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## Gas analysis — Preparation of calibration gas mixtures — Static volumetric method

*Analyse des gaz — Préparation des mélanges de gaz pour  
étalonnage — Méthode volumétrique statique*



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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.

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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 6144 was prepared by Technical Committee ISO/TC 158, *Analysis of gases*.

This second edition cancels and replaces the first edition (ISO 6144:1981), which has been technically revised.

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# Gas analysis — Preparation of calibration gas mixtures — Static volumetric method

## 1 Scope

This International Standard specifies a method for the preparation of calibration gas mixtures by a static volumetric method and provides a procedure for calculating the volumetric composition of the mixture. It can be used either with binary gas mixtures (containing one calibration component in a complementary gas, which is usually nitrogen or air<sup>[1, 2]</sup>) or with mixtures containing more than one component in the complementary gas. This International Standard also specifies how the expanded uncertainty in the volume fraction of each calibration component in the mixture is determined by a rigorous evaluation of all the measurement uncertainties involved, including those associated with the apparatus used for the preparation of the gas mixture and those associated with the experimental procedure itself.

NOTE 1 This International Standard is generally applicable to the preparation of calibration gas mixtures containing calibration components in the concentration range  $10 \times 10^{-9}$  (10 ppb — parts per billion) to  $50 \times 10^{-6}$  (50 ppm — parts per million) by volume. However, gas mixtures may be prepared at larger or smaller volume fractions, provided that the components used in the static dilution process are selected appropriately.

NOTE 2 A relative expanded uncertainty of not greater than  $\pm 1\%$  at a level of confidence of 95 % may be achievable at these concentrations, provided that:

- the purities of the parent gases have been determined by analysis and any significant impurities and the uncertainties in their measured concentrations have been taken into account;
- no significant adsorption effects or chemical reactions occur between the gaseous constituents and the internal surfaces of the apparatus, and there are no reactions between any of the gaseous components, i.e. between the calibration component and complementary gas or between the calibration components themselves;
- all the relevant apparatus used in the preparation of a calibration gas mixture have been calibrated with assigned measurement uncertainties which are appropriate to calculating the final expanded uncertainty for the calibration gas mixture prepared.

## 2 Normative references

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

ISO 7504, *Gas analysis — Vocabulary*

## 3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 7504 apply.

## 4 Principle

A calibration gas mixture consists of one or more calibration components in a complementary (diluent) gas, mixed in a suitable gas-mixing chamber. These calibration components are generally pure gases taken from cylinders, or from pure, volatile liquids that are allowed to evaporate into the gas-mixing chamber. The gas mixture is prepared using syringes to inject:

- either known volumes of gaseous calibration components (each at a pressure of about  $1 \times 10^5$  Pa);
- or known masses or volumes of liquid calibration components;

These are injected into a volume of complementary gas contained in the mixing chamber (which is also at a pressure of about  $1 \times 10^5$  Pa). Further complementary gas is then added to increase the overall pressure of the gas mixture to an accurately measured value above ambient atmospheric pressure. This final (above-atmospheric) pressure is required so that the calibration gas mixture will subsequently flow out of the mixing chamber and can be used to calibrate a gas analyser, which is usually operated at ambient pressure.

At each stage in the preparation procedure, the mixture is homogenized, usually by means of a suitable stirring device, and then left to equilibrate to ambient atmospheric temperature.

The volume fraction of each calibration component in the calibration gas mixture is determined by calculation of the ratio of the volume of the calibration component to the total volume of the mixture.

## 5 Apparatus

### 5.1 Gas-mixing chamber, consisting of the components specified in 5.1.1 to 5.1.8.

NOTE An example of a suitable gas-mixing chamber is described in Annex A.

**5.1.1 Vessel**, comprising the gas-mixing chamber itself, of sufficient internal volume to deliver the amount of calibration gas mixture required for any subsequent instrumental calibrations, manufactured of a suitable material that is inert to all the component gases, and designed both to be evacuable and to withstand the required above-atmospheric operating pressures. It shall also have vacuum/high-pressure flanges to allow access to the components that are mounted within the mixing chamber.

NOTE 1 Vessels with internal volumes of  $0,1 \text{ m}^3$  to  $0,5 \text{ m}^3$ , capable of operating up to pressures of about  $2 \times 10^5$  Pa (2 bar) and of maintaining a vacuum of better than  $0,1 \times 10^2$  Pa (0,1 mbar), have been found to be suitable (see Annex A).

NOTE 2 Mixing chambers manufactured from borosilicate glass or stainless steel have been found to be suitable for the commonly used gaseous species (e.g. gas mixtures which contain  $\text{SO}_2$ , NO,  $\text{NO}_2$ , CO and  $\text{C}_6\text{H}_6$  as the calibration components). However, care shall be taken in selecting the materials of the mixing chamber, and of the other components which come into contact with the gas mixtures, so that they do not affect the mixture's stability adversely — particularly when more reactive gas mixtures are to be prepared.

**5.1.2 Vacuum pump**, capable of evacuating the mixing chamber and its associated components to a low pressure, and including a suitable vacuum shut-off valve. This low pressure shall be defined either so that any gaseous contamination resulting from the residual low pressure has no effect on the accuracy of the concentration of the gas mixture prepared, or so that a quantitative correction for the effect of this residual low pressure may be made to the concentration of the mixture.

NOTE The residual gas pressure is generally due mainly to nitrogen from residual air. However, care must be taken to ensure that other gases that may react with the constituents of the gas mixture are not present at significant concentrations in this residual gas (e.g. traces of water vapour when acid gases are being used as calibration components, or traces of oxygen in the case when nitric oxide calibration mixtures are being prepared).

**5.1.3 Gas line**, used for the injection of the complementary gas, and including appropriate metering and shut-off valves.

**5.1.4 Pressure, vacuum and temperature gauges**, used to monitor these parameters inside the mixing vessel.

**5.1.5 Septum**, enabling a gas or liquid of known volume or mass to be injected into the mixing chamber from a metering syringe (5.2).

**5.1.6 Motor-driven gas-mixing device**, e.g. a fan, enabling the gaseous components in the gas-mixing chamber to be homogenized, and designed to provide satisfactory mixing of all the gaseous components to a given degree of homogeneity within a specified time. Experimental tests shall be carried out to demonstrate that the mixing device is able to achieve the required homogeneity within the specified time.

**5.1.7 Pressure relief valve**, used to ensure that the maximum internal safe working pressure specified for the mixing vessel and its associated components is not exceeded.

**5.1.8 Outlet-gas sampling line**, enabling the gas mixture prepared to be used for calibration purposes, and having a device for equalizing the internal pressure of the gas mixture in the mixing chamber with atmospheric pressure so as to enable the gas mixture to be determined at ambient pressure for calibration purposes.

**5.2 Calibrated metering syringe**, which can be used to inject, by means of a piston, a known volume of gas or liquid through a needle. The syringe shall have gastight seals to ensure that no significant leakage of the gas or liquid takes place.

NOTE 1 Glass syringes having polytetrafluoroethene (PTFE) bushings as seals, and with internal volumes of 10 ml, 5 ml, 1 ml, 0,5 ml and 0,1 ml, have been found to be suitable when used with mixing chambers of volumes which are in practical use, and when used to prepare gas mixtures for the calibration of ambient-air analysers.

NOTE 2 It is recommended that the internal volume of the syringe be measured experimentally with a maximum relative uncertainty of  $\pm 1\%$  (at a level of confidence of 95 %). In addition, the syringe should have a maximum leak rate of  $10 \times 10^2$  Pa (10 mbar) per hour after evacuation to 5 Pa ( $5 \times 10^{-2}$  mbar), in order that it has satisfactory leaktightness.

**5.3 Apparatus for filling the metering syringe**, consisting of the components specified in 5.3.1 to 5.3.9.

NOTE An example of a suitable set-up for filling the syringe is described in Annex A.

**5.3.1 Evacuatable gas reservoir**, capable of containing gas at above-atmospheric pressure so as to enable the metering syringe to be filled to that pressure, its internal surfaces being made of a material that does not react with any of the calibration components.

NOTE A gas reservoir with an internal volume of about 100 ml, capable of operating up to a pressure of  $1,4 \times 10^5$  Pa (1,4 bar) and of maintaining a vacuum of better than  $0,1 \times 10^2$  Pa (0,1 mbar), has been found suitable.

**5.3.2 High-pressure gas cylinder**, containing the selected pure gas component (or a pre-mixture containing a higher concentration of gas mixture).

**5.3.3 Pressure regulator**, used to enable the pressure of gas in the reservoir to be adjusted to a pre-defined pressure above that of the ambient atmosphere.

**5.3.4 Septum**, constructed of appropriate material, enabling the needle of the metering syringe to be introduced into the gas reservoir.

**5.3.5 Vacuum pump**, enabling the gas reservoir and its associated components to be evacuated to below the required vacuum.

NOTE It is important to ensure that any gaseous component which may be hazardous, and which is exhausted by the vacuum pump to the atmosphere, is vented in a safe way.

**5.3.6 Pressure gauge**, used to monitor the pressure of the gas in the reservoir during the various stages of the preparation procedure.

**5.3.7 Gas shut-off valves**, used to isolate the gas cylinder from the reservoir, and the gas reservoir from the vacuum pump.

**5.3.8 Pressure-relief valve**, capable of relieving a gas pressure selected to protect the apparatus (typically  $1,4 \times 10^5$  Pa). It should be vented to a safe location.

**5.3.9 Suitable vessel**, for use when the metering syringe is to be filled with a volatile liquid rather than a gas, and enabling the syringe to be filled in a manner that prevents the ingress into the syringe of any components other than the volatile liquid.

## 6 Procedure for preparing the calibration gas mixture

### 6.1 Determination of the volume of the gas-mixing chamber

There are a number of ways by which the internal volume of the gas-mixing chamber may be determined in practice. The major component of this volume will be the internal volume of the empty vessel itself and this is normally measured by filling it with water, or with another liquid of known density, and then determining the increase in mass due to this liquid. However, other methods may be used where these have the required accuracy. Following this, the internal volumes of the components within the gas-mixing chamber shall be determined by, for example, geometric measurement or liquid displacement. Corrections shall then be made for the volumes of these additional components when determining the net volume of the chamber. Corrections for some of the components (e.g. the gas-mixing device) will lead to a smaller volume whereas others (e.g. the pressure gauge and the outlet pipes leading to the shut-off valves) will lead to an increase in volume.

These measurements of the volumes of the components that make up the total gas-mixing chamber (see 5.1) may have been carried out at different temperatures. In such cases, corrections shall be made, where significant, to convert the measured volumes to a common ambient temperature. A further correction may need to be made if the complete mixing chamber with all its components is used at a different ambient temperature, provided such a correction is significant.

### 6.2 Conditioning the gas-mixing chamber before use

A new gas-mixing chamber will normally contain ambient air, and this may contain trace pollutants at levels that would affect the accuracy of the calibration gas mixture. In addition, the inside surfaces of the chamber may be contaminated with a surface layer which may react with some species which are put in the mixing chamber. It is therefore necessary to condition the mixing chamber before use so as to avoid any potential contamination of the calibration gas from these causes. Do this by evacuating the chamber to a pressure of less than  $5 \times 10^2$  Pa (5 mbar). Then fill the chamber to above-atmospheric pressure with the complementary gas which is to be used in the preparation of the calibration gas mixture. Subsequently, connect the outlet from the mixing chamber to a set of instruments designed to measure air pollutants (e.g. analysers which monitor  $\text{SO}_2$ ,  $\text{NO}_x$ , CO and hydrocarbons). These shall have sufficient detection sensitivity to determine whether significant concentrations of the relevant gaseous impurities exist in the complementary gas in the mixing chamber at this time. Allow the complementary gas in the mixing chamber to flow into these analysers, and observe the concentrations of any impurities detected.

Repeat this procedure, involving the evacuation of the mixing chamber followed by re-filling with complementary gas, several times or until all relevant gaseous impurities are below the concentrations required to prevent significant contamination of the calibration gas mixtures to be prepared in the chamber. In circumstances where this cannot be achieved, either clean the mixing chamber by other means so as to remove the contaminants, or make a suitable correction when calculating the concentration of the calibration component in the calibration gas mixture so as to allow for such impurities.

In circumstances where such an analysis of the impurities present in the complementary gas is the only one that is carried out, the detection limits of the analysers used shall represent the upper limits for the concentrations of the impurities which could be present in the calibration gas mixture. In these cases, the concentrations represented by these detection limits shall be taken into account in the determination of the expanded uncertainty of the prepared calibration gas mixture. In cases, however, where additional, more



sensitive, analyses of impurities are carried out by other means, the results of these analyses shall instead be incorporated into the expanded uncertainty of the calibration gas mixture.

After the mixing chamber has been pre-conditioned using the above procedure, it is possible that it might not be used for a significant period. If this is the case, re-fill the mixing chamber with the selected complementary gas at a pressure that is higher than ambient, so as to minimize further contamination which may arise from ingress of gaseous pollutants from the ambient atmosphere.

Subsequently, carry out the following steps to prepare the calibration gas mixture.

### 6.3 Filling the mixing chamber with the complementary gas

First evacuate the mixing chamber, using the vacuum pump (5.1.2), to a residual pressure such that contamination by components of the residual gas will have no significant effect on the accuracy and stability of the final calibration gas mixture (typically about  $5 \times 10^2$  Pa). Then fill the chamber with the selected complementary gas through the feed line (5.1.3) to about  $0,1 \times 10^5$  Pa (0,1 bar) above ambient pressure. The temperature of the complementary gas in the mixing chamber after filling will normally be above ambient temperature (due to adiabatic compression). Allow the gas to stand, therefore, so that it equilibrates to the temperature of the mixing chamber, and to that of the ambient atmosphere.

**NOTE** A temperature difference of 0,2 °C will introduce an uncertainty in the final volume fraction of a component of less than 0,1 % (relative) of the value of the concentration. In practice, therefore, it is sufficient to ensure that the complementary gas temperature and the ambient temperature are within 0,2 °C of each other.

After the temperature of the complementary gas and the external temperature have equilibrated, bring the pressure of the complementary gas in the mixing chamber to ambient pressure by opening the shut-off valve connected to the pressure relief valve (5.1.7). Record both the temperature and the pressure of the gas in the mixing chamber at this point, for use subsequently in the determination of the concentration of the calibration gas mixture.

### 6.4 Determination of the calibration component volume required

The required volume of the calibration component which is to be injected into the mixing chamber is calculated from the required composition of the final gas mixture, the volume of the mixing chamber itself, and the target value of the final gas pressure in the mixing chamber. Where a liquid is to be injected, it is important to know, at least approximately, the density of the calibration component in its liquid form so as to obtain the required concentration in the gaseous state when the final calibration gas mixture is produced.

The accuracy to which the internal volume of the syringe is known, and any leakage to the atmosphere through the needle or through the seals of the syringe, will make a contribution to the overall accuracy of the calibration gas mixture. An example of a method used to determine experimentally the volume of gas in the syringe, to demonstrate the leaktightness of the syringe, and to demonstrate the amount of gas loss through the needle is given in Annex B.

Select a syringe of appropriate volume so as to provide a final gas mixture with the required uncertainty in its concentration. In most cases, multiple injections using the selected syringe will be necessary. The uncertainty in the final volume fraction of the component is usually minimized by using a syringe that gives the minimum number of injections of calibration component into the mixing chamber. However, the choice of syringe will also depend, in practice, on the availability of a suitable syringe with the required uncertainty in its volume. Record the number of injections that are required.

### 6.5 Filling the syringe with the calibration component

#### 6.5.1 Gaseous calibration components

When gaseous calibration components are employed, use the apparatus described in 5.3 to fill the syringe. Then proceed using the following procedure.

First close the shut-off valve on the cylinder of calibration component. Then use the vacuum pump to evacuate the whole apparatus, including the reservoir, to a sufficiently low pressure to ensure that any gas left in the reservoir does not have a significant effect on the concentration or stability of the final gas mixture.

NOTE A residual pressure of about  $1 \times 10^2$  Pa (1 mbar) has generally been found to be suitable. However, this will depend, in practice, on the type of gas mixture being prepared and the concentration of the calibration component. It is recommended, therefore, that consideration be given to the residual gas pressure required when evaluating the uncertainty in the concentration of the calibration component in the gas mixture.

Close the shut-off valve between the vacuum pump and reservoir, and fill the reservoir with the calibration component up to a pressure of about  $1,4 \times 10^5$  Pa (1,4 bar). Re-evacuate the reservoir and then refill it with calibration component. Repeat this purging process a sufficient number of times so as to ensure that no gaseous impurities are left with the calibration component in the reservoir. After the final filling, check the gas pressure in the reservoir to ensure that sufficient over-pressure is available to fill the syringe.

NOTE Appropriate precautions should be taken to ensure that the calibration component, if hazardous, is vented safely when it is discharged from the apparatus.

Insert the needle of the selected empty metering syringe through the reservoir septum (5.3.4) into the reservoir. Then raise and lower the plunger of the syringe a sufficient number of times to flush the syringe with the calibration component and ensure that no significant contamination remains.

Fill the syringe completely by withdrawing the plunger to its full extent. Then remove the syringe needle from the septum and depress the plunger so that the syringe contains the target volume (taking suitable precautions, where applicable, to avoid any hazardous discharge of the calibration component into the atmosphere).

### 6.5.2 Liquid calibration components

The procedure for filling the selected metering syringe with liquids is, in principle, more straightforward than that for gaseous calibration components. However, it shall be designed so as to ensure that no significant amounts of contaminants, including air, are drawn into the syringe during filling.

## 6.6 Introduction of the calibration component into the mixing chamber

Introduce the needle of the syringe through the septum (5.1.5) of the gas-mixing chamber as quickly as possible after the volume of gas in the syringe has been brought to the target value but allowing sufficient time for the initially above-ambient pressure in the syringe to decay to atmospheric pressure. Where possible, determine experimentally, for each syringe used, the time taken to extract the syringe needle from the septum of the filling apparatus and inject the gas into the mixing chamber.

Depress the plunger of the syringe slowly, thereby injecting the calibration component into the mixing chamber, at the same time withdrawing the needle from the septum.

Carry out the number of repeat injections necessary (as determined in 6.4) to produce the required calibration gas concentration, using the above procedure for filling the syringe and injecting its contents into the mixing chamber.

Homogenize the gas mixture in the mixing chamber using the gas-mixing device (5.1.6). The time necessary to achieve the required homogeneity will depend both on the size and shape of the mixing chamber and on the performance of the mixing device, and this shall be investigated experimentally for the specific apparatus being used.

Where more than one calibration component is to be added, repeat the procedures in 6.5 and 6.6 for each of the additional calibration components.

## 6.7 Introduction of additional complementary gas

Increase the pressure by introducing additional complementary gas (up to the safe working pressure of the apparatus) so as to enable sufficient gas to be made available for instrumental calibrations (which are generally carried out using the calibration gas mixture at atmospheric pressure).

**NOTE** The size of the mixing chamber, combined with the pressure of the gas mixture in the chamber (more precisely, the excess pressure above atmospheric), defines the volume of gas which can be used for calibrations at ambient pressure.

Following introduction of this additional complementary gas, re-mix the gas in the mixing chamber using the gas-mixing device for a suitable length of time so that the required homogeneity is achieved.

Allow the mixture to re-equilibrate to ambient temperature (see Note to 6.3). Record the final pressure and temperature of the gas mixture as indicated by the gauges in the mixing chamber (see 5.1.4), for subsequent use in the determination of the concentration of the calibration gas mixture.

## 7 Calculation of the volume fraction of the calibration component in the gas mixture

### 7.1 Gaseous calibration components

The volume fraction of a calibration component  $x_g$  in a binary calibration gas mixture is calculated from the following equation:

$$\varphi(x) = \frac{p_1 \times V(x_g)}{p_2 \times V_{cg} + p_1 \times V(x_g)} \quad (1)$$

where

$\varphi(x)$  is the volume fraction of component  $x$  in the calibration gas mixture when it is used for the calibration of a gas analyser;

$V_{cg}$  is the volume of the complementary gas in the mixing chamber;

$V(x_g)$  is the volume of the gaseous component  $x_g$  in the syringe, referred to the same temperature as that of the mixing chamber;

$p_1$  is the pressure of the gas mixture in the mixing chamber before the final injection of complementary gas;

$p_2$  is the pressure of the gas mixture in the mixing chamber following the final injection of complementary gas.

Both volumes  $V(x_g)$  and  $V_{cg}$  shall be referred to the same ambient temperature [in practice, the temperature will be the same if the gas (or liquid) calibration component is injected from a syringe which is at the same temperature as that of the gas-mixing chamber].

A good approximation to, and simplification of, equation (1) can be derived if the volume  $V(x_g)$  is much less than  $V_{cg}$  when determined at the same temperature and pressure. In this case, the following equation results:

$$\varphi(x) = \frac{p_1 V(x_g)}{p_2 V_{cg}} \quad (2)$$

## 7.2 Liquid calibration components

In the same way as discussed in 7.1, the volume fraction, in a calibration gas mixture, of the calibration component gas obtained by evaporation of a liquid calibration component in the gas-mixing chamber is given by:

$$\varphi(x) = \frac{p_1 \times V(x_1)}{p_2 \times V_{cg} + p_1 \times V(x_1)} \quad (3)$$

where  $V(x_1)$  is the volume of calibration component  $x_1$  after it has evaporated to form a gas, expressed in the same units as  $V_1$  (see below);

In this case, where a calibration component is injected into the mixing chamber in the liquid phase using a syringe, followed by evaporation, the corresponding volume of the calibration component in the mixing chamber can be calculated as follows:

$$V(x_1) = \frac{V_1 \times \rho \times V_M}{M} \quad (4)$$

where

$V_1$  is the volume of calibration component  $x$  in liquid form;

$\rho$  is the density of the calibration component in liquid form at the temperature of use;

$M$  is the molar mass of the calibration component;

$V_M$  is the molar volume of the evaporated liquid, referred to the temperature and pressure of the mixing chamber at the time of injection of the liquid, assuming ideal-gas behaviour.

NOTE In equations (3) and (4), it has been assumed that the ideality law holds when converting from liquid to gas volumes. However, where appropriate, the compressibility of the liquid component should preferably be used instead in this calculation, where this can be derived from appropriate scientific literature.

In addition, by a similar approximation to that used to derive equation (2), for a binary calibration gas produced by liquid injection in the situation where  $V(x_1)$  is much less than  $V_{cg}$ , the final volume fraction  $\varphi(x)$  of the calibration component is given by:

$$\varphi(x) = \frac{p_1 V(x_1)}{p_2 V_{cg}} \quad (5)$$

where

$V(x_1)$  and  $V_{cg}$  are as defined above;

$p_1$  is the pressure of the gas mixture in the mixing chamber before the final injection of complementary gas;

$p_2$  is the pressure of the gas mixture in the mixing chamber following the final injection of complementary gas.

## 8 Determination of the uncertainty in the concentration of the calibration component in the gas mixture

### 8.1 Expanded uncertainty

The expanded uncertainty in the concentration (volume fraction) of the calibration component in a binary calibration gas mixture shall be determined, where practical, by experimental evaluation of the individual measurement uncertainties associated with *all* the influence variables. These individual uncertainties are then combined in a square-root sum-of-squares manner to produce the overall measurement uncertainty of the concentration in the calibration gas mixture. This is discussed below.

### 8.2 Influence variables related to the particular apparatus and preparation procedure used

#### 8.2.1 Uncertainty in the volume of the calibration component, $V(x_g)$ or $V(x_l)$ , injected into the mixing chamber

The exact volume of calibration component injected from the metering syringe into the mixing chamber is influenced by a number of factors, including the following:

- a) The internal volume of the syringe, corrected for the ambient temperature at which it is used, is initially defined by the syringe manufacturer, but it is recommended that the user also check it experimentally.

NOTE It is practical to obtain syringes with internal volumes which have been certified to better than  $\pm 0,5\%$  (relative) from commercial suppliers.

- b) Gaseous diffusion of the calibration component may take place through the needle of the syringe into the atmosphere. Clearly, the importance of this factor will depend, at least partially, on the time between extraction of the syringe needle from the septum of the filling reservoir and the time when the gas is injected into the mixing chamber.

This shall be determined experimentally, where possible, for each of the syringes used. However, experiments made with certain syringes used in practice have shown that there is no significant difference in the calibration component volume injected when the time between extraction of the syringe needle from the filling-reservoir septum and injection of the gas into the mixing chamber is varied from 5 s to 30 s.

- c) Gas may diffuse into the atmosphere through the seals of the syringe (this is unlikely to be significant, however, provided a sufficiently leaktight syringe is used, as specified in 6.4).

The uncertainties that result from all these sources shall be included in the uncertainty in the concentration of the calibration gas mixture. Annex B gives a specific example of the determination of the internal volume of a metering syringe.

#### 8.2.2 Uncertainty in the volume of the complementary gas, $V_{CG}$ , which arises from the uncertainty in the internal volume of the gas-mixing chamber

Each of the volume measurements used to determine the total volume of the gas-mixing chamber (described in 6.1) will be subject to a measurement uncertainty. These shall be combined, using the standard square-root sum-of-squares procedure to obtain the overall measurement uncertainty ascribed to the actual measured internal volume of the gas-mixing chamber.

It should also be noted (see 6.1) that each of the measurements of the volumes that make up the total may have been carried out at different ambient temperatures. Corrections may, therefore, have to be made to these in order to convert these volumes to a common ambient temperature, where such corrections are significant. This procedure will yield the volume of the mixing chamber at a specific ambient temperature. The mixing chamber will, however, be used at other ambient temperatures, and a correction shall, therefore, then be applied so as to define the volume of the gas-mixing chamber at the ambient temperature actually used. In these cases, any significant uncertainties arising from the corrections applied shall be included in the overall measurement uncertainty of the concentration of the calibration gas mixture.

### 8.2.3 Uncertainties in the measurement of the two pressures $p_1$ and $p_2$

These two pressure measurements contribute directly to the final volume fraction of the component [see equation (5)], and therefore the uncertainties in the measurements of these pressures shall be taken into account.

### 8.2.4 Uncertainties in the measurements of the ambient pressure and temperature to which both volumes $V(x)$ and $V_{cg}$ are referred

This is an item which, if significant, must be included somehow in the expanded uncertainty, since corrections are made to adjust from the working conditions of  $p$  and  $T$  in the vessel to the ambient conditions [see paragraph following equation (1)].

### 8.2.5 Uncertainties due to gaseous impurities in the calibration component and key impurities in the complementary gas

All gases contain impurities, and these may affect the exact volume fraction of the calibration component in the gas mixture when prepared by the static volumetric method or by any alternative method [e.g. gravimetric preparation (ISO 6142)<sup>[3]</sup> and dynamic volumetric preparation (the various parts of ISO 6145<sup>[4]</sup>)]. There is, therefore, a requirement for impurities in the calibration component and the complementary gas to be analysed, or the accuracy and/or stability of the prepared gas mixture may be degraded.

The effects of impurities in the calibration component gases on the accuracy of the gas mixture are generally different from those of impurities in the complementary gas, as discussed below:

- a) The calibration components in the calibrations which are used to determine  $x$  (see Clause 7) are assumed to comprise only the gaseous species selected. Therefore, any gaseous impurities in these components will give a gas mixture with a concentration of the specific calibration component which is systematically lower than that calculated using the method of Clause 7.

If no correction is made for the impurities present, the calculated concentrations of the calibration components will be in error by up to several percent (relative). The likely impurities in the calibration components shall therefore be analysed, and appropriate corrections made, if these impurities are at significant concentrations.

- b) Impurities in the complementary gas affect the concentration of the prepared gas mixture in a different way. For example:
- If calibration components are contained as impurities in the complementary gas, then the concentration of each component in the gas mixture will be higher than that calculated as in Clause 7. In this case, either the concentration of each calibration component in the complementary gas shall be determined with sufficient sensitivity so that it makes no significant contribution to the expanded uncertainty, or the concentration of each calibration component shall be shown to be below the detection limit of the measurement. In this latter case, the detection limit shall be included as a contribution to the expanded uncertainty in the volume fraction of that particular component in the complementary gas.
  - Alternatively, if the complementary gas contains impurities that will react with a calibration component, these will have a detrimental effect on the accuracy or stability of the final gas mixture. These impurities shall therefore be analysed with a detection sensitivity that is sufficient to demonstrate that they are not present in significant concentrations in the complementary gas, or an allowance for any instability occurring shall be made when calculating the expanded uncertainty in the volume fraction of the calibration component. A specific example of an expanded uncertainty determination including these component uncertainties is given in Annex C.

### 8.2.6 Uncertainty arising from the degree of stability of the calibration gas mixture between preparation and use

This will depend on:

- the species selected as the calibration component, and its reactivity with the inside walls and the other components of the mixing chamber (this may also be a function of the concentration of the calibration gas mixture);
- reactions between any trace impurities in the complementary gas or the calibration component (e.g. for mixtures of nitric oxide in nitrogen, trace concentrations of oxygen in the nitrogen will affect the stability of the mixture and this will be dependent on the concentration of nitric oxide in the gas mixture).

Tests shall, therefore, be carried out, where possible, to determine the stability, as a function of time, of the gas mixture prepared using specific components and a particular apparatus. A specific example of such a test is given in Annex D.

### 8.2.7 Uncertainty arising from the compressibility of the components of the gas mixture

This component of the uncertainty budget arises because the gas mixture will be used for calibration purposes at a pressure different from that at which it was prepared. However, since these pressures will be only slightly different from each other in practice, and since calibration components are generally at low concentrations, errors which arise in the volume concentration of the gas mixture as a result of the use of incorrect compressibility factors are unlikely to give rise to significant errors in the concentrations of the calibration components in the final mixture.

## 8.3 Calculation of the expanded uncertainty in the volume fraction of a component

All significant contributions to the uncertainty in the concentration of the final mixture shall be combined using a square-root sum-of-squares procedure to give the overall measurement uncertainty. This expanded uncertainty is generally then expressed at a level of confidence of 95 %, using a statistical  $t$ -factor which shall be derived from the appropriate number of degrees of freedom that contribute to this expanded uncertainty (for a large number of degrees of freedom, this involves a multiplicand of 2).

An example of how to calculate the expanded uncertainty in the concentration of the prepared gas mixture is given in Annex C.

## Annex A (informative)

### Example of an apparatus suitable for the preparation of calibration gas mixtures by the static volumetric method

#### A.1 General

The complete apparatus shall be leakproof. After evacuation to about 5 Pa ( $5 \times 10^{-2}$  mbar), the leak rate into the apparatus shall be less than  $10 \times 10^2$  Pa/h.

#### A.2 Mixing apparatus

A schematic outline is shown in Figure A.1.

**A.2.1 Manometer**, capable of measuring pressures between  $0,1 \times 10^5$  Pa and  $2,0 \times 10^5$  Pa (0,1 bar and 2,0 bar) to an uncertainty of  $1,0 \times 10^2$  Pa (1,0 mbar).

**A.2.2 Relief valve**, capable of relieving pressure at  $1,4 \times 10^5$  Pa (1,4 bar).

**A.2.3 Shut-off valves.**

**A.2.4 Pressure-equalization device.**

NOTE A wash bottle filled with water has been found suitable.

**A.2.5 Temperature sensors**, placed in the mixing chamber and on the outside shell, capable of measuring temperature differences to an uncertainty of 0,2 °C.

**A.2.6 Vacuum pump**, capable of generating a vacuum of 5 Pa ( $5 \times 10^{-2}$  mbar).

**A.2.7 Fan**, of sufficient integrity and size so that gas does not leak and adequate mixing is ensured.

#### A.3 Syringe-filling apparatus

**A.3.1 Reservoir**, gastight, with a volume of about 100 ml, with openings and connections as shown in Figure A.2, capable of being operated under a pressure of  $1,4 \times 10^5$  Pa and under a vacuum of  $0,1 \times 10^2$  Pa, made of a material that does not react with the calibration component gas.

**A.3.2 Manometer**, capable of measuring pressure between  $0,1 \times 10^5$  Pa and  $2,0 \times 10^5$  Pa to an uncertainty of  $1,0 \times 10^2$  Pa.

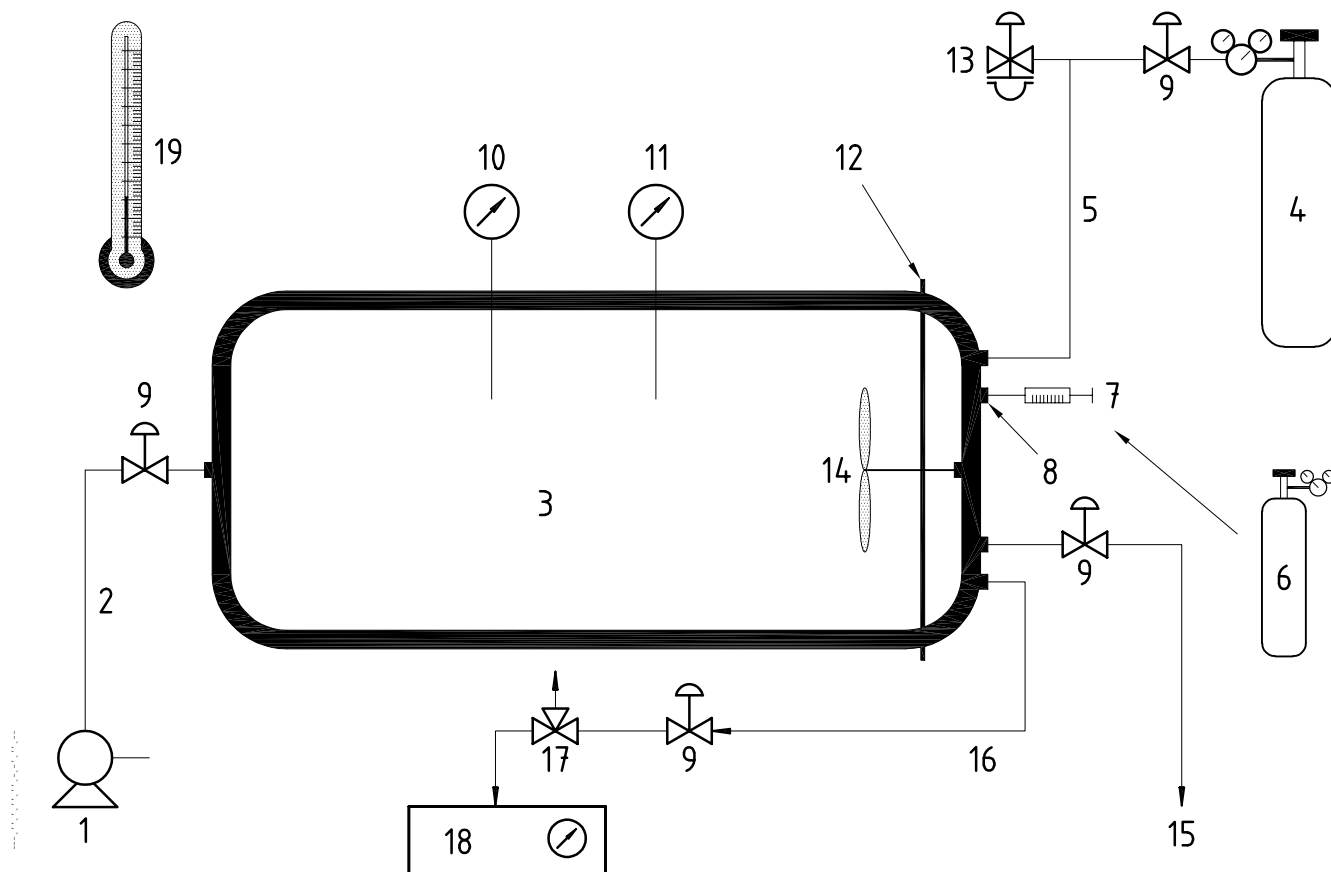
**A.3.3 Relief valve**, capable of relieving pressure at  $1,4 \times 10^5$  Pa and vented to a safe area.

**A.3.4 Shut-off valves.**

**A.3.5 Vacuum pump**, capable of generating a vacuum of 5 Pa.

**A.3.6 Septum**, made of e.g. silicone rubber.

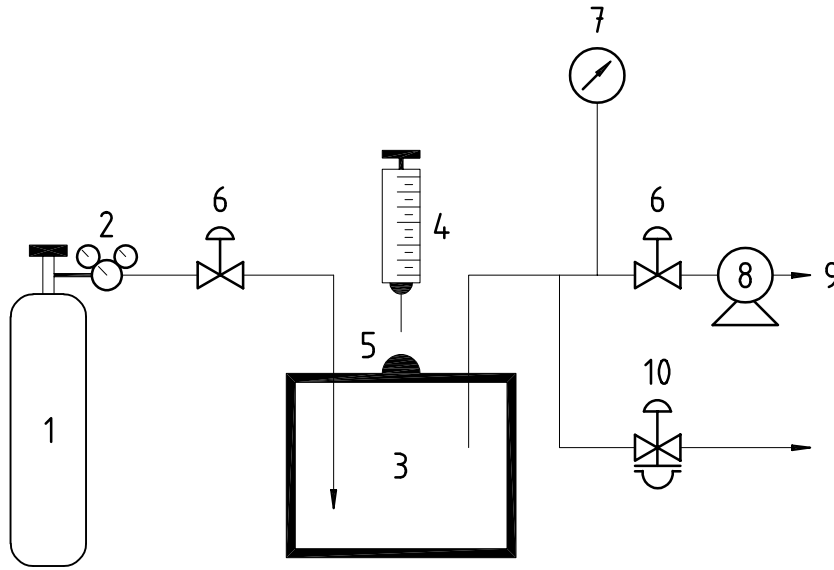




### Key

- |                                   |   |
|-----------------------------------|---|
| 1 vacuum pump                     | 11 temperature sensor for mixing chamber  |
| 2 connection line for vacuum pump | 12 plane-polished flanges for connection to standard glass parts (with screw connections) |
| 3 mixing chamber                  | 13 relief valve   |
| 4 complementary gas               | 14 motor-driven fan   |
| 5 feed line for complementary gas | 15 vent to safe location  |
| 6 calibration component           | 16 outlet for calibration gas mixture   |
| 7 metering syringe                | 17 pressure-equalization device   |
| 8 septum                          | 18 reference analyser   |
| 9 shut-off valve                  | 19 temperature sensor for measurement of ambient temperature                              |
| 10 pressure gauge                 |   |

**Figure A.1 — Schematic diagram of a mixing apparatus for the preparation of calibration gas mixtures by the static volumetric method**



**Key**

- |   |                          |    |                       |
|---|--------------------------|----|-----------------------|
| 1 | calibration component    | 6  | shut-off valve        |
| 2 | two-stage pressure valve | 7  | pressure gauge        |
| 3 | reservoir                | 8  | vacuum pump           |
| 4 | metering syringe         | 9  | vent to safe location |
| 5 | septum                   | 10 | relief valve          |

**Figure A.2 — Schematic diagram of set-up for filling a syringe with a gaseous calibration component**

**A.4 Syringe**

**A.4.1 Metering syringe**, gastight, with needle, with a maximum relative uncertainty of 1 %. Syringes of 0,1 ml, 1,0 ml and 10 ml, with PTFE bushings as seals, have been found suitable.

**A.5 Working materials**

**A.5.1 Complementary gas**, e.g. nitrogen or synthetic air, the purity requirements depending on the intended purpose.

**A.5.2 Calibration component**: pure gas, gas mixture or liquid, depending on the intended purpose.

## Annex B (informative)

### Example of determination of the volume of metering syringes

#### B.1 Determination of volume $V$ of syringe

The volumes of several NO and SO<sub>2</sub> syringes were determined by filling with water, weighing on a high-sensitivity balance (a Mettler AT201) and calculating the volume from the mass of liquid in the syringe (assuming a density of 0,998 g/cm<sup>3</sup> at 22 °C). Several replicate volume determinations were carried out in a continuous cycle. The results are shown in Table B.1.

**Table B.1 — Syringe volume**

NO syringe 1 $1 \times 10^{-6}$	NO syringe 2 $1 \times 10^{-6}$	NO syringe 2 $1 \times 10^{-6}$	NO syringe 3 $1 \times 10^{-6}$	NO syringe 4 $1 \times 10^{-6}$	SO <sub>2</sub> syringe 1 $1 \times 10^{-6}$	SO <sub>2</sub> syringe 2 $1 \times 10^{-6}$	SO <sub>2</sub> syringe 3 $1 \times 10^{-6}$
24,71	39,9	40,0	78,49	99,37	39,72	49,22	69,47
24,80	39,6	39,9	78,40	99,30	39,81	49,28	69,52
24,69	39,6	40,0	78,48	99,50	39,67	49,31	69,42
24,80	39,9	40,0	78,60	99,50	39,76	49,24	69,45
24,77	40,0	40,0	78,58	99,45	39,72	49,20	69,44
24,76	39,9	40,1	78,65	99,43	39,66	49,37	69,36
24,74	39,9	39,9	78,69	99,47	39,74	49,23	69,37
24,76	39,8	40,1	78,63	99,44	39,74	49,32	69,39
24,85	39,9	40,0	78,52	99,33	39,68	49,22	69,43
24,73	39,9	39,9	78,56	99,47	39,72	49,27	69,37
24,73	40,2	39,7	78,60	99,55	39,69	49,28	69,47
24,74	39,9	—	78,58	99,48	39,81	49,24	69,47
24,74	40,1	—	78,65	99,46	39,69	49,27	69,46
24,71	40,0	—	78,79	99,36	39,76	49,25	69,44
24,84	40,1	—	78,63	99,36	39,76	49,18	69,36

NOTE Data provided by European Commission's Joint Research Centre, Ispra, Italy.

## B.2 Uncertainty in the volume determination

The variations in the measured volume reflect variations in the filling and emptying processes and in the performance of the balance. The standard deviations of the estimates for  $V$  shown in Table B.1 are the square roots of  $u_{V1}^2$ , also given in Table B.2.

The balance was also subject to a linear deviation of + 0,02 mg (0,02 µl) from the true value in the range 0 g to 5 g. Assuming a rectangular distribution, the best estimate of the standard uncertainty for  $V$  is the square root of  $u_{V2}^2$ , also given in Table B.2.

**Table B.2 — Measured volumes of syringes**

Syringe	Average volume $l \times 10^{-6}$	$u_{V1}$ $l \times 10^{-6}$	$u_{V2}$ $l \times 10^{-6}$
NO syringe 1	24,71	$4,68 \times 10^{-2}$	$1,15 \times 10^{-2}$
NO syringe 2	39,86	$4,56 \times 10^{-2}$	$1,15 \times 10^{-2}$
NO syringe 3	78,43	$9,44 \times 10^{-2}$	$1,15 \times 10^{-2}$
NO syringe 4	99,23	$7,15 \times 10^{-2}$	$1,15 \times 10^{-2}$
SO <sub>2</sub> syringe 1	39,65	$4,56 \times 10^{-2}$	$1,15 \times 10^{-2}$
SO <sub>2</sub> syringe 2	49,16	$4,94 \times 10^{-2}$	$1,15 \times 10^{-2}$
SO <sub>2</sub> syringe 3	69,29	$4,86 \times 10^{-2}$	$1,15 \times 10^{-2}$

The uncertainties in Table B.2 were incorporated in an expanded uncertainty for the static volumetric method as outlined in Annex C.

Obviously, there are differences between injecting a gas with a syringe and injecting a liquid, but it is possible to make a good estimation of the volume, provided the precautions outlined in 6.5 are followed.

## Annex C (informative)

### Example of the determination of the uncertainty in the concentration of a calibration gas mixture prepared by the static volumetric method

#### C.1 Procedure

A syringe of known volume  $V(x_g)$  was filled with pure  $\text{SO}_2$  gas at atmospheric pressure and room temperature. This volume of  $\text{SO}_2$  was injected into a large vessel of known volume  $V_{cg}$  filled with hydrocarbon-free air at atmospheric pressure and room temperature. Further hydrocarbon-free air was then introduced into the vessel until the desired final pressure was obtained: this is normally about  $1,5 \times 10^5$  Pa (1 500 mbar) in order to permit easy use of the mixture. The mixture is ready for use when it reaches room temperature.

#### C.2 Model equation

$$\varphi(x) = \varphi(X) \times \frac{V(x_g)}{V_{cg} + V(x_g)} \times \frac{p_1}{p_2} \quad (\text{C.1})$$

This equation can be simplified by taking into account that  $V_{cg} + V(x_g) \approx V_{cg}$ , giving

$$\varphi(x) = \varphi(X) \times \frac{V(x_g)}{V_{cg}} \times \frac{p_1}{p_2} \quad (\text{C.2})$$

According to the *Guide to the expression of uncertainty in measurement*<sup>[5]</sup>, the combined uncertainty is given by equation (C.3). It is assumed that the variables are not correlated.

$$u_c^2[\varphi(x)] = \left( \frac{p_1 V(x_g)}{p_2 V_{cg}} \right)^2 u_{\varphi(X)}^2 + \left( \frac{\varphi(X) \times V(x_g)}{p_2 V_{cg}} \right)^2 u_{p_1}^2 + \left( \frac{\varphi(X) \times p_1}{p_2 V_{cg}} \right)^2 u_{V(x_g)}^2 + \left( \frac{\varphi(X) \times p_1 V(x_g)}{p_2^2 V_{cg}} \right)^2 u_{p_2}^2 + \left( \frac{\varphi(X) \times p_1 V(x_g)}{p_2 V_{cg}^2} \right)^2 u_{V_{cg}}^2 \quad (\text{C.3})$$

### C.3 List of quantities

#### C.3.1 General

The quantities concerned are listed in Table C.1.

**Table C.1 — List of quantities**

Quantity	Unit	Definition
$\varphi(x)$	—	Volume fraction of SO <sub>2</sub> in the resulting mixture
$\varphi(X)$	—	Volume fraction of SO <sub>2</sub> in the pure or concentrated SO <sub>2</sub> injected
$V(x_g)$	l	Volume of SO <sub>2</sub> injected, expressed in litres (or in the same units as $V_{cg}$ )
$V_{cg}$	l	Volume of hydrocarbon-free air, expressed in litres [or in the same units as $V(x_g)$ ]
$p_1$	Pa × 10 <sup>2</sup> (mbar)	Pressure of the SO <sub>2</sub> in the syringe (same units as $p_2$ )
$p_2$	Pa × 10 <sup>2</sup> (mbar)	Final pressure in the vessel (same units as $p_1$ )

#### C.3.2 $\varphi(x)$

Calculated from equation C.2 (see also Table C.1).

#### C.3.3 $\varphi(X)$

Type B uncertainty

Value: 0,999(9)

Half-width of distribution: 0,000 1

The volume fraction of SO<sub>2</sub> in the SO<sub>2</sub> injected,  $\varphi(X)$  (called purity hereafter), and its corresponding uncertainty, should be determined by the end-user or by an external laboratory accredited for such testing.

In this case, the purity of the SO<sub>2</sub> in the cylinder was given by the manufacturer, which was accredited for the determination of SO<sub>2</sub> contents in gas cylinders. However, in the absence of a certificate, the only information made available by the manufacturer was that the purity was better than 99,98 %. The lower and upper limits of the purity were chosen to be 0,999(8) and 1, with maximum probability that the purity is equal to 0,999(9) and zero probability that the purity is 0,999(8) or 1. The probability distribution is then triangular with 100 % probability that the purity lies within this interval. The standard uncertainty for  $\varphi(X)$  is given by

$$u[\varphi(X)] = \sqrt{\frac{0,000\ 1^2}{6}} = 40,8 \times 10^{-6}$$

#### C.3.4 $V(x_g)$

Type A uncertainty

Value: 0,000 039 65 l

Standard uncertainty:  $4,97 \times 10^{-8}$  l

Degrees of freedom: 18

The volume of the syringe used for injection was determined by filling it with water and calculating the volume from the mass of water in the syringe (assuming a density of 0,998 g/cm<sup>3</sup> at 22 °C). Fifteen replicate volume measurements were carried out in a continuous cycle. The variations in the measured volume reflect variations in the filling and emptying processes and in the performance of the balance. The standard deviation, for  $V(x_g) = 39,65 \mu\text{l}$ , is the square root of  $2,15 \times 10^{-15} \text{ l}^2$  with 14 degrees of freedom, calculated from the following volume measurements (in microlitres):

39,64	39,58	39,61
39,73	39,66	39,73
39,59	39,66	39,61
39,68	39,60	39,68
39,64	39,64	39,68

The weighings made using the balance are also subject to uncertainty. The repeatability and reproducibility of the balance was therefore evaluated by performing triplicate weighings of a certified 10 g mass on 18 different days spread over a period of 1 month. The reading of the balance was always within the certified value of the mass. An analysis of the variance did not reveal any significant difference between the between-day and within-day variations, so all weighings were used to estimate the standard uncertainty of the balance, which is the square root of  $3,12 \times 10^{-16} \text{ l}^2$  with 53 degrees of freedom.

Finally, the standard uncertainty for the volume of the syringe is given by

$$u[V(x_g)] = \sqrt{2,15 \times 10^{-15} + 3,12 \times 10^{-16}} = 4,97 \times 10^{-8} \text{ l}$$

with a number of degrees of freedom given by

$$v_{\text{eff}} = \frac{(4,97 \times 10^{-8})^4}{\frac{(\sqrt{2,15 \times 10^{-15}})^4}{14} + \frac{(\sqrt{3,12 \times 10^{-16}})^4}{53}} = 18,4$$

### C.3.5 $V_{\text{cg}}$

Type A uncertainty

Value: 111,84 l

Standard uncertainty: 0,111 84 l

Degrees of freedom: 2

The total volume was determined by filling the whole system with water. Three repetitions gave an average of 111,84 l with a standard uncertainty of 0,1 %. As the vessel was made of 4-mm-thick borosilicate glass, it was not expected to increase in volume at internal pressures up to  $1,7 \times 10^5 \text{ Pa}$ .

**C.3.6**  $p_1$

Type B uncertainty

Value:  $1\,013 \times 10^2$  Pa (1 013 mbar)

Expanded uncertainty:  $2,32 \times 10^2$  Pa (2,32 mbar)

Coverage factor: 2

SO<sub>2</sub> was injected at room pressure, which was measured with a barometer. The barometer manufacturer gave upper and lower limits of  $(1\,013 \pm 0,25) \times 10^2$  Pa. Assuming a rectangular distribution of the probability that the pressure lies between  $999,75 \times 10^2$  Pa and  $1\,000,25 \times 10^2$  Pa, the best estimate of the standard uncertainty is given by

$$u(p_1)_1 = \sqrt{\frac{(0,25 \times 10^2)^2}{3}} = 14,4 \text{ Pa}$$

The pressure is influenced by the time interval between withdrawing the syringe needle from the septum chamber and injecting the SO<sub>2</sub> into the vessel. The SO<sub>2</sub> concentration obtained with different time intervals between withdrawal of the syringe needle from the septum chamber and injection into the vessel was investigated. The results showed that there was little difference between injections after 5 s intervals and those after 15 s intervals, although a transient over-pressure of 0 % to 0,2 % cannot be ruled out. Assuming a rectangular distribution, the best estimate of the standard uncertainty is given by

$$u(p_1)_2 = \sqrt{\frac{(0,002 \times 1\,000 \times 10^2)^2}{3}} = 115 \text{ Pa}$$

Finally, the standard uncertainty of  $p_1$  is given by

$$u(p_1) = \sqrt{2,088\,3 \times 10^{-2} \times 10^4 + 1,33 \times 10^4} = 116 \text{ Pa}$$

**C.3.7**  $p_2$

Type B uncertainty

Value:  $1\,500 \times 10^2$  Pa (1 500 mbar)

Expanded uncertainty:  $1,78 \times 10^2$  Pa (1,78 mbar)

Coverage factor: 2

The manufacturer of the pressure sensor gave an accuracy of  $\pm 0,04$  % and a precision of  $\pm 0,025$  % of the reading. For a pressure of  $1,5 \times 10^5$  Pa, therefore, the precision claimed by the manufacturer was  $0,375 \times 10^2$  Pa. However, one would think that a digital display should have a precision of at least one digit, i.e.  $1 \times 10^2$  Pa. Assuming a rectangular distribution, the best estimate of the standard uncertainty for  $p_2$  is the sum of

$$u(p_2)_1 = \sqrt{\frac{(0,6 \times 10^2)^2}{3}} = 35 \text{ Pa}$$

and



$$u(p_2)_2 = \sqrt{\frac{(1 \times 10^2)^2}{3}} = 58 \text{ Pa}$$

The final pressure  $p_2$  of  $1,5 \times 10^5$  Pa (1 500 mbar) was not measured exactly until room temperature was reached. A vessel temperature  $0,5$  °C higher than room temperature has been observed to produce a deviation of  $1 \times 10^2$  Pa (1 mbar) in the final pressure  $p_2$ . Assuming a rectangular distribution, the best estimate of the standard uncertainty is given by

$$u(p_2)_3 = \sqrt{\frac{(1 \times 10^2)^2}{3}} = 58 \text{ Pa}$$

Finally, the standard uncertainty for  $p_2$  is given by

$$u(p_2) = \sqrt{35^2 + 58^2 + 58^2} = 89 \text{ Pa}$$

## C.4 Uncertainty budget

This is given in Table C.2.

Table C.2 — Uncertainty budget

Quantity	Value	Standard uncertainty	Degrees of freedom	Sensitivity coefficient	Uncertainty contribution	Index
$\varphi(X)$	0,999	$40,8 \times 10^{-6}$	$\infty$	$239 \times 10^{-9}$	$9,77 \times 10^{-12}$	0 %
$V(x_g)$	$39,650 0 \times 10^{-6}$ l	$49,7 \times 10^{-9}$ l	26	$6,03 \times 10^{-3}$	$300 \times 10^{-12}$	37,2 %
$V_{cg}$	111,840 l	0,118 l	2	$2,14 \times 10^{-9}$	$239 \times 10^{-12}$	23,7 %
$p_1$	$1,013 00 \times 10^5$ Pa	$1,16 \times 10^2$ Pa	50	$236 \times 10^{-12}$	$274 \times 10^{-12}$	30,8 %
$p_2$	$1,500 000 \times 10^5$ Pa	$0,890 \times 10^2$ Pa	50	$159 \times 10^{-12}$	$142 \times 10^{-12}$	8,3 %
$\varphi(x)$	$239,4 \times 10^{-9}$	$492 \times 10^{-12}$	26	—	—	—

### Result:

Quantity:  $\varphi(X)$

Value:  $239,4 \times 10^{-9}$

Relative expanded uncertainty:  $0,98 \times 10^{-9}$

Coverage factor: 2,0

## Annex D (informative)

### Example of the determination of the stability, as a function of time, of prepared calibration gas mixtures

#### D.1 Analytical methods

CO, NO/NO<sub>x</sub> and SO<sub>2</sub> calibration gas mixtures were prepared in a borosilicate glass vessel, using the static volumetric method described in this International Standard. The concentrations of the calibration components were then determined as the gas mixtures were passed to the analyser. It was possible to take about 50 l from the vessel before the pressure fell below that necessary to maintain the required flow-rate for the analyser.

NOTE For the CO calibration gas mixture, a smaller vessel and syringe were used than for the other gases.

The following methods of analysis were used:

- for CO non-dispersive infrared correlation spectroscopy;
- for NO/NO<sub>x</sub> chemiluminescence spectroscopy;
- for SO<sub>2</sub> UV fluorescence spectrometry.

#### D.2 Results

##### D.2.1 General

The results are shown in Tables D.1 to D.3 and Figures D.1 to D.3 [with acknowledgements to the National Reference Laboratory of the Federal Environmental Agency (UBA, Germany)].

NOTE Throughout the tables and figures, the concentration is by volume (1 ppb =  $1 \times 10^{-9}$  vol/vol and 1 ppm =  $1 \times 10^{-6}$  vol/vol) and the pressure is given in bars (1 bar =  $10^5$  Pa).

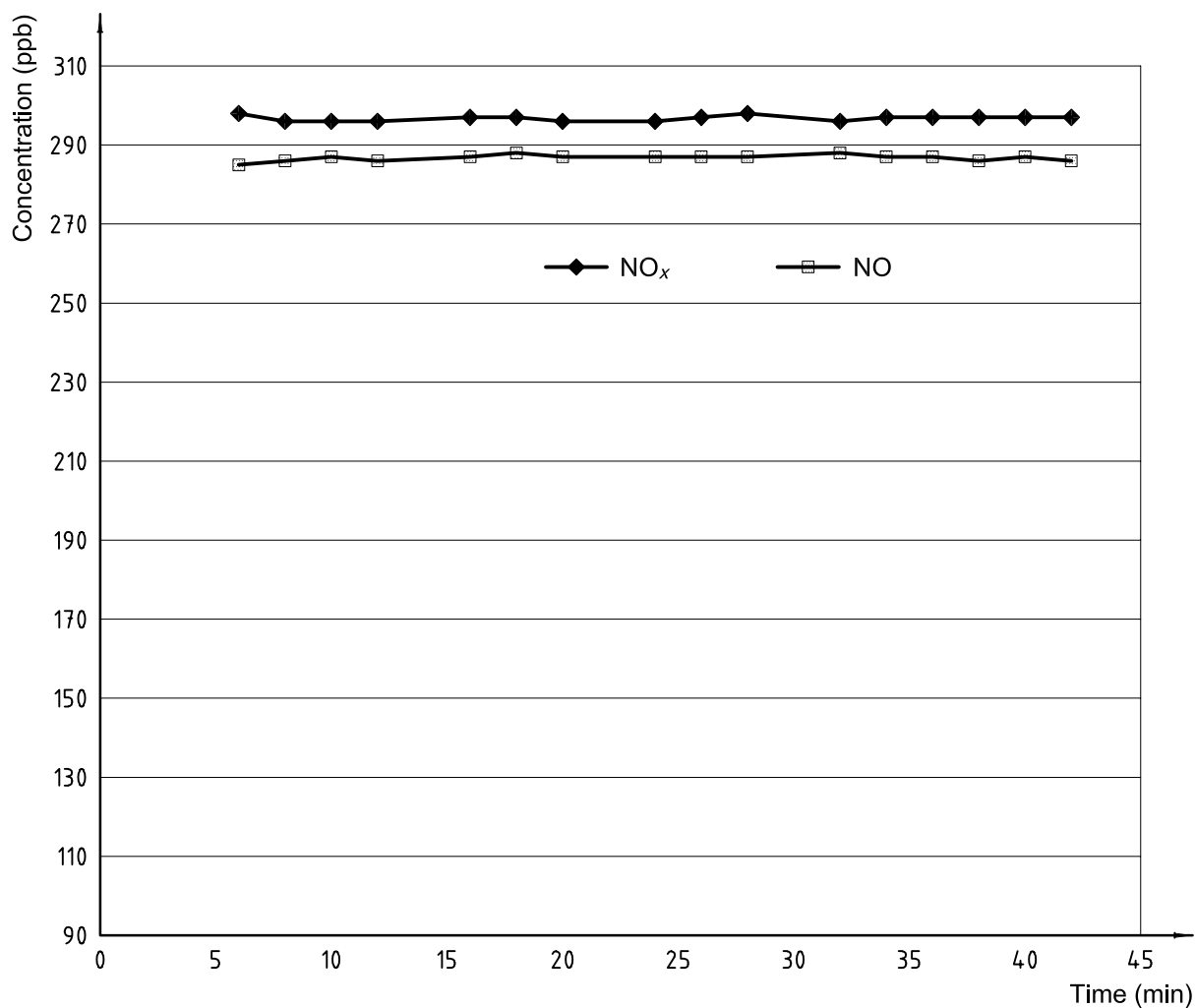
##### D.2.2 NO<sub>x</sub>/NO

The analyses were carried out under the following conditions:

Volume of vessel:	111,490 l
Volume of syringe	50 µl
Pressure in chamber	1,520 bar to 1,007 bar

Table D.1 — Stability of NO<sub>x</sub>/NO concentration during calibration

Time min	NO <sub>x</sub> concn. ppb	NO concn. ppb	Pressure bar
0	0	0	1,520
6	298	285	1,453
8	296	286	1,418
10	296	287	1,395
12	296	286	1,371
16	297	287	1,319
18	297	288	1,283
20	296	287	1,263
24	296	287	1,211
26	297	287	1,192
28	298	287	1,166
32	296	288	1,115
34	297	287	1,089
36	297	287	1,064
38	297	286	1,041
40	297	287	1,022
42	297	286	1,009



Calculated calibration concentration for NO<sub>x</sub>: 299 ppb  
 for NO: 299 ppb  
 Average measured value for NO<sub>x</sub>: 296,75 ppb  
 for NO: 286,75 ppb

**Figure D.1 — Stability of NO<sub>x</sub>/NO concentration during calibration**

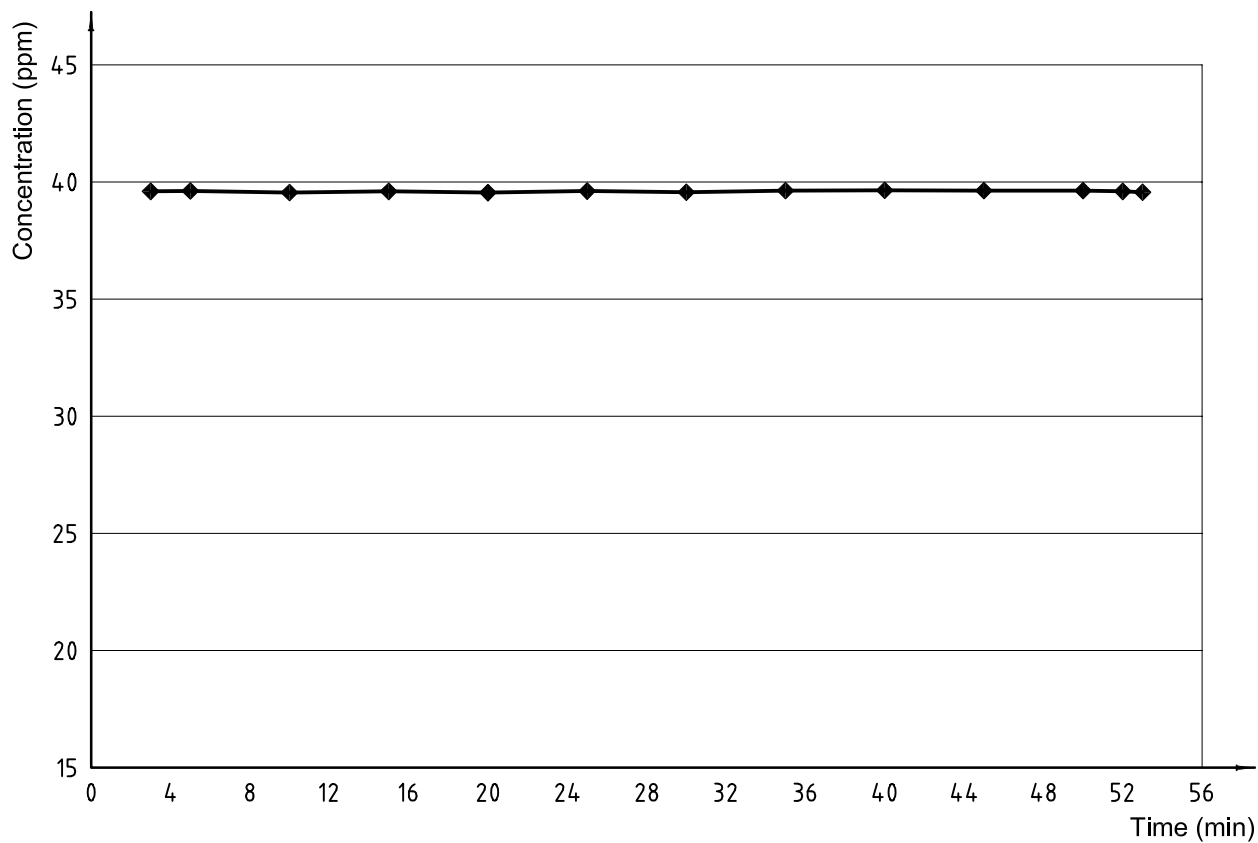
**D.2.3 CO**

The analyses were carried out under the following conditions:

Volume of vessel	14,019 l
Volume of syringe	5 000 µl
Pressure in chamber	9,140 bar to 1,002 bar

**Table D.2 — Stability of CO concentration during calibration**

<b>Time</b> min	<b>CO concn.</b> ppm	<b>Pressure</b> bar
0	0	9,140
3	39,60	7,700
5	39,61	7,494
10	39,56	6,964
15	39,60	6,400
20	39,56	6,005
25	39,61	5,487
30	39,59	5,014
35	39,64	4,223
40	39,65	3,438
45	39,63	2,630
50	39,64	1,856
52	39,60	1,075
53	39,57	1,015



Calculated calibration concentration: 39,63 ppm

Average measured value: 39,60 ppm

Figure D.2 — Stability of CO concentration during calibration

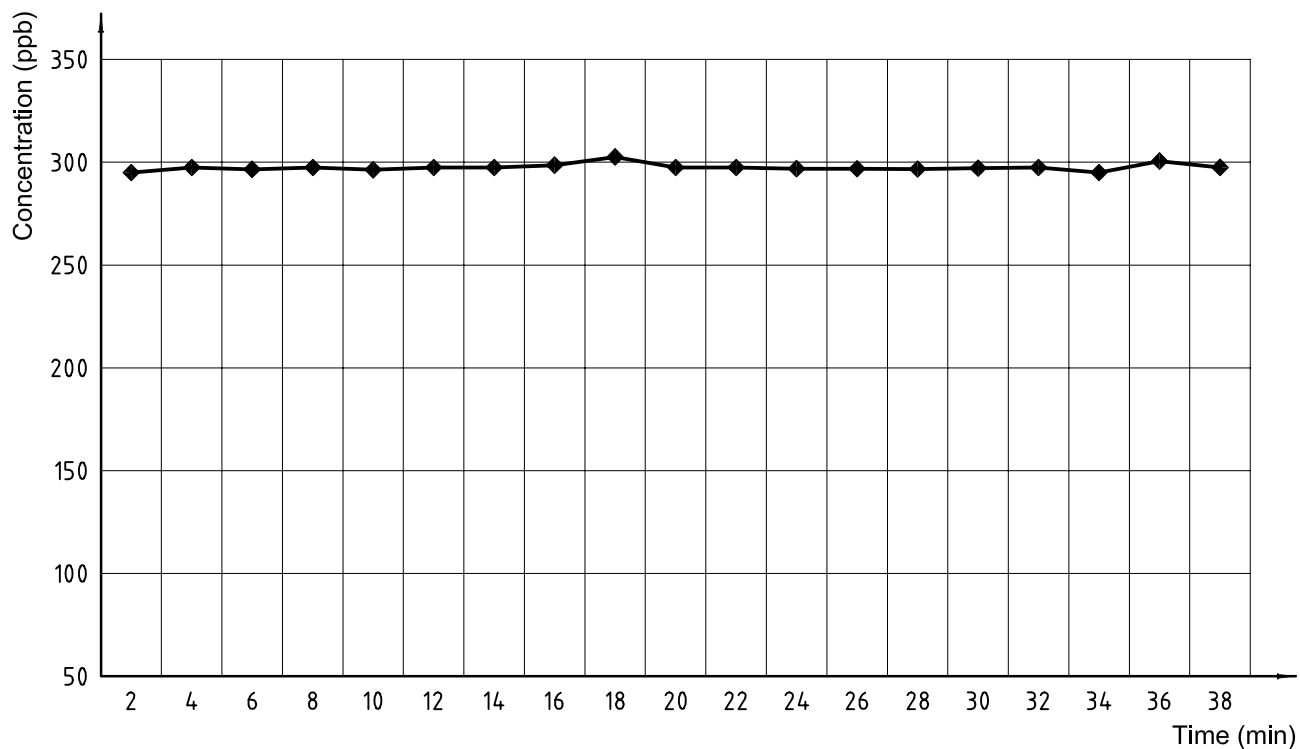
**D.2.4 SO<sub>2</sub>**

The analyses were carried out under the following conditions:

Volume of vessel: 111,490 l  
 Volume of syringe 50 µl  
 Pressure in chamber 1,526 bar to 1,002 8 bar

**Table D.3 — Stability of SO<sub>2</sub> concentration during calibration**

Time min	SO <sub>2</sub> concn. ppb	Pressure bar
0	0	1,526
2	295	1,496
4	298	1,478
6	297	1,460
8	298	1,442
10	296	1,416
12	298	1,387
14	298	1,360
16	299	1,332
18	302	1,307
20	298	1,277
22	298	1,253
24	297	1,228
26	297	1,200
28	297	1,166
30	297	1,135
32	298	1,105
34	295	1,073
36	301	1,035
38	298	1,014



Calculated calibration concentration: 299 ppb

Average measured value: 297,5 ppb

**Figure D.3 — Stability of SO<sub>2</sub> concentration during calibration**



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