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Gas analysis — Preparation of calibration gas mixtures —

Part 1:
Gravimetric method for Class I mixtures

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

Partie 1: Méthode gravimétrique pour les mélanges de Classe I

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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.

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).

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For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information

The committee responsible for this document is ISO/TC 158, *Analysis of gases*.

This first edition of ISO 6142-1 cancels and replaces ISO 6142:2001, which has been technically revised to update the methods of preparation, estimation of the uncertainty, and validation of the composition of gravimetrically prepared calibration gases. It also incorporates the Amendment ISO 6142:2001/Amd.1:2009.

ISO 6142 consists of the following parts, under the general title *Gas analysis — Preparation of calibration gas mixtures*:

— *Part 1: Gravimetric method for Class I mixtures*

A future part dealing with gravimetric method for Class II mixtures.

Introduction

The revision of ISO 6142 was initiated to provide better guidance to the users of this International Standard especially with respect to quality assurance measures and laboratory accreditation. In preparing the revision, it was decided to make accommodation for two types of calibration gas mixtures with different levels of quality assurance and with different levels of measurement uncertainty. The difference in the two classes can be summarized as follows:

Class I type calibration gas mixtures are prepared in accordance with this part of ISO 6142. The mixtures are individually verified. 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.

Class II type calibration gas mixtures are prepared in a similar manner to Class I calibration gas mixtures but these mixtures are not individually verified. Verification of Class II calibration gas mixtures can be based on random verification checks. These checks are monitored by means of statistical quality control to be described in a future part. For mixtures containing identical compounds and nominally identical amount–of–substance fractions, Class II type calibration gas mixtures will always have amount–of–substance fractions with larger uncertainties than their Class I counterparts.

Gas analysis — Preparation of calibration gas mixtures —

Part 1:
Gravimetric method for Class I mixtures

1 Scope

This part of ISO 6142 specifies a gravimetric method for the preparation of calibration gas mixtures in cylinders with traceable values for the amount-of-substance fraction (amount fraction) of one or more components. This part of ISO 6142 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 part of ISO 6142 is only applicable to mixtures of gaseous or totally vaporized components, which may be introduced into the cylinder in the gaseous or liquid state. Both binary and multi-component gas mixtures (including natural-gas type mixtures) are covered by this part of ISO 6142. Methods for the batch production of more than one mixture in a single process are not included in this part of ISO 6142.

This part of ISO 6142 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 unintentionally. This part of ISO 6142 also requires the impurities in each parent gas or liquid used in the preparation of the mixture to be assessed and quantified.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 6141, *Gas analysis — Contents of certificates for calibration gas mixtures*

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

ISO 7504, *Gas analysis — Vocabulary*

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

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

ISO 19229, *Gas analysis — Purity analysis and the treatment of purity data*

ISO/TS 29041, *Gas mixtures — Gravimetric preparation — Mastering correlations in composition*

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

IUPAC, Commission on atomic weights and isotopic abundances: Atomic weights of the elements

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 7504 and ISO/IEC Guide 98-3 apply.

4 Symbols

A_z	atomic weight of element *z*
b_i	estimated amount fraction drift rate of component *i*
k	coverage factor
L_{ij}	limit of detection of impurity *i* in parent gas or liquid *j*
M_i	molar mass of component *i*
M_j	molar mass of parent gas or liquid *j*
M_k	molar mass of component *k*
M_Ω	molar mass of the final mixture
m_j	mass added of parent gas or liquid *j*
m_Ω	mass of the final mixture
q	number of components in the mixture
r	number of parent gases or liquids
p_F	filling pressure
$p_{\mathrm{F},\Omega}$	filling pressure of the final mixture
$p_\mathrm{i}(T_\mathrm{L})$	saturated vapour pressure of component *i* at temperature T_L
R	ideal gas constant
T_F	filling temperature
T_L	lowest temperature to which the gas mixture will be exposed
t_d	decay time
t_s	shelf life of the mixture
$u(...)$	standard uncertainty (of the quantity in parentheses)
$U(...)$	expanded uncertainty (of the quantity in parentheses)
V_cyl	volume of the cylinder
ν_{zi}	stoichiometric coefficient for element *z*
w_i	mass fractions w_i of the components *i* in the final mixture
$w_{i,j}$	mass fraction of component *i* in parent gas or liquid *j*
x_c	amount-of-substance fraction of the “pure” component in the material being analysed
x_i	amount-of-substance fraction of component *i*
$x_{i,j}$	amount-of-substance fraction of component *i* in parent gas or liquid *j*
$x_{k,j}$	amount-of-substance fraction of component *k* in parent gas or liquid *j*
y_k^0	amount-of-substance fraction of component *k* at time $t = 0$

y_k^t	amount-of-substance fraction of component *k* at time *t*
y_i	amount-of-substance fraction of component *i* in the prepared mixture
y_k	amount-of-substance fraction of component *k* in the prepared mixture
$y_{k,\mathrm{ver}}$	analysed amount-of-substance fraction
Z_Ω	compressibility of the final mixture
Ω	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:

a) the determination of the masses added;

b) the conversion of the added masses to amounts of substance, by knowledge of their chemical purity and appropriate relative atomic and/or molecular masses;

c) the verification of the final mixture against independent reference gas mixtures.

For Class II type calibration gas mixtures, the individual verification of the final mixture against independent reference gas mixtures is not required. The verification of Class II type calibration gas mixtures is described in a future part.

The mass of each component is determined by weighing either the supply cylinder, 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 In the case of an addition of a small mass of a specified component, a highly sensitive balance is needed. If such a balance has insufficient capacity to weigh the final mixture, a small added mass can best be determined by weighing a low-volume supply cylinder before and after addition of the component to the main cylinder.

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 components in 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).

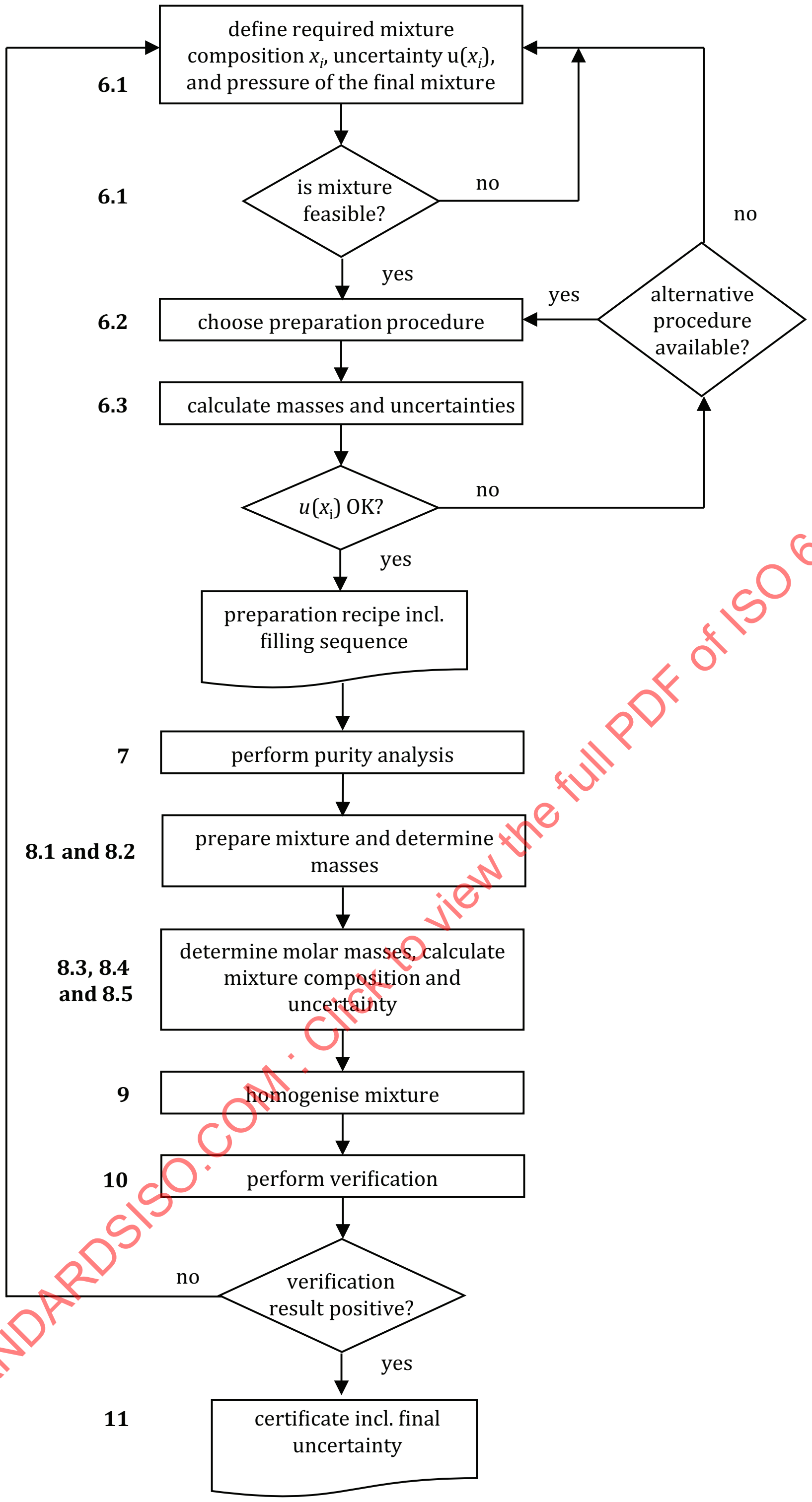


Figure 1 — Scheme for preparation of calibration gas mixtures using gravimetry

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 European Industrial Gases Association (EIGA) documents IGC 39 "The safe preparation of gas mixtures"[23] and IGC 139 "Safe preparation of compressed oxidant-fuel gas mixtures in cylinders"[24].

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

6.1.2 Reactions of mixture components

Before preparing a gas mixture, it is essential to consider possible chemical reactions of 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 the 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 16664 and in ISO 11114 (all parts)[25].

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 performance specifications of the balance to be used .

6.3 Calculation of target masses

Calculate the value of the target masses m_j, of each parent gas or liquid j, using Formula (1).

$$m_j = \frac{y_k \times M_k}{\sum_{i=1}^{q} y_i \times M_i} \times m_\Omega \tag{1}$$

where m_Ω is computed as

$$m_\Omega = \frac{p_{\mathrm{F},\Omega} \times V_{\mathrm{cyl}}}{Z_\Omega \times R \times T_\mathrm{F}} \sum_{i=1}^{q} y_i \times M_i \tag{2}$$

NOTE 1 Formula (1) applies to pure gases and liquids only.

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 2 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 this 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. The fill pressure is also set after consideration of the Joule-Thomson cooling curve (see Annex C).

— During the storage of the gas mixture, the storage temperature shall be set safely over the dew-point temperature of the mixture that depends upon its composition and filling pressure.

— 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

For the preparation of calibration gas mixtures, purity analysis is a critical step and the procedures to be followed shall be in accordance with ISO 19229. The presence of significant impurities in the parent materials should be minimized by selecting pure gases or liquids of sufficient high quality grades. The outcome of purity analysis will be a table tabulating the amount fractions of all measured and otherwise estimated impurities with their values and associated uncertainties.

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. In some cases, cylinder surface treatment steps will be required to allow for preparation of specific calibration gas mixtures.

NOTE 1 Most weighing procedures require the use of a tare. In this case it will be necessary to select two cylinders made from the same material that have nominally the same internal and external volumes. One will be required for the final mixture and one for use as the tare (see Annex A).

NOTE 2 Typical examples of cylinder surface treatment steps range from drying the interior of the cylinder in an oven to dedicated vapour deposition.

8.2 Determination of masses and their uncertainties

The mass of each component added to the cylinder shall be determined by weighing. 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 (electronic) 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 Atomic weights and molar masses

The molar masses of the components and their uncertainties are required for the conversion of mass fraction to amount fraction. The values of the atomic weights used to calculate molar masses shall be taken from the most recent publication of the commission on atomic weights and isotopic abundances of the International Union of Pure and Applied Chemistry (IUPAC). A practical approach for the interpretation of the standard atomic weights is given in Annex E.

For other conversions between quantities, 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 Formula (3):

$$y_k = \frac{\sum_{j=1}^{r}\left(\frac{x_{k,j} \times m_j}{\sum_{i=1}^{q} x_{i,j} \times M_i}\right)}{\sum_{j=1}^{r}\left(\frac{m_j}{\sum_{i=1}^{q} x_{i,j} \times M_i}\right)} \tag{3}$$

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

8.5 Calculation of gravimetric uncertainty

The uncertainty of the amount fraction computed from gravimetry [$u(y_{k,\text{grav}})$] is calculated by the application of the law of propagation of uncertainty to Formula (3):

$$u^2(y_{k,\text{grav}}) = \sum_{i=1}^{q}\left(\frac{\partial y_k}{\partial M_i}\right)^2 \times u^2(M_i) + \sum_{j=1}^{r}\left(\frac{\partial y_k}{\partial m_j}\right)^2 \times u^2(m_j) + \sum_{j=1}^{r}\sum_{i=1}^{q}\left(\frac{\partial y_k}{\partial x_{i,j}}\right)^2 \times u^2(x_{i,j}) \tag{4}$$

Expressions for the sensitivity coefficients appearing in Formula (4) are given in Annex G. The uncertainty in the mass of each of the parent gases [$u(m_j)$] can be calculated according to methods described in Annex A and Annex B.

Information on how to deal with correlated input parameters is given in ISO/TS 29041.

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.

NOTE 1 Homogeneity is defined in ISO 7504:2015 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 parent 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, by applying heat, or by other procedures (e.g. dip tube filling). The minimum duration of this homogenization should be based on prior experimental knowledge.

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.

NOTE 3 As indicated in ISO 16664, re-homogenization of the calibration gas mixture may be required for some specific mixtures after longer storage periods.

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 the amount fraction of component k using a linear decay model following Formula (5):

$$y_k^t = y_k^0 - b_k \cdot t_d \tag{5}$$

The drift rate shall be determined on a case-by-case basis; it cannot be predicted from first principles. This part of ISO 6142 can only be applied when the linear decay model [Formula (5)] 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 a reference material or certified reference material) as the time interval during which the producer of the reference material warrants its stability.

The contribution to the uncertainty in the amount fraction of component k 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 Formula (6):

$$u\ (y_{k,\mathrm{stab}}) = b_k \times t_s \tag{6}$$

NOTE 2 Formula (6) results in an absolute value for uncertainty.

NOTE 3 When no drift is observed, the value for b_k can be zero and the resulting uncertainty $u(y_{k,\mathrm{stab}})$ will also be zero.

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

NOTE 4 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.

Knowledge of composition of the gas mixture composition coupled with the chemical reactivity of the components and possible reactions shall be taken into account when designing a stability study. If the stability study provides sufficient evidence of stability of a 2-component calibration gas mixture at a certain relatively low amount fraction, a further testing at higher amount fractions is unnecessary. However, this is not the case for components that polymerise or react at higher amount fractions.

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 when 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 significant 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 of 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.

The stability period determined from the study is proportional to 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.

9.2.2.2 Chemical nature of components

The chemical nature of the components influences the stability of the gas mixture and shall be taken into account. 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. an oxygen impurity in nitrogen may react with nitric oxide. Careful consideration shall be made to ensure the reactivity of the components and the materials used give the mixture the best chance to remain stable. ISO 16664 (and ISO 11114 (all parts)[25]) shows material compatibility for some components and materials.

Knowledge of possible reactions between components can give information on the required purities of parent gases and pre-mixtures composition.

Gases such as saturated hydrocarbons and some permanent gases (for example N_2, Ar, He) can be considered as being unconditionally stable and these components when used in a gas mixture may only require a stability evaluation to a limited extent, whereas more reactive components such as SO_2, NO, NO_2 require a more rigorous stability evaluation and may involve the use of highly pure components and proprietary cylinder passivation techniques to allow the mixture to remain stable long enough for the end users requirements.

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 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 are then used to calculate the level at which the instrument can discriminate between two statistically different amount fractions, i.e. the instrument's resolution.

EXAMPLE A stability study involving a nitric oxide in nitrogen mixture at an amount fraction of 100 µmol/mol is being performed. A traceable reference gas is used to calibrate the instrument at nominally 100 µmol/mol and 10 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 µmol/mol. For two measurements to be statistically different, their difference needs at least to be twice the standard deviation, i.e. 0,28 µmol/mol. Therefore, the smallest difference which can be quantified is 0,28 µmol/mol, conversely if the stability measurements after calibration are less than 0,28 µmol/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 performed with at least two identical gas cylinders containing gas mixtures of the same nominal composition. The greater the number of cylinders involved in the study the more confidence can be gained in the claimed shelf life.

9.2.2.5 Duration of the study and frequency of analysis

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

NOTE A commercial consideration may result in a stability trial being conducted such that a potential customer may order another gas mixture on an annual basis. However, a technically driven approach may result in a study where the measurements are continued until the gas mixture has been degraded and a safety factor retrospectively applied. This needs to be assessed on a case-by-case basis.

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. One approach for assessing the stability of gas mixtures is given in ISO 16664:2004, Annex A.

9.2.4 Calculation of the preparation uncertainty

When calculating the uncertainty from stability, some relatively small drift effect may simply be accounted for in the final uncertainty when estimates can be derived from in house experiments or open literature. Examples are the possible effects of adsorption of certain components or the effect of the lowering of pressure inside the cylinders due to the use of the contained gas.

Formula (7) shall be used to calculate the preparation uncertainty:

$$u(y_{k,\mathrm{prep}})=\sqrt{u^2(y_{k,\mathrm{grav}})+u^2(y_{k,\mathrm{stab}})} \tag{7}$$

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.

The composition of a calibration gas mixture can only be considered 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;

— comparison with a calibration gas mixture prepared by a validated implementation of a dynamic method according to one of the parts of ISO 6145.[20]

In the case of verification of calibration gas mixtures where no appropriate reference gas mixtures are available and no dynamic method is applicable, verification can also be achieved by demonstrating consistency between several nominally similar prepared mixtures prepared by a method consistent with this part of ISO 6142.

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 analytical measurement used for the verification [$u(y_{k,\text{ver}})$] shall take account of the following:

- 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 following:

- 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:

$$\left|y_{k,\text{prep}} - y_{k,\text{ver}}\right| \le 2\sqrt{u^2(y_{k,\text{prep}}) + u^2(y_{k,\text{ver}})} \tag{8}$$

where the preparation uncertainty is calculated by Formula (7).

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 amount fraction of component *k* in the final mixture shall be calculated using Formula (9):

$$u_c(y_k) = \frac{1}{2}\sqrt{u^2(y_{k,\text{prep}}) + u^2(y_{k,\text{ver}}) + (y_{k,\text{prep}} - y_{k,\text{ver}})^2} \tag{9}$$

NOTE 1 A method for deriving Formula (9) is given in Annex H.

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

$$U(y_k) = k \times u_c(y_k) \tag{10}$$

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 level of approximately 95 %.

The certificate shall be prepared according to ISO 6141 and shall indicate that this is a Class I calibration gas mixture in accordance with ISO 6142-1.

The expiry date shall be calculated from the shelf life used in 9.2.

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 (electronic) 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 maximum 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 readability of 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 and readability of 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. 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 or its authorized representative, 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 References [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 mass 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 [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 6). 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. An evacuation step may be necessary to remove air trapped in dead volumes 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 temperature effects can be expected (Joule-Thomson effect). 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, close the pure gas or pre-mixture 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 examples

B.1 General

This Annex provides some examples of the implementation of the normative text in this part of ISO 6142 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 electronic balance.

a) Place the tare cylinder on the balance, and when stability is reached (usually within 1 min) record the value (T_1).

b) 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 min), note the reading on the balance terminal controller (X_1).

c) 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 mass of component added.

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

a) Place the tare cylinder on the balance, and when stability is reached (usually within 1 min), “tare” the reading on the terminal control unit such that it reads zero.

b) 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 min), note the reading on the balance terminal controller (X_1).

c) Tare the reading on the terminal control unit to zero and place the preparation cylinder at the side of the balance.

d) 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 a) to c) should be repeated until 3 consecutive readings in the series:

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

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 mass 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 l cylinder filled to approximately 100 bar. The uncertainties used for the weighings are: 10 mg for the cylinder on a top-pan balance, 0,20 mg for a “large” weighing vessel used to add a component to a cylinder, and 0,05 mg for a “small” vessel. Standard uncertainties are denoted by u and expanded uncertainties ($k = 2$) as U. Note, the values shown for $U(x)$ also include a contribution from the uncertainty of the molecular masses.

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-l cylinder on top-pan balance**		**“Large” vessel**	**“Small” vessel**
Nominal amount fraction (x)/ mol/mol	10^{-1}	10^{-2}	10^{-3}	10^{-4}
m_a/g	116,709	11,671	1,167 09	0,116 71
$u(m_a)$/mg	10	10	0,20	0,05
m_b/g	1 050,502	1 155,552	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 methane 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 methane gravimetrically

Method used for weighing minor component	**“Large” vessel**		**“Small” vessel**	
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	0,20	0,20	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
$[U(x)/x] \times 100$	0,012	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 ISO 19229 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 µmol/mol	Standard uncertainty in amount fraction µmol/mol[a]
N_2	GC-TCD	395	20
CO_2	GC-TCD	40	4
O_2	GC-TCD	13	10
H_2	GC-TCD	110	6
CH_4	GC-FID	12	7
H_2O	n/a[b]	10	5,77
CO	Calculated	999 420	26

[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 mentioned in ISO 19229, 6.3 was therefore used. The estimated GC-TCD method limit of detection was 20 µmol/mol, so an amount fraction value of half of this (i.e. 10 µmol/mol) was assigned and the standard uncertainty was calculated assuming a rectangular distribution.

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 Formula (C.1).

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

For $p_F > 5 \times 10^6$ Pa (50 bar), Formula (C.1) 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].

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
n-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 (C_3), 2-methylpropane (C_4) and *n*-butane (C_4) 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 C_3 and C_4 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 C_3 and C_4 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.

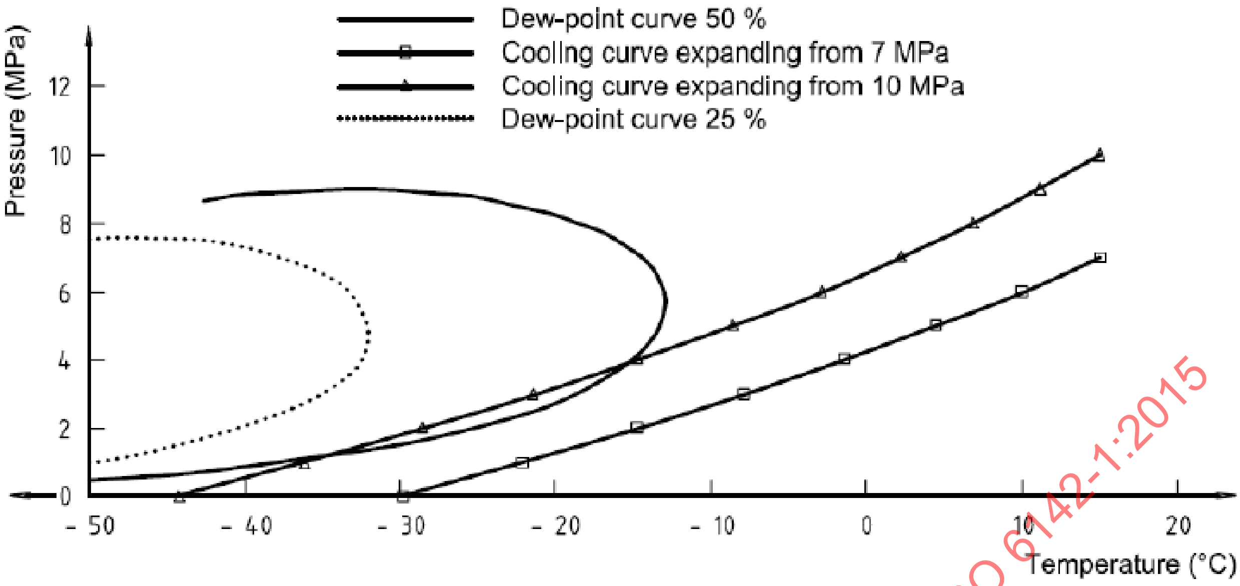


Figure C.1 — Example of dew-point curves and cooling curves

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, 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 saturated 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 6.4. For guidance on transport, see ISO 16664.

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 mass of liquid introduced.

The liquid is introduced into the evacuated 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 mass 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.

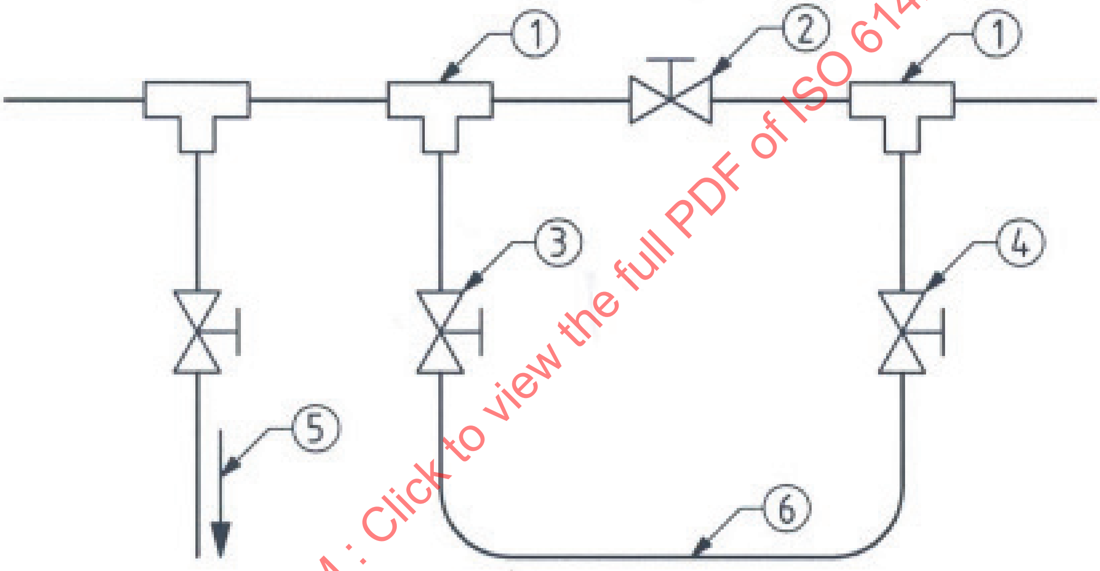
The evacuated receptacle is connected to a flask of liquid, and the vapour allowed to flow into the receptacle until the vapour pressures in the flask and in the receptacle are equal.

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 mass 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 with valve (2) open and 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 Mini cylinder method

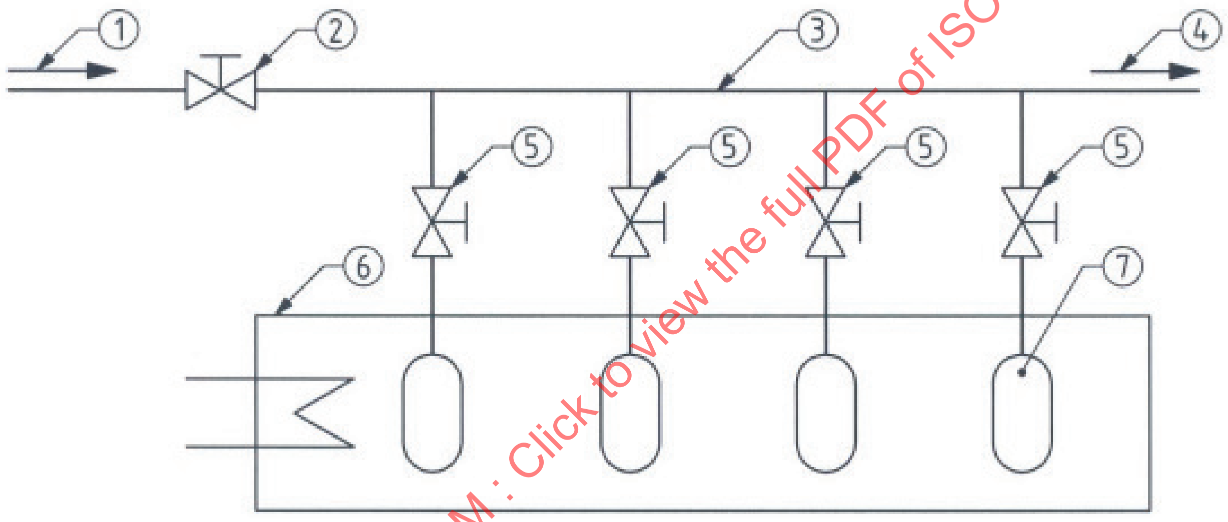
D.2.6.1 General

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

These mini cylinders 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 transfer line
5 shut off valves
6 heating system
7 mini cylinder

Figure D.3 — Mini cylinders in parallel

First, the calculated mass of each component is introduced into each of the evacuated mini cylinders (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 mini cylinder then is opened to balance the pressure in the filling system (transfer line, mini cylinder, and calibration gas cylinder).

This step is repeated for each mini cylinder.

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.

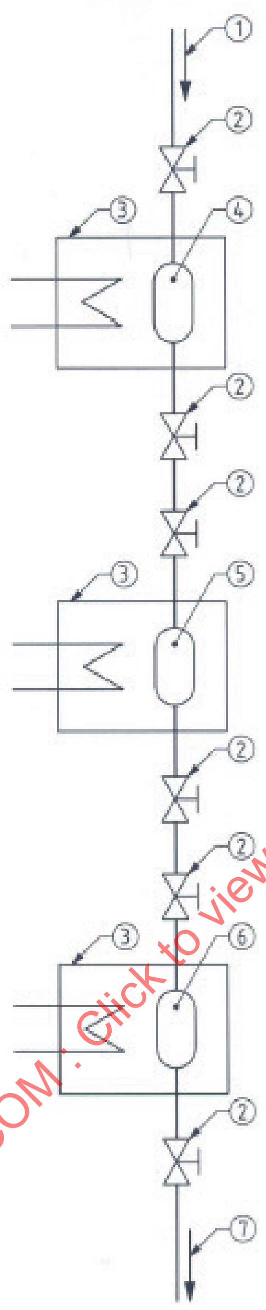
The exact mass of each component is determined by the weighing difference between the mini cylinders before and after the filling process (in the calibration gas cylinder).

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

D.2.6.3 Serial configuration

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

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



Key

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

Figure D.4 — Mini cylinders in series

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