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Gas analysis — General quality assurance aspects in the use of calibration gas mixtures — Guidelines

Analyse des gaz — Aspects généraux de l'assurance qualité dans l'utilisation de mélanges de gaz pour étalonnage — Lignes directrices

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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 2.

The main task of technical committees is to prepare International Standards. 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.

In other circumstances, particularly when there is an urgent market requirement for such documents, a technical committee may decide to publish other types of normative document:

— an ISO Publicly Available Specification (ISO/PAS) represents an agreement between technical experts in an ISO working group and is accepted for publication if it is approved by more than 50 % of the members of the parent committee casting a vote;

— an ISO Technical Specification (ISO/TS) represents an agreement between the members of a technical committee and is accepted for publication if it is approved by 2/3 of the members of the committee casting a vote.

An ISO/PAS or ISO/TS is reviewed after three years in order to decide whether it will be confirmed for a further three years, revised to become an International Standard, or withdrawn. If the ISO/PAS or ISO/TS is confirmed, it is reviewed again after a further three years, at which time it must either be transformed into an International Standard or be withdrawn.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO/TS 14167 was prepared by Technical Committee ISO/TC 158, *Analysis of gases*.

Introduction

Gas analyses are performed on samples covering a wide range of compositions.

All gas analyses fall into one of two categories:

— those for which calibration gas mixtures exist with compositions that are traceable to reference gas mixtures (e.g. primary or national standards);

— those for which the above do not exist.

In both cases, this Technical Specification provides the overall guidance on quality assurance aspects required to achieve a result with a valid measurement uncertainty.

It is applicable only to calibration gas mixtures of gaseous, or totally vaporized, components which do not react with each other or with the cylinder walls.

The user of this Technical Specification chooses, prior to any analyses, an appropriate measurement procedure depending on the application of the final results of the analyses and the requirements for a particular measurement uncertainty. This use may vary considerably, ranging from qualitative analysis to accurate quantitative analysis for which evidence has to be provided that claimed measurement uncertainty levels are met. Each type of measurement procedure involves a number of issues, which are considered beforehand. Typically, for gas analysis these include:

a) sampling;

b) selection and use of calibration gas mixtures;

c) selection and validation of measurement method;

d) identification of uncertainty sources;

e) quantification of uncertainty contributions;

f) documentation.

For a given measurement procedure, the effect of the above issues, influencing the uncertainty of the final measurement result, is calculated approximately. This may imply that several calculations have to be made in advance, with different sets of values for the parameters involved, before the required level of uncertainty is achieved. In practice, this calculation process is repeated until the desired target uncertainty is reached. This process of defining target uncertainties is an effective way of finding correct solutions for specific measurement procedures. The final analysis is then performed using this evaluated procedure.

To illustrate the use of this Technical Specification, two practical examples are given in Annex A.

Annex B gives information on the validation of reference gas mixtures in those cases where calibration gases of widely acknowledged composition do not exist.

Annex C describes the traditional hierarchy of reference gas mixtures.

The references are given in the Bibliography.

Gas analysis — General quality assurance aspects in the use of calibration gas mixtures — Guidelines

1 Scope

This Technical Specification provides guidance on the quality aspects in the field of gas analysis that are implemented in order to achieve a result with a valid measurement uncertainty.

It provides guidelines on quality aspects to be employed in gas analysis using calibration gas mixtures and their subsequent validation and/or verification, and the testing of the analytical performance of gas analysis instruments. These guidelines have the overall objective of defining procedures which will ensure that measurements of gas composition are reliable, comparable and consistent between different organizations and countries.

This Technical Specification explains, in particular, the concepts of measurement uncertainty and of traceability as effective quality assurance tools for defining the measurement uncertainty of particular measurement results. It also gives guidance on how to identify and estimate measurement uncertainty components of the result, and how to combine these uncertainty components in order to obtain the overall uncertainty.

2 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

2.1
traceability
property of a result of a measurement or the value of a standard whereby it can be related to stated references, usually national or international standards, through an unbroken chain of comparisons all having stated uncertainties

NOTE 1 The unbroken chain of comparisons is called a “traceability chain”.

NOTE 2 A calibration gas mixture is traceable at best to a primary reference gas mixture.

[VIM [1]]

2.2
uncertainty (of measurement)
parameter, associated with the result of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the measurand

NOTE 1 The parameter may be, for example, a standard deviation or a given multiple of it, or the half-width of an interval having a stated level of confidence.

NOTE 2 Uncertainty of measurement comprises, in general, many components. Some of these components may be evaluated from the statistical distribution of the results of series of measurements and can be characterized by experimental standard deviations. The other components, which can also be characterized by standard deviations, are evaluated from assumed probability distributions based on experience or other information.

NOTE 3 It is understood that the result of the measurement is the best estimate of the value of the measurand, and that all components of uncertainty, including those arising from systematic effects, such as components associated with corrections and reference standards, contribute to the dispersion.

NOTE 4 Uncertainty can be expressed as a standard uncertainty or, when multiplied by a coverage factor, as an expanded uncertainty.

[Adapted from GUM [2]]

2.3
uncertainty of a certified value
estimate attached to a certified value of a quantity which characterizes the range of values within which the "true value" is asserted to lie with a stated level of confidence

[ISO Guide 30:1992 [3]]

2.4
calibration gas mixture
gas mixture of sufficient stability and homogeneity whose composition is properly established for use in the calibration of a measuring instrument or for the validation of a measurement or gas analytical method

NOTE Calibration gas mixtures are the analogues of measurement standards in physical metrology

[ISO 7504:2001 [4]]

2.5
reference gas mixture

calibration gas mixture whose composition is sufficiently well established and stable to be used as a reference standard of composition from which other composition data are derived

NOTE Reference gas mixtures are the analogues of reference standards.

[ISO 7504:2001 [4]]

2.6
primary reference gas mixture
reference gas mixture which is designated, or generally accepted, as realizing a specific composition of the highest metrological quality

NOTE 1 Primary reference gas mixtures are the analogues of primary standards.

NOTE 2 Normally the use of primary reference gas mixtures is confined to comparisons with other primary reference gas mixtures of similar compositions and to secure secondary reference gas mixtures by comparison.

NOTE 3 Primary reference gas mixtures are sometimes designated as measurement standards by national metrology institutes, and may then be known as primary standard gas mixtures

[ISO 7504:2001 [4]]

2.7
secondary reference gas mixture
reference gas mixture whose composition is assigned by comparison with a primary reference gas mixture of similar composition, or with several such primary reference gas mixtures

NOTE 1 Secondary reference gas mixtures are the analogues of secondary standards.

NOTE 2 A secondary reference gas mixture may be used as a calibration gas mixture then having traceability to a primary reference gas mixture.

[ISO 7504:2001 [4]]

2.8
stability
attribute of a gas mixture, stored or used under specified conditions, to maintain its composition within its specified uncertainty limits for a specified period of time (maximum storage life) and over a specified range of pressure and of temperature

NOTE It is appropriate to specify the uncertainty limits for each component of interest.

[ISO 7504:2001 [4]]

2.9
homogeneity
state of a gas mixture wherein all of its components are distributed uniformly throughout the volume occupied by the gas mixture

NOTE Unless any other indication is given, it is normally to be assumed that the gas mixture is homogeneous in composition in time and space within the gas mixture.

[ISO 7504:2001 [4]]

2.10
validation
confirmation, through the provision of objective evidence, that the requirements for a specific intended use or application have been fulfilled

NOTE 1 In design and development, validation concerns the process of examining a product to determine conformity with user requirements.

NOTE 2 Validation is normally performed on the final product under defined operating conditions. It may be necessary in earlier stages.

NOTE 3 The term “validated” is used to designate the corresponding status.

NOTE 4 Multiple validations may be carried out if there are different intended uses.

NOTE 5 In gas composition analysis, validation refers to the confirmation that the method, as applied, is fit for the intended purpose.

[Adapted from ISO 7504:2001 [4]]

2.11
verification
Confirmation, through the provision of objective evidence, that the specified requirements have been fulfilled

NOTE 1 In design and development, verification concerns the process of examining the result of a given activity to determine the conformity with the stated requirements for that activity.

NOTE 2 The term “verified” is used to designate the corresponding status.

NOTE 3 In gas composition analysis, verification refers to an individual result that agrees with the result of an independent method.

[ISO 7504:2001 [4]]

3 Gas analysis using a comparison method

The acceptability of individual measurement results is improved when rigorous quality control provides evidence that the results are in agreement with results from:

a) measurements on similar samples by other laboratories;

b) previous measurements on similar samples by the same laboratory;

c) previous measurements on other samples.

Whenever links are made between measurement systems, these links have to be identified (traceability chain) and its strength quantified (uncertainty). In the following clauses, these concepts are elaborated as well as the quality control aspects of the steps in the measurement procedure.

Calibration gas mixtures should be prepared using either static or dynamic methods:

— Gravimetric preparation of fully gaseous gas mixtures is described in ISO 6142 [5].

— Static volumetric methods are described in ISO 6144 [6].

— The various parts of ISO 6145 [7] to [15] deal with a great number of dynamic methods for preparing gas mixtures. Mixtures prepared in accordance with any of these parts will have stated compositions and uncertainty evaluations.

Mixtures prepared by the methods given should first be verified before they can actually be used as calibration gas mixtures. ISO 6143 [16] gives a comparison method that is in most cases suited for verification purposes.

ISO 6141 [17] describes the contents of a certificate of a calibration gas mixture.

Figure 1 gives a scheme explaining gas analysis using a comparison method. The numbers in the boxes refer to references in the Bibliography.

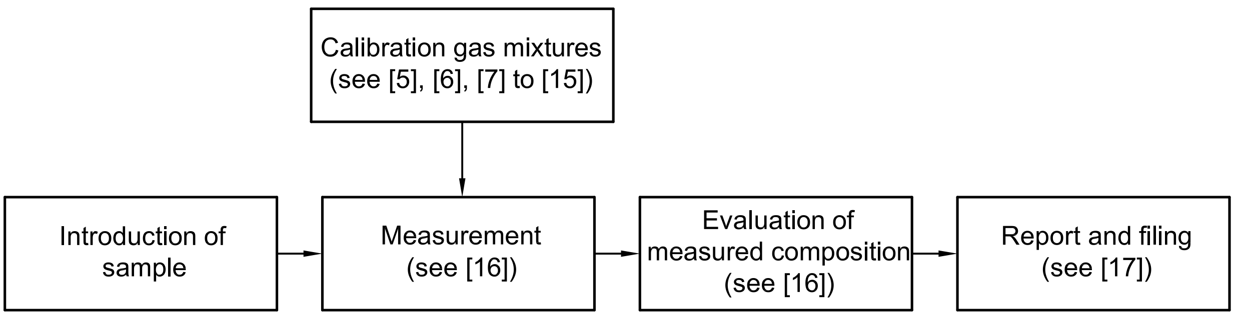

Figure 1 — Gas analysis scheme using a comparison method

4 Uncertainty

4.1 General

The main task of gas analysis is to determine the composition of gases, i.e. to measure the content of one or several specified target components (analytes) in a matrix gas. This clause mainly gives guidance on how to evaluate and express the uncertainty of results in gas composition analysis. However, the same principles and analogous procedures may be used to evaluate and express the uncertainty of results in the preparation of calibration gas mixtures or in other fields of gas analysis such as the direct measurement of physico-chemical properties of gases.

The uncertainty of an analytical procedure is determined in accordance with two fundamentally different strategies:

— the **step-by-step** approach (also called the bottom-up approach), where the uncertainty is calculated as a combination of various components, relating to building blocks of the overall procedure or to significant error sources;

— the **direct** approach (also called the top-down approach), where the uncertainty is determined directly by investigating the spread of results obtained on gases of known composition.

The step-by-step approach (see 4.2) requires a thorough investigation of the analytical procedure and proper assessment of component uncertainties. Its main tools are uncertainty budgets and uncertainty propagation, based on an appropriate mathematical model of the measurement process or the preparation process.

The direct approach (see 4.3) requires appropriate reference gases or reference analytical methods. In addition, the comparison measurements have to be performed under appropriate reproducibility conditions.

4.2 Step-by-step approach

This approach attempts to evaluate the uncertainty of the result of an analytical procedure by identifying the uncertainty components of that procedure. Each of the uncertainty components are evaluated to determine their contribution and are combined mathematically using the principles described in GUM [2]. This approach requires the user to produce a detailed uncertainty budget in a series of steps as follows:

a) Separate the analytical procedure into a series of well-designed steps, e.g. sample pre-treatment, measurement, data evaluation.

b) For each step, identify and list all factors that may influence the performance of this step and consequently give rise to uncertainty.

NOTE 1 It is understood that a correction is applied to every identified source of systematic error, leaving as a contribution to the overall uncertainty budget the uncertainty of the correction.

NOTE 2 In a number of International Standards produced by ISO/TC 158, comprehensive lists of uncertainty sources and assessments of their relevance are given. [5], [6], [7], [16]

NOTE 3 To prove the validity of the results, traceability to acknowledged measurement standards should be demonstrated where available.

c) Some of the identified uncertainties will have a large influence on the uncertainty of the method, and others only a small influence. To determine this influence, an estimate is now made of the contribution of each of the uncertainty sources to the final combined standard uncertainty. Each of the identified uncertainties should now be classed as being either significant or insignificant when compared to the combined standard uncertainty. Uncertainty sources classed as insignificant should be neglected. (Insignificant uncertainties may be classed as those which contribute less than 10 % to the combined standard uncertainty.)

d) For the uncertainty sources classed as significant, design a mathematical model describing the final result of the procedure, y, as a function of the input parameters (significant contributors) x_i (i = 1, 2, …, N), e.g. sample flow, pressure and temperature, recovery rates, measured instrument response, response function parameters, conversion factors and corrections:

$$y = f(x_1, x_2, \ldots, x_N) \tag{1}$$

e) For each significant uncertainty source, evaluate the contribution $u_i(y)$ to the uncertainty of the final result y as a **standard uncertainty**, that is as a standard deviation, either of a series of repeated measurement results (Type A evaluation) or of a hypothetical distribution expressing the available information about the respective quantity (Type B evaluation). The contribution to the total uncertainty due to x_i is $u_i(y)$, and is

determined as a product of a sensitivity coefficient c_i taken from the model in accordance with step d) and the standard uncertainty $u(x_i)$ of the respective input quantity:

$$u_i(y) \equiv |c_i|\, u(x_i) \tag{2}$$

where $c_i = \dfrac{\partial f}{\partial x_i}$

f) Consider possible correlations between different uncertainty contributions $u_i(y)$ and $u_j(y)$, determined in step e), e.g. due to use of the same measurement standard. If the correlation is determined as being significant, estimate the corresponding **covariance** $u_{ij}(y)$:

$$u_{ij}(y) = c_i c_j\, u(x_i, x_j) \tag{3}$$

g) Calculate the **combined standard uncertainty** $u(y)$ of the final result y as the root of the sum of squares of the component standard uncertainties and their possible covariances:

$$u_c{}^2(y) = \sum_{i=1}^{N} c_i{}^2 u^2(x_i) + 2\sum_{i=1}^{N-1} \sum_{j=i+1}^{N} c_i c_j\, u(x_i, x_j) \tag{4}$$

4.3 Direct approach

In this approach, the analytical procedure is applied to appropriate reference samples, and the results are compared with the reference values attributed to the reference samples. Alternatively, the procedure under investigation and an established reference method are applied in parallel to appropriate samples, and the results are compared. This comparison serves a double purpose:

a) By comparing the mean of repeated measurements with the corresponding reference value, any significant analytical bias is detected. In addition, an appropriate bias correction should be derived.

b) From the spread of results of repeated measurements and the uncertainty of the reference values, the uncertainty of the results of the analytical procedure, including a bias correction, is calculated. It is emphasized that a proper evaluation of the variability is necessary.

A more detailed description of this comparison and its evaluation are given in 5.2.

This approach is applied either by an individual laboratory or in an interlaboratory study. In the first case, it is essentially a calibration study. Then it is important to ensure that:

— the reference values and their uncertainties are well established;

— the calibration samples are representative of the range of samples to be analysed;

— the variability of the measurement conditions in the calibration study covers the variability in the intended applications.

In the second case of an interlaboratory study, the procedures described in the ISO 5725 series of International Standards [18] to [23] should be followed.

If neither suitable reference samples nor suitable reference methods are available, the comparison may be based on consensus values instead of reference values, as a substitute but by no means as an equivalent.