

Gas analysis — Preparation of calibration gas mixtures — Gravimetric method

Analyse des gaz — Préparation des mélanges de gaz pour étalonnage — Méthode gravimétrique

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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

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 6142 was prepared by Technical Committee ISO/TC 158, *Analysis of gases*.

This third edition cancels and replaces the second edition (ISO 6142:2001) and its amendment (ISO 6142:2001/Amd.1:2009), which have been revised to update the methods of preparation, estimation of the uncertainty and validation of the composition of gravimetrically prepared calibration gases.

Gas analysis — Preparation of calibration gas mixtures — Gravimetric method

1 Scope

This International Standard specifies a gravimetric method for the preparation of calibration gas mixtures in cylinders with traceable values for the amount-of-substance fraction (further: amount fraction) of one or more components. This International Standard describes a method for calculating the uncertainty associated with the amount fraction of each component. This uncertainty calculation requires the evaluation of the contributions to the uncertainty due to factors including the weighing process, the purity of the components, the stability of the mixture and the verification of the final mixture.

This International Standard is only applicable to mixtures of gaseous or totally vaporized components, which may be introduced into the cylinder in the gaseous or liquid state. The preparation of multi-component gas mixtures (including natural-gas type mixtures) is a special case of the gravimetric preparation method for binary mixtures described here. Multicomponent mixtures are therefore covered by this International Standard. This International Standard does not include methods for the batch production of more than one mixture in a single process.

The International Standard requires estimation of the stability of the mixture for its intended life time (maximum storage life), but it is not for use with components that react with each other or with the container material. The International Standard also requires the impurities in each material (liquid or gas) used in the preparation of the mixture to be assessed and quantified.

Provided rigorous and comprehensive quality assurance and quality control procedures are adopted during the preparation and verification of these mixtures, uncertainties may be achieved that are substantially smaller than by any other preparation method.

2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this International Standard. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 6141, *Gas analysis — Requirements for certificates for calibration gases and gas mixtures*

ISO 6143, *Gas analysis — Determination of the composition of calibration gas mixtures — Comparison methods*

ISO 7504, *Gas analysis — Vocabulary*

(ISO 12963:—¹), *Gas analysis — Measurement protocols and data evaluation techniques for general analytical applications*)

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

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

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

(IUPAC, *Commission on atomic weights and isotopic abundances: Atomic weights of the elements, biennial review*)

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 7504 apply.

4 Symbols

b_i	estimated drift rate of component i
k	coverage factor
$L_{i,A}$	limit of detection of impurity i in parent gas A
M_A	molar mass of parent gas A
M_i	molar mass of component i
M_Ω	molar mass of the final mixture
m_A	mass added of parent gas A
m_Ω	mass of the final mixture
n	number of components i in the mixture
P	number of parent gases A
p_F	filling pressure
$p_i(T_L)$	vapour pressure of component i at temperature T_L
T_F	filling temperature
T_L	lowest temperature to which the gas mixture will be exposed
t_d	decay time

1) To be published in 2014.

t_s	shelf life of component i in the mixture
w_i	mass fractions w_i of the components i in the final mixture
$w_{i,A}$	mass fraction of component i in parent gas A
x_c	amount-of-substance fraction of the 'pure' component in the material being analysed
x_i	amount-of-substance fraction of component i
$x_{i,A}$	amount-of-substance fraction of component i in parent gas A
x_i^0	amount-of-substance fraction component i at time $t = 0$
x_i^t	amount-of-substance fraction component i at time t
y_k	amount-of-substance fraction of component k in the prepared mixture
y_{ver}	analysed amount-of-substance fraction
Ω	composition of the final mixture

5 Principle

Calibration gas mixtures are prepared by transferring pure gases, pure liquids or gravimetrically prepared mixtures of known composition quantitatively into a cylinder in which the calibration gas will be contained. The traceability to the SI of amount fractions of these mixtures arises from the correct execution of three steps:

- 1) the determination of the masses added;
- 2) the conversion of the added masses to amounts of substance, by knowledge of their chemical purity and appropriate relative atomic and/or molecular masses;
- 3) the verification of the final mixture against independent reference gas mixtures.

The mass of each component is determined by weighing either the supply vessel, or the cylinder in which the calibration gas mixture will be contained, before and after each addition. The difference in these two weighings corresponds to the mass of the component added. The choice between these two weighing procedures depends on the uncertainty required for the amount fraction of the final mixture. Annex A provides more guidance on precautions to be taken when weighing, handling and filling cylinders.

NOTE The addition of small masses of a specified component may best be weighed in a low-volume supply cylinder (or other vessel) before and after addition on a highly sensitive balance. This case is used when the highly sensitive balance has insufficient capacity to weigh the final mixture.

A single-step preparation method may be used when the mass of each component added is large enough to be measured accurately. Alternatively, a multiple-step dilution method may be used to obtain a final mixture with acceptable uncertainty, particularly when low amount fractions are required. In this method "pre-mixtures" are prepared gravimetrically and used as parent gases in one or more of the steps.

An example of the steps used to prepare a calibration gas mixture is given in Annex B.

The determination of the purity of each material (liquid or gas) used in the preparation of the mixture is described in clause 7. Clause 8 describes the determination of masses and the calculation of preparation uncertainty. The homogeneity and stability of the gas mixture are dealt with in clause 9. The verification of the amount fraction of the final mixture against independent standards is described in clause 10. The calculation of the uncertainty of the calibration gas mixture is given in clause 11.

The gravimetric method scheme for preparing calibration gas mixtures, based on requirements for composition and the level of uncertainty, is given as a flowchart in Figure 1. The individual steps are explained in more detail in the following clauses (reference is given to the subclause for each step in Figure 1).

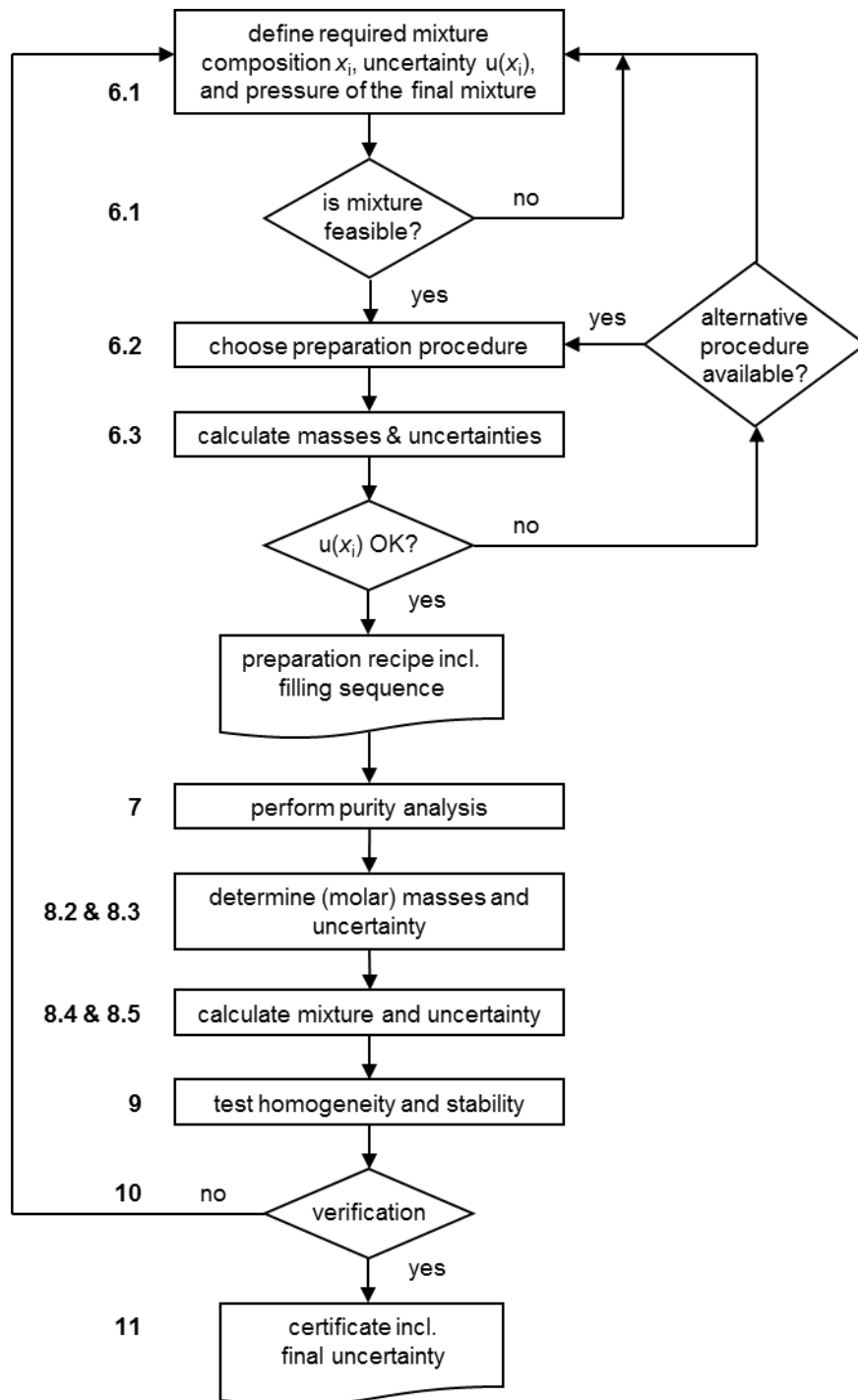


Figure 1 —Scheme for preparation of calibration gas mixtures using gravimetry

6 Planning the preparation of the mixture

6.1 Feasibility of preparing the gas mixture

6.1.1 Safety considerations

Gas mixtures potentially capable of reacting dangerously shall be excluded for safety reasons. National and local safety regulations should be followed.

NOTE Guidance is given in EIGA (European Industrial Gases Association) documents IGC 39 'The safe preparation of gas mixtures' and IGC 139 'Safe preparation of compressed oxidant-fuel gas mixtures in cylinders'.

The final pressure of the calibration gas mixture shall not exceed the stated maximum working pressure of the target cylinder.

6.1.2 Reactions between mixture components

Before preparing a gas mixture, it is essential to consider possible chemical reactions between the components of the mixture. A comprehensive compilation of combinations of components that may react is not available. Therefore, chemical expertise is necessary to assess the stability of a gas mixture and a risk analysis shall be performed.

6.1.3 Reactions with container materials

Before preparing a gas mixture, it is necessary to consider possible chemical reactions of mixture components with materials of a high-pressure cylinder, its valve and the transfer system. Special consideration shall be given to the attack by corrosive gases with metals and possible reactions with elastomers and greases used, for example, in the valve seat and seals. Such reactions shall be prevented by using only materials that are inert to all components of the mixture. If this is not possible, measures shall be taken to minimize corrosive attack on the materials with which the gases make contact so as to prevent any significant effect on mixture composition and any danger in storage and use.

NOTE Information on the compatibility of gases with container materials is given in ISO 11114 series.

6.2 Choice of preparation method

The following parameters shall be considered when choosing a preparation method:

- the target composition and uncertainty of the calibration gas mixture;
- the target filling pressure of the calibration gas mixture;
- the required tolerance for the preparation;
- the composition of any available parent gas mixture;
- the characteristics of the balance to be used with its determined performance specifications.

6.3 Calculation of target masses

Calculate the value of the target masses m_A , of each component A , using Equation (1).

$$m_A = \frac{x_{k,A} \times M_k}{\sum_{i=1}^n x_{i,A} \times M_i} \times m_{\Omega} \quad (1)$$

After the target masses have been calculated, a preparation procedure is selected and the uncertainties associated with the amount fractions are calculated (see 8.5). If these uncertainties are deemed unacceptable, another procedure shall be tried. It may be necessary to perform an iterative process to select a procedure with acceptable uncertainty.

NOTE The preparation method can include various filling methods, i.e. direct method, multiple step dilution or transfer method (use of small cylinder separately weighed on a low-capacity, high-resolution balance). More information on the various preparation methods is given in Annex A.

6.4 Condensation of components from the gas phase

When preparing, storing or handling gas mixtures that contain condensable components (see Annex C), the following measures shall be taken to prevent condensation because loss by condensation will change the gas phase composition.

- During the preparation of the gas mixture, the filling pressure shall be set safely below the dew-point vapour pressure of the final mixture at the filling temperature. To prevent condensation at intermediate stages, this condition shall be fulfilled for every intermediate mixture as well. If condensation of an intermediate mixture cannot be safely excluded, measures shall be taken to vaporize any possible condensate and to homogenize the gas phase at an appropriate later stage.
- During the storage of the gas mixture, the storage temperature shall be set so as to maintain the filling pressure safely below the dew-point vapour pressure of the mixture at that temperature.
- During the handling of the gas mixture, the same condition on the handling temperature applies. Furthermore, to prevent condensation during mixture transfer, the transfer lines shall be heated if required.

In Annex C, some guidance is given for estimating the maximum filling pressure for introducing components of a gas mixture at which no condensation of the condensable components is expected to occur. An example of this estimation is given in C.2 for a natural gas mixture.

7 Purity analysis

7.1 General

The determination of the impurities contained in each material (gas or liquid) used in the preparation has an impact on the uncertainty associated with the amount fraction of the component.

Assess and list all of the impurities that may be present in the material. These may be identified by means including:

- information provided with the material;
- previous experience of using the same or similar materials;
- knowledge of the process used to produce the material.

In order to decide the extent of purity analysis required, it is necessary to specify which of the potential impurities are 'critical' and which are 'significant' to the final composition of the mixture.

7.2 Assessment of critical and significant impurities

7.2.1 Critical impurities

A critical impurity is an impurity that meets one or more of the following criteria:

- An impurity in the major component (matrix) of a mixture that is also present as a minor component in the same mixture at low concentrations.

EXAMPLE If preparing a low-concentration oxygen in nitrogen mixture, oxygen may also be present as an impurity in the nitrogen.

- An impurity in a minor component in a multi-component mixture that is also present as another minor component in the same mixture.

EXAMPLE For natural gas mixtures, i-pentane is often found as an impurity in n-pentane and neo-pentane, as well as being added as a minor component in its own right.

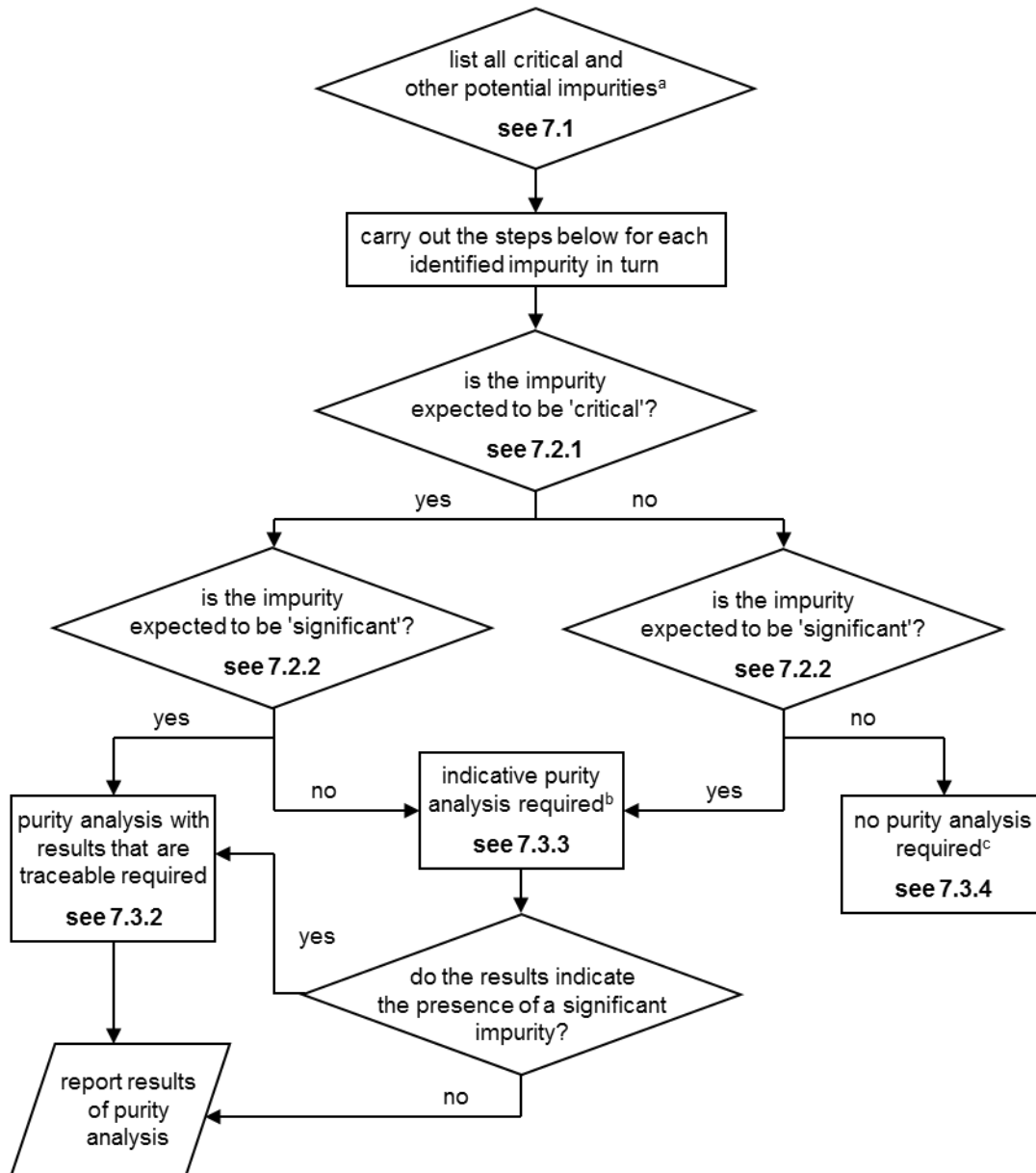
- An impurity that may be reactive with any other component in the mixture.

EXAMPLE If preparing a mixture of nitric oxide in nitrogen, any oxygen present as an impurity in the nitrogen may react with the nitric oxide to form nitrogen dioxide.

7.2.2 Significant impurities

A significant impurity is an impurity that is predicted to contribute more than 10 % of the target uncertainty in the final calibration gas mixture.

The above described steps are summarised as a flowchart in Figure 2. The use of the flowchart is explained in the following sections.



^a If an unpredicted or unknown impurity is identified during the course of a purity analysis, return to the start of the flowchart.

^b If preferred, a purity analysis with results that are traceable may be carried out instead of an indicative purity analysis.

^c If preferred, a traceable or indicative purity analysis may be carried.

Figure 2 — Purity analysis flowchart

7.3 Analysis of impurities

7.3.1 General

The extent of purity analysis required shall be determined by the outcome of the flowchart in Figure 2. Each of these levels is discussed in 7.3.2 to 7.3.4.

The process shown in the flowchart in Figure 2 shall be undertaken for each of the listed potential impurities. If any unpredicted or unknown impurities are identified at any later stage of purity analysis, the same process shall be repeated for these impurities.

Purity analysis may be carried out by one or more appropriate analytical techniques. In some instances, more than one technique may be needed.

EXAMPLE When determining the purity of methane, hydrocarbon impurities can most accurately be determined by gas chromatography with flame ionisation detection (GC-FID), whilst other impurities can be determined by GC with thermal conductivity detection (GC-TCD) or discharge ionisation detection (GC-DID).

For some materials (e.g. liquids and corrosive gases), it may not be practicable to analyse the material in its 'pure' state. In these cases, an alternative approach may be taken such as:

- A lower concentration gravimetric mixture may be prepared for purity analysis (using a carefully chosen matrix gas of known high purity). It should however be noted that this approach has a detrimental effect on the achievable limits of detection and that care should be taken to account for the purity of the matrix gas when calculating the purity of the component of interest.
- For liquids, the 'headspace' above the liquid may be analysed for purity. When this approach is taken, it should be noted that fractional distillation effects may cause the composition of the 'headspace' to differ from that of the pure liquid. An additional uncertainty component shall be included in the results to reflect this difference in composition.

When carrying out a purity analysis, care should be taken to check for any unexpected impurities (i.e. any observed impurities that were not identified as a potential impurity when following the assessment procedure in 7.2). For example, when using gas chromatography, unexpected impurities can be observed as unexpected peaks in the chromatogram. If one or more unexpected impurities are observed, each should be assessed as to whether it is 'critical' and/or 'significant', and the appropriate impurity analysis then carried out as determined by the flowchart in Figure 2.

7.3.2 Purity analysis with results that are traceable

To carry out a purity analysis with results that are traceable, calibrate the analyser(s) using reference gas mixtures with defined uncertainties, and quantify the impurity by direct comparison with these reference mixtures by use of methods described in ISO 6143 or (ISO 12963).

If data that have shown to be traceable are available from a third party (e.g. on a certificate of analysis provided by the manufacturer), these data may be used for this purpose. Traceability may be demonstrated, by, for example, the laboratory holding suitable accreditation for the analysis and/or using appropriate certified reference materials.

NOTE 1 A reference gas mixture is a mixture of appropriate metrological quality that is traceable, through an unbroken chain of comparisons with stated uncertainties, to a national or International Standard. An example is a gas mixture certified by a calibration laboratory accredited under ISO/IEC 17025.

NOTE 2 Where traceable gaseous standards are not available, certified reference materials can be available in liquid form with certified purity.

NOTE 3 Where traceable standards or certified reference materials are not available, it can be necessary to re-design the proposed preparation such that traceable purity analysis is not required. For example, by the use of starting materials with improved purity.

NOTE 4 Where traceable standards or certified reference materials are not available, it is sometimes possible to estimate the purity of starting materials by use of a standard addition-type method. Prepare a series of standards containing the 'pure' material at different concentrations, and extrapolate the analysed values back to zero.

7.3.3 Indicative purity analysis

In the field of gas analysis, an indicative purity analysis is one that is not traceable, for example an analysis that uses gas mixtures with non-traceable composition.

If data that are non-traceable are available from a third party (e.g. on a certificate of analysis provided by the manufacturer), these data may be used for the purpose of an indicative purity analysis only.

For all indicative purity analyses, an appropriate uncertainty component shall be included in the results established to account for a possible bias in the results.

7.3.4 No purity analysis

A purity analysis is not required for impurities that are both non-critical and insignificant.

7.3.5 Estimation of the amount fraction of unmeasured (but expected) impurities and its associated uncertainty

When carrying out a purity analysis with results that are traceable or an indicative purity analysis, an impurity may sometimes be expected to be present in a material (through either prior knowledge or information provided by a third party, such as the manufacturer of the material), but cannot be detected by, or is below the limit of detection of, the analytical method used.

In these instances, if a more suitable and/or sensitive analytical method is not available, the amount fraction of the expected impurity shall be set equal to half of the value of the limit of detection of the analytical method used.

The uncertainty of an amount fraction estimated in this manner is based upon a rectangular distribution between zero and the value of the detection limit of the analytical method, thus assuming that there is an equal likelihood that the impurity may be present in the material at a level up to the value of the detection limit. An undetected impurity therefore forms a rectangular probability distribution from which its standard uncertainty is given by Equation (2):

$$u(x_{i,A}) = \frac{L_{i,A}}{2 \times \sqrt{3}} \tag{2}$$

7.4 Determination of the amount fraction of the ‘pure’ component and its associated uncertainty

Tabulate the uncertainties of all the measured and unmeasured impurities in a manner similar to that shown in Table B.3. The amount fraction of the ‘pure’ component in the material being analysed is determined by Equation (3):

$$x_c = 1 - \sum_{i=1}^n x_{i,A} \tag{3}$$

The standard uncertainty in the amount fraction of the ‘pure’ component is determined using the law for the propagation of uncertainty described in ISO/IEC Guide 98-3 (GUM) and shown in Equation (4):

$$u^2(x_c) = \sum_{i=1}^n u^2(x_{i,A}) \tag{4}$$

The uncertainty in the amount fraction of each impurity shall be determined by combination of all relevant factors. These may include, but are not limited to, the uncertainties in calibration standards, analytical repeatability and reproducibility, and the use of relative response factors.

8 Determination of masses and calculation of preparation uncertainty

8.1 Preparation of cylinder

Select a cylinder for the preparation. Evacuate it to a pressure at which the residual gas will not contribute to the uncertainty of the final mixture.

NOTE Most weighing procedures require the use of a tare. In this case it will be necessary to select two cylinders for the procedure with nearly identical external volume. One will be required for the final mixture and one for use as the tare.

8.2 Determination of masses and their uncertainties

The mass of each component added to the cylinder shall be determined by weighing. The mass of each component shall be corrected for its purity as determined according to clause 6.

Precautions to be taken when weighing, handling and filling cylinders are given in Annex A.

The uncertainty of each mass added shall be evaluated. The evaluation shall take into account all sources of uncertainty, in particular the following:

- the accuracy of the balance including consideration of its calibration and its linearity;
- the repeatability of the balance readings including errors caused by the location of the cylinder on the balance;
- buoyancy effects;
- effects of moisture adsorption and dust on the outer surface of the cylinder;
- errors due to loss of material during transfer into the cylinder.

Guidance on the introduction of liquid components into gravimetrically prepared calibration gas mixtures is provided in Annex D. This annex is only applicable to mixtures whose final composition is totally vaporized and contain components that do not react with each other or interact with the cylinder wall.

8.3 Molar masses and uncertainties

The molar masses of the components, and their uncertainties, are required for the conversion of mass fraction to amount fraction. The values used shall be from the most recent publication of the commission on atomic weights and isotopic abundances of the International Union of Pure and Applied Chemistry (IUPAC). For other conversions between units ISO 14912 shall be used.

8.4 Calculation of the mixture composition

The amount fractions of the components in the final mixture are calculated using the Equation (5):

$$y_k = \frac{\sum_{A=1}^P \left(\frac{x_{k,A} \times m_A}{\sum_{i=1}^n x_{i,A} \times M_i} \right)}{\sum_{A=1}^P \left(\frac{m_A}{\sum_{i=1}^n x_{i,A} \times M_i} \right)} \quad (5)$$

NOTE A method for deriving this formula is given in Annex E.

8.5 Calculation of preparation uncertainty

The preparation uncertainty is calculated by the application of the law of propagation of uncertainty to Equation (5):

$$u_{prep}^2(y_k) = \sum_{i=1}^n \left(\frac{\partial y_k}{\partial M_i} \right)^2 \times u^2(M_i) + \sum_{A=1}^P \left(\frac{\partial y_k}{\partial m_A} \right)^2 \times u^2(m_A) + \sum_{A=1}^P \sum_{i=1}^n \left(\frac{\partial y_k}{\partial x_{i,A}} \right)^2 \times u^2(x_{i,A}) \quad (6)$$

The uncertainty in the weighing of each of the parent gases ($u(m_A)$) can be estimated according to methods described in Annex A and B.

9 Homogeneity and stability of the calibration gas mixture

9.1 Homogeneity

It is essential that a gas mixture is homogeneous before it is analysed or used as a calibration gas mixture.

NOTE 1 Homogeneity is defined in ISO 7504:2001 as the “state of a gas mixture wherein all of its components are distributed uniformly throughout the volume occupied by the gas mixture”.

In order to ensure the homogeneity of the gas mixture, it shall be homogenized after the last gas has been added and weighed. This can be done by rolling the cylinder in an orientation that is close to horizontal. Alternatively, homogenization can be achieved by laying the cylinder on its side for an extended period or by applying heat. The minimum duration of this homogenization varies for different components.

NOTE 2 When one of the components has a relative density substantially greater than the relative density of the balance gas, rolling the cylinder is not always sufficient to homogenize the gas due to their density difference.

9.2 Stability

9.2.1 General

The stability of a gas mixture is characterized by determining a quantitative value for the drift rate of component i using a linear decay model following the equation:

$$x_i^t = x_i^0 \times (1 - b_i \times t_d) \quad (7)$$

The drift rate shall be determined on a case-by-case basis, it cannot be predicted from first principles. This International Standard can only be applied when the linear decay model (Equation (7)) is applicable.

NOTE 1 ISO Guide 30 defines stability as the ability of a reference material, when stored under specified conditions, to maintain a stated property value within specified limits for specified period of time. ISO Guide 35 defines shelf life (of an RM/CRM) as the time interval during which the producer of the CRM warrants its stability.

The contribution to the uncertainty in the amount fraction of component i from limitations in the stability of the mixture is characterized by the uncertainty due to instability. The uncertainty due to instability is related to the drift rate of component i and the shelf life through the equation:

$$u_{stab}(x_i) = b_i \times t_s \quad (8)$$

NOTE 2 Values for t_s of 2 or 3 years are often used.

NOTE 3 Since the uncertainty due to instability contributes to the combined standard uncertainty of the amount fraction, two nominally identical gas mixtures with different values for the shelf life will have different uncertainties.

The approach proposed here may require modification to be applicable to the considerable number of components and amount fractions that are required in the analytical laboratory.

9.2.2 Assessing stability

9.2.2.1 Designing a stability study

A stability study is necessary to provide input data for the stability component in the overall expanded uncertainty budget. The stability rate constants for mixtures shall be determined empirically by experiment where the mixture cannot be shown to be unconditionally stable. Gas mixtures shall be prepared and analysed immediately after preparation then again at regular intervals until either the mixture has shown an unacceptable change in composition or until an acceptable stability period has been demonstrated.

The stability uncertainty component in some cases can be a significant uncertainty component and the design of the study is therefore crucial to assess the stability of the gas mixture accurately. The study shall be carefully designed to ensure that the gas mixture stability is being determined and not other parameters such as instrumental drift of the analyser. The design of the study shall also ensure as many parameters as possible are kept constant during the study to prevent these parameters influencing the results and hence the study. For example, sample gas flow and pressure, sampling equipment and instrument should always remain the same as well as carefully controlled environmental conditions such as the room temperature.

The design of the stability study is influenced by the chemical nature of the components in the mixture, the cylinder and valve type and the stability period required by the customer.

A stability study is typically performed as part of a preparation validation exercise. When statistical control methods are applied under a quality assurance regime, the results of the stability study can be used for similar mixtures using similar pure gases and cylinders.

9.2.2.2 Chemical nature of components

The chemical nature of the components influences the stability of the gas mixture. Some components are inherently reactive, e.g., HCl that can react with the walls of the cylinder and other components in the mixture. In other cases, the components can react with each other, e.g., oxygen impurity in nitrogen with nitric oxide. Careful consideration should be made to ensure the reactivity of the components and the materials used give the mixture the best chance to remain stable. ISO 16664 shows material compatibility for some components and materials.

Knowledge of possible reactions between components can give information on the required purities of components and pre-mixtures, for example a mixture of 10 ppm NO/N₂ needs to be prepared using nitrogen with oxygen impurity content less than 1 ppm. Similar considerations shall be made for other mixtures where reactions between components occur.

Unreactive gases such as saturated hydrocarbons and some permanent gases (N₂, Ar, He) can be considered as being unconditionally stable and these components when used in a gas mixture may only require a cursory stability evaluation, whereas more reactive species such as SO₂, NO, NO₂ require a more rigorous stability evaluation and may involve the use of highly pure components, proprietary cylinder passivation techniques to allow the mixture to remain stable long enough for the end users requirements.

The stability period determined from the study is proportional to the uncertainty of the stability component in the overall uncertainty budget, for example, a short stability period gives rise to a small stability uncertainty, whereas a long stability period gives rise to a larger stability uncertainty. The stability rate constants for mixtures shall be determined empirically by experiment where the mixture cannot be shown to be unconditionally stable.

9.2.2.3 Sampling and analysis methodology

ISO 16664 shall be used when considering sampling of reference gases and gas mixtures under test. Calibration of instrumentation using good quality calibration gases before and after measurement of the gases under test will highlight any instrumental drift. This is a fundamental requirement as gas mixture instability and instrumental drift shall be differentiated and without a careful approach these two effects will become confused.

Before the stability of a gas mixture can be ascertained, the analytical instrumentation shall be assessed so that its characteristics, i.e. repeatability and resolution can be demonstrated to be fit for purpose. Determinations of the repeatability of the instrument with the gas mixture involved in the stability study are necessary before the study can progress. Once the repeatability is determined, the data is then used to calculate the level at which the instrument can discriminate between two statistically different amount fractions, i.e. the instruments resolution.

EXAMPLE A stability study involving a nitric oxide in nitrogen mixture at an amount fraction of 100 $\mu\text{mol/mol}$ is being performed. A traceable reference gas is used to calibrate the instrument at nominally 100 $\mu\text{mol/mol}$ and ten repeat measurements of the reference gas are taken over a two minute period. The standard deviation, from this calibration step, is used to assess the repeatability of the instrument. The standard deviation is calculated to be 0,14 $\mu\text{mol/mol}$. Therefore to show that two measurements are statistically different the uncertainties will not overlap, i.e. twice the standard deviation 0, 28 $\mu\text{mol/mol}$. Therefore the smallest difference which can be quantified is 0,28 ppm, conversely if the stability measurements after calibration are less than 0,28 $\mu\text{mol/mol}$ then the gas mixture is stable.

9.2.2.4 Number of cylinders to be used in the study

The stability study shall be run at least two identical gas cylinders of nominally the same composition. The greater the number of cylinders involved in the study the more confidence can be gained in the claimed shelf life. Knowledge of the gas mixture and amount fraction coupled with the chemical reactivity of the species and possible reactions shall be taken into account when designing a stability study. If the stability study provides sufficient evidence of stability of a calibration gas mixture at a certain relatively low amount fraction a further testing at higher amount fractions is unnecessary.

9.2.2.5 Duration of the study and frequency of analysis

There are several constraints on the duration of a stability study.

NOTE 1 A commercial influence can wish to conduct a study so that a potential customer would order another gas cylinder on an annual basis for example. A technical driver can wish to conduct a study until the gas mixture was considered unstable then apply a retrospective time comfort factor. This needs to be assessed on a case-by-case basis.

NOTE 2 A common approach is to conduct a study which is one year longer than the typical shelf life of similar gas mixtures.

The kinetics involved in physicochemical reactions affecting stability is a function of concentration. Some reactions will occur quickly and others over a longer period. Making a number of measurements in the first few days is a good idea to check for short term stability and then less frequently over a longer period for long term stability.

9.2.3 Statistics for assessment stability

There are a number of methods available for the statistical treatment of the data collected in a stability study. A check that reference value plus the claimed uncertainty is within the analytical value plus the standard deviation of the measurement is simple to do.

10 Verification of calibration gas mixture composition

10.1 Objectives

The composition of a calibration gas mixture shall be verified experimentally to demonstrate that the composition of the calibration gas sampled from the cylinder is consistent with the composition calculated from the gravimetric preparation process. This verification acts to highlight errors in the preparation process of the individual gas mixture or the presence of any chemical reaction between the components, or between any component and the cylinder.

A calibration gas mixture can only have a composition and uncertainty that is traceable to the SI when it has been verified.

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

- demonstrating consistency between the prepared mixture and appropriate reference gas mixtures;
- demonstrating consistency between several nominally similar prepared mixtures prepared by a method consistent with this International Standard;
- comparison with a calibration gas mixture prepared by a validated implementation of a dynamic method according to one of the parts of ISO 6145.

10.2 Statistical tests for consistency and uncertainty due to verification

The results of the verification shall be subject to appropriate statistical procedures, for example those included in ISO 6143.

The calculation of the uncertainty of the analysis process used for the verification (u_{ver}) shall take account of:

- the number of the standards used and their uncertainty;
- the repeatability of the verification process;
- the number of times the verification process was repeated.

The calculation of the uncertainty of the analysis process used for verification may 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:

$$|y_k - y_{ver}| \leq 2u(y_k - y_{ver}) = 2\sqrt{u^2(y_k) + u^2(y_{ver})} \quad (9)$$

The uncertainty of the verification process shall not be less than the deviation of the result of the verification from the gravimetric value. It shall be calculated using

$$u_{ver}(y_i) = \frac{1}{2} \sqrt{u^2(y_k) + u^2(y_{ver}) + (y_k - y_{ver})^2} \quad (10)$$

11 Uncertainty of the calibration gas mixture and preparation of certificate

The amount fraction of component i in the final mixture on the certificate shall be the result of the calculation as described in 8.4.

The combined standard uncertainty of the certified value of the amount fraction of component i in the final mixture shall be calculated using:

$$u_c(x_i) = \frac{1}{2} \sqrt{u_{ver}^2(x_i) + u_{stab}^2(x_i) + u_{prep}^2(x_i)} \quad (11)$$

In order to avoid incorporating the same source of uncertainty in the calculation twice, if the stability uncertainty makes use of the results of data from the verification, then it may be acceptable to set either $u_{\text{ver}}(x_i)$ or $u_{\text{stab}}(x_i)$ equal to zero in equation (11).

The certificate shall report the expanded uncertainty and the coverage factor. The expanded uncertainty is calculated from the combined standard uncertainty:

$$U(x_i) = k \times u_c(x_i) \quad (12)$$

The uncertainty shall take account of the uncertainty of the verification process as shown in equation (12).

NOTE 1 Use $k = 2$, unless specific reasons necessitate an alternative.

NOTE 2 For a normal distribution, a coverage factor of $k = 2$ corresponds to a confidence interval of approximately 95 %.

The certificate shall be prepared according to ISO 6141.

When an expiry date is stated, it shall be calculated from the shelf life used in 8.2.

Annex A (informative)

Precautions to be taken when weighing, handling and filling cylinders

A.1 General

A number of sources of error influence the uncertainty of the final result. A list of potential sources of error is given below for each step in the preparation process. During the validation process of the preparation method these sources should be evaluated carefully. In some cases the applied method may not be influenced by one or more of the listed sources of error. Also additional sources of error may be applicable that are not listed in this annex. In some cases the magnitude of the error evaluated is small in comparison to the other sources of error and this error can then be neglected in the final uncertainty budget.

A.2 Weighing

A.2.1 Possible sources of uncertainty in weighing

The following are sources of error related to the balance and the weights:

- resolution of balance;
- accuracy of balance including linearity;
- zero point deviation;
- drift (thermal and time effects);
- instability due to draught;
- location of cylinder on the balance pan;
- errors in the weights used;
- buoyancy effects on the weights used.

A.2.2 Choice of the balance

Choose a balance with a total capacity suitable for weighing the mass of the cylinders and suitable resolution to correctly weigh the smallest mass of gas.

EXAMPLE In order to prepare gas mixtures in aluminium cylinders of a volume of about 5 l, a suitable balance would have a total capacity of 10 kg and would be capable of weighing to the nearest 0,4 mg. In some cases, the amount of minor component to be added requires the use of a small transfer cylinder (i.e. 200 ml volume cylinder). This small cylinder can be weighed on a more accurate balance with higher sensitivity (i.e. an analytical balance of 240 g capacity capable of reading to the nearest 0,05 mg).

A.2.3 Balance surroundings

The performance of the balance chosen and its ability to prepare accurate calibration gas mixtures can be compromised if the surroundings of the balance are inappropriate. For example, draughts caused by air conditioning, temperature variations resulting from direct sunlight or air conditioning, and vibration can all

hinder the performance of the balance. Moreover, changes in the surrounding temperature and humidity can result in drift.

Therefore, it is best to place the balance in surroundings which meet the manufacturer's recommendations. Continuous logging of temperature, atmospheric pressure and humidity are recommended if changes in these conditions can significantly influence the weighing results. Further experiments should be carried out to demonstrate that the performance of the balance is satisfactory.

A.2.4 Performance of the balance

It is recommended that the balance be installed by the manufacturer, and its performance checked and calibrated on a regular basis.

Depending on the type of balance and the weighing method used, the performance of the balance should be checked for the following aspects:

- sensitivity;
- linearity;
- drift (zero and span);
- repeatability;
- stability;
- influence of changing environmental conditions.

A.2.5 Use of balance, weights and weighing

Gas cylinders are large objects which displace significant volumes of air whose mass varies proportionally with the temperature and humidity.

Changes in this buoyancy effect, resulting from changes in atmospheric pressure, should be compensated for by comparative weighing against a similar reference cylinder or by calculation. The density of the air can be calculated with the equation for the determination of the density of moist air (see [12] and [13]).

Apart from the temperature effect described in A.2.3, it is also important to minimize the effect on the weighing results due to variations in temperature which occur during cylinder filling. It is important that experiments be carried out so as to determine to what extent temperature stabilization is needed after filling for minimizing these effects.

If the amount fractions of the calibration gas mixtures are intended to be traceable to international or national gravimetric standards, then the weights used during the weighing process or in calibration of the balance should be traceable. Similarly the instruments used to measure the surrounding temperature and pressure, so as to calculate the buoyancy correction, should also be traceable to either national or international standards.

A.3 Cylinders

A.3.1 Possible sources of uncertainty

Sources of error related to the gas cylinder include the following:

- mechanical handling of cylinder due to:
 - loss of metal, paint or labels from surface of cylinder;

- loss of metal from threads of valve/fitting;
- dirt on cylinder, valve or associated fitting;
- adsorption/desorption effects on the external cylinder surface;
- buoyancy effects resulting from:
 - the cylinder itself;
 - differences in temperature of the cylinder from surrounding air due to e.g. filling with gas;
 - change of cylinder volume during filling;
 - change of density of air due to:
 - temperature;
 - air pressure;
 - humidity and carbon dioxide content;
- uncertainty in determination of external cylinder volume.

A.3.2 Choice of cylinders

Cylinder material, size and valve should be chosen such that the cylinder can be safely handled and the material is compatible with the components which are to be contained in the cylinder.

A.3.3 Handling cylinders

Water-vapour contamination inside cylinders can cause unwanted reactions with the gases that are to be contained in these cylinders. To eliminate this contamination, consideration should be given to vacuum-heating new cylinders by placing them in an oven and evacuating any vaporized contaminants using a vacuum pump. However, vacuum heating should not be performed in cases where it may damage the internal surface treatment of the cylinder.

Each cylinder should be leak-tested under vacuum and working-pressure conditions. Leakage can be indicated by suitable vacuum-pressure indicators or by weighing the cylinder over a period of time. When weighing, consideration should be given to the effects described in A.2.3 and A.2.5 concerning changes in conditions of the surroundings and effects due to pressurization.

Cylinders, their valves and threads should be clean and free from loose paint in order to minimize possible mass changes during preparation. When using very sensitive balances, cylinders should be handled with gloved hands and, during operations other than weighing, protected with a polyethylene mesh sleeve. The base of the cylinders should be protected by mats from knocks against the floor which may possibly remove paint or metal.

In order to avoid abrasion and wear of metal fittings and their threads, the necessary fitting should preferably be permanently attached to the cylinder valve and connections from it to the gas-transfer apparatus made with proprietary O-ring sealed connections.

A.3.4 Safety considerations

National regulations relating to the frequency of testing of cylinders should be observed, and re-tests carried out by an approved body.

No organic oils or greases should be allowed into contact with cylinders or their fittings, nor chlorinated solvents allowed into contact with aluminium cylinders. The maximum working pressure of cylinders, usually two-thirds of the test pressure, should never be exceeded.

All pipe-work and fittings should be suitable for their pressure and intended purpose and have compatible threads. Fittings should be assembled in accordance with their manufacturer's instructions.

The gas transfer apparatus should be designed to withstand 1,5 times its maximum operating pressure and leak-tested at this pressure using appropriate means. It is recommended that it be protected from over-pressure by a pressure-relief valve which is installed so as to discharge outside of the preparation area. If a vacuum pump is part of the transfer apparatus, it should also be protected from pressurization resulting from incorrect operation by a pressure-relief valve. Furthermore, a vent should be connected to a manually operated valve and installed so as to clear high pressure gas from the apparatus outside the preparation area.

A.4 Filling cylinders

A.4.1 Sources of uncertainty

Sources of error related to the component gases include the following:

- residual gas in cylinder;
- leakage of:
 - air into the cylinder after evacuation;
 - gas from the cylinder valve during filling;
 - gas from the cylinder after filling;
 - gas from cylinder into transport lines;
- gas remaining in transfer system when mass loss method is used;
- adsorption/reaction of components on internal cylinder surface;
- reaction between components;
- impurities in the parent gases used;
- insufficient homogenization;
- uncertainty of molecular mass.

A.4.2 Principal methods for preparing calibration gas mixtures

The following are the three principal methods for the preparation of calibration gas mixtures.

- a) Pure gases or pre-mixtures of known composition are added to a weighed evacuated cylinder in amounts quantified by weighing.
- b) A certain amount of gas is removed from a cylinder containing a known mass of gas mixture of known composition. The remaining quantifiable amount of gas mixture is then diluted by the addition of a further gas, whose mass is again determined.

- c) In order to reduce the uncertainty of measurement of a minor component, transfer this component from a smaller container, which can be weighed on a high-resolution balance.

These methods are outlined below [except that the procedures for methods a) and b) are essentially the same], together with the precautions to be taken in carrying them out.

A.4.3 Preparation using pure gases or pre-mixtures

Determine the filling sequence first (see clause 4). Evacuate the cylinder to a pressure such that the mass of residual gas in the cylinder is less than the weighing uncertainty. Disconnect the evacuated cylinder from the vacuum pump and, after temperature equilibration, weigh it to constant mass.

Connect the cylinder to the transfer apparatus and flush the connecting tubing with the first pure gas, or pre-mixture. A flushing procedure should be defined to minimize effects of contamination of the final mixture due to remaining gases in the transfer apparatus.

After sufficient flushing (and evacuation) open the pure gas or pre-mixture cylinder valve and introduce the gas into the transfer apparatus and tubing and open the valve of the cylinder to be filled. Carry out the addition of gas to the cylinder slowly so as to reduce temperature effects. In the case of gas mixtures, where condensation can occur, this effect may lead to partial condensation of some components. Due to adiabatic expansion (Joule-Thomson effect), temperature effects can be expected. These effects can lead to errors if pressure indication is used for targeting the mass of the gas component. This expansion can also lead to condensation.

With the cylinder valve fully open, continue adding the gas until either the pressure gauge indicates that sufficient amount of gas has been added, or a top-loading balance on which the cylinder stands indicates the approximate mass. Close the cylinder valve, disconnect the cylinder and, after temperature equilibration, re-weigh the cylinder to constant mass.

Repeat this procedure for the second and subsequent gases. As the cylinder valve is opened, make sure the pressure of each gas in the apparatus and transfer line is regulated so as to remain higher than the pressure of gas in the cylinder. This will prevent gas from the cylinder re-entering the transfer line. After the last gas has been added and weighed, homogenize the cylinder contents before use.

A.4.4 Preparation by transfer of a minor component from a separate cylinder

Once the mass of the minor component has been determined by weighing it in a small cylinder using a low-capacity balance, connect this cylinder to the transfer apparatus. Evacuate the "larger" cylinder to be filled, weigh it, and connect it to the transfer apparatus as described in A.4.2. After sufficiently flushing the transfer lines with the next gas to be added, evacuate the transfer lines and open the cylinder valves, allowing the gas in the smaller cylinder to be transferred to the larger cylinder. Then close the valve of the larger cylinder. By successively pressurizing the transfer apparatus and the smaller cylinder with the next component, transfer this component to the larger cylinder and flush this cylinder and transfer lines. However, make sure before opening the valve of the larger cylinder, to check that the pressure in the transfer apparatus is higher than the actual pressure in the larger cylinder. Once the addition of this component has been completed, remove the larger cylinder and weigh it. If the smaller cylinder, or its valve, cannot withstand the final pressure used for transferring this component, the smaller cylinder can be removed from the transfer apparatus and weighed again. The difference in mass before and after addition of this component from the smaller cylinder corresponds to the mass added to the larger cylinder.

Annex B (informative)

Practical example

B.1 Introduction

This annex provides some examples of the implementation of the normative text in this International Standard and is complementary to Annex A.

B.2 Cylinder weighing procedure

The most important elements of a procedure to weigh a gas cylinder are included in the following examples:

Example 1 using a top-pan balance.

- 1) Place the tare cylinder on the balance, and when stability is reached (usually within 1 minute) record the value (T_1).
- 2) Remove the tare cylinder and place at the side of the balance. Place the target cylinder on the balance pan. After stability is reached (usually within 1 minute), note the reading on the balance terminal controller (X_1).
- 3) Compute the difference $X_1 - T_1$.

Repeat the sequence, until three consecutive values of $X_n - T_n$ fall within an interval of 20 mg. The average of these 3 readings is the value of the mass of the cylinder minus that of the tare.

This sequence is repeated each time a gas is added during the preparation. The difference in the weight between successive steps is the weight of component added.

Example 2 using a top-pan balance and using the “tare” function on the balance controller:

- 1) Place the tare cylinder on the balance, and when stability is reached (usually within 1 minute), “tare” the reading on the terminal control unit such that it reads zero.
- 2) Remove the tare cylinder and place at the side of the balance. Place the target cylinder on the balance pan. After stability is reached (usually within 1 minute), note the reading on the balance terminal controller (X_1).
- 3) Tare the reading on the terminal control unit to zero and place the preparation cylinder at the side of the balance.
- 4) Place the tare cylinder on the balance and when stability is reached note the reading on the balance terminal controller (X_2) (this reading will be negative). Tare the reading on the terminal control unit to zero.

Steps 1) to 3) should be repeated until 3 consecutive readings in the series:

$$X_1, -X_2, X_3, -X_4, X_5, -X_6, X_7, -X_8, \dots$$

fall within an interval of 20 mg. The average of these 3 readings is the value of the mass of the cylinder minus that of the tare.

This sequence is repeated each time a gas is added during the preparation. The difference in the weight between successive steps is the weight of component added.

B.3 Examples of masses added and uncertainties

Table B.1 shows the values and uncertainties for the masses required for the dilution of pure carbon monoxide in pure nitrogen gravimetrically. The example is based on the use of a 10 litre cylinder filled to approximately 100 bar. The uncertainties used for the weighings are: 10 mg for the cylinder on a top-pan balance, 0,2 mg for the “large” loop and 0,05 mg for the “small” loop. Standard uncertainties are denoted by u , and expanded uncertainties ($k = 2$) as U . Note, the values shown for $U(x)$ also includes a contribution from the uncertainty of the molecular weights.

Table B.1 — Values and uncertainties for the masses required for the dilution of pure carbon monoxide in pure nitrogen gravimetrically

Method used for weighing minor component	10-litre cylinder on top-pan balance		'Large' loop 40 ml volume	'Small' loop 5 ml volume
	10^{-1}	10^{-2}	10^{-3}	10^{-4}
Nominal amount fraction (x) / mol/mol	10^{-1}	10^{-2}	10^{-3}	10^{-4}
m_a / g	116,709	11,671	1,167	0,116 71
$u(m_a)$ / mg	10	10	0,2	0,05
m_b / g	1 050,502	1 115,552	1 166,057	1 167,108
$u(m_b)$ / mg	10	10	10	10
$(U(x)/x) \times 100$	0,016	0,170	0,035	0,086

Table B.2 shows values and uncertainties for the masses required for the dilution of pure n-hexane in pure nitrogen gravimetrically. All other parameters are the same as for Table B.1.

Table B.2 — Values and uncertainties for the masses required for the dilution of pure n-hexane in pure nitrogen gravimetrically

Method used for weighing minor component	'Large' loop 40 ml volume		'Small' loop 5 ml volume	
	10^{-3}	10^{-4}	10^{-4}	10^{-5}
Nominal amount fraction (x) / mol/mol	10^{-3}	10^{-4}	10^{-4}	10^{-5}
m_a / g	3,590 64	0,359 06	0,359 06	0,035 91
$u(m_a)$ / mg	0,2	0,2	0,05	0,05
m_b / g	667,767 4	668,368 9	668,368 9	668,429 1
$u(m_b)$ / mg	10	10	10	10
$(U(x)/x) \times 100$	0,015	0,112	0,029	0,278

B.4 Example of purity table

Table B.3 shows an example of a purity table for carbon monoxide. The results of the calculation as described in 7.4 for the example data in this table are given in the bottom row.

Table B.3 — Example purity table for carbon monoxide

Impurity	Measurement technique	Amount fraction $\mu\text{mol/mol}$	Standard uncertainty in amount fraction $\mu\text{mol/mol}^a$	Probability distribution	Divisor	Contribution to combined uncertainty $\mu\text{mol/mol}$
N ₂	GC-TCD	395	20	Normal	1	20
CO ₂	GC-TCD	40	4	Normal	1	4
O ₂	GC-TCD	13	10	Normal	1	10
H ₂	GC-TCD	110	6	Normal	1	6
CH ₄	GC-FID	12	7	Normal	1	7
H ₂ O	n/a ^b	10	10	Rectangular	$\sqrt{3}$	5,77
CO	Calculated	999 420	-	Normal	-	25

^a The uncertainty in the amount fraction of each impurity shall be determined by combination of all relevant factors. These may include, but are not limited to, the uncertainties in calibration standards, analytical repeatability and reproducibility.

^b In the example shown in this table, water was expected to be an impurity, but could not be measured by any of the techniques available in the laboratory, nor was any data provided by the manufacturer. The approach in 7.3.5 was therefore used, i.e. an amount fraction of half of the estimated GC-TCD method limit of detection was assigned.

Annex C (informative)

Guidelines for estimating filling pressures so as to avoid condensation of condensable components in gas mixtures

C.1 Estimation of filling pressure limits for general gas mixtures

A condensable component is defined as a component that may become a liquid during preparation, use or outdoor storage of the gas mixture of which it is part.

So as to keep such components completely in the gaseous phase, the filling pressure, p_F , should be limited. If no information is available to calculate the limit of the filling pressure, this limit can be estimated using the simple approximation (which is rather restrictive) given in Equation (C.1).

$$p_F \leq \frac{1}{\sum_{i=1}^n \left[\frac{x_i}{p_i(T_L)} \right]} \quad (\text{C.1})$$

For $p_F > 5 \times 10^6$ Pa (50 bar), Equation (6) is likely to give considerably conservative values.

In order to avoid condensation, the difference between the filling temperature, T_F , and T_L (at which the vapour pressure of the condensable components is chosen) should not be too small.

Information concerning the vapour pressure of a component can be found in the literature listed in references [1] to [11] of the Bibliography.

C.2 Application — Natural gas

C.2.1 Component vapour pressures

The maximum pressure (at 20 °C) at which a component can be introduced into the cylinder is given in Table C.1. These pressures are derived from the partial pressures of the individual components.

The pressures given in Table C.1 are the highest available for the “pure” component. If a partly prepared mixture is at a pressure greater than that which is available for a “pure” component, then that component cannot be added in the “pure” state. These pressures should not be seen as those which can be used in mixtures, regardless of the content of other components, because addition of more than one hydrocarbon at pressures approaching their vapour pressures can lead to the formation of a liquid phase in the cylinder. Although the final mixture, after the addition of methane as the major component, will behave as a single gaseous phase, the possibility of liquid being deposited during the preparation should be avoided.

If liquid is deposited in the cylinder during preparation, then:

- there is uncertainty about the time required for all liquid to re-enter the gas phase and form a homogeneous mixture, or about whether it ever will re-enter the gas phase, and
- the reduction in volume resulting from liquid formation means that the predicted filling pressures no longer bear a relationship to the added masses.

If a computer program is available to calculate phase properties, it should be used to ensure that the mixture stays entirely in the gas phase throughout the preparation. If such a program is not available, components should not be added to more than 50 % of their vapour pressures at ambient temperature, and preferably to no more than 25 %.

Table C.1 — Maximum filling pressures based on vapour pressures of the pure components

Component	Pressure kPa	Component	Pressure kPa
<i>n</i> -Butane	162	Carbon dioxide	4 590
2-Methylpropane	234	Methane	> 20 000
Propane	500	Nitrogen	> 20 000
Hydrogen	> 20 000	Oxygen	> 20 000
Ethane	3 400	Helium	> 20 000

C.2.2 Final-mixture phase behaviour

In addition to the phase behaviour of the intermediate mixtures, the properties of the final mixture should also be considered. It is a characteristic of hydrocarbon mixtures that the maximum dew-point temperature, i.e. the temperature below which components separate into the liquid phase, occurs at some intermediate pressure, below and above which the dew-point temperature is lower. By contrast, ideal gas predictions would always associate the highest dew-point temperature with the highest pressure.

Figure C.1 shows an example of the dew-point curve for a calibration gas mixture in which the concentrations of propane (C3), 2-methylpropane (C4) and *n*-butane (C4) correspond to 50 % of their vapour pressures at 15 °C. This curve has been calculated using a phase property program. The maximum dew-point temperature is

13 °C at 5,5 MPa. This means that the mixture should be stable during transport and storage in warm or temperate climates. However, when the mixture is used, it will be expanded from the cylinder pressure through a pressure regulator or other pressure-control device, and Joule-Thomson cooling will occur during this operation.

Figure C.1 also shows the cooling curves from 15 °C and 7,0 MPa, and from 15 °C and 10,0 MPa. When expanding from 7,0 MPa, the cooling curve does not impinge upon the two-phase region, whereas it does when expanding from 10,0 MPa. Some liquid will separate from the gas as it passes through the regulator and the composition of the gas exiting will not be the same as that entering. A mixture with such concentrations of C3 and C4 components can therefore be used from a fill pressure of 7,0 MPa, but should not be used from a fill pressure of 10,0 MPa, even though the mixture itself is stable at this pressure. Figure C.1 also includes the dew-point curve for a similar calibration gas mixture, but in which the C3 and C4 components are present at 25 % of their vapour pressures. The maximum dew-point temperature falls to -32 °C at 5,0 MPa, giving a larger safety margin such that no condensation occurs on expansion from 10,0 MPa.

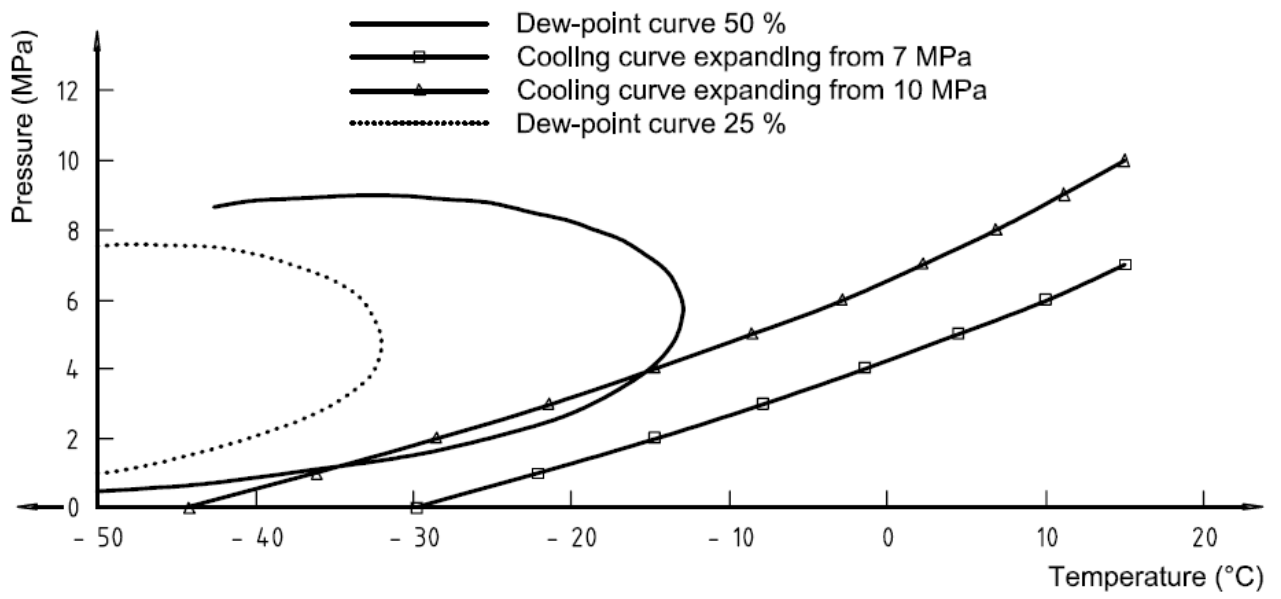


Figure C.1 — Example of dew-point curves and cooling curves

Annex D (normative)

Liquid introduction

D.1 Principle

The introduction of a liquid component into a gas mixture requires dedicated introduction methods and equipment. As the gas mixtures are prepared gravimetrically and as the amount of liquid is normally small due to the vapour pressure, a highly sensitive, low capacity balance is required. The liquid is either introduced into an evacuated cylinder, where it vaporizes, or is introduced as a volume of vaporized liquid.

In some cases, a liquid component may be introduced directly into the cylinder as long as the cylinder undergoes a final mixing stage to ensure complete homogenization.

Several methods of liquid introduction are described that result in a good calibration gas preparation. For a better understanding, some are described in more detail. Other methods may exist with equal or even better performance.

D.2 Methods

D.2.1 General guidance

It is important that the liquid fully vaporizes in the gas mixture and that it also remains in the gaseous phase. Normally the vapour pressure of a component at specified conditions is used to calculate the maximum amount of liquid to be introduced.

IMPORTANT — To prevent condensation the fraction of the vapour pressure shall be kept low enough in relation to the dew-point. This limits the maximum amount fraction to be produced at a certain pressure.

NOTE A maximum of 70 % is usually found sufficient. This is a safety measure for transport conditions, which may differ from production conditions. See also 4.2.2. For guidance on transport see ISO 16664 ^[19].

D.2.2 Syringe method

A gas-tight syringe is filled with the liquid to be introduced. A syringe with a graduated scale is useful for estimating the amount of liquid in the syringe. It is best to first weigh the syringe after filling it, then to weigh it again after injection. The difference between these two weighings corresponds to the amount of liquid introduced.

The liquid is introduced into the vacuum cylinder by injection through a septum that is closed off during pressurization with the matrix gas. An example of this setup is shown in Figure D.1.



Figure D.1 — Example of introduction via syringe

When using this method, it is important to eliminate the loss of component in the syringe and especially in the needle. It is therefore recommended to replace the needle after filling and before weighing. Especially with very volatile components, the remaining liquid droplets may vaporize during weighing.

D.2.3 Glass tube method

A glass tube with one open end is weighed, then filled with liquid. After filling, the tube is sealed by melting the open end of the glass tube. The sealed tube is weighed again. The difference between the two weighings corresponds to the amount of liquid introduced. The glass tube is then packed into the filling line, or even in the gas cylinder, and broken by the high-pressure matrix gas.

It is important to prevent the broken glass from entering the cylinder valve during the filling process and later use.

The sealing of the glass tube will cause some vaporization of the liquid introduced into the tube.

This effect should be evaluated for the different liquids as the effect increases with more volatile components. To prevent this, cool the tube before sealing.

D.2.4 Vapour in a receptacle

This method uses a certain quantity of vapour in a closed receptacle. The receptacle may have various shapes, but spheres are mostly used.

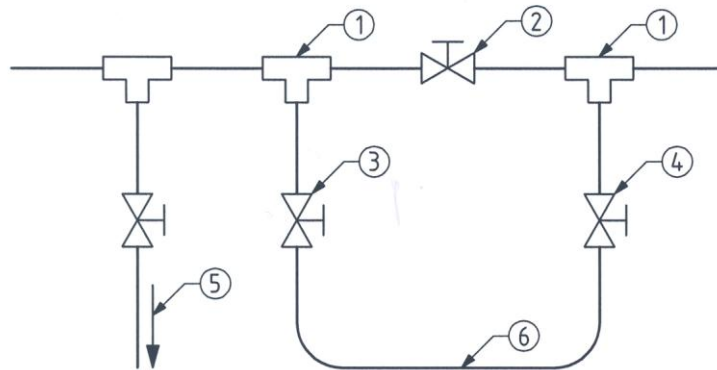
The evacuated receptacle is connected to a flask of liquid, and the vapour allowed to flow into the receptacle until the vapour pressures in the flask and in the receptacle are equal.

It is important that the temperature of the receptacle and the transfer lines be higher than the temperature of the flask of liquid to avoid condensation.

After the system is equilibrated, the receptacle is disconnected and accurately weighed. After weighing, it is connected to the final evacuated cylinder. After equilibration, the receptacle is weighed again to determine the amount of vapour transferred into the cylinder.

D.2.5 U-tube method

A U-tube is typically constructed from stainless steel (see Figure D.2). The length of the U-tube is designed so that the volume is nominally the same as the volume of liquid required. Different volume tubes can easily be made by altering the U-tube length.



- Key**
- 1 T-type connector
 - 2, 3, 4 shut off valves
 - 5 vacuum
 - 6 U-tube line

Figure D.2 — U-tube construction

The U-tube is dismantled so that the U part retains the two shut off valves (3 and 4). The U-tube with open valves is then weighed on a high accuracy balance. Both valves are opened and liquid is then introduced into the U-tube and the valves are then closed. The U-tube plus the liquid is again weighed. The difference between the weighing readings corresponds to the mass of liquid. The U-tube is then reconnected to the filling assembly. One end of the filling assembly is connected to the cylinder to be filled and the other to a gaseous component which is to be introduced. The system excluding the U-tube is then evacuated (valve 2 open, valves 3 and 4 closed).

The gas to be introduced is then allowed to fill the filling assembly. Valve 2 is then closed and valves 3 and 4 are then opened. The filling gas pushes the liquid into the recipient cylinder. Before the final mass of gas has been achieved in the recipient cylinder, valves 3 and 4 should be closed and valve 2 opened. This is to remove any liquid trapped behind valve 2. Once the required mass of gas has been transferred, the recipient cylinder is isolated.

The U-tube method has the advantage that liquids can be introduced into the recipient cylinder at any stage of the cylinder filling process. Unfortunately, the U-tube method can introduce some air contaminants into the recipient cylinder if the correct tube length is not used. Air above the liquid in the U-tube should be kept to a minimum.

D.2.6 Minicylinder method

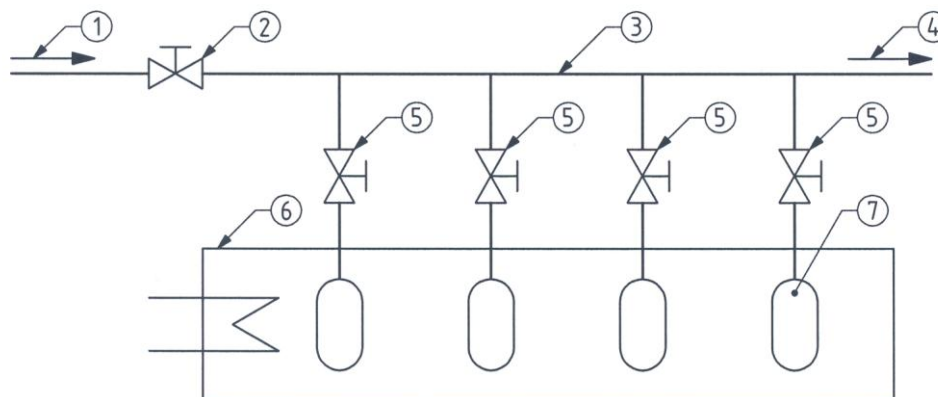
D.2.6.1 General

This method uses a set of minicylinders filled with liquid to be transferred into the calibration gas cylinder.

These minicylinders can be configured in parallel or in series.

D.2.6.2 Parallel configurations

An example for a typical configuration is shown in Figure D.3.



Key

- 1 inlet
- 2 inlet valve
- 3 transfer line
- 4 outlet
- 5 shut off valves
- 6 heating system
- 7 minicylinder

Figure D.3 — Minicylinders in parallel

First, the calculated mass of each component is introduced into each of the evacuated minicylinders (7).

These components are introduced one after the other into the calibration gas cylinder, starting with the component of lowest vapour pressure.

After evacuation of the complete filling system, inlet valve 2 is closed and the valve of the evacuated calibration gas cylinder opened.

The shut off valve (5) of the first minicylinder then is opened to balance the pressure in the filling system (transfer line, minicylinder and calibration gas cylinder).

This step is repeated for each minicylinder.

The remaining components in the transfer system are purged with the matrix gas (pure gas or pre-mixture) or an additional component (pure gas or pre-mixture) through the outlet (4) into the calibration gas cylinder.

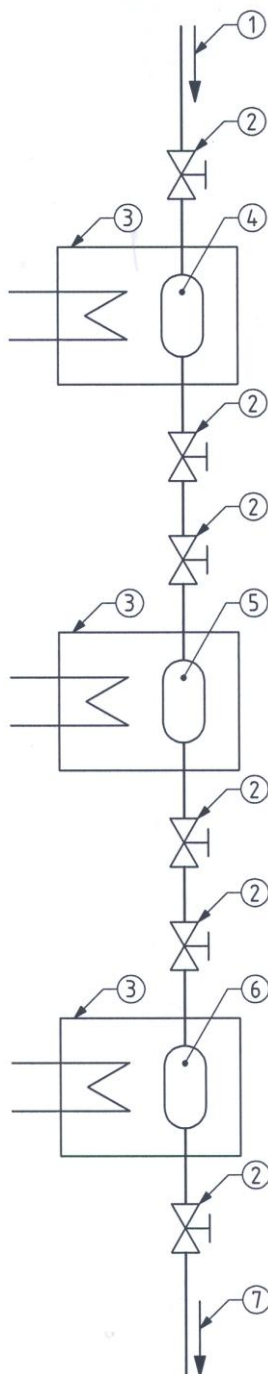
The exact mass of each component is determined by the weighing difference between the minicylinders before and after the filling process (in the calibration gas cylinder).

For components with vapour pressures lower than the vapour pressure of *n*-butane, the minicylinders should be heated during the filling process.

D.2.6.3 Serial configuration

A similar approach is used with three minicylinders combined in line (see Figure D.4).

Again, first the calculated mass of each component is introduced into the evacuated minicylinders.



Key

- 1 inlet transfer line
- 2 two-way valves
- 3 heating system
- 4, 5, 6 minicylinders
- 7 outlet transfer line

Figure D.4 — Minicylinders in series

These components are introduced one after the other through the outlet (7) into the calibration gas cylinder, starting with the component in minicylinder 6.

Starting with the outlet valve of minicylinder 6, one valve after the other, excluding the inlet valve of minicylinder 4, is opened to balance the pressure in the system.

Thereafter, the inlet valve of minicylinder 4 is opened to purge the remaining components with matrix gas (pure gas or pre-mixture) or an additional component (pure gas or pre-mixture) through the outlet (7) into the calibration gas cylinder.

The exact mass of each component is determined by the weighing difference between the evacuated and the filled minicylinders.

NOTE The mass of the remaining air in the connections between the minicylinders and in the transfer line from minicylinder 6 to the calibration gas cylinder can be calculated from these volumes.

The uncertainty contributions should be well estimated.

In cases where 3-way valves are installed for the evacuation of the connections between the minicylinders and in front of minicylinder 6, no remaining air need be considered.

Annex E (informative)

Derivation of the equation for calculating the calibration gas mixture composition

Let $i = 1, 2, \dots, n$ denote the components (including quantified impurities) of the final calibration gas mixture Ω .

Let $A = 1, 2, \dots, P$ denote the parent gases used in the preparation.

The composition of the final mixture Ω is calculated from the following input data:

- m_A is the mass of parent gas A in the final mixture Ω ;
- $x_{i,A}$ is the amount fraction of component i in parent gas A ;
- M_i is the molar mass of component i .

NOTE In this approach, all parent gases are formally considered as n -component mixtures. Typically most of the amount fractions $x_{i,A}$ will be zero.

From the data above, a set of auxiliary data can be determined as follows:

- M_A is the molar mass of parent gas A , given by:

$$M_A = \sum_{i=1}^n x_{i,A} \times M_i \quad (\text{E.1})$$

- $w_{i,A}$ is the mass fraction of component i in parent gas A , given by:

$$w_{i,A} = x_{i,A} \times \frac{M_i}{M_A} \quad (\text{E.2})$$

The composition of the final mixture is derived from the input data in a two-step procedure:

- a) calculate the mass composition, i.e. the mass fractions w_k of the components k in the final mixture;
- b) convert the mass composition to molar composition, i.e. from the mass fractions w_k to the amount fractions x_k of the components k in the final mixture.

The mass fractions w_i are given by:

$$w_k = \frac{\sum_{A=1}^P w_{k,A} \times m_A}{m_\Omega} \quad (\text{E.3})$$

where m_Ω is the mass of the final mixture.

Using Equation (E.2) the mass fractions $w_{k,A}$ are substituted by amount fractions $x_{k,A}$ as follows:

$$w_k = \frac{\sum_{A=1}^P x_{k,A} \times \frac{M_k}{M_A} \times m_A}{m_\Omega} \quad (\text{E.4})$$

Equation (E.4) gives the mass composition of the final calibration gas mixture as a function of the input data, i.e. the molar composition of the parent gases, the molar masses of the mixture components, and the masses of the parent gases determined by weighing.

In the final step the mass fractions w_k are converted into amount fractions x_k , using Equation (E.2) again and applying it to the final mixture Ω .

The result is:

$$y_k = \frac{\sum_{A=1}^P x_{k,A} \times \frac{m_A}{M_A}}{\frac{m_\Omega}{M_\Omega}} \quad (\text{E.5})$$

where M_Ω is the molar mass of the final mixture.

Using the identity

$$\frac{m_\Omega}{M_\Omega} = \sum_{A=1}^P \frac{m_A}{M_A} \quad (\text{E.6})$$

the following result is obtained:

$$y_k = \frac{\sum_{A=1}^P x_{k,A} \times \frac{m_A}{M_A}}{\sum_{A=1}^P \frac{m_A}{M_A}} \quad (\text{E.7})$$

M_A is given in Equation (E.1); this gives the final equation:

$$y_k = \frac{\sum_{A=1}^P \left(\frac{x_{k,A} \times m_A}{\sum_{i=1}^n x_{i,A} \times M_i} \right)}{\sum_{A=1}^P \left(\frac{m_A}{\sum_{i=1}^n x_{i,A} \times M_i} \right)} \quad (\text{E.8})$$

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