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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.

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 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.

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[1, 2]) 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 10×10^{-9} (10 ppb — parts per billion) to 50×10^{-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 ± 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 of 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 1×10^5 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 1×10^5 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 m^3 to 0,5 m^3, capable of operating up to pressures of about 2×10^5 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 SO_2, NO, NO_2, CO and C_6H_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 10×10^2 Pa (10 mbar) per hour after evacuation to 5 Pa (5×10^{-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 Evacuable 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 5×10^2 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 SO_2, 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 5×10^2 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 1×10^2 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:

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

where

$\varphi(x)$ is the volume fraction of component x_g 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:

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

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

where $V(x_l)$ is the volume of calibration component x_l after it has evaporated to form a gas, expressed in the same units as V_l (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:

$$V(x_l) = \frac{V_l \times \rho \times V_M}{M}$$ (4)

where

V_l is the volume of calibration component x in liquid form;

ρ 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 $V(x_l)$ is much less than V_{cg}, the final volume fraction (x) of the calibration component is given by:

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

where

$V(x_l)$ 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.