INTERNATIONAL STANDARD

ISO 14167

First edition
2018-11

Gas analysis — General quality aspects and metrological traceability of calibration gas mixtures

Analyse des gaz — Aspects généraux sur la qualité et traçabilité des mélanges de gaz pour étalonnage

Reference number
ISO 14167:2018(E)

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Published in Switzerland

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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 documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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

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

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

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.

This first edition of ISO 14167 cancels and replaces ISO/TS 14167:2003, which has been technically revised. The main changes compared to the previous edition are as follows:

- the description of quality assurance aspects has been improved;
- the relationship between ISO/TC 158 standards has been described;
- the metrological traceability and metrological hierarchy of calibration gas mixtures has been elaborated upon.

Gas analysis — General quality aspects and metrological traceability of calibration gas mixtures

1 Scope

This document provides requirements and guidelines on the necessary quality assurance required to produce calibration gas mixtures that are demonstrably stable and comparable. It shows that this is achieved by demonstrating that the composition of the calibration gas mixture is metrologically traceable to the SI.

This document shows that calibration gas mixtures can be prepared according to methods that have measurements that are completely described in SI units. It describes procedures for verifying that the composition of such gas mixtures is correct within the stated measurement uncertainty. Guidance is given as to how to conduct the evaluation of uncertainty in these procedures.

This document also shows how a calibration gas mixture with unknown composition can be calibrated by reference to traceable standard gas mixtures.

This document covers the commonalities and differences of quality management schemes in use by producers of calibration gas mixtures, most notably those described in ISO/IEC 17025 and ISO 17034. These systems lead to gas mixtures with different characteristics, and this document explains these differences and their implications.

Calibration gas mixtures, as prepared and certified for composition in accordance with this document, are used for the calibration of equipment, the performance evaluation of methods, measurement procedures and equipment.

2 Normative references

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

ISO Guide 30, *Reference materials — Selected terms and definitions*

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

ISO/IEC Guide 98-3/Suppl 1, *Supplement 1 to the Guide to the expression of uncertainty in measurement — Propagation of distributions using a Monte Carlo method*

ISO/IEC Guide 98-3/Suppl 2, *Supplement 2 to the Guide to the expression of uncertainty in measurement — Extension to any number of output quantities*

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

ISO 6142 (all parts), *Gas analysis — Preparation of calibration gas mixtures*

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

ISO 6144, *Gas analysis — Preparation of calibration gas mixtures — Static volumetric method*

ISO 6145-1, *Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods — Part 1: Methods of calibration*

ISO 6145-2, *Gas analysis — Preparation of calibration gas mixtures using dynamic methods — Part 2: Piston pumps*

ISO 6145-4, *Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods — Part 4: Continuous syringe injection method*

ISO 6145-5, *Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods — Part 5: Capillary calibration devices*

ISO 6145-6, *Gas analysis — Preparation of calibration gas mixtures using dynamic methods — Part 6: Critical flow orifices*

ISO 6145-7, *Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods — Part 7: Thermal mass-flow controllers*

ISO 6145-8, *Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods — Part 8: Diffusion method*

ISO 6145-9, *Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods — Part 9: Saturation method*

ISO 6145-10, *Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods — Part 10: Permeation method*

ISO 6145-11, *Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods — Part 11: Electrochemical generation*

ISO 7504, *Gas analysis — Vocabulary*

ISO 12963, *Gas analysis — Comparison methods for the determination of the composition of gas mixtures based on one- and two-point calibration*

ISO 14912, *Gas analysis — Conversion of gas mixture composition data*

ISO 16664, *Gas analysis — Handling of calibration gases and gas mixtures — Guidelines*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 7504, ISO Guide 30 and ISO/IEC Guide 99 apply.

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

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

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

4 Symbols

i,k	indices for components in a gas or gas mixture
j	index for a parent gas
M	molar mass
m	mass
q_m	mass flow rate
n	amount of substance

q_n	amount-of-substance flow rate
p	pressure
q	number of components in the gas mixture
R	ideal gas constant
r	number of parent gases
T	temperature
V	volume
q_V	volume flow rate
v	mass fraction of a component in a parent gas
w	mass fraction of a component in a gas mixture
x	amount-of-substance fraction of a component in a parent gas
y	amount-of-substance fraction of a component in a gas mixture
Z	compressibility factor
φ	volume fraction of a component in a parent gas
ϕ	volume fraction of a component in a gas mixture

5 Preparation of gas mixtures

5.1 Static and dynamic methods

Gas mixtures can be prepared using either static or dynamic methods. Static methods mix portions of gas, dynamic methods mix flows of gas. These portions are commonly quantified as masses (gravimetric methods) or volumes (volumetric methods).

Static methods lead to the preparation of a calibration gas mixture in a cylinder, and are generally used for components that are stable in cylinders. Static methods can be gravimetric [covered in ISO 6142 (all parts)] or volumetric (covered in ISO 6144). These methods are employed to produce compressed calibration gas mixtures in cylinders. High-pressure gas mixtures are usually prepared gravimetrically. The volumetric method of ISO 6144 is commonly used in connection with a vessel (gas mixing chamber) and operated at lower pressures, but still well above ambient pressure. The filling pressure is determined by the request of the customer and limited by the physical properties of the gas mixture, more specifically the condensation behaviour. Static gravimetric preparation of calibration gas mixtures shall be done in accordance with ISO 6142 (all parts). For the static volumetric preparation of calibration gas mixtures, ISO 6144 shall be used.

Dynamic methods are described by the ISO 6145 series. These methods are based on the principle that mixing gases with constant flow rates leads to a gas mixture with a defined composition. The appropriate part(s) of ISO 6145 shall be used for the dynamic preparation of calibration gas mixtures.

Both types of methods have their strengths and weaknesses. The most suitable preparation method is determined based on the constituents and the composition of the desired gas mixture, and the practical circumstances of use, among other factors.

Some producers use a manometric method to prepare a calibration gas mixture of a specified composition. Such gas mixtures can be characterized to become calibration gas mixtures using a comparison method as described in Clause 6.

5.2 Purity of parent gases

The composition of parent gases plays a role in gas mixture preparation. It is not always necessary to perform a rigorous purity analysis, neither is it always acceptable to compute the composition of calibration gas mixtures while ignoring the effects of impurities. In ISO 19229, criteria are given regarding to what extent purity analysis is required. These shall be followed both in static and dynamic gas mixture preparation. The resulting purity data can be expressed in different forms, of which the amount-of-substance and volume fractions are the most commonly used. Dynamic gravimetric methods often require the use of purity data expressed in mass fractions. As necessary, purity data shall be converted using the appropriate conversion method as described in ISO 14912.

5.3 Use of gas mixtures as parent gases

Most of the written standards for gas mixture preparation, such as ISO 6142 (all parts), ISO 6144 and the ISO 6145 series, describe methods for working with pure gases. These methods are, however, also applied for preparing calibration gas mixtures using other gas mixtures as parent gases. Although this use is not always formally covered by the scope of the International Standards mentioned above, it is common practice in the entire gas analysis area. The rationale behind this use is that there are practical limitations with respect to the dilution factors that can be achieved with the desired accuracy for the various methods.

Complex multicomponent calibration gas mixtures, such as synthetic natural gas mixtures and stack gas mixtures, are practically always prepared using a multistage preparation process. The expressions used for computing composition, as summarized in 5.4 and 5.5, are also valid for calibration gas mixtures prepared from a combination of pure gases and gas mixtures.

5.4 Gravimetric methods

In gravimetric gas mixture preparation, the masses of the transferred parent gases (or liquids) are recorded. When using pure materials, the composition can directly be calculated from the masses of the parent gases j, which are in this case identical to the masses of the components i. The mass fraction of a component k is computed as:

$$w_k = \frac{m_k}{\sum_{i=1}^{q} m_i} \tag{1}$$

If the molar composition is desired, by using the molar masses of the components i, the amount-of-substance fraction of a component k is computed as:

$$y_k = \frac{m_k / M_k}{\sum_{i=1}^{q} m_i / M_i} \tag{2}$$

It is important to recognize that the amount-of-substance of a component k is computed as $n_k = m_k / M_k$.

Both Formula (1) and Formula (2) underline the primary character of gravimetric methods: the composition can be calculated from first principles, without the need to refer to measurement standards of the same kind, that is, the use of calibration gas mixtures or other standards characterized for composition.

In practice however, the formulae are insufficient for an accurate computation of the composition of the prepared gas mixture, because the materials used for producing the mixture are not pure. To deal with the impurities, all parent gases (and liquids) shall be considered as mixtures themselves. The methods for purity analysis (see ISO 19229) as well as those for characterizing the composition of the gas mixtures used can involve the use of measurement standards of the same kind, thus compromising the primary character of the preparation method. The appreciation of the composition of the parent gases (or liquids) leads to expressions that are much more complex than Formulae (1) and (2).

The mass fraction of a component *k* is now computed by calculating the mass of component *k* across all parent gases and dividing this mass by the total mass of the mixture:

$$w_k = \frac{\sum_{j=1}^{r} m_j v_{k,j}}{\sum_{j=1}^{r} m_j} \tag{3}$$

where $v_{k,j}$ denotes the mass fraction of component *k* in parent gas *j*.

Similarly, the composition expressed in amount-of-substance fractions can be computed while appreciating the composition of the parent gases. The expression for the amount-of-substance fraction of a component *k* in the gas mixture is computed as:

$$y_k = \frac{\sum_{j=1}^{r} \left(\frac{x_{k,j} m_j}{\sum_{i=1}^{q} x_{i,j} M_i} \right)}{\sum_{j=1}^{r} \left(\frac{m_j}{\sum_{i=1}^{q} x_{i,j} M_i} \right)} \tag{4}$$

This expression is well known from ISO 6142-1. A derivation of this expression is given in this document. The numerator of Formula (4) equals the amount-of-substance of component *k*, whereas the denominator equals the total amount-of-substance of the mixture.

Formulae (3) and (4) are widely used in gas metrology. They not only apply to gas mixtures prepared from pure gases, but can also be used for gas mixtures prepared from other gas mixtures.

Dynamic gravimetric methods shall be employed using the same models as the static methods, where the masses are replaced by the corresponding mass flow rates. The molar composition of a dynamically prepared gas mixture shall be computed from:

$$y_k = \frac{\sum_{j=1}^{r} \left(\frac{x_{k,j} \left(q_m\right)_j}{\sum_{i=1}^{q} x_{i,j} M_i} \right)}{\sum_{j=1}^{r} \left(\frac{\left(q_m\right)_j}{\sum_{i=1}^{q} x_{i,j} M_i} \right)} \tag{5}$$

Formula (5) differs from Formula (4) only in that it takes the mass flow rates rather than the masses to compute the composition. A prerequisite for the validity of using Formula (5) is that the mass flow rates are constant within a narrow range, the width of which determines the measurement uncertainty.

NOTE Formula (3) can be reworked in a similar manner to apply to dynamic methods.

5.5 Volumetric methods

In volumetric gas mixture preparation, the volumes of the transferred parent gases (or liquids) are recorded. When using pure materials, the composition can be directly calculated from the volumes of the parent gases *j*, which are in this case identical to the volumes of the components *i*. The volume fraction of a component *k* is calculated as:

$$\phi_k = \frac{V_k}{\sum_{i=1}^{q} V_i} \tag{6}$$

provided that the temperature and pressure of all parent gases are the same.

Similar to the case of gravimetric methods, the amount-of-substance can be computed from the gas volumes. The amount-of-substance of component *k* shall be computed as:

$$n_k = \frac{p_k V_k}{R T_k} \tag{7}$$

assuming that the gas is an ideal gas. The amount-of-substance fraction of component *k* is computed as:

$$y_k = \frac{n_k}{\sum_{i=1}^{q} n_i} \tag{8}$$

where the amount-of-substance is computed using Formula (7).

Formulae (6) and (8) underline the primary character of volumetric methods: the composition can be calculated from first principles, without the need to refer to measurement standards of the same kind, that is, the use of calibration gas mixtures or other standards characterized for composition.

In practice, however, Formulae (6) and (8) are insufficient for an accurate computation of the composition of the prepared gas mixture, because the materials used for producing the mixture are not pure. To deal with the impurities, all parent gases (and liquid) shall be considered as mixtures themselves. The methods for purity analysis (see ISO 19229), as well as those for characterizing the composition of the gas mixtures used, can involve the use of measurement standards of the same kind, thus compromising the primary character of the preparation method.

A further issue that specifically applies to the volumetric methods is that for an accurate composition the parent gases need to be considered as *real gases*, which means that the conversion of volume to amount-of-substance shall take into account the compressibility factor of the parent gas. Formula (7) thus becomes:

$$n_k = \frac{p_k V_k}{R T_k Z_k} \tag{9}$$

The compressibility factor, *Z*, is a function of the temperature, pressure and composition. Valid methods for computing the compressibility factor are given in, among others, ISO 14912. Equations-of-state can also be used for this purpose.

Effects of the presence of impurities in the parent gases, and the necessity to compute the composition of the gas mixture at a given temperature and pressure, lead to the expression for a volume fraction as shown in Formula (10):

$$\phi_k = \frac{\sum_{j=1}^{r} V_j p_j T_j^{-1} Z_{ref,j} Z_j^{-1} \varphi_{k,j}}{\sum_{j=1}^{r} V_j p_j T_j^{-1} Z_{ref,j} Z_j^{-1}} \tag{10}$$

where Z_{ref} denotes the compressibility factor under reference conditions.

Likewise, the amount-of-substance fraction of a component k in the prepared gas mixture can be computed from:

$$y_k = \frac{\sum_{j=1}^{r} n_j x_{k,j}}{\sum_{j=1}^{r} n_j} \tag{11}$$

where the amount-of-substance n_j is computed using Formula (9).

Dynamic volumetric methods can be employed using the same models as the static methods. In the case of dynamic methods, the volume flow rates are measured rather than the static volumes. The molar composition of a dynamically prepared gas mixture is computed using Formula (11), where the amount-of-substance flow rate is computed from the volume flow rate as shown in Formula (12):

$$(q_n)_k = \frac{p_k (q_V)_k}{R T_k Z_k} \tag{12}$$

5.6 Hybrid methods

Some methods for the preparation of calibration gas mixtures combine principles from gravimetric and volumetric gas mixture preparation. An example of such a method is the use of the permeation method (ISO 6145-10) for dynamically preparing calibration gas mixtures.

6 Composition of calibration gas mixtures by comparison

6.1 General

The methods in Clause 5 describe how the composition of a calibration gas mixture is computed from preparation data, including the data from a purity assessment. Another widely applied approach to determine the composition of a gas mixture is the use of a comparison method. In this approach, the contents of one or more components in a gas mixture are computed from the observed instrument responses and converted into contents (e.g. amount-of-substance, mass, or volume fractions) through the calibration data.

The calibration gas mixtures used for this purpose shall have been verified in accordance with ISO 6143 or ISO 12963 (see Clause 7) prior to use. When using a calibration gas mixture that has been produced in accordance with the requirements of ISO/IEC 17025[4], ISO 17034[5] or a combination thereof, and coming with a certificate in accordance with ISO 6141, it shall be presumed that the calibration gas mixture meets this requirement.

Calibration gas mixtures thus characterized for composition can be certified following the requirements of ISO/IEC 17025[4] or ISO 17034[5]. It is sometimes perceived that calibration gas mixtures certified on preparation data would be superior to those certified by means of a comparison method. Such a statement should not be generally made, as there can be effects in the gas mixture preparation methods that make these methods less reliable than well-performed analytical measurements. A decision as to whether the gas mixture preparation data or the analytical data should be used for certification should be rendered on a case-by-case basis, rather than perceived superiority.

6.2 Multipoint calibration

Multipoint calibration is the most comprehensive way of calibrating analytical equipment. Such a calibration shall be carried out in accordance with ISO 6143. For the most commonly used calibration and analysis functions, up to seven calibration gas mixtures are required, which can be prepared gravimetrically or volumetrically, dynamically or statically, as appropriate. The method of ISO 6143 is not only suitable for cases where the composition is expressed in amount-of-substance fractions, but can also be used for other quantities, such as mass or volume fractions.

The use of dynamic methods for gas mixture preparation in connection with ISO 6143 is particularly attractive because of the greater flexibility in choosing the points along the calibration curve. Multipoint calibration can be performed with statically prepared calibration gas mixtures as well, but choosing other compositions usually requires more work.

The use of the multipoint calibration is not restricted to the assignment of a value to the content of a component in a gas mixture to be characterized, this form of calibration is also an indispensable tool for validating simpler calibration approaches (see 6.3) which involve assessing the linearity of the analyser. In the natural gas area, the multipoint calibration is described alongside the single point calibration in ISO 6974-1[7] and ISO 6974-2[8]. The performance evaluation of natural gas analysers shall, according to ISO 6974-1, be carried out in accordance with ISO 10723[9], which in turn relies on the multipoint calibration method described in ISO 6974-1.

6.3 Simple calibration approaches

It is not always necessary to perform a multipoint calibration. There can be situations where a simpler approach is more practicable, in particular when taking field measurements (i.e. measurements outside a laboratory). Several approaches exist using a single or two calibration gas mixtures. Some commonly used single point calibration methods include (see ISO 12963):

a) single point exact-match calibration (SPEM);

b) single-point through origin calibration (SPO).

Some two-point calibration methods include:

c) two-point calibration using a single point and a blank (TPB);

d) two-point calibration: bracketing using two calibration gas mixtures (TPC).

The difference between the SPEM and the SPO is that in the SPEM, a calibration gas mixture is prepared that matches the gas mixture to be analysed, whereas in the SPO the composition of the calibration gas mixture can be quite distant from the gas mixture to be analysed. Because of the closeness of the calibration gas mixture and the mixture to be analysed, SPEM is insensitive to nonlinearity or zero deviation of the analyser, so a performance evaluation involving a multipoint calibration is not necessary.

SPO assumes that the analysis function is a straight line through the origin and thus is sensitive to both zero deviation and nonlinearity. TPB assesses, in comparison with SPO, the zero point deviation through the use of a zero gas, and is therefore only sensitive to nonlinearity of the analyser. TPC, also known as bracketing, uses two calibration gas mixtures and is sensitive to nonlinearity only.

The use of SPO, TPB, and TPC shall be preceded by a performance evaluation in accordance with ISO 12963 involving a multipoint calibration. The (average) bias over the analytical range to be used shall either be corrected for or added to the uncertainty budget. The variance of the bias, as well as its pooled standard uncertainty, shall be appreciated. The Monte Carlo method of ISO 10723[9] meets these requirements, but the calculations can also be performed in analytical form, requiring the coefficients and the associated variances and covariances from the multipoint calibration only (see ISO 12963).

7 Verification of composition of gas mixtures

7.1 Objectives

If the preparation data are used for calculating the composition of newly prepared calibration gas mixtures, then it should be verified experimentally that the composition of the calibration gas sampled is consistent with the composition calculated from the preparation data. The requirements for the rigour and frequency used for verification differs between standards: ISO 6142-1 requires verification of each gas mixture individually, whereas the ISO 6145 series allow the verification of one or more newly prepared calibration gas mixtures from a batch, or from a series as prepared using a dynamic method. This verification acts to detect errors in, for example, the preparation process of the calibration gas mixture(s) or the presence of any chemical reaction between the components, or (especially for static preparation methods) between any component and the cylinder.

The composition of a newly prepared calibration gas mixture shall only be considered as metrologically traceable to the SI when it has been verified, either individually or as part of a larger batch or series.

Verification of the composition of a calibration gas mixture can be achieved by:

- demonstrating consistency between the prepared mixture and appropriately verified calibration gas mixtures;
- comparison with a calibration gas mixture prepared by a validated implementation of another preparation method.

In the case of verification of calibration gas mixtures where no appropriately verified calibration gas mixtures are available and no alternative preparation method is applicable, verification can also be achieved by demonstrating consistency between several nominally similar prepared mixtures prepared using the same method.

NOTE “Appropriately verified calibration gas mixture” denotes a calibration gas mixture that has been subject to a previous verification. Depending on the regime and frequency required by the preparation method, such verification may have been a batch verification.

The frequency with which a verification measurement is required depends on several factors. For achieving the smallest uncertainties, such as those necessary for maintaining the measurement standards of national metrology institutes[1] (NMIs) or designated institutes[2], every time a gas mixture (or, with a dynamic method, a series of gas mixtures) is prepared, the composition shall be verified. If such small uncertainties are not required, then a lower frequency can be applied.

7.2 Statistical tests for consistency and uncertainty due to verification

The results of the verification shall be subject to appropriate valid statistical procedures, such as those included in ISO 6143 or ISO 12963.

The calculation of the uncertainty of the analytical measurement used for the verification shall take account of:

- the number of the standards used and their uncertainty;
- the repeatability of the verification process;

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[1] National metrology institutes are institutes designated by their nation states to develop, improve and maintain primary national measurement standards for one or more quantities.

[2] Designated institutes are not national metrology institutes, but are designated for a specific area to develop, improve and maintain primary national measurement standards for one or more quantities for their nation.

— where applicable, the number of times the verification process was repeated.

The calculation of the uncertainty due to the analysis process used for verification should, as appropriate, also take account of:

— the performance of the same method when used for the analysis and verification of similar mixtures made previously;

— participation in proficiency tests or comparisons;

— the implementation of a quality system that monitors the performance of the preparation and analysis methods, and triggers corrective action when they deviate beyond accepted limits.

The calibration mixture passes the verification if it passes the criterion in Formula (13), where the preparation uncertainty $u(y_{k,\text{prep}})$ is calculated using a suitable method (see also Clause 9).

$$\left|y_{k,\text{prep}} - y_{k,\text{ver}}\right| \le 2\sqrt{u^2(y_{k,\text{prep}}) + u^2(y_{k,\text{ver}})} \quad (13)$$

where

$y_{k,\text{prep}}$ is the amount-of-substance fraction as calculated from preparation (see also Clause 5);

$y_{k,\text{ver}}$ is the amount-of-substance fraction obtained from determining this fraction analytically (see also Clause 6).

Formula (13) also applies to other quantities expressing content, such as mass or volume fractions, or amount-of-substance concentrations. It is important to compare quantities of the same kind (so, for example, mass fractions with mass fractions).

7.3 Maintaining measurement standards

NMIs and the gas industry maintain measurement standards for use in, for example, the verification of calibration gas mixtures (see 7.2) and the characterization of the composition of calibration gas mixtures for one or more components (see Clause 6). Given that measurement standards in the form of static calibration gas mixtures are consumed during their use, procedures shall be in place and implemented to ensure:

a) timely replacement of calibration gas mixtures approaching their minimum utilization pressure;

b) timely replacement or recertification of calibration gas mixtures approaching their expiry date;

c) availability of calibration gas mixtures at all times for the calibration points relevant to the calibration approach used (see 6.2 and 6.3);

d) availability of means to independently assess the stability of the measurement standards used (see 7.4).

When other methods are used, such as methods for dynamic gas mixture preparation, procedures shall be in place and implemented to monitor the stability of these calibration gas mixtures produced with these methods. Such methods can also be used as an independent means to confirm the stability of static calibration gas mixtures and vice versa.

Multipoint calibration involving statically prepared calibration gas mixtures (6.2) of an analyser enables, every time that the procedure is used, the verification of the relative position of the calibration points with respect to one another. This verification process can be an element in confirming the continued stability of the calibration gas mixtures, provided that freshly prepared calibration gas mixtures are used in combination with older ones. For some types of gas mixtures, their compositions are subject to gradual change over time. Such effects shall be evaluated and appropriate corrections to the composition shall be developed. These corrections and their associated measurement uncertainty shall be applied when using such measurement standards.

7.4 Assessing gas mixture stability

When preparing calibration gas mixtures, stability issues should be considered. The stability of gas mixtures with respect to the composition depends on the reactivity of the components and interactions with, for example, the cylinder surface, transfer lines and valves. Assessing gas mixture stability is only necessary when an organization prepares calibration gas mixtures, either for internal use, or, after certification, for sale to a customer.

An organization purchasing a calibration gas mixture may expect that the compositional data remain valid within the stated expanded uncertainty for the period of time stated on the certificate (see also ISO 6141). The only condition for the user's side is that they shall follow the guidance given in ISO 16664 with respect to the appropriate storage and use of calibration gas mixtures. It is generally recommended that, where possible, the composition of a newly purchased calibration gas mixture is compared against one that has been in use for some time, to confirm the compatibility of the calibration gas mixtures.

In static gas mixture preparation in particular, issues with respect to the stability of the composition can arise. These issues can have various causes. In dynamic gas mixture preparation, stability issues usually play a lesser role, because these gas mixtures are typically used shortly after their preparation, so that many of the slower mechanisms that cause a gradual change of the composition do not occur to a meaningful extent.

A stability study is necessary to provide data for the uncertainty contribution due to (in)stability. The stability rate constants for mixtures should be determined empirically by experiment when the mixture cannot be shown to be unconditionally stable over the relevant time span. Gas mixtures should be compared immediately after preparation and then again at regular intervals until either the mixture has shown an unacceptable change in composition or an acceptable stability period has been demonstrated. The processing of data from a stability study should be performed in accordance with ISO Guide 35 and ISO 6142-1.

7.5 Initial losses, chemical reactions and other effects

Most International Standards (e.g. ISO 6142-1, ISO 6144, ISO 6145) for calibration gas mixture preparation limit the range of applications in their scope to those in which initial losses, chemical reactions and other permanent effects do not occur.

Unsafe situations shall be prevented at all times (see for guidance, e.g. IGC 39[1] and IGC 139[2]). Such situations can arise, for example, when preparing a synthetic natural gas mixture with a low level of oxygen. A route, involving multiple stages of calibration gas mixture preparation, is needed to introduce the required quantity of oxygen gas without crossing an explosion limit[2].

Initial losses of one or more components cannot always be prevented. Such losses can occur because of, for example, adsorption or chemical reactions. An appropriate correction for the contents of the components concerned shall be developed. Typically, such development requires the application of comparison techniques and often also different preparation techniques. As such a correction is determined with limited accuracy, its measurement uncertainty shall be evaluated. When applying the correction, its uncertainty shall be taken into account in calculating the measurement uncertainty of the composition of the calibration gas mixture.

Chemical reactions are usually unwanted as well. The descriptions of the methods for gas mixture preparation (e.g. ISO 6142-1, ISO 6144, the ISO 6145 series) require consideration of the possibility of chemical reactions between the components of a gas mixture. There are, however, types of static gas mixtures prepared by means of a reaction. A well-known example is the preparation of mixtures of nitrogen dioxide from a mixture of nitrogen monoxide in nitrogen and nitrogen by adding some oxygen to convert the nitrogen monoxide into nitrogen dioxide. This approach has proved to be superior over a preparation starting with pure nitrogen dioxide.

8 Metrological traceability and quality assurance

8.1 Preparation methods

A measurement result is metrologically traceable if it can be linked through an unbroken chain of calibrations, each with a stated uncertainty, to the international system of units (SI). The preparation methods introduced in Clause 5 allow calculating the composition of the mixture prepared from quantities which are not necessarily traceable to the same units used to express the composition of the mixture. Most of them could be operated without using measurement standards of quantities of the same kind.

EXAMPLE In gravimetric gas mixture preparation, the composition, expressed in amount-of-substance fractions, is usually computed from the masses of pure gases used and the molar masses of the components. In theory, none of these input data require the use of measurement standards with quantities of the same kind as the ones used for expressing the composition of the calibration gas mixture being produced. In reality, however, starting materials for gas mixture preparation are not pure and a purity analysis is performed on the nominally pure gases, followed by calculating the fraction of the main component. This approach usually involves the use of calibration gas mixtures with quantities of the same kind as the gas mixture produced (e.g. the amount-of-substance fraction of a component). Strictly, therefore, these preparation methods are, as usually implemented, no longer *primary*.

Even if spectroscopy is used, absorption cross sections that have been determined involving measurement standards of quantities of the same kind (chemical composition) are needed.

The definition of a primary method states that it operates without reference to a standard of the quantity being measured. In order to provide results that are traceable to the SI, it is also essential that all terms in the measurement equation be fully described in terms of SI units. Such a method then also conforms to the CCQM definition of a primary method of measurement.

Another important element of establishing metrological traceability is a comprehensive evaluation of all factors influencing the measurement uncertainty of the result. By implication, this requires that the method is sufficiently well understood and described that such an uncertainty evaluation can be performed with confidence.

As a quality assurance measure, the documentary standards for calibration gas mixture preparation [e.g. ISO 6142-1, ISO 6144, ISO 6145 (all parts)] shall be followed. These standards require the demonstration of metrological traceability by subjecting a newly prepared calibration gas mixture to a verification measurement (see also Clause 7). Once the comparability of the newly prepared gas mixture is demonstrated, the composition as calculated is considered metrologically traceable. The verification measurement usually contributes to the overall uncertainty assigned to the composition of the prepared calibration gas mixture.

The verification step involves reference to a standard of the quantity, in this case a gas mixture of similar composition[3]. This is the fundamental reason why the preparation of gas mixtures outside an NMI is not considered a primary method or a primary realization of the amount-of-substance fraction in gas mixtures, as only NMIs can use their own realizations of such measurement standards for this purpose. Other organizations are required to obtain their metrological traceability through an NMI of their choice.

NMIs are required to demonstrate the equivalence of the measurement standards they maintain in key comparisons. These comparisons establish and document the ability of each NMI to realize measurement standards of chemical composition in the form of gas mixtures at a primary level – the highest metrological level – and represent a mutual "verification" process between NMIs. This process, governed by the CIPM MRA[11] and documented in the Key Comparison Database (KCDB)[12], fully accounts for the uncertainties associated with the realization of these primary measurement standards and is the only process considered to verify the ability to produce such standards.

8.2 Comparison methods

For comparison methods (see Clause 6), the situation is slightly different. In this situation, metrological traceability is achieved by using calibration gas mixtures that come with a certificate (see also ISO 6141) documenting the metrological traceability of (parts of) the composition, and by performing a comprehensive evaluation of the measurement uncertainty. Provided that all known effects, such as interferences, losses of the component(s) of interest, etc., are accounted for, such comparison methods are capable of providing results with metrological traceability.

8.3 Conversion of composition data

Any measurement result is expressed in a specific unit. In gas metrology, commonly used units for expressing the chemical composition of a gas mixture include (sub)multiples of mol/mol (amount-of-substance fraction), kg/kg (mass fraction), kg/m^3 (mass concentration). Results expressed on one measurement scale can be converted to another measurement scale. Conversions of the corresponding quantities are described in ISO 14912. It is important to note that when such a conversion is done, the highest reference point of the metrological traceability chain changes. This highest reference point is the SI unit in which the content is expressed. These conversions shall be carried out with care, and their measurement uncertainty should be evaluated duly; see ISO 14912 for further guidance.

NOTE These conversions are similar to expressing temperature in degrees Celsius instead of kelvin; also in this case a conversion is necessary and the measurement scales are different. The conversion between the temperature scales is, however, exact; it does not change the measurement uncertainty of the result. The conversion of quantities expressing content is usually not without additional uncertainty, as the conversion factor has an associated uncertainty (see ISO 14912).

8.4 Transfer of metrological traceability

Metrological traceability is often transferred in gas analysis through well-characterized calibration gas mixtures in cylinders. Figure 1 illustrates some of these mechanisms. The national primary standard does not always consist of a set of primary standard gas mixtures (PSMs). In some cases, a well-characterized dynamic preparation facility is used instead. The equivalence of the national primary gas standards is achieved through key comparisons (see also 8.1). Two commonly used approaches are shown in Figure 2.

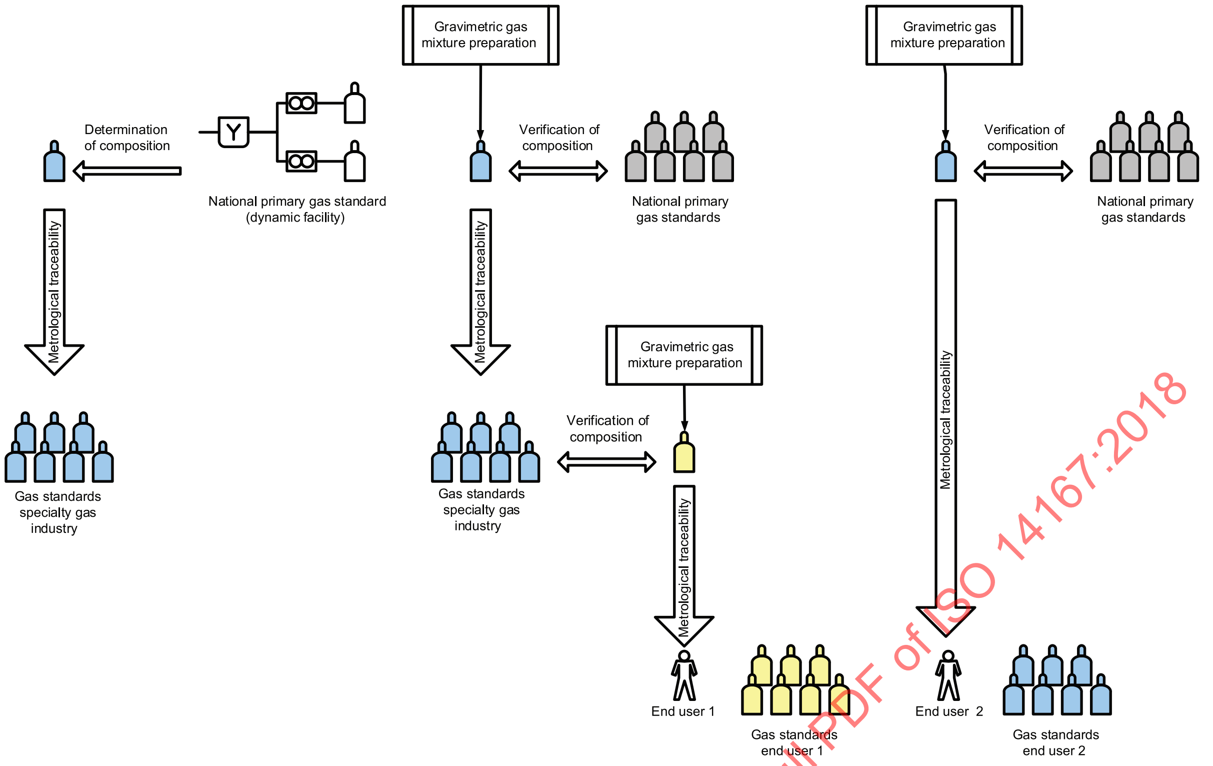
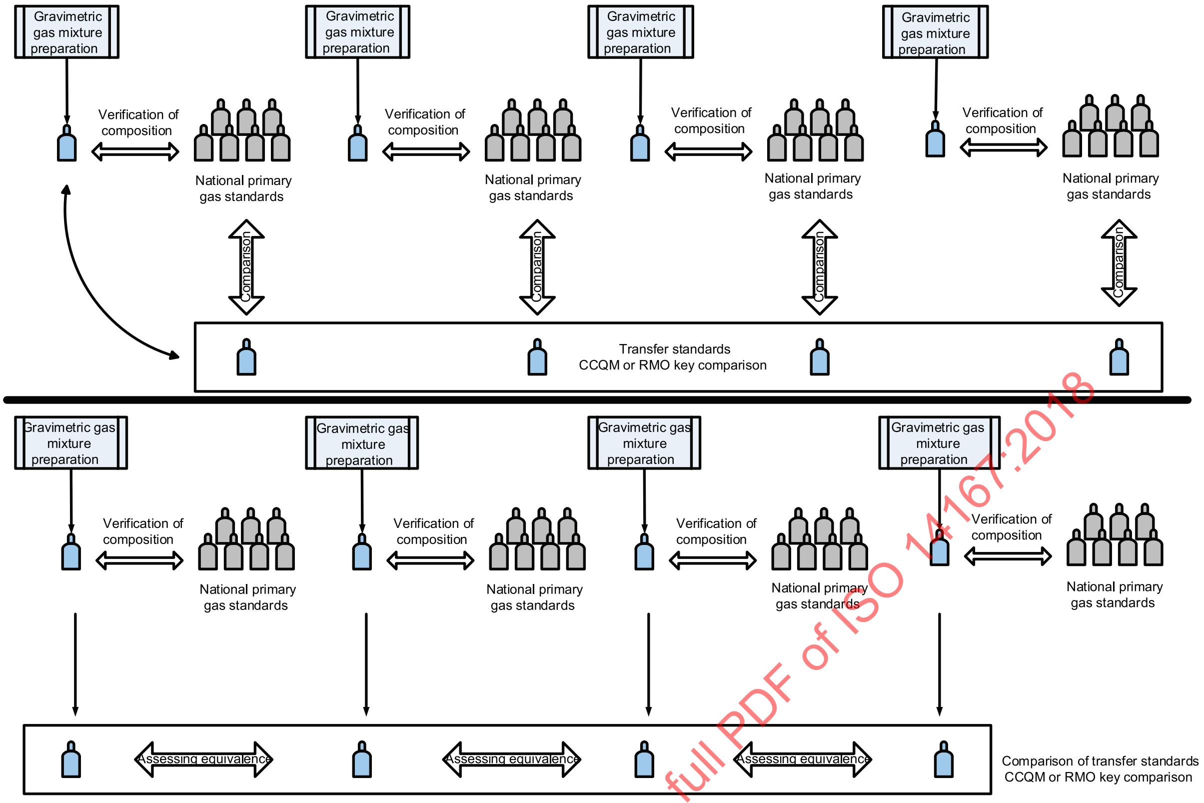


Figure 1 — Mechanisms for disseminating metrological traceability using calibration gas mixtures in cylinders



NOTE NMIs either calibrate a transfer standard using their own standards (top) or submit a transfer standard they prepared for a direct comparison in one NMI (bottom).

Figure 2 — Assessment of the equivalence of national primary gas standards by means of key comparisons

More generally, the transfer of metrological traceability in gas metrology can be achieved by one of the following means.

a) The use of a calibration gas mixture in a cylinder prepared using a static preparation method, with the values assigned on the basis of:

   1) the preparation method, including a verification measurement;

   2) a comparison method.

b) The use of a preconfigured and validated apparatus for dynamic gas mixture preparation.

c) The calibration of measurement equipment suitable for taking gas composition measurements.

d) The provision of reference values for the purpose of proficiency testing.

The calibration gas mixtures considered under list item a) are certified reference materials (CRMs) in the context of ISO 17034[5] and ISO Guide 35[6], provided that the certificate contains an expiry date. If such a date is missing, the user can still use such gas mixtures for calibration, but shall verify from time to time that the composition of the gas mixture is still valid within the stated uncertainty by independent means (e.g. the use of another CRM).

Calibration gas mixtures under a) are traded under various (trade) names and often a distinction is made between mixtures certified on the basis of preparation and analytical data and the uncertainty information accompanying these data. The name given to mixtures should recognize their position in the traceability hierarchy. Certain names will, therefore, be unique to NMIs – for instance "National Primary Standard". Apart from possible differences in the uncertainty and the expiry date on the certificate, from the viewpoint of transferring metrological traceability, calibration gas mixtures from

NMIs or other organizations can be used, provided that these meet the requirements stipulated in this document.

The highest metrological grade of measurement standards in gas metrology are maintained by NMIs (see also Annex A). ”Highest metrological grade” is to be understood in the context described above – the primary realization of chemical composition in gas mixtures. The smallest uncertainties are often available from NMIs, as they have the shortest metrological traceability chain. Other organizations are required to obtain their metrological traceability from NMIs[4], so that the uncertainties they attain when producing and certifying calibration gas mixtures are (slightly) higher than those of the NMIs for the same type of gas mixtures. The verification measurement usually contributes to the overall uncertainty attributed to the composition of the prepared calibration gas mixture and this is usually larger than the uncertainty of the mixture used in the verification. For many types of calibration gas mixtures, the primary measurement standards maintained by NMIs are mixtures prepared with static gravimetry. In other cases, such measurement standards are realized using dynamic methods, for example because of the reactivity of one or more constituents, adsorption effects, and so on.

8.5 Quality assurance and quality control

Metrological traceability cannot be established without appropriate quality control. Such quality controls include the verification of newly prepared gas mixtures (see 7.1 to 7.3) and the regular checking of the measurement methods used for the characterization of calibration gas mixtures (see Clause 6) or the verification of the composition of gas mixtures.

An organization should participate in interlaboratory comparisons aimed at evaluating the proficiency in measurement (“proficiency tests”[13]), or, in the case of NMIs, demonstrating the equivalence of national measurement standards (“key comparisons”). Neither the participation in proficiency tests nor in key comparisons establishes metrological traceability of measurement results.

The principal idea behind this kind of interlaboratory comparison is that the participating organization uses its own means to provide a measurement result that is metrologically traceable, which is then assessed against an assigned value (proficiency test) or key comparison reference value (key comparison). When the assessment demonstrates equivalence (e.g. a satisfactory score in a proficiency test), no further follow-up actions are required. Otherwise, the measurement or calibration service should be improved so that it provides equivalent results.

9 Evaluating measurement uncertainty

9.1 General

The evaluation of measurement uncertainty shall be carried out using methods that are consistent with ISO/IEC Guide 98-3 (GUM) and its two supplements. The evaluation procedures described in the written standards used in the gas analysis area are usually based on the law of propagation of uncertainty from the GUM. Although the law of propagation of uncertainty applies strictly only to linear measurement models, it has been demonstrated that it can be applied satisfactorily to the models described in Clause 5 for computing gas mixture compositions, as long as only values for the contents and associated standard uncertainties are needed[16].

The rigour with which the uncertainty evaluation should be carried out depends, among other things, on the uncertainty to be achieved. Uncertainty budgets should cover all relevant components of uncertainty, i.e. all components that can contribute non-negligibly to the uncertainty about the quantity of interest (e.g. an amount-of-substance, mass or volume fraction). When designing and developing procedures for evaluating measurement uncertainty, it is important to consider the scope of such methods. Components of uncertainty highly relevant for one group of gas mixtures can be quite irrelevant for another group, and vice versa.

Assumptions that are made in calculations, such as the use of equations for ideal gases (see 5.5) or relying on the linearity of an analyser (see 6.3), should be validated and the effects of such simplifications should be included in the evaluation of measurement uncertainty. Corrections that are