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Gas analysis — Preparation of calibration gas mixtures —

Part 1: Gravimetric method for Class I mixtures

Analyse des gaz — Préparation des mélanges de gaz pour étalonnage —
Partie 1: Méthode gravimétrique pour les mélanges de Classe I

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Foreword

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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 documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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

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

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

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

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

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

Introduction

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

Class I type calibration gas mixtures are prepared in accordance with this part of ISO 6142. The mixtures are individually verified. Provided rigorous and comprehensive quality assurance and quality control procedures are adopted during the preparation and verification of these mixtures, uncertainties may be achieved that are substantially smaller than by any other preparation method.

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

Gas analysis — Preparation of calibration gas mixtures —

Part 1: Gravimetric method for Class I mixtures

1 Scope

This part of ISO 6142 specifies a gravimetric method for the preparation of calibration gas mixtures in cylinders with traceable values for the amount-of-substance fraction (amount fraction) of one or more components. This part of ISO 6142 describes a method for calculating the uncertainty associated with the amount fraction of each component. This uncertainty calculation requires the evaluation of the contributions to the uncertainty due to factors including the weighing process, the purity of the components, the stability of the mixture, and the verification of the final mixture.

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

This part of ISO 6142 requires estimation of the stability of the mixture for its intended life time (maximum storage life), but it is not for use with components that react with each other unintentionally. This part of ISO 6142 also requires the impurities in each parent gas or liquid used in the preparation of the mixture to be assessed and quantified.

2 Normative references

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

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

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

ISO 7504, *Gas analysis — Vocabulary*

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

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

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

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

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

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

3 Terms and definitions

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

4 Symbols

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

y_k^t amount-of-substance fraction of component k at time t

y_i amount-of-substance fraction of component i in the prepared mixture

y_k amount-of-substance fraction of component k in the prepared mixture

$y_{k,\mathrm{ver}}$ analysed amount-of-substance fraction

Z_Ω compressibility of the final mixture

Ω final mixture

5 Principle

Calibration gas mixtures are prepared by transferring pure gases, pure liquids, or gravimetrically prepared mixtures of known composition quantitatively into a cylinder in which the calibration gas will be contained. The traceability to the SI of amount fractions of these mixtures arises from the correct execution of three steps:

a) the determination of the masses added;

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

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

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

The mass of each component is determined by weighing either the supply cylinder, or the cylinder in which the calibration gas mixture will be contained, before and after each addition. The difference in these two weighings corresponds to the mass of the component added. The choice between these two weighing procedures depends on the uncertainty required for the amount fraction of the final mixture. Annex A provides more guidance on precautions to be taken when weighing, handling, and filling cylinders.

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

A single-step preparation method may be used when the mass of each component added is large enough to be measured accurately. Alternatively, a multiple-step dilution method may be used to obtain a final mixture with acceptable uncertainty, particularly when low amount fractions are required. In this method, “pre-mixtures” are prepared gravimetrically and used as parent gases in one or more of the steps.

An example of the steps used to prepare a calibration gas mixture is given in Annex B.

The determination of the purity of each material (liquid or gas) used in the preparation of the mixture is described in Clause 7. Clause 8 describes the determination of masses and the calculation of preparation uncertainty. The homogeneity and stability of the gas mixture are dealt with in Clause 9. The verification of the amount fraction of the components in the final mixture against independent standards is described in Clause 10. The calculation of the uncertainty of the calibration gas mixture is given in Clause 11.

The gravimetric method scheme for preparing calibration gas mixtures, based on requirements for composition and the level of uncertainty, is given as a flowchart in Figure 1. The individual steps are explained in more detail in the following clauses (reference is given to the subclause for each step in Figure 1).

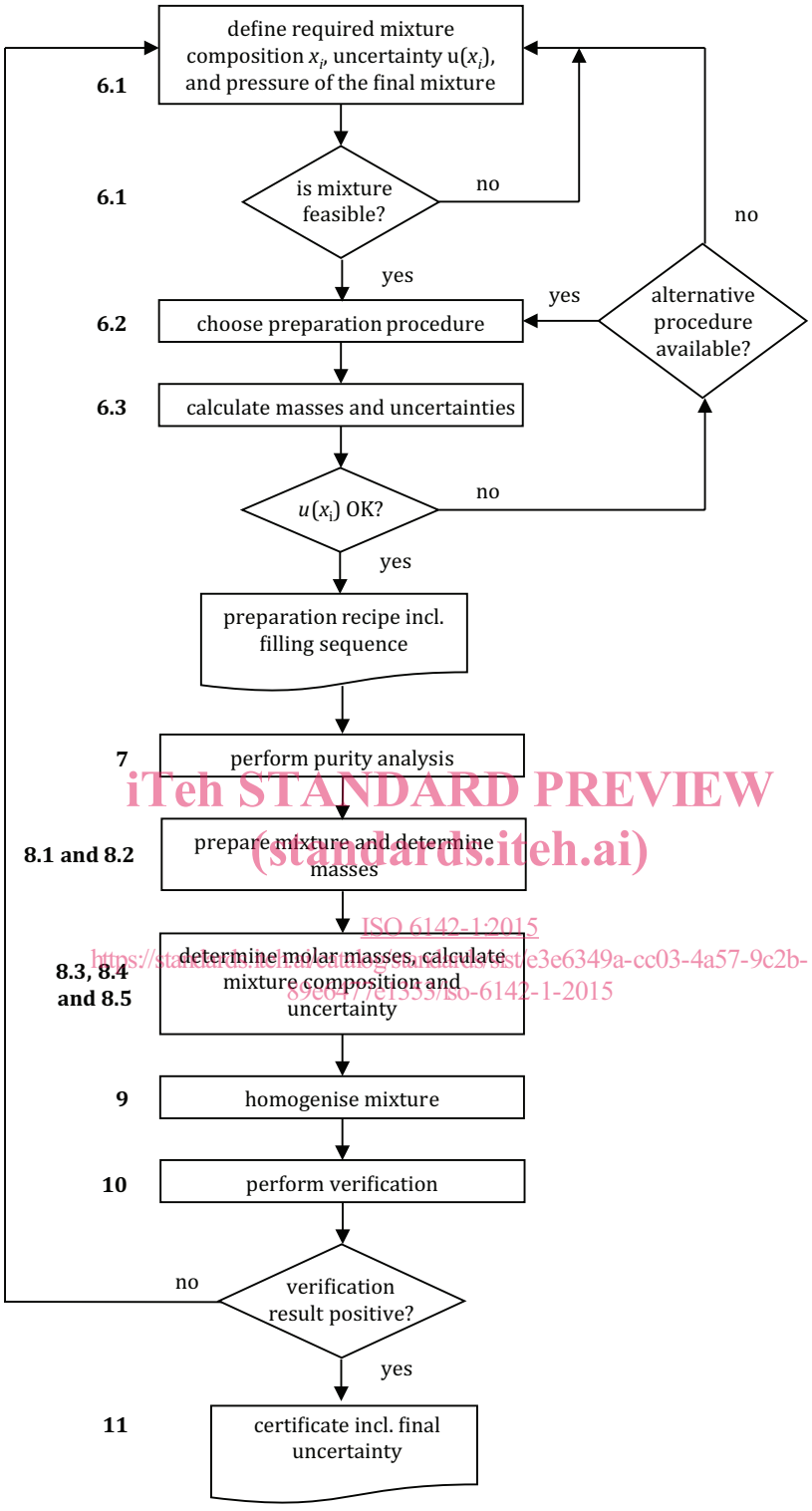

Figure 1 — Scheme for preparation of calibration gas mixtures using gravimetry

6 Planning the preparation of the mixture

6.1 Feasibility of preparing the gas mixture

6.1.1 Safety considerations

Gas mixtures potentially capable of reacting dangerously shall be excluded for safety reasons. National and local safety regulations should be followed.

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

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

6.1.2 Reactions of mixture components

Before preparing a gas mixture, it is essential to consider possible chemical reactions of the components of the mixture. A comprehensive compilation of combinations of components that may react is not available. Therefore, chemical expertise is necessary to assess the stability of a gas mixture and a risk analysis shall be performed.

6.1.3 Reactions with container materials

Before preparing a gas mixture, it is necessary to consider possible chemical reactions of mixture components with the materials of a high-pressure cylinder, its valve and the transfer system. Special consideration shall be given to the attack by corrosive gases with metals and possible reactions with elastomers and greases used, for example, in the valve seat and seals. Such reactions shall be prevented by using only materials that are inert to all components of the mixture. If this is not possible, measures shall be taken to minimize corrosive attack on the materials with which the gases make contact so as to prevent any significant effect on mixture composition and any danger in storage and use.

NOTE Information on the compatibility of gases with container materials is given in ISO 16664 and in ISO 11114 (all parts)[25].

6.2 Choice of preparation method

The following parameters shall be considered when choosing a preparation method:

— the target composition and uncertainty of the calibration gas mixture;

— the target filling pressure of the calibration gas mixture;

— the required tolerance for the preparation;

— the composition of any available parent gas mixture;

— the performance specifications of the balance to be used .

6.3 Calculation of target masses

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

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

where m_Ω is computed as

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

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

After the target masses have been calculated, a preparation procedure is selected and the uncertainties associated with the amount fractions are calculated (see 8.5). If these uncertainties are deemed unacceptable, another procedure shall be tried. It may be necessary to perform an iterative process to select a procedure with acceptable uncertainty.

NOTE 2 The preparation method can include various filling methods, i.e. direct method, multiple step dilution, or transfer method (use of small cylinder separately weighed on a low-capacity, high-resolution balance). More information on the various preparation methods is given in Annex A.

6.4 Condensation of components from the gas phase

When preparing, storing, or handling gas mixtures that contain condensable components (see Annex C), the following measures shall be taken to prevent condensation because this will change the gas phase composition.

— During the preparation of the gas mixture, the filling pressure shall be set safely below the dew-point vapour pressure of the final mixture at the filling temperature. To prevent condensation at intermediate stages, this condition shall be fulfilled for every intermediate mixture as well. If condensation of an intermediate mixture cannot be safely excluded, measures shall be taken to vaporize any possible condensate and to homogenize the gas phase at an appropriate later stage. The fill pressure is also set after consideration of the Joule-Thomson cooling curve (see Annex C).

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

— During the handling of the gas mixture, the same condition on the handling temperature applies. Furthermore, to prevent condensation during mixture transfer, the transfer lines shall be heated if required.

In Annex C, some guidance is given for estimating the maximum filling pressure for introducing components of a gas mixture at which no condensation of the condensable components is expected to occur. An example of this estimation is given in C.2 for a natural gas mixture.

7 Purity analysis

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

8 Determination of masses and calculation of preparation uncertainty

8.1 Preparation of cylinder

Select a cylinder for the preparation. Evacuate it to a pressure at which the residual gas will not contribute to the uncertainty of the final mixture. In some cases, cylinder surface treatment steps will be required to allow for preparation of specific calibration gas mixtures.

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

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

8.2 Determination of masses and their uncertainties

The mass of each component added to the cylinder shall be determined by weighing. Precautions to be taken when weighing, handling, and filling cylinders are given in Annex A.

The uncertainty of each mass added shall be evaluated. The evaluation shall take into account all sources of uncertainty, in particular the following:

— the accuracy of the (electronic) balance including consideration of its calibration and its linearity;

— the repeatability of the balance readings including errors caused by the location of the cylinder on the balance;

— buoyancy effects;

— effects of moisture adsorption and dust on the outer surface of the cylinder;

— errors due to loss of material during transfer into the cylinder.

Guidance on the introduction of liquid components into gravimetrically prepared calibration gas mixtures is provided in Annex D. This annex is only applicable to mixtures whose final composition is totally vaporized and contain components that do not react with each other or interact with the cylinder wall.

8.3 Atomic weights and molar masses

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

For other conversions between quantities, ISO 14912 shall be used.