INTERNATIONAL STANDARD

ISO 6142

Second edition
2001-04-01

Gas analysis — Preparation of calibration gas mixtures — Gravimetric method

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

Reference number
ISO 6142:2001(E)

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Printed in Switzerland

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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 3.

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 International Standard may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

International Standard ISO 6142 was prepared by Technical Committee ISO/TC 158, *Analysis of gases,* in collaboration with ISO/TC 193, *Natural gas*.

This second edition cancels and replaces the first edition (ISO 6142:1981), which has been revised to update the methods of preparation, estimation of the uncertainty and of validation of gravimetrically prepared calibration gases.

Annexes A to G of this International Standard are for information only.

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 of which the target accuracy of the composition has been pre-defined. It is applicable only to mixtures of gaseous or totally vaporized components which do not react with each other or with the cylinder walls. A procedure is given for a method of preparation based on requirements for the final gas mixture composition to be within pre-set levels of uncertainty. Multi-component gas mixtures (including natural gas) and multiple dilution mixtures are included in this International Standard and are considered to be special cases of the single component gravimetric preparation method.

This International Standard also describes the procedure for verifying the composition of gravimetrically prepared calibration gases. Provided rigorous and comprehensive quality assurance and quality control procedures are adopted during the preparation and validation of these gravimetric gas mixtures, calibration gases of the highest accuracy can be obtained for a wide range of gas mixtures, in comparison with other methods of preparing such gases.

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:—[1], *Gas analysis — Comparison methods for determining and checking the composition of calibration gas mixtures.*

ISO/IEC 17025, *General requirements for the competence of testing and calibration laboratories*.

IUPAC, *Commission on atomic weights and isotopic abundances: Atomic Weights of the Elements, biennial review*.

3 Principle

Calibration gas mixtures are prepared by transferring parent gases (pure gases or gravimetrically prepared mixtures of known composition) quantitatively from supply cylinders to the cylinder in which the calibration gas mixture will be contained. The amount of gaseous component added from the parent gas is determined by weighing after each successive addition.

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[1] To be published. (Revision of ISO 6143:1981)

The amount of parent gas added to the cylinder in which the calibration gas mixture will be contained is determined by weighing either the supply cylinder or, alternatively, 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 gas added. The choice between these two weighing methods depends on which one represents the most suitable procedure for preparing the specified mixture. For example, the addition of small amounts of a specified component may best be performed by weighing a small, low-volume supply cylinder, before and after addition, on a highly sensitive, low-capacity balance.

A single-step preparation method may be used where the amount of each gaseous component required is large enough to accurately measure the mass of the cylinder, in which the calibration gas mixture will be contained, at each addition within the required composition uncertainty of the final calibration gas mixture. Alternatively, a multiple dilution method may be used to obtain a final mixture with acceptable uncertainty, particularly when low concentrations of the minor components are required. In this method, “pre-mixtures” are gravimetrically prepared and used as parent gases in one or more dilution steps.

The mass fraction of each component in the final calibration gas mixture is then given by the quotient of the mass of that component to the total mass of the mixture.

The gravimetric method scheme for preparing calibration gas mixtures, based on pre-set requirements for composition and the level of uncertainty, is given as a flow chart in Figure 1. The individual steps are explained in more detail in clause 4 (reference is given to the subclause for each step in Figure 1). An example of the gravimetric method scheme for preparing a calibration gas mixture following the Figure 1 flow chart is given in annex A.

4 Preparation of the mixture

4.1 Mixture composition and uncertainty

The composition of the final gas mixture is, by the principle of the gravimetric method, defined by the mass of each component. Gas composition is preferentially expressed as a mole fraction (mol/mol). If other quantities of composition are required (for example mass concentration or volume fraction) then the applicable conditions (pressure and temperature) shall be given and the additional uncertainty contributions shall be determined and considered in the calculation of the uncertainty in the composition of the calibration gas. The uncertainty of the final mixture composition is expressed as an expanded uncertainty, i.e. the combined standard uncertainty multiplied by a coverage factor.

The molar masses of the components, and their uncertainties, needed for the conversion of mass fraction to mole fraction, shall be derived using the most recent publication of the commission on atomic weights and isotopic abundances of the International Union of Pure and Applied Chemistry (IUPAC).

4.2 Feasibility of obtaining the gas mixture

4.2.1 General

Gas mixtures potentially capable of reacting dangerously shall be excluded for safety reasons. These phenomena shall be taken into account when considering the feasibility of preparing the required gas mixture, described in 4.2.2 to 4.2.4.

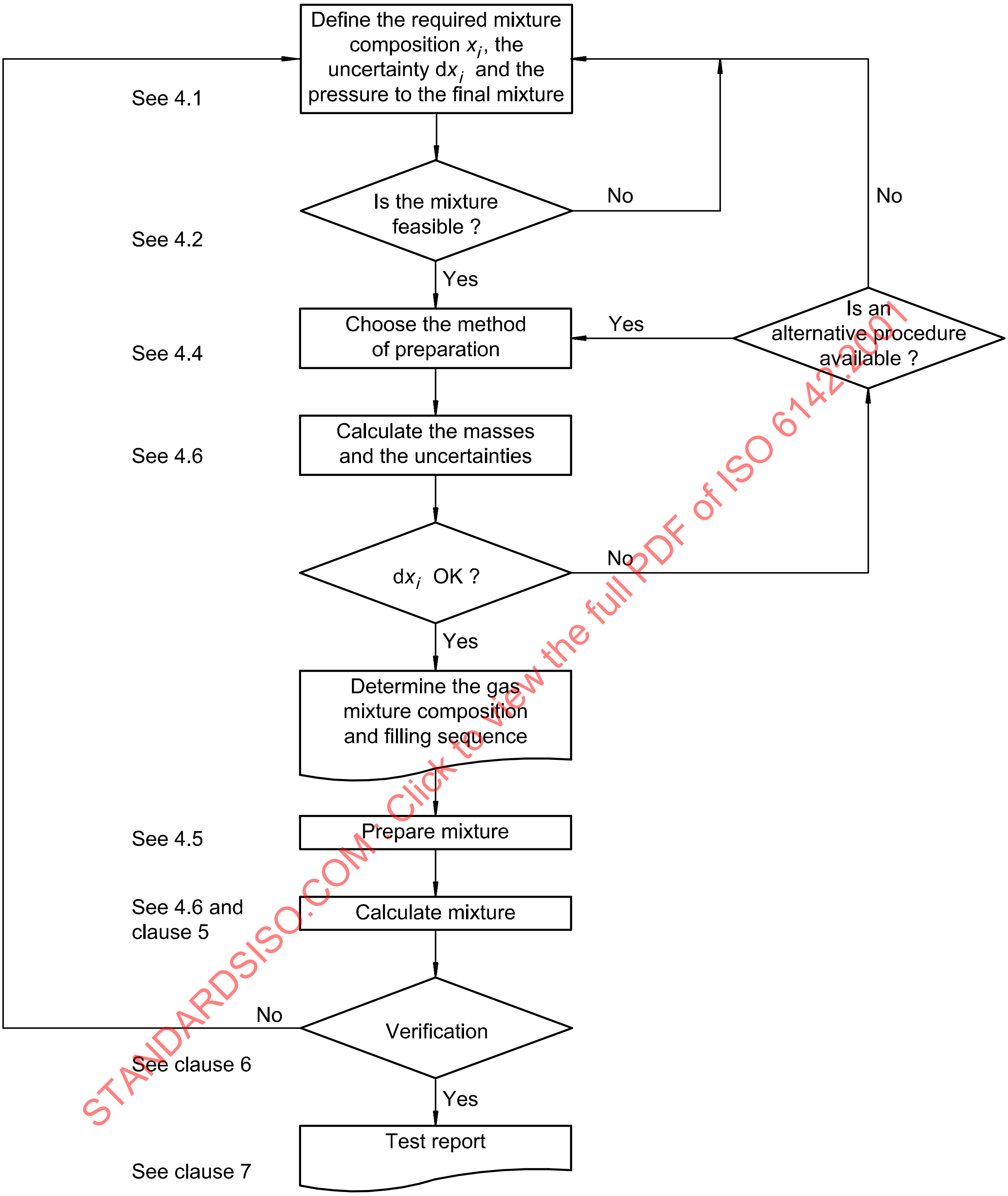

Figure 1 — Gravimetric method scheme for preparing calibration gas mixtures

4.2.2 Condensation of the vapour to either a liquid or a solid phase

When preparing, storing or handling gas mixtures which contain condensable components (see annex B), 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 informative annex B, 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 B.2 for a natural gas mixture.

4.2.3 Reactions between mixture components

Before preparing a gas mixture, it is necessary to consider possible chemical reactions between the components of the mixture. The method cannot be used to prepare mixtures

- containing potentially interactive substances (e.g. hydrochloric acid and ammonia),
- producing other possible dangerous reactions including explosions (e.g. mixtures containing flammable gases and oxygen),
- producing strong exothermic polymerizations (e.g. hydrogen cyanide), and
- which can decompose (e.g. acetylene).

Exceptionally this method can be used for substances undergoing dimerization, such as NO_2 to N_2O_4, which is a reversible reaction.

A comprehensive compilation of reactive combinations is not available. Therefore, chemical expertise is necessary to assess the stability of a gas mixture.

For dangerous reactions and dangerous combinations, to be excluded for safety reasons, some information can be found in regulations on dangerous goods and in gas supplier handbooks.

4.2.4 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 should 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.

Information on the compatibility of gases with container materials is given in gas sampling guidelines, corrosion tables and gas supplier handbooks.

4.3 Purity analysis of primary gas standards

The accuracy achievable by the gravimetric method will depend significantly on the purity of the parent gases used for the preparation of the calibration gas mixture. Impurities in the parent gases are often one of the most critical contributors to the uncertainty of the final mixture composition. The uncertainty contributions depend on the amount of impurities present in the pure, parent gases and upon the accuracy with which these impurities have been measured. In many cases the purity of the major component (matrix gas) is of most importance. This is especially true when the mole fraction of the minor component is low and is likely to be an impurity in the major component. It is also important to evaluate critical impurities that may react with the minor component (e.g. oxygen present in pure nitrogen will react with NO to form NO_2). The result of purity analysis of parent gases shall be incorporated into a purity table containing the mole (or mass) fractions of all components with accompanying uncertainties derived from analysis.

Generally, impurities in a nominally “pure” parent gas are established by analysis and the mole fraction of the major component is conventionally determined by difference such that

$$x_{\text{pure}} = 1 - \sum_{i=1}^{N} x_i \tag{1}$$

where

x_i is the mole fraction of impurity i, determined by analysis;

N is the number of impurities likely to be present in the final mixture;

x_{pure} is the mole fraction “purity” of the “pure” parent gas.

When an impurity, likely to be present in the “pure” parent gas, is not detectable by the analytical method used, the mole fraction of the expected impurity shall be set equal to half of the value of the detection limit of the analytical method. The uncertainty of the determination of this mole fraction is based upon a rectangular distribution between zero and the value of the detection limit of the analytical method. In this way, the gravimetric method assumes that there is an equal likelihood that the impurity may be present in the “pure” parent gas at a level up to its value of the detection limit. Hence, the content of an undetected impurity forms a rectangular distribution from which its standard uncertainty is defined as half the value of the detection limit divided by $\sqrt{3}$.

4.4 Choice of preparation procedure

When choosing a suitable preparation procedure, a number of considerations shall be made to ensure the most appropriate method is used. The following is a list of parameters which shall be considered:

- pressure at which the gases are available and possibility of condensation (see annex B);
- maximum filling pressure of the cylinder to be used;
- established composition of each parent gas mixture used;
- filling method, i.e. direct method, multiple dilution, transfer method (use of small cylinder separately weighed on a low-capacity, high-resolution balance);
- characteristics of the type of balance to be used with its determined performance specifications;
- requirements for the preparation tolerance.

First calculate the value of the masses desired, or target masses m_i, of each component i, using equation (2).

$$m_i = \frac{x_i M_i}{\sum_{j=1}^{N} x_j M_j} \cdot m_\mathrm{f} \tag{2}$$

where

x_i is the mole fraction of component i;

x_j is the mole fraction of component j;

M_i is the molar mass of component i;

M_j is the molar mass of component j;

N is the number of components in the final mixture;

m_f is the mass of final mixture.

After the target masses have been calculated, a preparation procedure is selected and the uncertainties associated with the preparation process are calculated. If the calculated uncertainty for that procedure proves to be unacceptable, another procedure shall be adopted. It may be necessary to perform an iterative process to select a procedure with acceptable uncertainty.

These considerations result in a preparation procedure whereby a filling sequence consisting of several stages is selected in which gases are transferred into a cylinder in which the calibration gas mixture will be contained and subsequently weighed. Each stage has its own associated uncertainty and when combined, remain within the required level of uncertainty. This procedure shall be used in the subsequent preparation.

4.5 Preparation of the mixture

Precautions to be taken when weighing, handling and filling cylinders are given for information in annex C.

To achieve the intended composition of the mixture, a tool is required. Normally the parameters used in targeting this composition are pressure and/or mass. When pressure is used for targeting this composition, temperature effects, resulting from the pressurization and the compressibility of the introduced components, is of importance. In particular, non-ideal behaviour of certain components makes it difficult to establish a simple relationship between added pressure and added mass. However, the compression factor, which quantifies these deviations from ideal behaviour, is a function of pressure, temperature and composition and can be calculated and used to predict the required pressure.

A more direct way of targeting the desired masses is by use of a balance on which the cylinder is placed to observe the difference in mass which occurs during transfer.

4.6 Calculation of the mixture composition

The mole fractions of the components in the final mixture are calculated using equation (3):

$$x_i = \frac{\sum_{A=1}^{P} \left(\frac{x_{i,A} \cdot m_A}{\sum_{i=1}^{n} x_{i,A} \cdot M_i} \right)}{\sum_{A=1}^{P} \left(\frac{m_A}{\sum_{i=1}^{n} x_{i,A} \cdot M_i} \right)} \tag{3}$$

where

x_i	is the mole fraction of the component i in the final mixture, $i = 1,..., n$;
P	is the total number of the parent gases;
n	is the total number of the components in the final mixture;
m_A	is the mass of the parent gas A determined by weighing, $A = 1,..., P$;
M_i	is the molar mass of the component i, $i = 1,…, n$;
$x_{i,A}$	is the mole fraction of the component i, $i = 1,…, n$, in parent gas A, $A = 1,..., P$.

A method for deriving this formula is given for information in annex D.

5 Calculation of uncertainty

5.1.1 The uncertainty in the values of the mole or mass fractions of the components in a gravimetrically prepared calibration gas mixture indicates the dispersion of values which can reasonably be attributed to these fractions.

The procedure for evaluating the uncertainty may be summarized in 5.1.2 to 5.1.7.

5.1.2 Identify the steps taken in the preparation procedure. Following equation (3) in 4.6, three categories can be identified that will influence the uncertainty:

- the uncertainty in the weighing of the parent gases;
- the uncertainty in the purity of the parent gases;
- the uncertainty in molar masses.

NOTE The parent gases may themselves be gravimetrically prepared mixtures.

5.1.3 For each step in the gravimetric preparation procedure, a list shall be made of all sources of uncertainty, i.e., a list of all factors that may influence the resulting composition. A list of possible error sources is given for information in annex E. Some of these uncertainty contributions, for example the standard deviation in the repeated weighings, can be determined by repeated measurements (type A evaluation). For a well-characterized measurement under statistical control, a combined or pooled estimate of variance s_p^2 (or a pooled experimental standard deviation s_p) that characterizes the measurement may be available. In such cases, when the value of the measurand q is determined from n independent observations, the experimental variance of the arithmetic mean $\overline{q}$

of the mean observations is more closely estimated by s_{p}^2/n than by s_{q}^2/n and the standard uncertainty more closely estimated by $u = s_{\mathrm{p}}/\sqrt{n}$. For uncertainty contributions that cannot be estimated by repeated measurements (type B evaluation), a realistic evaluation should be made to estimate this contribution. This applies, for example, to adsorption/desorption effects and thermal effects on the cylinder that influence the balance. Variations in some parameters can be decreased by monitoring and/or controlling these and then calculating the appropriate correction factors. For example, the uncertainty of the buoyancy effect may be decreased by accurately monitoring the ambient pressure, humidity and temperature conditions and using these to calculate the density of air at the time of weighing. Each significant uncertainty contribution shall be evaluated as a standard uncertainty, i.e. as a single standard deviation.

NOTE More details about type A and type B evaluations of standard uncertainty are given in the Guide to expression of uncertainty in measurement [17].

5.1.4 For each contribution to the total uncertainty, decide which ones merit evaluation (significant contributions) and which ones can be neglected (insignificant contributions). As the total certainty is the sum of squared contributions, a contribution equalling less than 1/10 of the largest contribution can safely be neglected.

NOTE This method cannot always be applicable to the purity analysis of the parent gases, as some insignificant impurities can be critical to the mixture under preparation (for example, some impurities can react with the minor component). In such cases, an evaluation of the influence of the parent gas purity on the contribution to total uncertainty is necessary.

5.1.5 The combined uncertainty due to the contributions from the molar masses of the components, the weighing results and the purity analyses is obtained by uncertainty propagation of equation (3) in 4.6. In this equation, the targeted component quantities x_i are expressed as functions of a number of input quantities y_1, y_2, ..., y_q, i.e.

$$x_i = f_i(y_1, y_2, \ldots, y_q) \tag{4}$$

Here the input quantities y_i comprise the molar masses M_j, the parent gas masses m_A, and the mole fractions $x_{j,A}$. According to the rules of uncertainty propagation the standard uncertainties $u(x_i)$ are given as follows:

$$u^2(x_i) = \sum_{r=1}^{q} \left(\frac{\partial f_i}{\partial y_r} \right)^2 \cdot u^2(y_r) + 2 \sum_{r=1}^{q-1} \sum_{s=r+1}^{q} \left(\frac{\partial f_i}{\partial y_r} \right) \left(\frac{\partial f_i}{\partial y_s} \right) \cdot u(y_r, y_s) \tag{5}$$

In this equation $u(y_r)$ are the standard uncertainties of the input quantities, and $u(y_r, y_s)$ are the covariances between different input quantities, should these be correlated.

Correlations can be made, for example, between different parent gas masses m_A, m_B, if these are determined as differences between the results of successive weighings. Correlations can also be made between the mole fractions $x_{j,A}$, $x_{k,A}$ of different components in the same parent gas, due to the fact that these mole fractions add up to unity. To avoid making such correlations, the primary input quantities can be considered instead. For example, in the case of parent gas masses, these are the results of successive weighings, starting with the empty cylinder in which the calibration gas mixture is to be contained (see informative annex C). In the case of the mole fractions of parent gas components, the problem of correlation can be resolved by expressing the mole fraction of the main component as the difference of the sum of the mole fractions of all the other components from unity (see 4.3), which are generally uncorrelated. If, in this manner, the targeted component quantities x_i have been expressed as functions of uncorrelated input quantities z_1, z_2, ..., z_p, i.e.

$$x_i = g_i(z_1, z_2, \ldots, z_p) \tag{6}$$

the combined uncertainties $u(x_i)$ are simply given by:

$$u^2(x_i) = \sum_{t=1}^{p} \left(\frac{\partial g_i}{\partial z_t} \right)^2 \cdot u^2(z_t) \tag{7}$$

or by:

$$u^2(x_i) = \sum_{t=1}^{p} \left[c_i \cdot u(z_t) \right]^2 \equiv \sum_{t=1}^{p} u_t^2(x_i) \tag{8}$$

where c_i, the sensitivity coefficient is given by:

$$c_i \equiv \frac{\partial g_i}{\partial z_t}, \quad u_t(x_i) \equiv \left| c_i \right| \cdot u(z_t)$$

5.1.6 The total uncertainty is given by the result of this calculation, combined with the contributions from all other sources of significant error. Simple methods for evaluating uncertainty contributions based on estimates of maximum errors are described in annex F.

NOTE The total uncertainty is only applicable to stand-alone applications of single analyte contents. In any joint application of several analyte contents or the complete composition, covariances have to be taken into account, whose estimation is beyond the scope of this International Standard.

5.1.7 In order to obtain the expanded uncertainty, the combined standard uncertainty is multiplied by the coverage factor, k.

NOTE 1 A coverage factor, k, is typically in the range from 2 to 3.

NOTE 2 Within ISO TC 158, a coverage factor of $k = 2$ has been agreed, unless specific reasons necessitate another choice.

NOTE 3 For a normal distribution, a coverage factor of $k = 2$ corresponds to a coverage probability of approximately 95 %.

More information on the estimation of corrections and correction uncertainty is given for information in annex F. A computer program implementing the recommended methods for calculating gas mixture composition as well as uncertainty is given for information in annex G.

6 Verification of calibration gas mixture composition

6.1 Objectives

The objective of verifying the composition of a calibration gas mixture is to check that the composition, calculated from the gravimetric process, is consistent with measurements made on the mixture by independent means, for example by an analytical comparison method. This verification acts to highlight significant errors in the preparation process of the individual gas mixture. Moreover, further checks may be required over a period of time to demonstrate the stability of specific mixtures.

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

a) establishing consistency between prepared mixtures and appropriate traceable standards (see note);

b) establishing consistency between several nominally similar prepared mixtures;

c) monitoring continuing production of validated mixtures using a suitable statistical process control method.

NOTE A traceable standard refers to a mixture of appropriate metrological quality that is traceable, through an unbroken chain of comparisons with stated uncertainties, to a national or an International Standard.

When seeking to verify a prepared mixture and confirm its composition, the mixture components may all be in a range where suitable traceable standards are readily available, so that consistency may easily be demonstrated. However, often the reason for relying on gravimetric preparation is that one or more components are outside the range where traceable standards already exist, so verification shall be performed by other methods, such as demonstrating internal consistency of prepared mixtures and the capability of the process in suitable ranges where traceable standards are available.

In practice, one of the two cases in 6.2 and 6.3 can be used for verification of the composition of a freshly prepared calibration gas mixture.

6.2 Traceable standards available for direct comparison with the mixture

Each single gravimetrically prepared calibration gas mixture should be verified with traceable standards following the procedure described in 6.1 of ISO 6143:—.

6.3 Traceable standards not available for direct comparison with the mixture

When the approach described in 6.2 cannot be used, the following subsequent steps should be used for the verification of the prepared calibration gas mixture.

a) Prepare at least five calibration gas mixtures with the required mole or mass fraction lying within the expected linear range of the analytical method. Prepare these mixtures independently, i.e. no two mixtures should be made from the same parent gas mixture. Verify that they are consistent with each other, following the procedure described in 6.2 of ISO 6143:—.

b) Verify the preparation procedure. Use the same preparation procedure as in a) to prepare a “check” gas mixture consisting of components having traceable standards available. Verify the composition of this check mixture using the procedure given in 6.1 of ISO 6143:—. If the value of the composition obtained analytically is consistent with the gravimetric value, then this provides some evidence that the preparation procedure is suitable. It is preferable to use a “check” component which is similar chemically to the component of interest.

c) In cases where the composition of the component of interest in a multi-component mixture falls outside the range of traceable standards available or when no traceable standards exist for that component, comparison with gas mixture(s) prepared by another standardized method may be required for the verification of that component (e.g. dynamic volumetric methods ISO 6145 [19]).

7 Test report

The test report shall be prepared in accordance with the general requirements of ISO/IEC 17025. Requirements on the contents of certificates for calibration gases are specified in ISO 6141.

The following information shall be given in the test report:

a) a reference to this International Standard, i.e. ISO 6142;

b) the preparation procedure;

c) a purity table for all the parent gases;

d) the masses of gases transferred at each stage in the preparation procedure;

e) a list of the contributions to the composition uncertainty;

f) the details of all of the verification procedures;

g) the final composition, including the expanded uncertainty.

Annex A
(informative)

Practical example

A.1 Introduction

In order to facilitate understanding of this International Standard, especially the calculation of the composition and the calculation of uncertainty, an example is given. The magnitude of the uncertainties and the instrumentation presented should not be regarded as representative for a typical preparation process. The result of the analysis will depend on the equipment available. The example follows the flow chart in Figure 1.

A.2 Starting parameters

Mixture:	1×10^{-3} mol/mol carbon monoxide in nitrogen desired expanded relative uncertainty: 0,5 %, $k = 2$
Desired total pressure:	150×10^{5} Pa (150 bar)
Cylinder:	5×10^{-3} m^3 aluminium
Component purities:	carbon monoxide $99,9 \times 10^{-2}$ mol/mol nitrogen $99,999 \times 10^{-2}$ mol/mol
Balance:	mechanical, capacity 10 kg
Readability of balance:	1 mg
Weighing uncertainty for a 5 l cylinder:	± 4 mg per weighing (pooled experimental standard deviation s_p)
Number of weighings:	3

A.3 Evaluation of mixture feasibility

The components of this mixture are not reactive with each other. Furthermore, it is known from previous experience that mixtures containing considerably lower concentrations of carbon monoxide in nitrogen are stable in aluminium cylinders. Thus, there is no risk of reaction between the components nor reaction between the components and the cylinder. If the stability is not known, tests should be performed beforehand. It is known, for example, that mixtures with carbon monoxide prepared in steel cylinders can be unstable.

There is no risk of condensation of carbon monoxide. The mixture is feasible and there should be no problem its stability.

A.4 Choice of preparation procedure

A calculation should first be performed, to establish whether the chosen gas mixture can be prepared directly or whether multi-stage dilutions or pre-mixtures are required.

The masses targeted are calculated as follows:

$$m_i = \frac{x_i \times p_\mathrm{f} \times V_\mathrm{cyl} \times M_i}{R \times T \times Z_\mathrm{f}} \qquad \text{(A.1)}$$

where

m_i is the mass, expressed in grams, of component i in the mixture;

x_i is the intended mole fraction of component i;

p_f is the final fill pressure, expressed in pascals, of the mixture;

V_cyl is the volume, expressed in cubic metres, of the cylinder;

M_i is the molar mass, expressed in grams per mole, of component i;

R is the gas constant (8,314 51 J/mol·K);

T is the temperature, expressed in kelvin;

Z_f is the compression factor of the mixture at T and p_f.

In this example

$x_\mathrm{CO} = 1 \times 10^{-3}$ mol/mol

$p_\mathrm{f} = 150 \times 10^5$ Pa

$V_\mathrm{cyl} = 5 \times 10^{-3}$ m^3

$M_\mathrm{CO} = 28{,}010\ 4$ g/mol

$T = 294$ K

$Z_\mathrm{f} = 1{,}0$

$x_{\mathrm{N}_2} = 99{,}9 \times 10^{-2}$ mol/mol

$M_{\mathrm{N}_2} = 28{,}013\,48$ g/mol

$m_\mathrm{CO} = 0{,}86$ g

$m_{\mathrm{N}_2} = 858{,}6$ g

The weighing technique used is well-characterized and under statistical control. The pooled estimate of standard deviation s_p is 4 mg; the standard uncertainty is $u = s_\mathrm{p} / \sqrt{n}$; in this case, it is equal to 2,3 mg. The estimated mass of carbon monoxide is 860 mg. A standard uncertainty of 2,3 mg makes a contribution of 0,27 % relative to the final uncertainty. The requested expanded uncertainty compared to this uncertainty contribution is already so close to the limit that it should be minimized.

Consequently, it would be best to perform a multi-step dilution or to weigh the carbon monoxide in a separate smaller container on a low-capacity balance. In this example, the first method is evaluated and a pre-mixture is prepared.

In order to limit the uncertainty contribution of weighing the carbon monoxide to at most 0,05 %, a mass of at least 8 g of carbon monoxide should be weighed.

For the pre-mixture, a mass of 8,5 g of carbon monoxide is chosen. If the total pressure of the mixture is 150×10^5 Pa, the maximum amount of $\mathrm{N_2 + CO}$ should be 850 g.

The approximated mole fraction of the pre-mixture of CO (x_pm) is 1×10^{-2} mol/mol.

This pre-mixture should then be diluted by a factor 10 to reach the final mole fraction of 1×10^{-3} mol/mol.

The masses targeted can be calculated using equation (A.1) assuming a 10 % dilution.

$x_{pm} = 10 \times 10^{-2}$ mol/mol
$p_f = 150 \times 10^5$ Pa
$V_{cyl} = 5 \times 10^{-3}$ m^3
$M_{mix} = 28{,}013\ 44$ g/mol
$T = 294$ K
$Z_f = 1{,}0$

$x_{N2} = 90 \times 10^{-2}$ mol/mol
$M_{N2} = 28{,}013\ 48$ g/mol
$m_{pm} = 85{,}9$ g
$m_{N2} = 773{,}5$ g

A.5 Evaluation of sources of uncertainty

A.5.1 General

The sources of uncertainty are identified in three categories, as described in A.5.2 to A.5.4.

A.5.2 Uncertainty in the weighings (category 1)

A.5.2.1 Balance (u_m)

The uncertainty given in A.2 has been determined by repeated weighing of a cylinder which has undergone a simulated filling process. The uncertainty thus incorporates the following components: resolution of balance, drift, incorrect zero point, effect of location of the cylinder on the pan, typical changes (not those which are occasionally large ones) in mass due to handling and connection of cylinder and adsorption phenomena occurring when the cylinder is at constant temperature. This evaluation gives a pooled estimate of standard uncertainty in the mass determination of a component of $s_p = 4$ mg; the standard uncertainty is $u = s_p / \sqrt{n}$, in this case 2,3 mg.

A.5.2.2 Weights (u_w)

The substitution method is used in weighing and to avoid linearity and adjustment errors, it is expedient to add auxiliary weights of known mass to keep the weighing difference between the mixture and reference cylinder small.

The weights used in this example are made of stainless steel and calibrated against national standards and comply with OIML class E2. The calibration certificate for these weights shows an associated expanded uncertainty on the 1 g mass piece (which is the smallest mass piece used and has the largest relative uncertainty). Usually this is reported as 1/3 of the maximum allowable error.

The maximum allowable error is 0,06 mg. Thus the expanded uncertainty, U_w, is 0,02 mg (coverage factor $k = 2$). For each added mass piece the expanded uncertainty can be calculated in a similar way. The density of the mass pieces is listed in the certificate as (7 850 ± 50) kg/m^3. This uncertainty is rather high. However, the nominal value of the mass pieces, the calibrated correction and uncertainty in the correction are normally listed in terms of the *conventional mass*. This means that the mass pieces are equal to the masses of reference weights with a density of 8 000 kg/m^3 when weighing with an air density of 1,2 kg/m^3. In this case, the uncertainty is 0,002 kg/m^3 (k=1).

A.5.2.3 Buoyancy effects (u_B), (u_{exp})

A buoyancy correction for the difference in cylinder volume, between mixture and sample, has to be calculated, because the atmospheric density may change between the sets of weighings; sometimes it is even necessary to carry out weighings after overnight temperature stabilization. In the worst case, the difference in air density is 0,1 kg/m^3 and difference in volume of the two cylinders is 0,2 l, i.e. 0,000 2 m^3. Therefore, the difference in mass between the mixture cylinder and the reference cylinder may differ by 0,02 g due to changes in atmospheric density. One can only ignore the difference in volume if the air density does not change. A more accurate estimation can be made by measuring the temperature, pressure and humidity of the environmental air while weighing.

Buoyancy effects arise from the multiplicative effect of differences in atmospheric conditions between weighings and differences in the volumes of the items being weighed.

The density of the air can be calculated with the equation for the determination of the density of moist air (Giacomo[12], Davis[13]).

For the temperature range from 0 °C to 27 °C, a simplified formula can be used to calculate the density of air with an uncertainty of 1×10^{-4} kg/m^3:

$$\rho = \frac{3{,}484\,88\,p - \left(8{,}083\,7 + 737{,}4 \times 10^{-3}\,t + 975{,}25 \times 10^{-6}\,t^3\right) \times h}{(273{,}15 + t) \times 10^3} \qquad \text{(A.2)}$$

where

ρ is the density of air, expressed in kilograms per cubic metre;

p is the pressure, expressed in pascals;

t is the temperature, expressed in degrees Celsius;

h is the relative humidity, expressed as a fraction (% RH).

Conditions	Density of air
24 °C, 986 hPa, 80 % RH	1,145 8 kg/m^3
18 °C, 1 040 hPa, 20 % RH	1,242 9 kg/m^3

The example above shows that the maximum difference in air density between two weighings is less than 0,1 kg/m^3 (or 0,1 g/l) unless circumstances are exceptional.

In this example, weighing is performed using a balance with equal arms and a reference cylinder as tare mass. The difference in volume is due to differences in cylinder volume and the weights used. For cylinders of 5 l capacity, the external volume (being the sum of internal volume and metal volume) can differ up to 0,2 l. The volume of the weights used when the carbon monoxide is added, is about 0,001 1 l for the pre-mixture (8,5 g divided by the density of about 8 000 kg/m^3) and about 0,011 l for the final mixture (86 g divided by the density of about 8 000 kg/m^3).

If carbon monoxide is added to the cylinder, the uncertainty of the cylinder can be 20 mg (0,1 g/l multiplied by 0,201 1 l), giving a relative uncertainty of about 2×10^{-3}. For the pre-mixture, this can be converted to a relative uncertainty of 2×10^{-4}. These uncertainties may possibly be too large. However, they can be reduced by measuring the air density parameters. If the temperature is estimated with ± 0,5 °C uncertainty, the atmospheric pressure with ± 5 hPa and the relative humidity with ± 10 % RH, the maximum uncertainty on the air density becomes less than 0,003 g/l. In this case, the relative uncertainty for the addition of carbon monoxide is about 6×10^{-5} and 5×10^{-6} for the pre-mixture.

To correct the weighing result for the buoyancy effect for the difference in mass pieces placed on the balance, the following formula should be used [14]:

$$m_\mathrm{m} = m_\mathrm{R} + \rho_\mathrm{a}\,(V_\mathrm{m} - V_\mathrm{R}) + \Delta m_\mathrm{w} \qquad \text{(A.3)}$$

where

m_m is the mass of mixture cylinder;

m_R is the mass of reference cylinder;

ρ_a is the air density;

V_m is the volume of mixture cylinder, plus mass pieces;

V_R is the volume of reference cylinder, plus mass pieces;

Δm_w is the difference between the weighing readings of the gas mixture and reference cylinder.

The term $\rho_a (V_m - V_R)$ designates the correction for air buoyancy.

The effect of the difference in cylinder volume can be avoided by performing relative weighings against the same reference cylinder during each weighing in the preparation step. If the mass difference is determined between the sample cylinder and the reference cylinder for the empty weighing and for the weighings after filling, the amount of gas is determined by subtraction of the mass differences. Every weighing takes into account the difference in cylinder volume.

The expansion of the cylinder due to the increase in pressure of 15 MPa [150 bar[2]] will be about 0,02 l. This buoyancy effect is proportional to the filling pressure. Therefore, taking into account the extreme values of air density, this effect corresponds to an increase of at least 22,9 mg and at most 24,8 mg. The average value is 23,8 mg and the standard uncertainty $u_{exp} = 23{,}8/\sqrt{3} = 13{,}7$ mg.

A.5.2.4 Residual gas (u_R)

The cylinder is purged with nitrogen and evacuated to a pressure of 0,1 kPa (1 mbar) before filling.

Using equation (A.1) the additional nitrogen is about 5,7 mg.

The uncertainty in this estimation originates from the pressure reading. Assuming that the absolute error is 0,1 kPa (1 mbar), the standard uncertainty can be calculated as being $u_R = 5{,}7/\sqrt{3} = 3{,}3$ mg.

A.5.3 Uncertainty in the purity of the gases (u_{CO}, u_{N2}) (category 2)

The carbon monoxide is stated to be 99,9 % pure. Therefore, it is assumed that at most it contains a mole fraction of 1 000 × 10^{-6} mol/mol [1 000 ppm[3]] of impurities. In this example, these impurities are not analysed individually; the purity specified by the manufacturer of the pure CO shall be used to make a purity table. The reason for this is that the CO is to be diluted and the extra effort of an individual analyses has no effect on the final uncertainty. Furthermore, the pure CO will not contain any critical impurities with regard to the methods used in this example. The “detection limit approach” is used for the calculation of the uncertainty, assuming a rectangular distribution, when impurities are rather low. In this example, it is assumed that information has been received from the manufacturer that the N_2 content of CO is less than 700 × 10^{-6} mol/mol (< 700 ppm) but greater than 100 × 10^{-6} mol/mol (> 100 ppm), a rectangular distribution from 100 × 10^{-6} mol/mol to 700 × 10^{-6} mol/mol is therefore assumed. Asking the manufacturer as much information as possible is advised, as this assists in giving the best estimation.

The final standard uncertainty in the carbon monoxide amounts u_{CO} is 185 × 10^{-6} mol/mol, being the square root of the sum of squares of the uncertainties of the listed impurities. Using manufacturers general specifications for purity data may not always be useful. General purity information of manufacturers is often listed as a mean value for large batches of cylinders. Some impurities may be included in the matrix gas (Ar in pure N_2) or are not listed. A more robust method would be to use the results of an individual analysis including uncertainties. In some cases, purity analysis just before preparation is advisable.

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[2] 1 bar = 10^5 N/m^2 = 0,1 MPa

[3] 1 ppm = 1 × 10^{-6} mol/mol. The use of ppm is depreciated.

The nitrogen is of 99,999 % purity. The maximum impurity in the nitrogen is 10×10^{-6} mol/mol. The CO concentration in the final mixture is $1\,000 \times 10^{-6}$ mol/mol. If the 10×10^{-6} mol/mol impurity in the nitrogen is only CO, the uncertainty contribution can be 1 % maximum. The desired value of relative expanded uncertainty is 0,5 %, thus making this impurity unacceptable. A better quality nitrogen should be chosen. The contribution to the final uncertainty is 0,1 %, if the maximum impurity is 1×10^{-6} mol/mol (1 ppm) (99,9999 % quality). Another option is to analyse the impurities of the pure nitrogen in order to determine the amount of CO in the nitrogen. For this example, a purity analysis of the pure N_2 was performed with suitable analytical techniques. The analyser was calibrated with applicable gravimetrically prepared mixtures with stated uncertainty. The outcome of the purity analysis is listed in a purity table.

The nitrogen contains $(1 \pm 0{,}2) \times 10^{-6}$ mol/mol of CO. The total uncertainty in the nitrogen was calculated with the squared addition of the uncertainties for the impurities and amounts u_{N_2} is $1{,}19 \times 10^{-6}$ mol/mol.

Table A.1 — Purity table for CO

Component	General manufacturer specifications 10^{-6} mol/mol	Distribution	Mole fraction 10^{-6} mol/mol	Uncertainty 10^{-6} mol/mol
H_2O	$\leqslant 20$	Rectangular	10	6
N_2	Between 100 and 700	Rectangular	400	174
CO_2	$\leqslant 50$	Rectangular	25	14
O_2	$\leqslant 20$	Rectangular	10	6
H_2	$\leqslant 200$	Rectangular	100	58
CH_4	$\leqslant 25$	Rectangular	12	7
CO	$\geqslant 998\,985$	—	999 443	185

Table A.2 — Purity table for N_2

Component	Mole fraction 10^{-6} mol/mol	Uncertainty
H_2O	2	0,5
CO	1	0,2
CO_2	1	0,2
O_2	2	0,2
Ar	25	1
CH_4	0,5	0,2
N_2	999 968,5	1,19

A.5.4 Uncertainty in molar mass (u_M) (category 3)

The molar mass of the components and the related uncertainties are calculated from the atomic weights given in the IUPAC publication on the Atomic weights of the Elements.

Component	Molar mass	Standard uncertainty, u_M
Carbon monoxide	28,010 4	0,001 0
Nitrogen	28,013 48	0,000 10

A.5.5 Other sources of error

Temperature differences may cause unequal thermal expansion of the balance arms, thus having a significant influence on the result of the weighing. Placing a recently filled warm cylinder on the balance pan is an example of such an effect. A warm cylinder also gives convective air currents along the vertical surface, developing vertical forces[15]. The volume of a warm cylinder is larger, influencing the buoyancy. The error originating from all thermal effects can be as large as 100 mg. The cylinder should be in thermal equilibrium with the balance before it is weighed.

The error caused by adsorption/desorption phenomena varies with the surface treatment of the cylinder and is influenced by variations in temperature. When the balance gas is added into the cylinder, this effect is the most significant, because the cylinder heats up significantly. Tests with the type of cylinder used should be made. When a small amount of gas is added to the cylinder the temperature does not change. In both cases adsorption/desorption phenomena at constant temperature are included in the test mentioned under A.5.2.4.

A.5.6 Calculations of composition and uncertainty

A.5.6.1 Calculations of the pre-mixture

The vacuum cylinder is weighed.

A 50 g mass piece is used to correct the difference in mass between the reference cylinder and the mixture cylinder. The certificate lists a conventional mass of (50,000 210 ± 0,000 030) g.

Three observations of the difference in mass between the mixture cylinder (M) and the reference cylinder (R) are obtained using the substitution method and the substitution scheme RMMR, RMMR, RMMR:

Observation	Cylinder	Balance reading	Weighing difference Δm
1	reference	0,010	
	mixture + 50	0,022	
	mixture + 50	0,018	
	reference	0,012	–0,009
2	reference	0,016	
	mixture + 50	0,027	
	mixture + 50	0,024	
	reference	0,013	–0,011
3	reference	0,012	
	mixture + 50	0,025	
	mixture + 50	0,023	
	reference	0,010	–0,013

Arithmetic mean: $\overline{\Delta m}$ = – 0,011 g

Pooled estimate of standard deviation: $s_p(\Delta m)$ = 4 mg

Standard uncertainty: $u(\Delta m)$ = 2,3 mg

During the weighing the temperature is measured to be: (19,5 ± 0,5) °C, humidity: (40 ± 10) % RH and barometric pressure: (1 005 ± 2) hPa.

Using equation (A.2) in A.5.2.3, the air density is calculated to be: 1,192 7 kg/m^3.

As the cylinder volume is part of every weighing, correction is only made for the mass pieces. The volume of the 50 g piece is: 50,000 21 g / 8 000 g·l^{-1} = 6,25 ml.

Calculating the air buoyancy term $\rho_a (V_m - V_R)$: 1,192 7 g × l^{-1} (0,006 25 l) = 0,007 45 g.

The uncertainty in this term is given by:

$$u_B^2 = \rho_a^2 \left(\mathrm{d}V_m^2 + \mathrm{d}V_R^2 \right) + \left(V_m + V_R \right)^2 \mathrm{d}\rho_a^2 \tag{A.4}$$

Giving for this example:

$$\mathrm{d}V_m^2 = \left(\frac{m_w}{\rho_w^2} \right)^2 \mathrm{d}\rho_w^2 + \left(\frac{1}{\rho_w} \right)^2 \mathrm{d}m_w^2 = \left[\frac{50{,}000\ 21}{(8\ 000)^2} \right]^2 (0{,}002)^2 + \left(\frac{1}{8\ 000} \right)^2 (0{,}000\ 015)^2 = 6 \times 10^{-14}$$

$$\mathrm{d}V_R^2 = 0$$

$$\mathrm{d}\rho_a = 0{,}003$$

This gives a total uncertainty on the buoyancy term: u_B = 0,000 019 g.

The weighing of CO and N_2 is performed in the same way and results in:

Arithmetic mean: $\bar{\Delta} m(\mathrm{CO})$ = −0,515 g

Pooled estimate of standard deviation: $s_p(\Delta m)$ = 4 mg

Standard uncertainty: $u(\Delta m)$ = 2,3 mg

For CO, four mass pieces are used namely:

(20,000 96 ± 0,000 025) g + (10,000 067 ± 0,000 020) g + (9,999 9 ± 0,000 020) g + (1,999 985 ± 0,000 012) g.

Total mass is 42,000 912 g, expanded uncertainty is 0,039 6 mg.

Arithmetic mean: $\bar{\Delta} m(N_2)$ = 0,024 g

Pooled estimate of standard deviation: $s_p(\Delta m)$ = 4 mg

Standard uncertainty: $u(\Delta m)$ = 2,3 mg

For N_2, mass pieces of 500 g, 200 g, 50 g, 20 g, 10 g, 10 g and 1 g are used with a total conventional mass of 791,118 0 g, and the expanded uncertainty is 0,275 mg (this mass is added to the reference cylinder).

The 20 g and 10 g mass pieces are also used in the weighing of the CO introducing a correlation. Reviewing the uncertainty sources, the uncertainty contribution of the mass pieces is negligible, making this covariance term negligible as well.

The contributions to uncertainty are summarized in Tables A.3 to A.5.

Table A.3 — Uncertainty contributions for vacuum

Value $\overline{x}_i$	Estimate x_i	Standard uncertainty $u(x_i)$	Probability distribution	Sensitivity coefficient c_i	Uncertainty contribution $u_i(y)$
m_m	50,000 210 g	0,015 mg	Normal	1	0,015 mg
u_m	– 0,011 g	2,3 mg	Normal	1	2,3 mg
u_B	0,007 45 g	0,019 mg	Normal	1	0,019 mg
m_x	49,996 660 g	—	—	—	2,3 mg

Table A.4 — Uncertainty contributions for CO

Value $\overline{x}_i$	Estimate x_i	Standard uncertainty $u(x_i)$	Probability distribution	Sensitivity coefficient c_i	Uncertainty contribution $u_i(y)$
m_m	42,000 912 g	0,019 8 mg	Normal	1	0,019 8 mg
u_m	–0,515 g	2,3 mg	Normal	1	2,3 mg
u_B	0,006 26 g	0,016 mg	Normal	1	0,016 mg
m_x	41,492 172 g	—	—	—	2,3 mg

Table A.5 — Uncertainty contributions for N_2

Value $\overline{x}_i$	Estimate x_i	Standard uncertainty $u(x_i)$	Probability distribution	Sensitivity coefficient c_i	Uncertainty contribution $u_i(y)$
m_R	791,118 0 g	0,14 mg	Normal	1	0,14 mg
u_m	0,024 g	2,3 mg	Normal	1	2,3 mg
u_B	0,117 9 g	0,297 mg	Normal	1	0,297 mg
u_exp	0,023 8	13,7 mg	Rectangular	1	13,7 mg
u_R	0,005 7 g	3,3 mg	Rectangular	1	3,3 mg
m_x	791,289 4 g	—	—	—	14,28 mg

The amount of CO and N_2 can now be calculated:

CO: (49,996 66 – 41,492 172) = 8,504 488 ± 0,003 253 g

N_2: (791,289 4 + 41,492 172) = 832,781 572 ± 0,014 464 g

In this way, the above estimates are correlated. In both of these calculations, the result of the CO weighing is taken into account. To avoid any correlation between the two, CO should be weighed twice; using the first weighing of the vacuum weighing to estimate the amount of CO, then using the second weighing to estimate the amount of N_2.

Equation (5) in 5.1.5 is used to calculate the uncertainties, for this purpose it can be written as:

$$u^2(x_i) = \sum_{i=1}^{n} \left(\frac{\partial x_i}{\partial M_i} \right)^2 \cdot u^2(M_i) + \sum_{A=1}^{p} \left(\frac{\partial x_i}{\partial m_A} \right)^2 \cdot u^2(m_A) + \sum_{A=1}^{p} \sum_{i=1}^{n} \left(\frac{\partial x_i}{\partial x_{iA}} \right)^2 \cdot u^2(x_{iA}) \tag{A.5}$$

where

$u(M_i)$ is the uncertainty in the molar mass (A.5.3) and can be fully neglected for this purpose;

$u(m_A)$ is the uncertainty on the weighings (A.5.1) and is the sum of squares of the uncertainties listed above;

$u(x_{iA})$ is the uncertainty in the purity analysis.

Applying equation (3) in 4.6, the purity for the pre-mixture is calculated and given in Table A.6.

Table A.6 — Purity table for final mixture

Component	**Mole fraction** (10^{-6})	**Uncertainty** (10^{-6})
H_2O	2,08	0,50
CO	10 176,90	4,29
CO_2	1,24	0,24
O_2	2,08	0,21
Ar	24,75	0,99
CH_4	0,62	0,21
N_2	989 791,31	5,61
H_2	1,02	0,59

A.5.6.2 Calculation of the final mixture

After the pre-mixtures, the final mixture can be calculated. The method of calculation is similar to the pre-mixture. It is assumed that during preparation (85,881 5 ± 0,003 3) g of the pre-mixture has been weighed into the cylinder. It is also assumed that the mass of nitrogen, (774,321 4 ± 0,014) g N_2, has been weighed. The purity of both the pre-mixture and N_2 is given in the purity tables above.

The molar mass of the pre-mixture is $(0{,}01 \times 28{,}010\,4 + 0{,}99 \times 28{,}013\,48) = 28{,}013\,45$ and of N_2: 28,013 48.

Table A.7 — Purity table for final mixture

Component	Mole fraction (10^{-6})	Uncertainty (10^{-6})
H_2O	2,01	0,45
CO	1 016,95	0,46
CO_2	1,02	0,18
O_2	2,01	0,18
Ar	24,97	0,90
CH_4	0,51	0,18
N_2	998 952,42	1,22
H_2	0,10	0,06

The objective is to obtain a relative uncertainty of 0,5 % for the CO mole fraction. From Table A.7, it can be seen that the mole fraction of CO is $1\,016{,}95 \times 10^{-6}$. The relative expanded uncertainty is $0{,}92 \times 10^{-6}$, which is less than 0,1 %.

The next step in the preparation process is to verify the mixture. Traceable standards of CO in N_2 are available and therefore the situation prescribed in 6.1 is applicable. A suitable analyser is used, GC-TCD or ND-IR for example, to determine the assigned content and uncertainty of the freshly prepared mixture. The analyser is calibrated with traceable standards all in accordance with the procedures prescribed in ISO 6143.

The compatibility criterion used is:

$$\left| x_{\text{grav}} - x_{\text{anal}} \right| \leqslant 2\sqrt{u\left(x_{\text{grav}}\right)^2 + u\left(x_{\text{anal}}\right)^2} \qquad \text{(A.6)}$$

where x_{grav} and x_{anal} denote the gravimetrically measured mole fraction ($= 1\,016{,}95 \times 10^{-6}$) and the analytically measured mole fraction, respectively the analytical content (determined using the analyser), and $u(x_{\text{grav}})$ ($= 0{,}45 \times 10^{-6}$) and $u(x_{\text{anal}})$ denote the standard uncertainties of these quantities.

Annex B
(informative)

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

B.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 (B.1).

$$p_F \leqslant \frac{1}{\sum_{j=1}^{n}\left[\frac{x_j}{p_j(T_L)}\right]} \tag{B.1}$$

where

T_L is the lowest temperature to which the gas mixture will be exposed;

n is the number of components;

x_j is the mole fraction of component j;

$p_j(T_L)$ is the vapour pressure of component j at temperature T_L.

For $p_F > 5 \times 10^6$ Pa (50 bar), equation (B.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) shall 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.

B.2 Application — Natural gas

B.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 B.1. These pressures are derived from the partial pressures of the individual components.

The pressures given in Table B.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 B.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

B.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 B.1 shows 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 B.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 B.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.

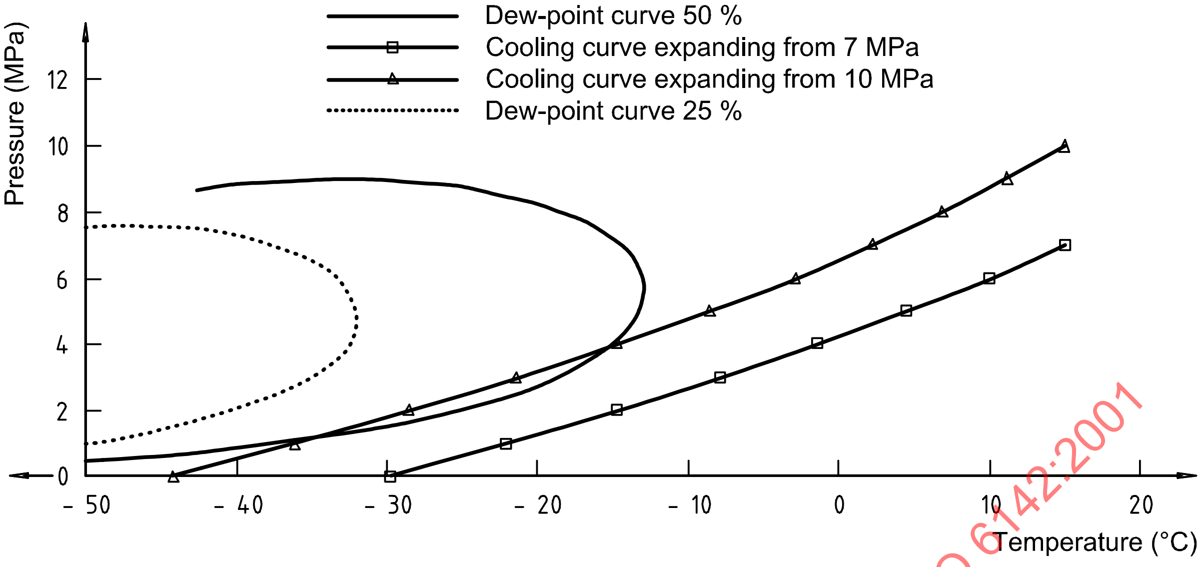

Figure B.1 — Dew-point curves and cooling curves

Annex C
(informative)

Precautions to be taken when weighing, handling and filling cylinders

C.1 Weighing

C.1.1 Choice of the balance

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

C.1.2 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.

C.1.3 Performance of the balance

It is recommended that the balance be installed by the manufacturer, and its performance checked and certified 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 conditions due to the surroundings.

C.1.4 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 rectified by comparative weighing against a similar reference cylinder or by calculation.

Apart from the temperature effect described in C.1.2, 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 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.

C.2 Cylinders

C.2.1 Choice of cylinders

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

C.2.2 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 C.1.2 and C.1.4 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.

C.2.3 Safety considerations

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

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.

C.3 Filling cylinders

C.3.1 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 low-capacity 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.

C.3.2 Preparation using pure gases or pre-mixtures

Determine the fill sequence first (see 4.4). 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. This is often done by rolling the cylinder. The minimum duration of this homogenization process should be determined experimentally beforehand.

The following aspects of possible condensation should be considered.

— Condensation can occur during the filling of the cylinder although there is no theoretical reason to expect this problem. Filling with the balance gas can compress the already present component without fully mixing with it and can result in condensation.

- During the homogenization process of partially condensed mixtures, it is sometimes difficult to remove the condensed phase from the cylinder wall.
- When one of the components has a relative density higher than the relative density of the balance gas, simply rolling the cylinder may not be sufficient to homogenize the gas due to their density difference. Homogenization can possibly be established by laying the cylinder on its side for a longer period or by applying heat during rolling.

C.3.3 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 C.3.1. 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 D
(informative)

Derivation of the equation for calculating the calibration gas mixture composition

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

Let $A = 1, 2, \ldots, P$ 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 mole 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 mole 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 (average) molar mass of parent gas A, given by:

$$M_A = \sum_{i=1}^{n} x_{i,A} \cdot M_i \tag{D.1}$$

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

$$w_{i,A} = x_{i,A} \cdot \frac{M_i}{M_A} \tag{D.2}$$

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_i of the components i in the final mixture;

b) convert the mass composition to molar composition, i.e. from the mass fractions w_i to the mole fractions x_i of the components i in the final mixture.

The mass fractions w_i are given by:

$$w_i = \frac{\sum_{A=1}^{P} w_{i,A} \cdot m_A}{m_\Omega} \tag{D.3}$$

where m_Ω is the mass of the final mixture.