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ISO 6142-2

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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

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Foreword

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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

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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/

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.

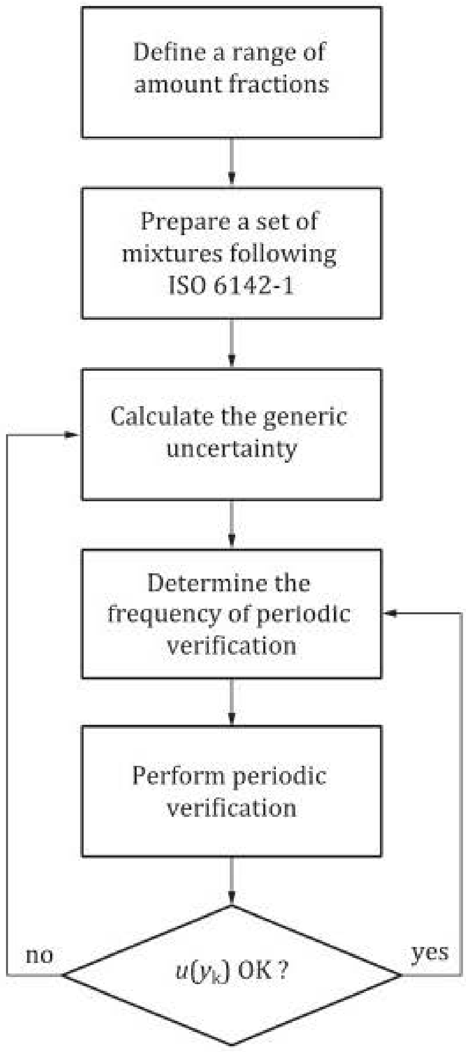


Figure 1 — Scheme for the gravimetric method of preparing Class II calibration gas mixtures, individual preparation

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.

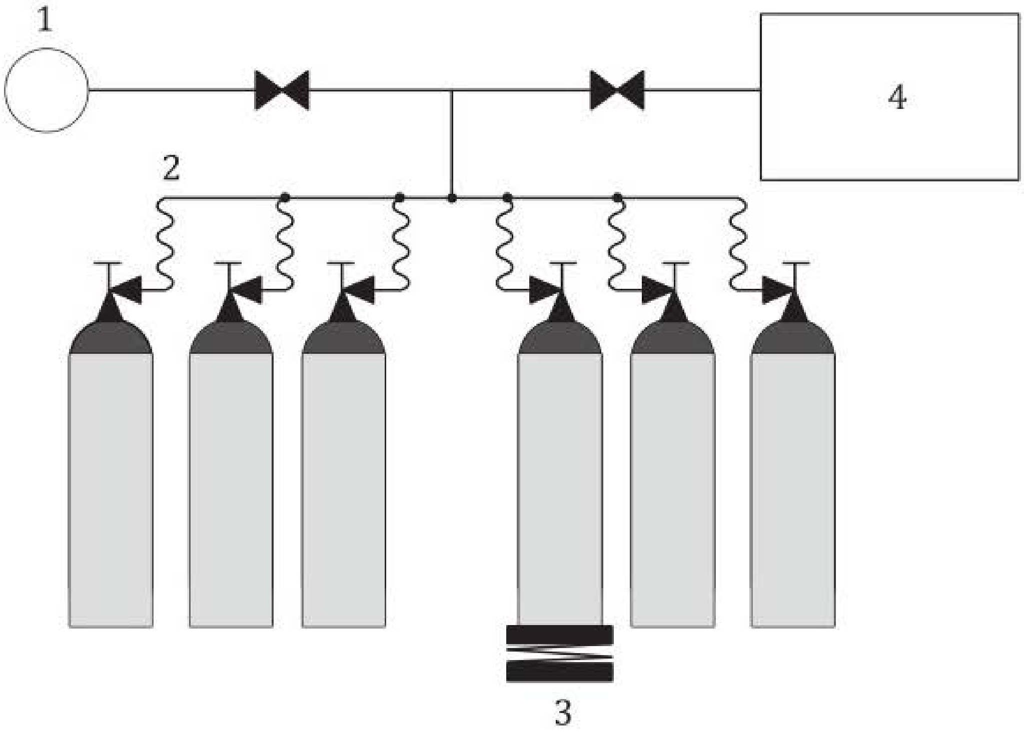
The batch homogeneity can be improved by using a symmetrical manifold and similar length and diameter of filling lines to each cylinder (see Figure 2).

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.