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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 des mélanges 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

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~~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 ~~in accordance with~~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 ~~accordance~~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 maycan 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 wholethe text in such a way that some or in part, are normatively referenced inall of their content constitutes requirements of this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 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 ~~terminological~~terminology databases for use in standardization at the following addresses:

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

— IEC Electropedia: available at ~~https://www.electropedia.org/~~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
~~$y_{k,ver}$~~ $y_{k,\mathrm{ver}}$	amount fraction of the component k measured by analysis in course of validation of the mixture
~~$y_{k,prep}$~~ $y_{k,\mathrm{prep}}$	amount fraction of the component k calculated in the preparation of the mixture
~~v_k~~ v_k	difference between the amount fraction from preparation and verification for the component k ~~$v_k = \left(y_{k,prep} - y_{k,ver}\right)$~~ $v_k = \left(y_{k,\mathrm{prep}} - y_{k,\mathrm{ver}}\right)$
~~s_{bb}~~ 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~~ n_0	number of individual analyses performed on a component in a mixture
z	total number of mixtures in the batch

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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_{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.

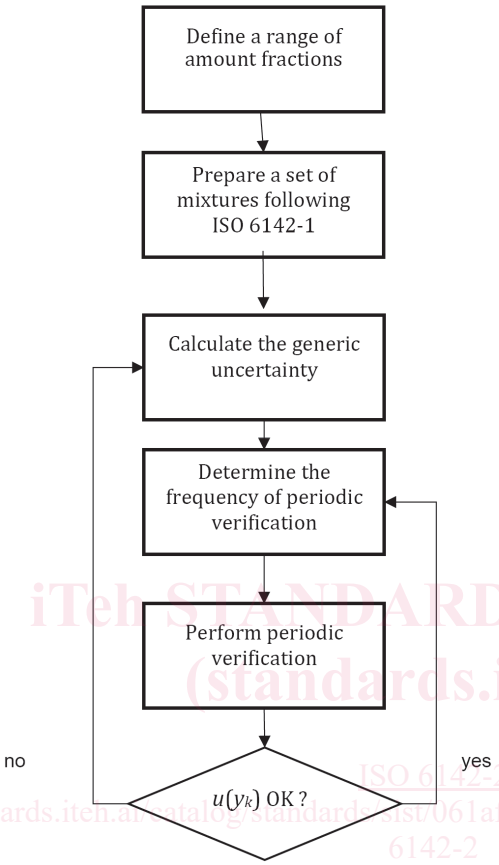
The filling of calibration gas mixtures in a batch is described in the Clause 7 with a description of the filling process and the uncertainty calculation.

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.



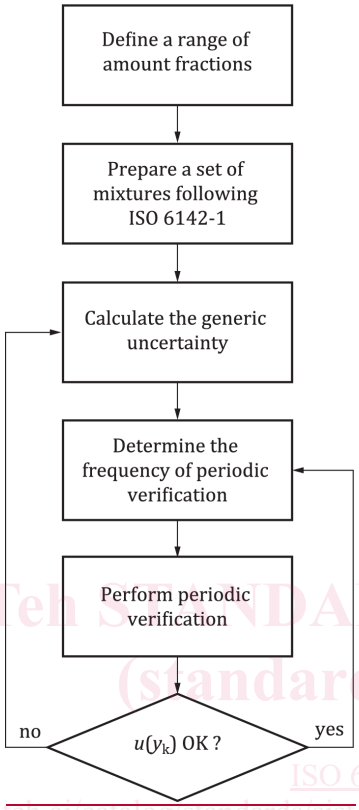


Figure 1 — Scheme for the gravimetric method of preparing Class II calibration gas mixtures, individual preparation

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):

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

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