM})_{\text{meas}}$, and an uncertainty caused by the limited resolution of the MFM, $u(\text{MFM})_{\text{resol}}$. The latter component of the uncertainty has to be taken into account because, before each measurement, the MFMs are re-zeroed. A deviation in this zeroing will cause a deviation in the measured value. The uncertainty caused by it is calculated using a Type B evaluation with a rectangular probability distribution as given by Equation (A.5):

$$u(\text{MFM})_{\text{resol}} = \frac{\Delta(\text{MFM})_{\text{min}}}{2 \times \sqrt{3}} \quad \text{(A.5)}$$

Equation (A.4) may be rewritten, using Equation (A.5), in the following way:

$$u_{\text{rel}}(Q_m) = \sqrt{u_{\text{rel}}{}^2(Q_m)_{\text{cal}} + u_{\text{rel}}{}^2(\text{MFM})_{\text{meas}} + u_{\text{rel}}{}^2(\text{MFM})_{\text{resol}}} \quad \text{(A.6)}$$

Another quantity influencing the uncertainty of the mass flows which has to be taken into account is the influence of impurities in the components on the MFM signal. It is assumed that the thermal properties of the impurities are similar to those of the pure components. Beside this, the calibrations of the MFMs are carried out with gases similar to those used for the preparation of the gas mixtures.

The uncertainties of the purity correction factors are known from a purity analysis, or the purity values given by the manufacturer are used as the uncertainties.

The actual values used for the calculation in this example are listed in Table A.2.

Table A.2 — Calculation values

Parameter	CO_2	CO	C_3H_8	N_2	**Remarks**
s(MFM), ml/min	0,025	0,011 5	0,695 × 10^{-3}	0,086	Measurement results
$u_{\text{rel}}(\text{MFM})_{\text{meas}}$, %	0,001 7	0,003 2	0,003 1	0,001	Type A evaluation
$\Delta(\text{MFM})_{\text{min}}$, ml/min	0,1	0,05	0,002	0,5	Resolution of MFM
$u_{\text{rel}}(\text{MFM})_{\text{resol}}$, %	0,039	0,081	0,053	0,032	Type B evaluation
$u_{\text{rel}}(q_m)_{\text{cal}}$, %	0,113	0,095	0,271	0,076	Type B evaluation
$u_{\text{rel}}(q_m)$, %	0,119	0,125	0,276	0,083	Combined uncertainty

NOTE s(MFM) is the standard deviation calculated from the readings displayed on the MFM. It is used to calculate the uncertainty of the MFM measurement, $u(\text{MFM})_{\text{meas}}$, as a standard deviation of the mean.

The relative standard uncertainties of the mole fractions are calculated using Equation (A.3) with the standard uncertainties of the mass flows, molar masses and purity factors and with the calculated mole fractions. Table A.3 shows the resulting values calculated for the example.

Table A.3 — Results

Parameter	CO_2	CO	C_3H_8	N_2
$x(l)$, × 10^{-2}	13,523	3,196	0,206 0	83,075
$u_{\text{rel}}(q_m)$, %	0,119	0,125	0,276	0,083
$u_{\text{rel}}(f)$, %	0,005	0,03	0,05	0,000 5
$u_{\text{rel}}(M)$, %	0,001 2	0,001 5	0,001 2	0,000 5
$u_{\text{rel}}[x(l)]$, %	0,124	0,143	0,288	0,022
$u[x(l)]$, × 10^{-2}	1,678 × 10^{-2}	4,574 × 10^{-3}	5,939 × 10^{-4}	1,808 × 10^{-2}

The results of the calculations represent the composition of the resulting gas mixture and the expanded uncertainties of the mole fractions with coverage factor $k = 2$:

$$x(CO_2) = (13{,}523 \pm 0{,}034) \times 10^{-2}\ \text{mol/mol}$$

$$x(CO) = (3{,}196 \pm 0{,}009) \times 10^{-2}\ \text{mol/mol}$$

$$x(C_3H_8) = (0{,}206\,0 \pm 0{,}001\,2) \times 10^{-2}\ \text{mol/mol}$$

$$x(N_2) = (83{,}075 \pm 0{,}036) \times 10^{-2}\ \text{mol/mol}$$

Annex B
(informative)

Example where traceable standards are not available

This annex discusses possible methods for assuring the quality of the concentrations of reference and calibration gas mixtures, where reference gas mixtures with known and validated gas compositions are **not** available. A particular example is when no reference gas mixtures are available with concentrations which are traceable to nationally held gas standards. In such cases, it is necessary to develop a special process for verifying the concentration of the prepared reference or calibration gas mixtures. It is also important to develop this verification process where there is a requirement that the measurement uncertainty of the analysed composition(s) of the gas mixture is to be stated correctly and its validity confirmed. The process is shown schematically in Figure B.1.

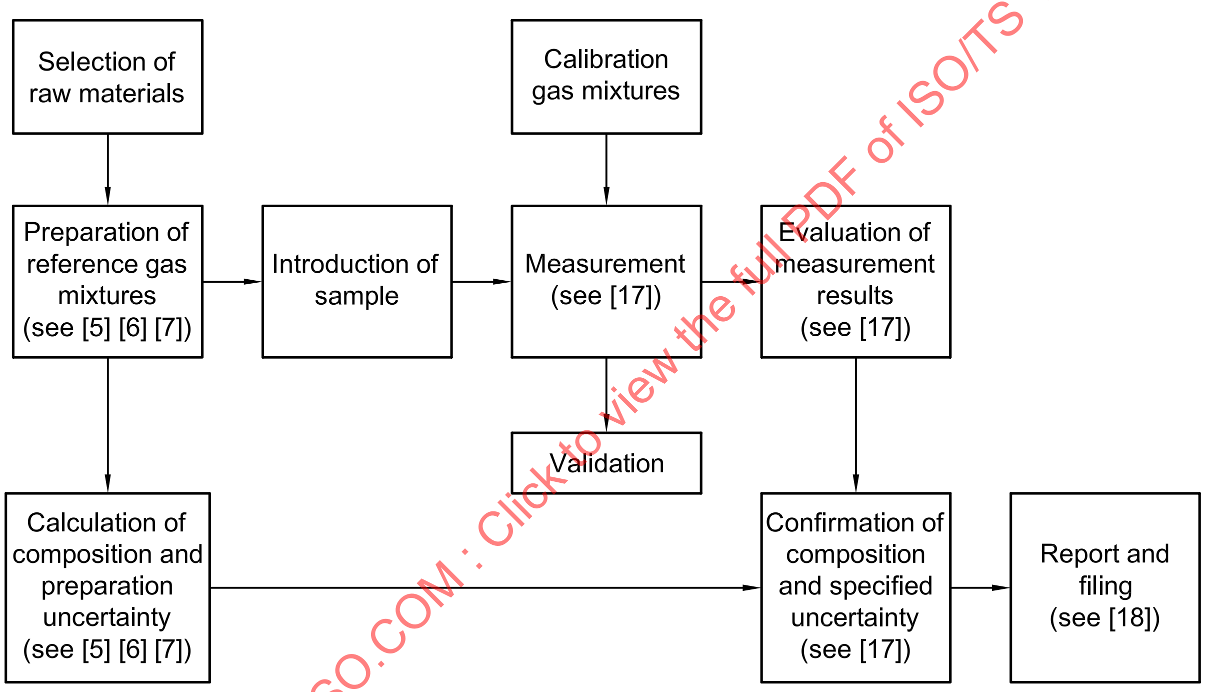

Figure B.1 — Preparation of reference gas mixtures and confirmation of composition

It should be noted that the quality assurance approach described below is not only applicable to the verification of a reference or calibration gas mixture when no externally produced gas mixtures with authenticated compositions are available. It is also the approach used to build up new suites of reference gas mixtures with verified uncertainties in their stated concentrations — either to provide suites of national standards or for other purposes.

The outcome of the confirmation step, where calculated and measured values are compared, taking into account a pre-set uncertainty level, is a simple yes/no decision. If the answer is no, this process should be repeated.

The raw materials can be pure gases, volatile liquids or gas mixtures. The selection of the quality depends on the required uncertainty of the composition of the desired gas mixture.

The preparation method depends on a number of producer/product/economy-related topics like availability of sufficiently pure gases, cylinders, preparation facilities, required uncertainties, etc., and is strongly producer-related.

For information on preparation, a number of International Standards are available (see the Bibliography). Based upon the preparation data and purity-analysis data, a composition, which includes the preparation uncertainty, is calculated and evaluated.

Annex C
(informative)

Hierarchy of reference gas mixtures

C.1 General

A well-defined hierarchy of measurement standards exists already in a wide range of physical fields, and these are continually being extended by research and development work, particularly where the hierarchy needs to be traceable to national or to International Standards. A similar situation exists with certain hierarchies of calibration gas mixtures. However, unlike other measurement fields, reference gas mixtures are required for a very diverse range of gaseous species as well as spanning a very wide range of concentrations. Therefore, although a considerable number of hierarchies of reference gas mixtures currently exist (particularly those which are traceable to verified national or other primary standards), they do not cover every gaseous species or all concentrations.

As with the hierarchy of measurement standards in physics, the hierarchy of calibration gas mixtures, as presented in this Technical Specification, is based on analytical comparison of lower-level standards with standards of the next-higher level. In contrast to metrology in physics, where this comparison is often performed in a one-to-one mode, validation of gas mixture composition usually requires analytical comparison with several higher-level reference gas mixtures.

The scheme in Figure C.1 presents not only the hierarchy of reference gas mixtures on the basis of uncertainty, but also the traceability chain for reference gas mixtures used in gas analysis.

C.2 Level 0: SI units for gas mixture composition

In metrological terminology, reference gas mixtures are measurement standards which have particular levels of gas mixture composition. In the case of binary mixtures, typically consisting of a “target” component of interest and a “balance” component, the supplied quantity is the contents of the target component, expressed e.g. as a mole fraction, a volume fraction or a mass concentration, in terms of combinations of units such as mol/mol, m^3/m^3 and kg/m^3.

C.3 Level 1: Primary reference gas mixtures

By definition, a primary reference gas mixture has a particular composition with the highest quality level, the quality concerning primarily the uncertainty and the stability. The specifications of primary quality can vary dramatically between different gas mixture types, as e.g. in the case of percentage levels of carbon monoxide in nitrogen as opposed to that of ambient levels of sulfur dioxide in air.

Primary reference gas mixtures are prepared gravimetrically. Appropriate weighing techniques combined with knowledge of parent gas composition have, in principle, the potential to give mixtures with relatively small uncertainties. The technique chosen depends on the concentration of the component of interest and the required stability of the mixture. Mixtures may be blended in a high-pressure cylinder, or they may be blended dynamically (e.g. in permeation tubes). The most accurate technique is the successive weighing, into a pressure cylinder, of samples of parent gases (either pure gases or previously prepared gas mixtures). Prior to preparation, analysis of these parent gases for relevant impurities is strongly recommended. The uncertainty of the resulting mixture composition is established using uncertainty propagation methods, by determining and combining the uncertainty contributions from all the various steps and influences involved [5].