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Gas analysis — Handling of calibration gases and gas mixtures — Guidelines

Analyse des gaz — Manutention des gaz et des mélanges de gaz pour étalonnage — Lignes directrices

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Contents

Page

Foreword iv

Introduction v

1 Scope 1

2 Terms and definitions 1

3 Transport and storage 4
3.1 General remarks 4
3.2 Low temperature 4
3.3 High temperature 4
3.4 Water 4
3.5 Storage and handling 4

4 Mode of withdrawal 5
4.1 General 5
4.2 Minimum utilization pressure 5
4.3 Temperature 5
4.4 Pressure reduction and flow 5
4.5 Replacement, change of cylinder positions 5

5 Transfer system 6
5.1 Purging procedure 6
5.2 Considerations when designing and constructing gas transfer lines 7

6 Stability 13

Annex A (informative) **Check on the stability of calibration gas mixtures by end-users** 14

Bibliography 17

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.

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 16664 was prepared by Technical Committee ISO/TC 158, *Analysis of gases*.

Introduction

This International Standard uses the terms “calibration gas” for both gas mixtures and pure gases as the limiting case of gas mixtures.

The quality of calibration gases in cylinders as certified by producers is defined by

a) the correct analyte content;

b) a known uncertainty which is appropriate for its intended use;

c) the stability;

d) the homogeneity.

During its utilization period, the quality of calibration gases is influenced by

— storage conditions at the manufacturer’s and user’s sites;

— transport conditions;

— modes of calibration gas withdrawal and transfer;

— the transfer system employed.

Gas analysis — Handling of calibration gases and gas mixtures — Guidelines

SAFETY PRECAUTIONS — National and International safety regulations concerning storage, use and transportation of pure gases and gas mixtures are to be followed in addition to this International Standard.

1 Scope

This International Standard describes factors that may influence the composition of pure gases and homogeneous gas mixtures used for calibration purposes. This International Standard only applies to gases or gas mixtures that are within the “utilization period”, and it pays special attention to

— storage of calibration gas cylinders;

— calibration gas withdrawal from cylinders;

— transfer of calibration gas from cylinders to the point of calibration.

It also outlines a method of assessing the stability for a gas mixture, and takes into account the gas composition uncertainty given on the certificate and the users measurement uncertainty.

2 Terms and definitions

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

2.1
calibration gas
pure gas or gas mixture used for calibration

2.2
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

[ISO 7504:2001]

2.3
component
chemical substance present in, or a material used in the preparation of, a gas mixture

NOTE 1 In practice, the term component is used variously to mean either:

a) a distinct pure chemical substance; or

b) a material such as:

— a pure substance mixed with small amounts of inadvertent impurities,

— a well defined mixture, such as air,

— a less well defined mixture, such as natural gas.

NOTE 2 In circumstances where it is required to distinguish unambiguously between the individual distinct chemical substances present in a gas mixture and the materials used in gas mixture preparation, then the chemical substances shall be referred to as “constituents”. When a constituent is or has been the subject of quantitative analysis, it may be referred to as an “analyte”.

NOTE 3 In the preparation of gas mixtures, materials such as gases, vapours and gas mixtures, including their impurities, are sometimes called “parent gases”.

[ISO 7504:2001]

2.4
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 with respect to composition and properties at all points in the gas mixture.

[ISO 7504:2001]

2.5
impurity
component present, but not wanted, in a gas mixture

NOTE 1 Impurities found in a gas mixture originate from the parent gases or are introduced during or after its production.

NOTE 2 An impurity affecting the intended use of a gas mixture is called a “critical impurity”.

NOTE 3 If the fraction of a gas mixture component is close to unity, and if the other components are of no special interest, such a gas mixture is considered, in general, as a “pure gas” consisting of that predominant component containing some impurities.

NOTE 4 The “purity” of a “pure gas” is quantified usually by the difference between unity and the sum of the fractions of all specified impurities.

[adapted from ISO 7504:2001]

2.6
leak rate
volume of fluid leaking from the system per unit of time due to incomplete sealing of materials

2.7
leak tightness
conformity to a specified leak rate

2.8
response time
time interval between the instant when a stimulus is subjected to a specified abrupt change and the instant when the response reaches and remains within specified limits around its final steady value

[VIM]

2.9
stability
attribute of a gas mixture, stored or used under specified conditions, to maintain its composition within 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]

2.10
maximum storage life
period after which the stored gas mixture shall not be used

NOTE 1 This period is usually identified as that for which the producer assures that the gas mixture maintains its composition within the specified limits when it is stored in accordance with requirements based upon maximum filling pressure, minimum utilization pressure, and minimum and maximum applicable temperature.

NOTE 2 The end of this period may be indicated by an “expiry date”.

[ISO 7504:2001]

2.11
transfer system
gas-conducting system which begins at the cylinder valve and ends at the gas sample inlet to the measuring instrument and includes all structural elements

2.12
uncertainty
⟨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 also can 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 a measurement is the best estimate of the value of a 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.

[GUM; ISO 7504:2001]

2.13
utilization period
time between the date of certification and the expiry date

2.14
permeability
property of a material of transmitting gases and liquids by passage through one surface and out at another surface by diffusion and sorption processes

NOTE Not to be confused with porosity.

[ISO 472:1999]

3 Transport and storage

3.1 General remarks

After preparation of the calibration gas, the gas cylinder will be transported to the user. The environment in which the cylinders are transported is not normally regulated in terms of temperature and humidity. Low temperatures may have a detrimental impact on the mixture composition, especially when condensable components are present in the mixture. As a consequence of this, environmental conditions during transport and storage should never exceed those recommended by the manufacturer.

Gas cylinders and especially cylinder valves shall be free of grease and other lubricants. During storage and transportation, cylinder valves shall be closed, sealing nuts shall be tightened and protection caps shall be attached.

The gas cylinders are transported in several ways, e.g. by air, railway, road and on water. In some specific cases, the temperature restrictions may be such that not every means of transport is acceptable.

3.2 Low temperature

The gas cylinder may be exposed to low temperatures during storage and transportation. For gas mixtures containing condensable components, it is important that the cylinder is not stored or transported at temperatures below those recommended by the manufacturer. If the mixture is exposed to temperatures below the stated range, some components may condense and this will change the composition of the mixture.

If the mixture has been exposed to temperatures lower than those recommended by the manufacturer, the certificate from the manufacturer is no longer valid. In this case, it is very important that the mixture shall not be used before the manufacturer is asked for further advice. He may advise homogenizing the mixture before usage.

3.3 High temperature

Avoid high temperatures (heating) close to the cylinder, e.g. from welding flames, blowlamps, ovens or other intensive heat sources. High temperatures will result in higher pressures leading to potentially hazardous situations. In addition, elevated temperatures may result in decomposition of thermally unstable species.

3.4 Water

Gas cylinders shall be protected from excessive humidity during transport. Transportation by boat may result in the cylinder being sprayed with water; this and/or excessive humidity may cause corrosion of the cylinder valve. Always protect the cylinder from precipitation to prevent corrosion. If the cylinders are stored outdoors protected by a roof, the cylinder base should also be protected from water accumulating on the floor by raising it above the ground.

3.5 Storage and handling

The best way to store calibration gas mixtures for a longer period is by laying the cylinders in a horizontal position, well protected against rolling and falling. For safety reasons, it is necessary to separate cylinders containing flammable gases from cylinders containing oxidizing components.

WARNING — For general safety reasons, never heat cylinders above 45° C.

Mixtures containing condensable components may require rehomogenization if stored for longer periods of time and if exposure to temperatures below the condensation point cannot be excluded. This may be done by bringing up the cylinders to ambient temperature and rotating them into a horizontal position for an appropriate period of time, which may depend on the matrix gas and the components (see 4.2).

NOTE After rehomogenization, it is necessary to contact the manufacturer in order to verify the validity of the calibration gas.

4 Mode of withdrawal

4.1 General

In the withdrawal of the gas from the cylinder through the transfer system, a number of aspects shall be considered.

4.2 Minimum utilization pressure

The information attached to the cylinder indicates, if applicable, a pressure value below which the gas should not be used. It has been reported that in some cases under a certain pressure, gas molecules that were attached to the cylinder wall come off this cylinder wall when the cylinder pressure drops, resulting in a higher mole fraction.

NOTE In addition to this effect on the stability of the gas mixture, it is important from the point of view of the manufacturer that a cylinder is not completely emptied, as the cylinder could then be contaminated with environmental air. This especially applies to specially treated cylinders where stability is an issue.

4.3 Temperature

Gas mixtures containing condensable components are often limited to a certain temperature range by the manufacturer. In calculating such a mixture, the manufacturer will assume a certain temperature of usage to calculate the vapour pressure at that specific temperature. Normally a safety tolerance is included to allow use of the mixture within a certain temperature range; however outside this range the condensable component may condensate, resulting in a change of gas mixture composition. In analysing gas mixtures, it is recommended to allow all cylinders to reach temperature equilibrium. Differences in temperature of different gas mixtures will influence the response of the gas analyser to these mixtures, according to the gas law (Boyle, Gay-Lussac).

4.4 Pressure reduction and flow

Normally, the withdrawal of gas from a cylinder is regulated by a pressure reducer and/or flow controller (needle valve, mass-flow controller, capillary, etc.). Due to the reversible adiabatic expansion of the gas when withdrawing the gas from the cylinder, cooling of the gas in the cylinder will occur. Furthermore, Joule Thomson cooling and/or heating will change the temperature of the transported gas itself. Again, especially with mixtures containing condensable components, condensation might occur due to these temperature effects. It is important that the pressure drop across flow controllers is minimized. Flow characteristics of flow controllers are normally specified by the manufacturer and give sufficient information to judge whether the requested flow can be controlled by the chosen flow controllers. In calculating the pressure drop, tube sizing (inside diameter and length) shall also be considered.

External heating of the gas at or before the reducer and using more than one reducer to drop the pressure in stages could help to minimize the danger of condensation.

4.5 Replacement, change of cylinder positions

Re-connecting cylinders always has the danger of creating a leaking connection, which shall be avoided for several reasons. In an optimum set-up, the reducer should remain on the cylinder and the cylinder is preferably left with some gas inside. This will help to reduce the number of purge cycles to flush the reducer prior to analysis. Even in this optimum set-up, some environmental air diffusion into the reducer over time may occur, even if this is pressurized.

NOTE In the long run, there will usually be some diffusion from O_2 and H_2O from the environment into the reducing valve, even if this is pressurized.