BS EN ISO 16664:2008

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

ICS 71.040.40

British Standards

National foreword

This British Standard is the UK implementation of EN ISO 16664:2008. It is identical with ISO 16664:2004. It supersedes BS ISO 16664:2004 which is withdrawn.

The UK participation in its preparation was entrusted to Technical Committee PTI/15, Natural gas and gas analysis.

A list of organizations represented on this committee can be obtained on request to its secretary.

This publication does not purport to include all the necessary provisions of a contract. Users are responsible for its correct application.

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Foreword

The text of ISO 16664:2004 has been prepared by Technical Committee ISO/TC 158 “Analysis of gases” of the International Organization for Standardization (ISO) and has been taken over as EN ISO 16664:2008 by Technical Committee CEN/SS N21 “Gaseous fuels and combustible gas” the secretariat of which is held by CMC.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by February 2009, and conflicting national standards shall be withdrawn at the latest by February 2009.

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Endorsement notice

The text of ISO 16664:2004 has been approved by CEN as a EN ISO 16664:2008 without any modification.

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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.

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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.

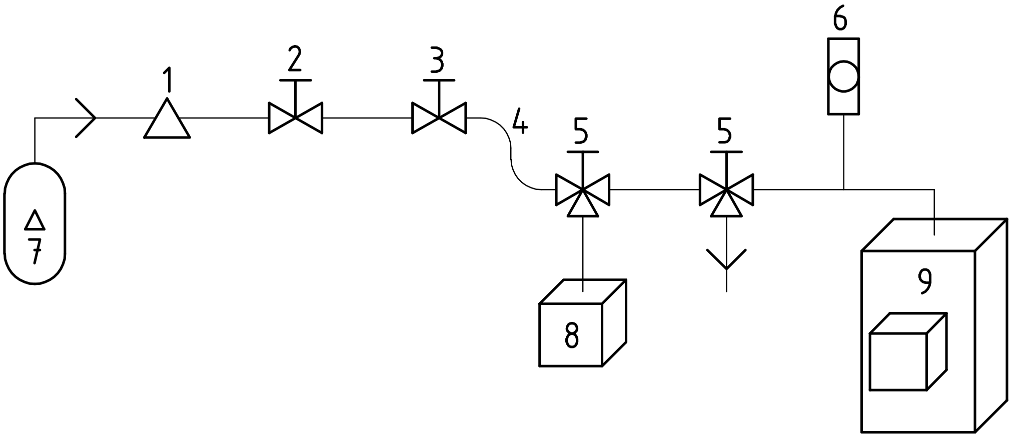
5 Transfer system

5.1 Purging procedure

The transfer-line integrity, including the leak tightness and cleanliness of all the components (pressure regulator, valves, transfer line, connections, etc.), shall be guaranteed. In order to guarantee this, an appropriate purging procedure shall be used. There are several simple methods that may be used to purge the transfer system; the most effective method uses a vacuum pump. In any case, it is important to open the cylinder valve only partially and only for a very short time (i.e. 0,5 s), both for safety reasons and in order to avoid back contamination.

If a vacuum pump is available, then the purging procedure should be as follows (see also Figure 1).

Sequentially evacuate and pressurize the entire transfer line with the gas mixture to be used. This procedure should be repeated several times, typically, three cycles are sufficient. Make sure that pressure regulators are suited for evacuation and that the purging cycle starts with evacuation.



Key

1	evacuable pressure regulator
2	dose valve
3	shut-off valve
4	transfer line
5	three-way valve
6	excess-flow line with flow indicator (applicable only for extractive monitors)
7	gas mixture
8	vacuum pump
9	motor with sample pump

Figure 1 — Arrangement for a periodic purging procedure for monitor systems

If a vacuum pump is not available, the following procedure is recommended.

Sequentially pressurize and vent the transfer system with the gas mixture to be used. This method is not as effective as the vacuum method, hence more cycles, typically five to eight, are required. The number of cycles depends on the concentration of the measurand; low-concentration mixtures require more steps. However, this method is prone to back contamination and should not be used for oxygen-sensitive mixtures; for these mixtures, the evacuation method is strongly recommended.

For both methods, the insertion of a stop valve after the pressure regulator is recommended for safety reasons.

5.2 Considerations when designing and constructing gas transfer lines

5.2.1 Modes of gas sampling

The design of the gas transfer line is dependent on the sample introduction method used by the analyser. Typically there are two methods of sample introduction.

a) Extractive analysers use a sample pump to move the calibration and zero gases from the sampling point to the point of analysis. The sample pump may be located upstream of the analyser and in this mode the gas is forced into the analyser. Conversely, the sample pump may also be located downstream of the analyser and in this mode the gas is forced through the analyser. In both cases, the transfer system shall include an excess-flow line to prevent over-pressurising the analyser and sample pump. The excess-flow line shall be located at the end of the transfer line and before the analyser in a “T” orientation (see Figure 1). The length of the excess-flow line shall be sufficient to prevent ambient air from the laboratory being pumped into the analyser when valve switching occurs during normal instrument operation (a typical length for an excess-flow line is approximately 1 m). It is also pertinent to use a flow indicator on the output of the excess-flow line to indicate that excess flow is occurring. Calibrations and analyses, performed using extractive analysers without excess flow through this line, are invalid.

b) Non-extractive analysers rely on pressure from gas cylinders to cause the gas to flow through the transfer line and analyser, and hence do not require an excess-flow line. However, many analysers, especially optical instruments, are sensitive to gas pressure and gas flow; it is therefore important to ensure the sample and calibration gases are introduced into the analyser under identical conditions.

5.2.2 Pressure- and flow-reducing equipment

It is important to use the most appropriate pressure- and flow-reduction equipment for a particular requirement. In general terms, this means the equipment needs to be fit for a purpose. The equipment should regulate to the required pressure and flow and should be constructed of the most appropriate material for the gas used. In many cases, the integrity of high quality and expensive calibration gas has been compromised through the use of poor quality or inappropriate pressure- and flow-reduction equipment.

Reactive gases, for example, require extensive purging of the “wetted” areas of the transfer line and, in particular, the pressure regulator. The use of “low-volume” regulators reduces the wetted surface area and hence reduces the level of purging required. For non-reactive gases, such as CO_2 and inert gases, most types of regulators may be used; however care shall be taken with respect to material compatibility. Table 1 outlines some details covering gas/material compatibilities when considering selection of pressure- and flow-reducing equipment. As this chart is rather general, it is advised to further check the suitability of the transfer system.

NOTE Additional information on material compatibility is found in References [5] to [9].

5.2.3 Material for the construction of transfer lines

As mentioned in 5.2.2, the choice of material for the construction of pressure-reducing equipment is extremely important, especially when considering the measurement of more reactive gases. In addition to this, the choice of transfer-line material is also important. Table 1 outlines the most commonly used gases and their level of compatibility with a range of materials.

When using polymeric transfer lines, it is also important to consider their permeability by certain gases and water vapour. For example, PTFE is very inert and suitable for a large range of gases; however, the permeability of this material makes it unsuitable for use with water-soluble gases, as water vapour can easily permeate into the transfer line.

It is also strongly recommended not to use polymeric or rubber-based material of unknown origin in the construction of transfer lines.

Table 1 — Material compatibility

Gas	Material																													
	Stainless steel			Copper/ brass			Hastelloy [f]/ monel [g]/ nickel			Aluminium			Polytetra-fluor-ethene			Polyether ether-ketone			Polyether-ether-ketone, silica-lined			Glass/ quartz			Fluorinated-ethene-propene			Silica-lined stainless steel		
	b	c	d	b	c	d	b	c	d	b	c	d	b	c	d	b	c	d	b	c	d	b	c	d	b	c	d	b	c	d
inert gas	+	+	+	+	+	+	+	+	+	+	+	+	+	o *	–	+	+	o	+	+	+	+	+	+	+	+	+	+	+	+
O_2	+	+	+	+	+	+	+	+	+	+	+	+	+	o	–	+	+	o	+	+	+	+	+	+	+	+	o	+	+	+
CO_2	+	+	+	+	+	+	+	+	+	+	+	+	+	+	o	o	o	–	+	+	+	+	+	+	+	+	+	+	+	+
CO	o	+	+	+	+	+	***	+	+	+	+	+	+	+	o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
alkanes	+	+	+	+	+	+	+	+	+	+	+	+	+	+	o	+	+	o	+	+	+	+	+	+	+	+	+	+	+	+
alkenes	+	+	+	+	+	o	+	+	+	+	+	+	+	o	–	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
aromatics	+	+	+	–	–	–	+	+	+	+	+	+	+	o	–	+	+	+	+	+	+	+	+	+	+	+	o	+	+	+
NO	+	+	+	+	+	+	+	+	+	+	+	+	o	o	o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
NO_2	+	+	+	–	–	–	+	+	+	o	***	***	o	o	o	***	+	+	***	***	***	+	+	+	o	o	o	+	+	+
Cl_2	o	o	o	+	+	+	+	+	+	***	***	***	+	+	+	+	+	+	+	***	***	+	+	+	+	+	+	+	+	+
HCl	o**	o **	o **	o	o	o	+	+	+	–	–	o**	+	+	–	***	***	***	***	***	***	+	+	+	+	+	+	+	+	+
NH_3	+	+	+	–	–	–	+	+	+	***	***	***	–	–	–	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
H_2S	+	+	–	–	–	–	+	+	+	+	+	+		o	o	o	o	o	o	o	o	+	+	+	***	o	o	+	+	+
SO_2	+	+	+	o	o	o	+	+	+	+	+	+	+	+	o	+	+	+	+	+	+	+	+	+	+	+	o	+	+	+

[a] See 5.2.3 for further recommendations.

[b] Mole fraction, $> 1\ \%$.

[c] Mole fraction, $\geqslant 0{,}001\ \% \leqslant 1\ \%$.

[d] Mole fraction $< 0{,}001\ \%$.

[e] Symbols are as follows:

+ = suitable;

o = of limited suitability;

– = not suitable;

* = not suitable for helium;

** = suitable only after passivation;

*** = no experience available; usage not recommended for safety reasons.

[f] Hastelloy is an example of a suitable product available commercially. This information is given for the convenience of users of this part of ISO 16664 and does not constitute an endorsement by ISO of this product.

[g] Monel is an example of a suitable product available commercially. This information is given for the convenience of users of this part of ISO 16664 and does not constitute an endorsement by ISO of this product.

5.2.4 General methods and examples of sampling systems

For continuous gas analysers, two flow charts are presented giving examples of procedures to test the integrity of the sampling system.

The first flow chart (given in Figure 2) explains a simple procedure to check the selected transfer system through the repeatability of the analyser readings.

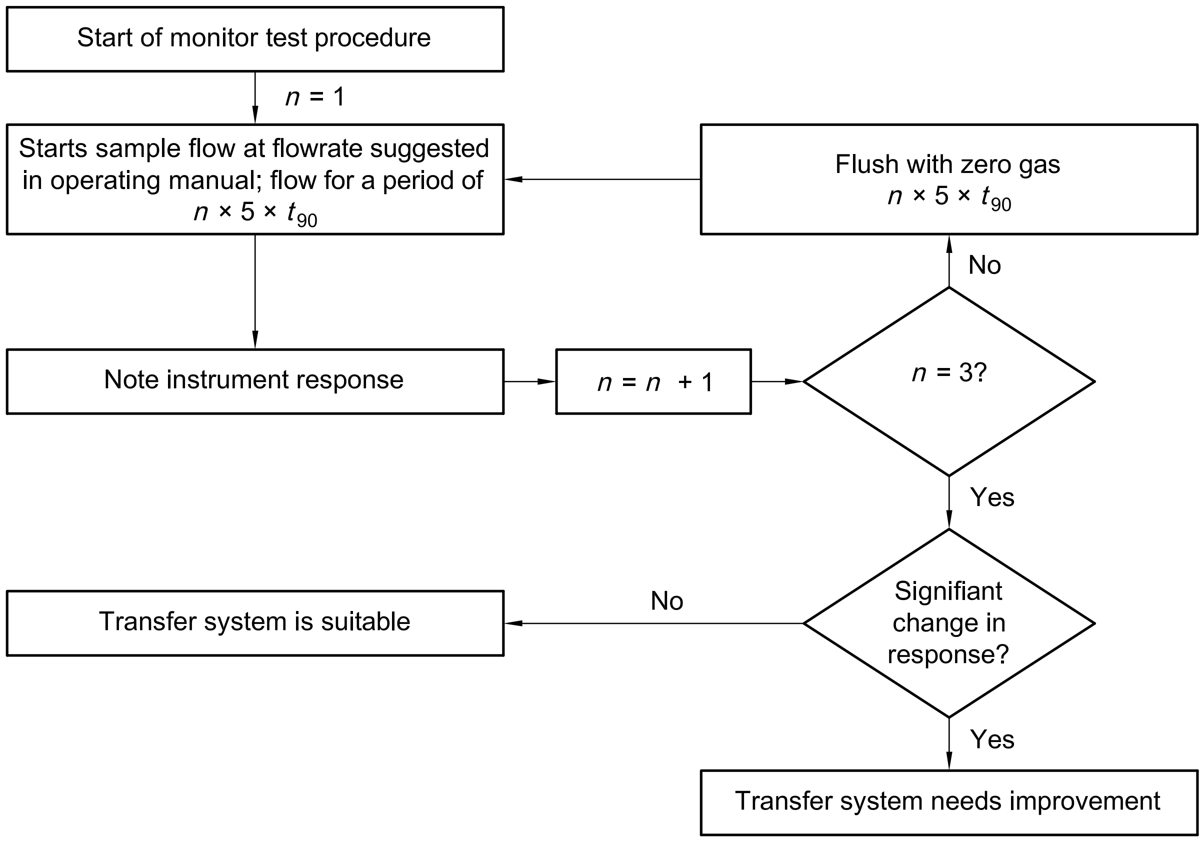
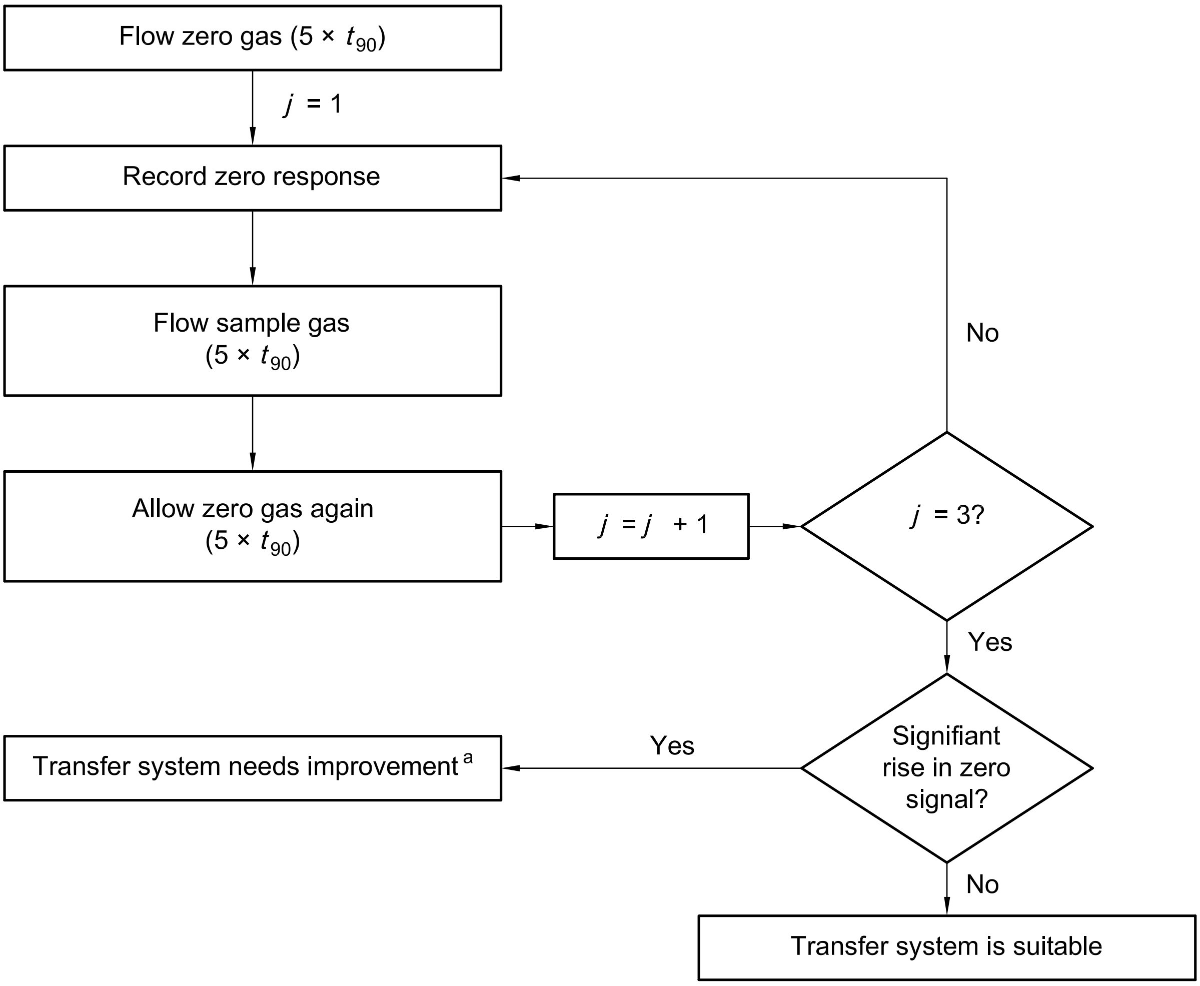


Figure 2 — Flow chart of the test procedure for suitability of transfer system for continuous gas analysers

The second flow chart (Figure 3) explains a procedure to test the transfer system for memory effects.

In both procedures it is helpful to attach a chart recorder to the output signal.



[a] When the outcome of this test shows that the transfer system needs improvement, double the flow and/or heat the transfer lines and repeat the procedure.

Figure 3 — Flow chart of the check on memory effects in the transfer systems

The typical response time t_{90} is normally specified in the operating manual and may be defined as the time between the introduction of the gas and the time that 90 % of the concentration change is displayed on the monitor.

The judgement whether a change in response is significant depends on the aimed accuracy; the change in response should be greater than the specified zero and span drift.

The third flow chart (Figure 4) presents an effective method to check the suitability of the transfer system for a GC application (see Figure 5). The check for any leaks by controlling the presence of oxygen is only applicable with an oxygen-sensitive detector [e.g. gas chromatograph/thermal conductivity detector (GC/TCD), gas chromatograph/discharge ionization detector (GC/DID) or gas chromatograph/mass spectrometer (GC/MS)]. In this method, the sample flow is changed from target flow down to ¼ of this flow.

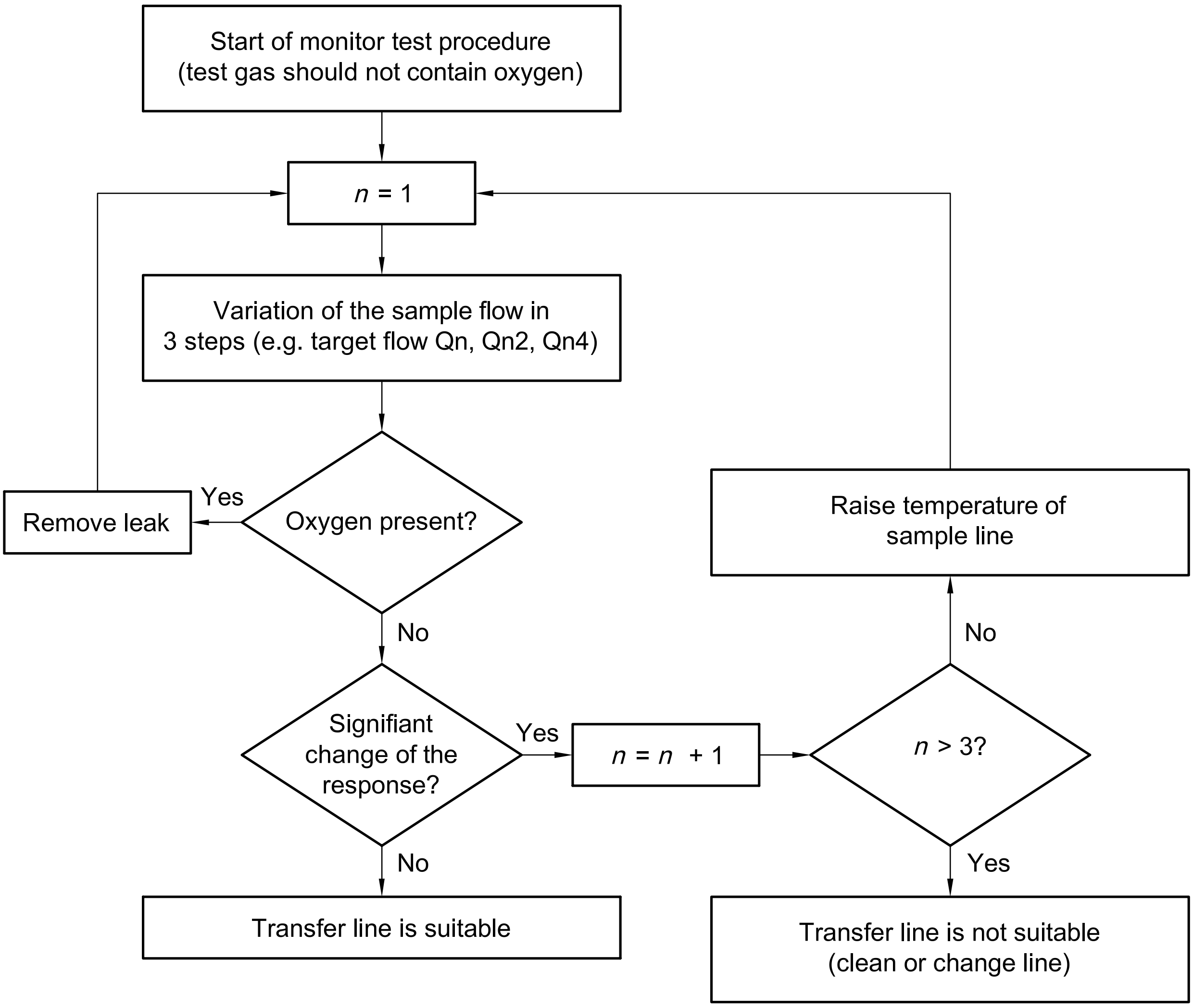
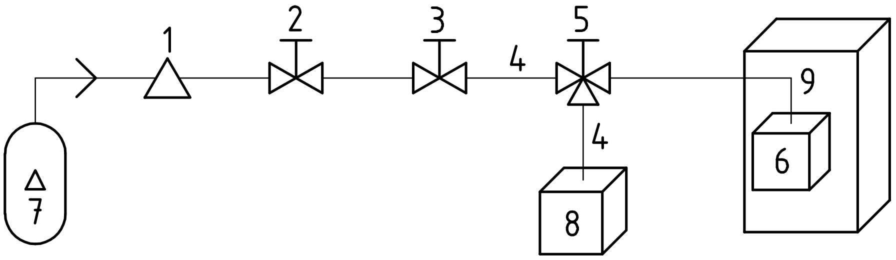


Figure 4 — Flow chart of the suitability test procedure for a transfer system for GCs with an oxygen-sensitive detector



Key

1	evacuable pressure regulator
2	dose valve
3	shut-off valve
4	transfer line
5	three-way valve
6	gas sample inlet system
7	gas mixture
8	vacuum pump
9	gas chromatograph

Figure 5 — Arrangement for a periodic purging procedure with a GC

6 Stability

The previous clauses discuss all precautions to be taken by the user of the gas mixtures to ensure that the integrity of the gas mixture as supplied by the manufacturer is not compromised during use. However, sometimes-unexpected influences do interfere and the continuing stability of the mixture should be demonstrated. A possible method to check the stability of calibration gases is given in Annex A (informative).

Annex A
(informative)

Check on the stability of calibration gas mixtures by end-users

After manufacturing, the composition of the calibration gas mixture is analysed at time t_0 with an analytical instrument calibrated with suitable standards. The results of this measurement are x_0 and $u(x_0)$, the content of the component x and its standard measurement uncertainty, respectively.

A second analysis with a calibrated analytical instrument is performed at $t_1 > t_0$, yielding the result x_1 and $u(x_1)$. The values of x_1 and $u(x_1)$ are usually different from x_0 and $u(x_0)$.

Testing on a 95 % confidence interval and assuming normal distribution, the test statistic D is given by the weighted difference:

$$D = \frac{|x_0 - x_1|}{\sqrt{u^2(x_0) + u^2(x_1)}} \qquad \text{(A.1)}$$

and provides a statistical test as follows:

- $D \leqslant 2$ no significant instability;
- $D > 2$ significant instability.

This simple test method is only valuable if the uncertainties $u(x_0)$ and $u(x_1)$ are comparable.

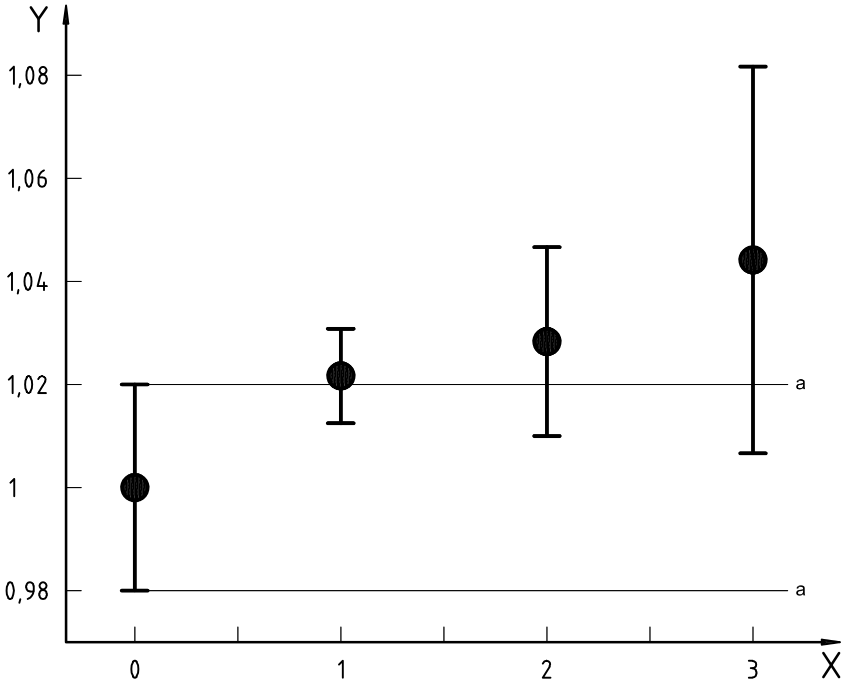
What happens when the uncertainties are not comparable is shown with the examples below and in Figure A.1.

In the limiting case, $D = 2$, i.e. where the test shows marginal stability, the effect of comparability of the uncertainties is illustrated for three cases of the ratio of standard measurement uncertainties of the form $F = u(x_0)/u(x_1)$, where x_0 is assumed to be 1 and $u(x_0) / x_0$ is 0,01, i.e. 1 %.

The ratios shown are

- $F_1 = 0{,}5$ at $t_1 = 1$ (the uncertainty of the second analysis is half the uncertainty of the first);
- $F_2 = 1$ at $t_2 = 2$ (the uncertainty of the second analysis is equal to the uncertainty of the first);
- $F_3 = 2$ at $t_3 = 3$ (the uncertainty of the second analysis is double the uncertainty of the first);

and thus cover a reasonably wide range of uncertainty ratios.



Key

X time

Y composition

[a] Represent $k = 2$ (± 2 standard uncertainties) of the initial measurement at t_0.

Figure A.1 — Limiting case $D = 2$ for the stability test statistic for three cases of the ratio of standard measurement uncertainties $F = u(x_0)/u(x_1)$

EXAMPLE To clarify the effect once more, two numerical examples are given:

1)

i	t_0	t_1
x_i	200×10^{-9}	188×10^{-9}
$u(x_i)$	4×10^{-9}	5×10^{-9}

Result: $D = 1{,}87$; mixture is stable.

2)

i	t_0	t_1
x_i	200×10^{-9}	188×10^{-9}
$u(x_i)$	2×10^{-9}	4×10^{-9}

Result: $D = 2{,}68$; mixture is not stable.

In evaluating the stability of a gas mixture, it is important to realize that a significant difference is not necessarily due to changes of composition but may also be caused by drift of instruments, degradation of calibration standards, bias between analytical procedures, bias of calibration standards, etc. Therefore, a negative test result (i.e. significant difference) has to be complemented by further investigations to confirm that the difference is due to degradation of the mixture.

For more information on how to check for stability and what the responsibilities of the user and the manufacturer of the calibration gas are in respect to stability of the mixture, see also ISO 17025[10] and Clause 8 and 9.5 of ISO Guide 35[11].

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