

Methods for

Preparation of calibration gas mixtures —

Part 3: Static volumetric methods

[ISO title: Gas analysis — Preparation of calibration gas mixtures — Static volumetric methods]

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- British Gas Corporation
- British Industrial Measuring and Control Apparatus Manufacturers' Association (BEAMA)
- Cement Makers' Federation
- Chemical Industries Association
- Department of Energy (Electricity Division)
- Department of Energy (Gas Standards)
- Department of Industry
- Department of Industry (Laboratory of the Government Chemist)
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- Society of Chemical Industry
- Society of Glass Technology
- Society of Motor Manufacturers and Traders Limited
- Water-tube Boilermakers' Association

The following bodies were also represented in the drafting of the standard through subcommittees and panels:

- British Compressed Gases Association
- Department of Industry (National Physical Laboratory)
- Sira Limited

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National foreword

This British Standard has been prepared under the direction of the Environment and Pollution Standards Committee. It is identical with ISO 6144:1981 “*Gas analysis — Preparation of calibration gas mixtures — Static volumetric methods*” published by the International Organization for Standardization (ISO). ISO 6144 was prepared as a result of discussions in Technical Committee 158, Gas analysis, in which the UK has participated.

BS 4559 was first published in 1970 as a single standard under the title “*Methods for the preparation of gaseous mixtures*”. The present revision is being issued in Parts to incorporate methods prepared by ISO/TC 158 and to provide for revision, where necessary, of the methods included in the 1970 edition which was withdrawn in 1981.

Terminology and conventions. The text of the International Standard has been approved as suitable for publication as a British Standard without deviation. Some terminology and certain conventions are not identical with those used in British Standards; attention is drawn especially to the following.

Wherever the words “International Standard” appear, referring to this standard, they should be read as “British Standard”.

The comma has been used as a decimal marker. In British Standards it is current practice to use a full point on the baseline as the decimal marker.

A British Standard does not purport to include all the necessary provisions of a contract. Users of British Standards are responsible for their correct application.

Compliance with a British Standard does not of itself confer immunity from legal obligations.

Summary of pages

This document comprises a front cover, an inside front cover, pages i and ii, pages 1 to 14, an inside back cover and a back cover.

This standard has been updated (see copyright date) and may have had amendments incorporated. This will be indicated in the amendment table on the inside front cover.

1 Scope and field of application

This International Standard specifies static volumetric methods for the preparation of calibration gas mixtures at pressures close to atmospheric pressure.

The methods are applicable to gas mixtures having concentrations between 10^{-6} and 10^{-1} (V/V) for which the relative uncertainty is between 10^{-3} and 10^{-2} .

2 Principles of the methods

2.1 General principles

Operations are carried out in three stages at a given temperature:

- a) Measurement: a container of known volume v is filled with the component to be analysed at a measured pressure p close to or, most often, equal to atmospheric pressure.
- b) Transfer: the volume v of the component is transferred into a receiver of known volume V in which at least a partial vacuum has been created beforehand.
- c) Dilution: the filling of this receiver is completed by means of the chosen complementary gas until the desired final pressure P is obtained; this is usually greater than atmospheric pressure to permit easy use of the mixture.

The volume concentration C_1 of the component, obtained after the first dilution, is practically equal at these pressure levels to the molar fraction concentration, and is given by the formula

$$C_1 = C_0 \frac{p_1 v_1}{P_1 V_1} = C_0 D_1 \quad \dots (1)$$

where

C_0 is the initial concentration of the component used ($C_0 \approx 1$);

D_1 is the dilution factor for the first operation.

The procedure described above is usually sufficient to give a relative uncertainty of less than 10^{-2} on concentrations of 10^{-3} to 10^{-1} (V/V).

In fact, values p and P act as correction factors in this case in order to achieve the volume concentration. For this reason, only the non-dimensional ratio p/P is significant and it is therefore possible to measure p and P with a simple system such as a mercury gauge. When the molar concentration is given, the corrections for the compressibility factor Z should be taken into account, if necessary.

In the present state of knowledge regarding "compressibility" factors Z for gas mixtures, it is assumed that the variation of Z for a binary mixture is a linear function of the concentrations of the components. For gas mixtures for calibration with a minor polar component in a complementary gas not very different from ideal gases, the correction factor Z is therefore only significant on the level of measurement [i.e. $(p_1 v_1)/Z_1$]¹⁾. For gas mixtures in which the complementary gas shows considerable deviations in relation to ideal gases, the correction factors Z shall be calculated using the same hypothesis of linearity; it does not seem desirable to go into any further detail on other corrections in the light of the present final purpose for which calibration gas mixtures are intended.

In the case of mixtures of lower concentrations [10^{-6} to 10^{-4} (V/V)], it is necessary to carry out a succession of dilutions in order to obtain an acceptable accuracy: a primary mixture of concentration C_1 between 10^{-3} and 10^{-1} is prepared and then diluted using the same procedure (measurement, transfer, dilution). The desired final concentration C_2 for the second stage dilution is given by the formula:

$$C_2 = C_1 D_2$$

where

C_1 is the concentration of the component in the mixture after the first dilution;

D_2 is the dilution factor for the second dilution, calculated from the pressure and volume data as in formula (1), i.e.

$$D_2 = \frac{P_2 v_2}{P_2 V_2}$$

where

p_2, v_2 are the values for the pressure and volume of the mixture at concentration C_1 ;

P_2, V_2 are the corresponding values for the receiver containing the final gas concentration C_2 .

¹⁾ In order to eliminate this source of error, for a component of low concentration and which is not ideal, the volume v_1 can, for example, be filled by a mixture obtained by a gravimetric method in which the component is at a sufficiently low concentration for the correction Z to be negligible.

It follows, therefore, that

$$C_2 = C_1 \frac{p_2 v_2}{P_2 V_2} = C_0 \frac{p_1 v_1}{P_1 V_1} \times \frac{p_2 v_2}{P_2 V_2} \quad \dots (2)$$

A third dilution may also be carried out which gives (with similar notations):

$$\begin{aligned} C_3 &= C_2 D_3 = C_2 \frac{p_3 v_3}{P_3 V_3} \\ &= C_0 \frac{p_1 v_1}{P_1 V_1} \times \frac{p_2 v_2}{P_2 V_2} \times \frac{p_3 v_3}{P_3 V_3} \end{aligned}$$

2.2 Precautions to be taken, evaluation of uncertainties

2.2.1 In order to achieve valid results using the dilution procedure described in 2.1:

- use containers and transfer lines which are made of materials which do not give rise to absorption phenomena with the intended constituents, for example glass and PTFE;
- carry out the operations so as to avoid increasing the temperature of the measuring vessel or the receiver at the time of filling by using gloves, for example, when handling.

2.2.2 As there are practical difficulties in evaluating uncertainty by statistical methods, the values recorded are those defined by the following error calculation derived from formula 2.

$$\begin{aligned} \frac{\Delta C_n}{C_n} &= \frac{\Delta C_0}{C_0} + \sum_1^n \frac{\Delta p}{p} + \sum_1^n \frac{\Delta P}{P} + \\ &+ \sum_1^n \frac{\Delta v}{v} + \sum_1^n \frac{\Delta V}{V} \quad \dots (3) \end{aligned}$$

where n is the number of dilutions.

2.2.3 As in other methods, account has to be taken of the purity corrections of the constituent samples and of the complementary gas used:

- constituent sample:** it is usually considered as having a concentration $C > 1 - y$, where y is the maximum quantity of impurity in the component. For the purpose of calculations, one may assume $C = 1 - \frac{y}{2}$ and for the level of error calculation, one can introduce $\pm \frac{y}{2}$.
- sample of complementary gas:** for mixtures of low component concentrations, it is often necessary to measure the residual component concentration $C_c \pm \Delta C_c$ in the complementary gas used, and to add this to the concentration calculated from the data from the dilution coefficients.

The effect on the error calculation is generally negligible at high concentrations.

At low concentrations, formula (3) becomes

$$\begin{aligned} \frac{\Delta C_2}{C_2} &= \frac{\Delta C_0}{C_0} + \sum \frac{\Delta p}{p} + \sum \frac{\Delta V}{V} + \frac{\Delta C_c}{C_2} \quad \dots (3') \\ &= \frac{\Delta C_0 D}{C_0 D} + \frac{\Delta C_c}{C_2} \end{aligned}$$

3 Examples of use

3.1 Method using glass vessels

3.1.1 Principle

Measurement of the component to be analysed is carried out in calibrated gas pipettes having capacities of approximately 10 to 400 cm³.

These pipettes are calibrated by weighing water or mercury: the volumes are determined with accuracies varying from 0,01 to 0,1 cm³ for pipettes of capacity 10 to 400 cm³.

Filling (see Figure 1) of these calibrated gas pipettes, which are fitted with polytetrafluoroethylene (PTFE) vacuum stopcocks, is carried out by sweeping with the component to be analysed: a fairly long outlet tube prevents ambient air flowing backwards towards the pipette.

Transfer of the measured volume into the mixture receiver (see Figure 2) takes place through glass tubes. When glass tubes are joined by rubber tubing, the contact area between the rubber and the gases should be minimal. Firstly, a vacuum is created in the receiver and the measured component is conveyed from the calibrated gas pipette towards the receiver by sweeping with the diluent gas.

Filling of the receiver with the diluent gas is completed slowly (see Figure 2); the mercury gauge may be used since the component is never in contact with the mercury. Filling of the receiver is adjusted to twice atmospheric pressure for convenience in transferring the mixture for subsequent use.

3.1.2 Apparatus

3.1.2.1 Flask, made of thick borosilicate glass, of capacity approximately 3 dm³, containing three PTFE tubes ($V < 0,3$ cm³), fitted with two PTFE vacuum stopcocks of 3 mm bore.

3.1.2.2 U-tube mercury manometer, the height of the two limbs being approximately 1 m; the right limb has, at the top, two PTFE vacuum stopcocks of 2 mm bore.

3.1.2.3 Water valve

3.1.2.4 Paraffin oil bubbler

3.1.2.5 Gas meter