International Standard

ISO 6142-2

First edition
2024-02

Gas analysis — Preparation of calibration gas mixtures —

Part 2: Gravimetric method for Class II mixtures

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

Partie 2: Méthode gravimétrique pour les mélanges de Classe II

Reference number
ISO 6142-2:2024(en)

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Published in Switzerland

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO document 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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This document was prepared by Technical Committee ISO/TC 158, *Analysis of gases*.

A list of all parts in the ISO 6142 series can be found on the ISO website

Any feedback or questions on this document should be directed to the user’s national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

The revision of ISO 6142 was initiated to provide better guidance to the users of this document especially with respect to quality assurance measures and laboratory accreditation. In preparing the revision, it was decided to accommodate 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 according to ISO 6142-1. 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, measurement uncertainties can be achieved that are substantially smaller than by any other preparation method.

Class II calibration gas mixtures may be prepared individually or in batches and certified with an associate generic measurement uncertainty.

Individually prepared Class II calibration gas mixtures are produced in a similar manner to Class I calibration gas mixtures, but these mixtures are not individually verified. Verification of individually prepared Class II calibration gas mixtures is based on periodic verification checks.

Class II type calibration gas mixtures, which are produced in batches, extend the principles of gravimetric preparation described in ISO 6142-1.

For mixtures containing identical components and nominally identical amount-of-substance fractions, Class II type calibration gas mixtures will usually have amount–of–substance fractions with larger measurement uncertainties than their Class I counterparts.

This document was developed to be in agreement with ISO 6142-1.

Gas analysis — Preparation of calibration gas mixtures —

Part 2:
Gravimetric method for Class II mixtures

1 Scope

This document describes the static gravimetric preparation of Class II calibration gas mixtures and describes a method for calculating the measurement uncertainty associated with the amount fraction of each component. In addition to all of the contributions to the measurement uncertainty mentioned in ISO 6142-1, this document also considers the uncertainty resulting from the validation process for Class II mixtures that are not individually verified, as is the case for Class I mixtures.

This document extends the uncertainty evaluation described in ISO 6142-1 to include the effects of batch production and the verification process. It provides guidance on how to derive an uncertainty budget that is representative of a particular category of mixtures.

Methods for the batch production of more than one mixture in a single process are included in this document.

This document is only applicable to mixtures of gaseous or totally vaporized components, which can be introduced into the cylinder in the gaseous or liquid state. Both binary and multi-component gas mixtures are covered by this document.

This document is limited to non-reactive molecules/components that are greater than or equal to an amount fraction of 100 µmol/mol. This document excludes components that react with each other, or with common mixture contaminants such as water vapour or oxygen or react with the inner surface of the cylinder and valve in the form of absorption or adsorption.

2 Normative references

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

ISO 6142-1:2015, *Gas analysis — Preparation of calibration gas mixtures — Part 1: Gravimetric method for Class I mixtures*

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

ISO 7504, *Gas analysis — Vocabulary*

3 Terms and definitions

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

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

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

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

3.1
generic uncertainty
uncertainty assigned to the amount fraction of a component of a *category of mixtures* (3.2), representative for all mixtures belonging to such a category

Note 1 to entry: This uncertainty is calculated from the validation process and not calculated individually for each cylinder. The generic uncertainty is usually expressed as a relative expanded uncertainty.

3.2
category of mixtures
group of mixtures that have the same filling method and analytical verification method and whose properties are sufficiently similar that the uncertainty of the composition of these mixtures can be described by a single *generic uncertainty* (3.1) statement

4 Symbols

n	number of replicates in the validation
$u(...)$	standard uncertainty (of the quantity in parentheses)
$U(...)$	expanded uncertainty (of the quantity in parentheses)
$u(v_k)$	Standard uncertainty for the validation process for component k
y_k	amount fraction of component k
$y_{k,\mathrm{ver}}$	amount fraction of the component k measured by analysis in course of validation of the mixture
$y_{k,\mathrm{prep}}$	amount fraction of the component k calculated in the preparation of the mixture
v_k	difference between the amount fraction from preparation and verification for the component k $v_k = \left(y_{k,\mathrm{prep}} - y_{k,\mathrm{ver}}\right)$
s_{bb}	between-unit component of variance from a homogeneity study, expressed as standard deviation.
$\mathrm{MS}_{\mathrm{among}}$	Mean Square between groups (from ANOVA)
$\mathrm{MS}_{\mathrm{within}}$	Mean Square within the groups (from ANOVA)
n_0	number of individual analyses performed on a component in a mixture
z	total number of mixtures in the batch
a	number of mixtures analysed from the total batch
y_{avg}	average amount of substance fraction value for component in the batch
A	Analytical results expressed as instrumental response
$U_{\mathrm{rel}}(...)$	relative expanded uncertainty (of the quantity in parentheses)

5 Principle

Class II calibration gas mixtures are prepared using the principles of preparation detailed in ISO 6142-1, and mixtures can be prepared individually or by batch production using a validated gravimetric process; however, the individual verification of the final mixture against independent reference gas mixtures is not required.

The process for the gravimetric method of preparing Class II calibration gas mixtures with individual preparation is given as a flowchart in ISO 6142-1:2015, Figure 1. Class II mixtures are typically mixtures that are prepared on a frequent basis and by a defined preparation procedure.

In the validation process for this method of preparation, the uncertainty of the calibration gas mixtures is evaluated as described in ISO 6142-1:2015, Clause 11. Statistical process control of the validation process is required. For a number of frequently produced mixtures, the average of the calculated uncertainties is then used to derive a generic uncertainty for a defined range of amount fractions and compositions. Further details are given in Clause 6 and Clause 9.

The filling of calibration gas mixtures in a batch is described in the Clause 7 with a description of the filling process and the uncertainty calculation.

The continued validity of this generic uncertainty shall be periodically re-confirmed following the procedures described in Clause 8.

6 Individual cylinder production

6.1 General

The process for the individual preparation of Class II calibration gas mixture is shown in Figure 1.

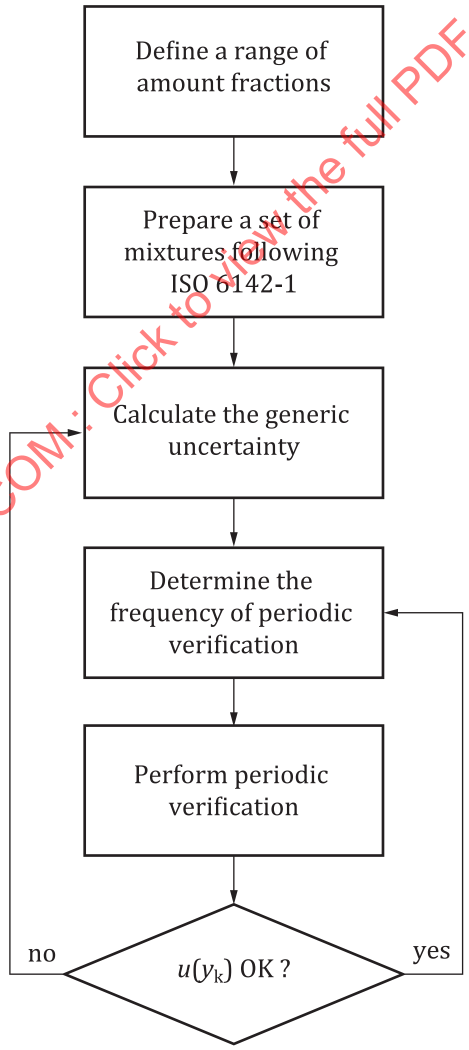


Figure 1 — Scheme for the gravimetric method of preparing Class II calibration gas mixtures, individual preparation

6.2 Estimation of generic uncertainty of the calibration gas mixtures

For each defined range of components and amount of substance, a set of preferably n = 10, but at least 6 gravimetric mixtures shall be prepared and verified in accordance with ISO 6142-1 under specified conditions.

The results of the individual verification shall be reviewed against the following criteria:

— all mixtures shall pass the verification criterion described in ISO 6142-1:2015, 10.2;

— the standard deviation of the mean of the expanded uncertainties shall be lower than a half of the intended expanded generic uncertainty;

— in the generic uncertainty an additional uncertainty component from the validation process, $u(v_k)$ is added, see Formula (1):

$$u(v_{\mathrm{k}})^2 = \frac{1}{n-1}\sum_{i=1}^{n}\left(v_{k,i} - \overline{v_k}\right)^2 \tag{1}$$

Where v_k denotes the difference between the amount fraction of the component k calculated from preparation and verification and n is the number of mixtures involved in the validation process.

An alternate approach is the use of a model from meta-analysis, such as the DerSimonian-Laird model.

The combined standard uncertainty of the amount fraction of component k in the final mixture shall be calculated using Formula (9) in ISO 6142-1 amended as follows:

$$u_c(y_k) = \frac{1}{2}\sqrt{u^2(y_{k,\mathrm{prep}}) + u^2(y_{k,\mathrm{ver}}) + \left(\left|y_{k,\mathrm{prep}} - y_{k,\mathrm{ver}}\right|\right)^2 + u(v_k)^2} \tag{2}$$

The generic uncertainty shall be calculated from the mean of the expanded uncertainties and shall be rounded up to a value with typically 2 significant figures.

Examples of the estimation of a generic uncertainty are given in Annex A.

Information on when the estimation of the generic uncertainty should be repeated is given in Clause 8.

7 Batch production

7.1 General

Batch filling offers productivity advantages over individual gravimetric step-by-step filling. The one-way ANOVA is used to determine the between bottle variation ($s_{\mathrm{bb},k}$) of the batch filling process for the component of interest k. This is then used to calculate the batch uncertainty by adding the s_{bb} value to the gravimetric uncertainty of the cylinder on the balance. Further guidance on performing a one-way ANOVA is described in ISO Guide 35[1].

7.2 Batch filling process

The gravimetric production of gas mixtures with nominally identical composition can be achieved by preparing a batch of identical cylinders and connecting the cylinders to a filling manifold and placing one cylinder on a high resolution, high-capacity balance. The addition of the component gases shall be controlled by the measurement and recording of the masses of gases added to the cylinder located on the balance.

The cylinder shall be weighed after each addition of gas to determine the mass of each component gas added into the controlling cylinder located on the balance. Specifically:

— connect all cylinders to be filled to the manifold and place one cylinder on the balance;

— evacuate all of the cylinders connected to the manifold and record the tare mass of the cylinder on the balance;

— fill the cylinder sequentially with the gaseous components to the target masses specified in the filling instruction for the mixture;

— continue until the mixture filling process is completed;

— homogenize the mixtures, for example by rolling the cylinders.

Random effects, slight variations in cylinder pre-treatment (e.g. vacuum) and the design of the manifold can result in deviations in the individual amount fractions of gas mixtures prepared in batch processes. These effects shall be expressed as an additional uncertainty component (batch uncertainty) in the gravimetric preparation process.

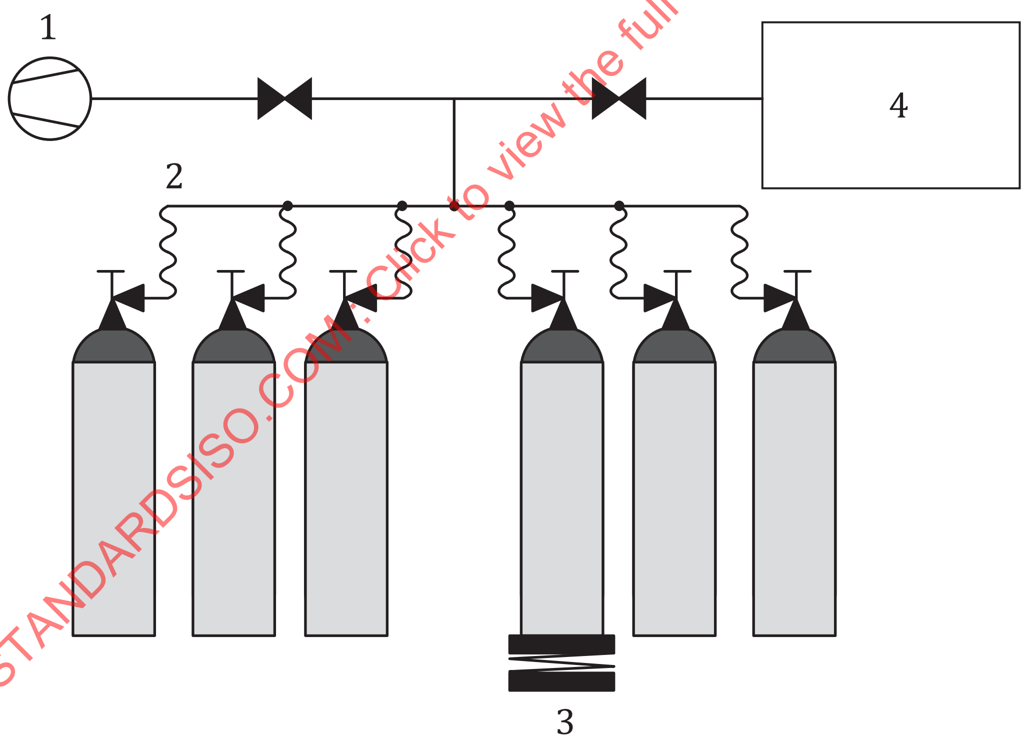
The batch homogeneity can be improved by using a symmetrical manifold and similar length and diameter of filling lines to each cylinder (see Figure 2).

To determine the homogeneity and the uncertainty contribution due to batch inhomogeneity the following actions shall be completed:

— complete the filling process as described in this subclause;

— analyse all cylinders individually. The number of replicate analyses have an influence on the generic uncertainty;

— perform the one-way ANOVA as described in Annex B, this will result in the batch uncertainty.



Key

1 vacuum pump

2 manifold

3 balance

4 supply gases: pure gases and pre-mixes cabinet

Figure 2 — Schematic diagram of filling system

7.3 Calculation of the measurement uncertainty

The batch inhomogeneity is equal to the between-bottle standard deviation s_{bb}. The between-bottle homogeneity study is based on a 100 % batch analysis. The number of replicate analyses depends on the desired measurement uncertainty.

Formula (3) is given for batch filling uncertainty for the component k,

$$u_c(y_k) = \frac{1}{2}\sqrt{u^2(y_{k,\text{prep}}) + u^2(y_{k,\text{ver}}) + (y_{k,\text{prep}} - y_{k,\text{ver}})^2 + s^2_{\text{bb},k}} \quad (3)$$

The values $y_{k,\text{prep}}$ and $y_{k,\text{ver}}$ are calculated from the cylinder on the balance.

8 Requirements for repeated verifications and document control

Class II mixtures shall use the principles of preparation detailed in ISO 6142-1 where each mixture is prepared individually (Clause 6) or follow the batch production using a validated gravimetric process as detailed in Clause 7 of this document.

The individual verification of the final mixture against independent reference gas mixtures is not required, however the analytical capabilities used to determine the generic uncertainty should be maintained.

The estimation of the generic uncertainty of the calibration gas mixture remains valid in a defined production system that was used in the estimation of the generic uncertainty.

The verification shall be completed at least every 12 months for each category of mixture to ensure the continued validity of the generic uncertainty assigned to the mixture.

The verification shall be repeated when a significant change might affect the measurement uncertainty such as changes:

— in the raw materials;

— in the filling process. These changes include the set-up of the preparation facility, the use of other weighing equipment and the use of other cylinder types and/or valves;

— in analytical capabilities, instrument selection and analytical method.

If there is any doubt about the stated generic uncertainty, for example in the case of a complaint from a customer, the manufacturer of the Class II calibration gas mixture shall perform an individual analysis to confirm the generic uncertainty using the same analytical equipment and set up that was used during the estimation of the generic uncertainty.

Verification procedures may also be used, when applicable, to address corrective actions.

The data to underpin the estimated uncertainty and the decisions taken in the classification of the groups and ranges of components shall be documented and available for at least three years after the generic uncertainty estimation has been superseded by new estimates. This enables the reproduction of original data in the event of production queries or customer complaints.

In case the verification indicates that the generic uncertainty for a specific range of amount of substance fractions and compositions cannot be confirmed, the procedure described in 6.2 and 7.3 shall be repeated and an adjusted generic uncertainty shall be determined.

9 Defining ranges of components and amount fractions by category of mixtures

The concept of category of mixtures is used to organize and simplify the validation processes, stability studies and frequency of the periodic verification. This is defined as a category of mixtures with the same characteristics in relation to the experimental design and filling processes. This allows the determination of the sources of measurement uncertainty and the validation of the filling processes by analytical verification.

The estimation of ranges of amount fractions (categories) depends on the specific chemical characteristics, physical properties and the production setup used, this is in order to end up with the same generic uncertainties. This is not applicable to all components and chemical expertise is required to define the limits of amount fraction ranges (category) with identical generic uncertainties.

When defining a range of composition for a category of mixtures, the uncertainty calculated for a component shall be valid in relative value for amount fractions above the composition considered and in an absolute value for amount fractions below this value.

For example, considering 1 mmol/mol: if the relative uncertainty at 1 mmol/mol is 2 % this is also valid for concentrations above 1 mmol/mol and the absolute value (0,002 mmol/mol) is applicable to all amount fractions below 1 mmol/mol. If the resulting uncertainties are not satisfactory, a producer of calibration gas mixtures should prepare extra mixtures to define additional ranges.

The estimation of the generic uncertainties will typically be performed for binary gas mixtures. However, multi-component mixtures, such as the typical automotive calibration gas mixtures containing carbon monoxide, carbon dioxide and propane in a nitrogen matrix, can be used to estimate generic uncertainties for 4 component gas mixtures as well as for mixtures of single components in nitrogen. Such an approach will result in identical generic uncertainties for the 4-component mixture and the binary mixtures. If lower uncertainties are required for binary mixtures containing these components, they shall be recalculated and separately estimated.

An example is given in informative Annex C.

10 Preparation of certificate

The amount fraction of component *k* in the final mixture on the certificate shall be the result of the calculation as described in ISO 6142-1:2015, Formula 3.

The certificate shall report the generic expanded uncertainty and the coverage factor.

The expanded (generic) uncertainty is calculated from the combined standard uncertainty, as shown in Formula (4):

$$U(y_k) = k \times u_c(y_k) \tag{4}$$

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

The certificate shall be prepared according to ISO 6141 and shall indicate that this is a Class II calibration gas mixture in accordance with ISO 6142-2 and whether it is individually prepared, or batch prepared.

The manufacturer of the calibration gas mixture shall specify the shelf-life and conditions to maintain the stability as specified on the certificate. The stability of calibration gas mixtures shall be evaluated in accordance with ISO 6142-1:2015, 9.2.

Annex A
(informative)

Practical example of the calculation of the generic uncertainty - Individual filling

The generic uncertainty for a category of mixture should be determined in the following way, the gravimetric uncertainty is calculated for each component and amount fraction range and the other sources of uncertainty such as stability, verification and validation are determined for the category of mixture by considering the worst-case scenario for each source using the guidelines below.

EXAMPLE Carbon dioxide (CO_2) in Nitrogen

A 1 mmol/mol mixture is selected for the determination of the generic uncertainty.

A mixture of 1 mmol/mol carbon dioxide in nitrogen is filled into a cylinder of 10 litre water capacity at approximately 150 bar. Other cylinders of the same amount fraction are individually filled under the same conditions and are verified by analysis.

10 cylinders are filled, and their preparation uncertainty is calculated according to ISO 6142-1:2015, Formula (7).

$$u_{k,\text{prep}} = \sqrt{u^2\left(y_{k,\text{grav}}\right) + u^2\left(y_{k,\text{stab}}\right)} \tag{A.1}$$

In this example, as the components of the mixture are CO_2 and nitrogen, which are unconditionally stable, $u(y_{k,\text{stab}})$ is set to zero.

To achieve the intended measurement uncertainty, a gravimetrically prepared gas premix of 20 % CO_2 in nitrogen is used, with a mass of 95,9 g.

The 10 cylinders are verified by analysis with traceable calibration standards using the bracketing system described in ISO 12963[2]. In this example the calibration standards have a relative expanded uncertainty of 0,4 % for the CO_2 amount fraction and the analytical relative expanded uncertainty is 0,6 %. The prepared gas mixture passes the verification if it meets the criterion given in ISO 6142-1:2015, Formula (8).

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

Table A.1 shows the gravimetric and verification amount fractions with their standard uncertainties and the result for the calculation of the verification criterion.

Table A.1 — Gravimetric and verification amount fractions with their standard uncertainties and the verification

cylinder	$y_{k,\text{grav}}$ mmol/mol	$u(y_{k,\text{grav}})$ mmol/mol	$y_{k,\text{ver}}$ mmol/mol	$u(y_{k,\text{ver}})$ mmol/mol	$\frac{\left\|y_{k,prep} - y_{k,ver}\right\|}{\sqrt{u^2\left(y_{k,prep}\right) + u^2\left(y_{k,ver}\right)}} \le 2$
1	1,000 8	0,005 0	1,004 9	0,006 0	0,52
2	0,998 9	0,005 0	1,005 9	0,006 0	0,90
3	0,998 9	0,005 0	1,006 9	0,006 0	1,02
4	1,000 6	0,005 0	1,008 5	0,006 0	1,01
5	1,000 6	0,005 0	0,998 3	0,006 0	0,29
6	0,998 8	0,005 0	0,999 6	0,006 0	0,10

Table A.1 *(continued)*

cylinder	$y_{k,\text{grav}}$ mmol/mol	$u(y_{k,\text{grav}})$ mmol/mol	$y_{k,\text{ver}}$ mmol/mol	$u(y_{k,\text{ver}})$ mmol/mol	$\frac{\lvert y_{k,prep} - y_{k,ver}\rvert}{\sqrt{u^2(y_{k,prep}) + u^2(y_{k,ver})}} \leq 2$
7	0,998 9	0,005 0	1,006 7	0,006 0	1,00
8	1,000 7	0,005 0	1,002	0,006 0	0,17
9	1,000 7	0,005 0	1,006 7	0,006 0	0,77
10	1,000 7	0,005 0	1,005 8	0,006 0	0,65
$y_{k,\text{grav}}$	is the gravimetric amount fraction				
$u(y_{k,\text{grav}})$	is the standard gravimetric amount fraction uncertainty				
$y_{k,\text{ver}}$	is the amount fraction obtained in the verification				
$u(y_{k,\text{ver}})$	is the standard verification uncertainty				

As all the 10 calibration mixtures pass the test, the uncertainty from the validation process can be evaluated according to ISO 6142-1:2015, Formula (1).

Table A.2 shows the gravimetric and verification amount fractions, their differences and the standard uncertainty of the validation process calculated according to Formula (A.2).

Table A.2 — Gravimetric and verification amount fractions, their differences and the standard uncertainty of the validation process

cylinder	$y_{k,\text{grav}}$ mmol/mol	$y_{k,\text{ver}}$ mmol/mol	$(y_{k,\text{prep}}-y_{k,\text{ver}})$ mmol/mol	$\overline{\lvert y_{k,\text{prep}} - y_{k,\text{ver}}\rvert}$ mmol/mol	$u(v)$ mmol/mol
1	1,000 8	1,004 9	-0,004 1	0,004 6	0,003 6
2	0,998 9	1,005 9	-0,007 0		
3	0,998 9	1,006 9	-0,008 0		
4	1,000 6	1,008 5	-0,007 9		
5	1,000 6	0,998 3	0,002 3		
6	0,998 8	0,999 6	-0,000 8		
7	0,998 9	1,006 7	-0,007 8		
8	1,000 7	1,002	-0,001 3		
9	1,000 7	1,006 7	-0,006 0		
10	1,000 7	1,005 8	-0,005 1		

The uncertainties for each cylinder and the generic uncertainty are shown in Table A.3.

The generic uncertainty is calculated by rounding up the maximum uncertainty found in the 10 cylinders.

Table A.3 — Uncertainties involved in the Class II preparation, individual production

$u(y_{k,\text{prep}})$ mmol/mol	$u(y_{k,\text{ver}})$ mmol/mol	$\overline{\lvert y_{k,\text{prep}} - y_{k,\text{ver}}\rvert}$ mmol/mol	$u(v)$ mmol/mol	$u_c(y_k)$ mmol/mol	$U_c(y_k)$ mmol/mol
0,005 0	0,006 0	0,004 6	0,003 6	0,004 9	0,009 8

The relative expanded uncertainty is determined by rounding up to a higher value than the values achieved in the validation. In this example the relative expanded generic uncertainty is 1,0 %.

A similar table should be produced for different amount fractions to enable the calculation of the generic uncertainty for a range of CO_2 in nitrogen mixtures.

Annex B
(informative)

A practical example of the calculation of the generic uncertainty – Batch filling

The example below shows how the generic batch uncertainty, s_{bb} for carbon monoxide (CO) is determined in a multicomponent mixture and how this value can be influenced by the number of analyses performed.

EXAMPLE

A batch of 10 cylinders is filled with a multicomponent mixture with the nominal amount of substance fractions of: 3,5 cmol/mol CO, 14 cmol/mol CO_2 and 2 000 µmol/mol C_3H_8 in a N_2 balance. After the filling process, the cylinders are safely disconnected and homogenized. This is followed by the individual analysis of all of the mixtures.

Two approaches are used:

— each minor component of the mixture in each cylinder is analysed twice, and the analytical results are entered in a table with 10 rows and 2 columns (Table B.1).

— each minor component of the mixture in each cylinder is analysed five times, and the analytical results are entered in a table with 10 rows and 5 columns (Table B.2).

Table B.1 — Results of the analysis for carbon monoxide in cmol/mol

Cyl no.	Amount fraction $y_{(CO)}$		AVG
	y_1	y_2	$y(CO)$
5602397	3,500	3,500	3,500
5602438	3,499	3,504	3,501
5602375	3,512	3,508	3,510
5602493	3,498	3,506	3,502
5602491	3,501	3,510	3,505
5602486	3,504	3,504	3,504
5602417	3,510	3,517	3,513
5602478	3,507	3,504	3,506
5600718	3,510	3,504	3,507
5601587	3,514	3,517	3,516
		$y_{(avg,avg)}$ =	3,506

Table B.2 — Results of the analysis for carbon monoxide in cmol/mol

Cyl no.	Amount fraction $y_{(CO)}$					AVG
	y_1	y_2	y_3	y_4	y_5	$y(CO)$
5602397	3,500	3,500	3,501	3,502	3,501	3,501
5602438	3,499	3,504	3,505	3,504	3,506	3,504
5602375	3,512	3,508	3,510	3,510	3,514	3,511
5602493	3,498	3,506	3,511	3,513	3,512	3,508
5602491	3,501	3,510	3,513	3,511	3,510	3,509
5602486	3,504	3,504	3,506	3,503	3,506	3,505
5602417	3,510	3,517	3,507	3,511	3,511	3,511

Table B.2 *(continued)*

Cyl no.	Amount fraction $y_{(CO)}$					AVG $y(CO)$
	y_1	y_2	y_3	y_4	y_5	
5602478	3,507	3,504	3,508	3,510	3,509	3,508
5600718	3,510	3,504	3,503	3,510	3,508	3,507
5601587	3,514	3,517	3,511	3,515	3,516	3,515
					$y_{(avg,avg)}$ =	3,508

In both cases the one-way ANOVA analysis is performed using spreadsheet-based software. The between-bottle standard deviation s_{bb} is the square root of the between-group variance derived from the ANOVA analysis, which is calculated using Formula (B.1):

$$S_{bb}{}^2 = \frac{MS_{among} - MS_{within}}{n_0} \tag{B.1}$$

where:

MS_{among} is the mean aquare between groups (from ANOVA),

MS_{within} is the mean square within the groups (from ANOVA),

n_0 is the number of replicates for each cylinder,

$u^2\ (s_{bb})$ $s^2{}_{bb}$.

In the case where two analyses are performed, the results of the ANOVA are given in Table B.3.

Table B.3 — Results of ANOVA

Analysis of variance			
DOF num 9	Variation between samples **Sum of squares** 4,764 × 10^{-4}	Variance between samples **Mean squares** 5,294 × 10^{-5}	**F(test)=** 3,66
DOF denum 10	Analytical variation **Sum of squares** 1,445 × 10^{-4}	Analytical variance **Mean squares** 1,445 × 10^{-5}	
CO avg value of batch Between-Bottle Homogeneity	= $y_{(avg,avg)}$ = = $s_{bb(rel)}$ =	3,506 cmol/mol 0,125 %	
Key DOF num = degrees of freedom between groups DOF denum = degrees of freedom within groups			

In the case where five analyses are performed, the results of the ANOVA are as follows (Table B.4).

Table B.4 — Results of ANOVA

Analysis of variance			
DOF num	Variation between samples **Sum of squares**	Variance between samples **Mean squares**	**F(test)=**
9	$7{,}289 \times 10^{-4}$	$8{,}099 \times 10^{-5}$	7,38
DOF denum	Analytical variation **Sum of squares**	Analytical variance **Mean squares**	
40	$4{,}392 \times 10^{-4}$	$1{,}098 \times 10^{-5}$	
CO avg value of batch	$= y_{(avg,avg)} =$	3,508 cmol/mol	
Between-Bottle Homogeneity	$= s_{bb(rel)} =$	0,107 %	
Key DOF num = degrees of freedom between groups DOF denum = degrees of freedom within groups			

In Table B.5, the $S_{bb,k}$ between bottle homogeneity uncertainty for each component k in the mixture is provided.

Table B.5 — Results of ANOVA

Analyte	z	a	n_0	y_{avg} [cmol/mol]	$s_{bb,k(rel)}$ [%]
Carbon Monoxide	10	10	5	3,508	0,107 %
Carbon Dioxide	10	10	5	13,77	0,092 %
Propane	10	10	5	0,202 1	0,081 %
Key z = total number of mixtures in the batch a = number of mixtures analysed from the total batch n_0 = Number of replicates for each cylinder y_{avg} = average amount of substance fraction value for component in the batch					

Annex C
(informative)

Example mixture categories

An example of a category of mixture determination for a binary mixture of methane in nitrogen is considered with each range having the same individual filling process and verification method. The mixture is prepared in a cylinder of 10 litre water capacity at 150 bar.

To determine the ranges, it is useful to consider the target uncertainty required and the possible use of a premix.

Moreover, it is important to consider that the calculated uncertainty for methane shall be valid in relative value for amount fractions above the amount fraction considered and in absolute value for amount fractions below.

Pure component CH_4 and N_2

Selected mixture for the validation: 25 cmol/mol methane in nitrogen

Selected mixture for the validation	$U(y_k)$ **cmol/mol**	$U_{rel}(y_k)$ **%**	$U_{rel}(y_k)$*rounded* **%**
25 cmol/mol methane in nitrogen	0,106	0,424	0,5

$U_{rel}(y_k)$ = 0,5 % is applicable from 25 cmol/mol and above.

$U(y_k)$ = 0,106 cmol/mol is applicable up to 25 cmol/mol from an amount fraction defined by the producer according to the target uncertainty required.

Lower amount fraction Mixture	$U(y_k)$ **cmol/mol**	$U_{rel}(y_k)$ **%**	$U_{rel}(y_k)$*rounded* **%**	**Considerations**
15 cmol/mol methane in nitrogen	0,106	0,71	0,8	The uncertainty is acceptable
5 cmol/mol methane in nitrogen	0,106	2,12	2,5	No, the uncertainty is too high

The categories of mixture are:

Amount fraction CH_4 **in** N_2 **cmol/mol**	$U(y_k)$ **cmol/mol**	$U_{rel}(y_k)$ **rounded %**
$CH_4 > 25$	0,106	0,5
$15 < CH_4 < 25$	0,106	0,8 - 0,5

Following the same approach, the categories are defined.

Pure component CH_4 and N_2

Selected mixture for the validation: 5 cmol/mol methane in nitrogen

Selected mixture for the validation	$U(y_k)$ **cmol/mol**	$U_{rel}(y_k)$ **%**	$U_{rel}(y_k)$ **rounded %**
5 cmol/mol methane in nitrogen	0,044	0,88	1