

Methods for

Preparation of calibration gas mixtures —

Part 5: Dynamic volumetric methods —

Section 5.1 Review of methods of calibration

[ISO title: Gas analysis — Preparation of calibration gas mixtures — Dynamic volumetric methods — Part 1: Methods of calibration]

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Committees responsible for this British Standard

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- British Ceramic Research Association
- British Coal
- British Gas plc
- Cement Makers' Federation
- Chemical Industries Association
- Department of Energy (Gas Standards)
- Department of Trade and Industry (Electronics Application Division)
- Department of Trade and Industry (Laboratory of the Government Chemist)
- Department of Trade and Industry (Warren Spring Laboratory)
- Electricity Supply Industry in England and Wales
- GAMBICA (BEAMA Ltd.)
- Institute of Petroleum
- Institution of Chemical Engineers
- Institution of Gas Engineers
- 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
- British Laboratory Ware Association

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National foreword

This Section of BS 4559 has been prepared under the direction of the Environment and Pollution Standards Committee. It is identical with ISO 6145-1:1986 “*Gas analysis — Preparation of calibration gas mixtures — Dynamic volumetric methods — Part 1: Methods of calibration*”, published by the International Organization for Standardization (ISO). This Part of ISO 6145 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 implement 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by ISO/TC 158 and to provide for revision, where necessary, of the methods included in the 1970 edition which was withdrawn in 1981.

Part 5 of this standard covers the preparation of mixtures using dynamic volumetric methods. This Section covers methods of calibration. Other Sections in this Part of BS 4559 are as follows.

- Section 5.2: *Volumetric pumps method*¹⁾;
- Section 5.3: *Periodic injections into a flowing gas stream*;
- Section 5.4: *Continuous injection method*;
- Section 5.5: *Capillary method*¹⁾;
- Section 5.6: *Sonic orifices*;
- Section 5.7: *Mass flow controllers method*¹⁾;
- Section 5.8: *Diffusion method*¹⁾.

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.

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.

Wherever the words “International Standard” and “part 1 of ISO 6145” appear, referring to this standard, they should be read as “British Standard” and “Section 5.1 of BS 4559” respectively.

In British Standards, it is current practice to use the symbol “L” for litre (and in its submultiples) rather than “l” and to use the spelling “sulphur”, etc. instead of “sulfur”, etc.

Cross-references

International Standard	Corresponding British Standard
	BS 4559 <i>Methods for preparation of calibration gas mixtures</i> Part 1 <i>Weighing methods</i>
ISO 6142:1981	Section 1.1:1983 <i>Mixtures containing components fully vaporizable under ambient conditions</i> (Identical) Part 5 <i>Dynamic volumetric methods</i>
ISO 6145-3:1986	Section 5.3:1987 <i>Periodic injections into a flowing gas stream</i> (Identical)
ISO 6145-4:1986	Section 5.4:1987 <i>Continuous injection method</i> (Identical)

¹⁾ In preparation.

International Standard	Corresponding British Standard
ISO 6145-6:1986	Section 5.6:1987 <i>Sonic orifices</i> (Identical)
ISO 6147:1979	Part 6:1981 <i>Saturation method</i> (Identical)
ISO 6349:1979	Part 7:1981 <i>Permeation method</i> (Identical)
ISO 7395:1984	Part 8:1985 <i>Mass dynamic method</i> (Identical)

It is intended to implement Parts 2, 5, 7 and 8 of ISO 6145 and ISO 8959-2 as British Standards upon publication of the ISO standards.

A British Standard implementing ISO 6143 is currently in preparation and it is intended to publish this as a further Part of BS 4559.

Textual errors. When adopting the text of the International Standard, the textual errors given below were discovered. They have been marked in the text and have been reported to ISO in a proposal to amend the text of the International Standard.

a) In **3.2.3.3.1**, paragraph 1, lines 5 and 6, “may not necessarily correspond” should be read as “corresponds”.

b) In **3.2.3.3.1**, item b), reference is made to burette A of Figure 6 but the burette is not marked in the figure. The identification “Burette A” should be inserted in the position marked by the asterisk in Figure 6.

NOTE In the title of **3.2.2.2.4**, “accross” should be read as “across”.

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 to iv, pages 1 to 24, 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.

0 Introduction

Dynamic volumetric methods consist of the introduction of a given flow rate q_A of gas A into a constant flow rate q_B of a complementary gas B. Gas A can be either a pure component I or a mixture, defined by its concentration C_{IA} of the component I, obtained by another preparation method.

The flow rate of the resultant mixture M of gases A and B, in which the concentration²⁾ of component I is C_{IM} , is taken as q_M . The value of the final concentration C_{IM} is calculated from the flow rates of gases A and B or from the ratio q_A/q_B or may be obtained from the measurement of the concentration of component I in the resulting mixture, as given by the equation

$$C_{IM} = C_{IA} \left(\frac{q_A}{q_A + q_B} \right)$$

It is assumed with this equation that C_{IB} , the concentration of component I in gas B, is zero.

The introduction of gas A can be continuous (e.g. permeation tube) or pseudo-continuous (e.g. piston volumetric pump). A mixing chamber should be inserted in the system before the analyser and is particularly essential in the case of pseudo-continuous introduction. The flow rate of component A is measured either directly in terms of volume or mass, or indirectly by measuring the variation of a physical property.

The dynamic volumetric preparation techniques produce a continuous flow rate of calibration gas mixtures into the analyser but do not generally allow the build-up of a reserve by storage under pressure.

The main techniques used for the preparation of the mixtures are:

- a) volumetric pumps;
- b) periodic injection;
- c) continuous injection;
- d) capillary;
- e) sonic orifices;
- f) mass flow controllers;
- g) diffusion;
- h) permeation.

In all cases, and most particularly if very dilute mixtures are concerned, the materials used for the apparatus should be chosen as a function of their resistance to corrosion and low absorption capacity (usually glass, PTFE or stainless steel). It should, however, be pointed out that the phenomena are less important for dynamic volumetric methods than for static methods.

Numerous variants or combinations of the main techniques can be considered and mixtures of several constituents can also be prepared by successive dilutions.

Some of these techniques allow calculation of the final concentration of the gas mixture from basic physical information (e.g. mass rates of diffusion, flow through capillaries). However, since all techniques are dynamic and rely on stable flow rates, this International Standard emphasizes calibration of the techniques by measurement of the individual flow rates or their ratios, or by determination of the final mixture concentration. The accuracy of the composition of the calibration gas mixture is determined by the method of calibration. The dynamic volumetric technique used has a level of precision associated with it. Information on the final mixture composition depends both on the calibration method and on the preparation technique.

1 Scope and field of application

The International Standard constitutes part 1 of ISO 6145, which deals with the various dynamic volumetric methods used in the preparation of calibration gas mixtures.

It describes the calibration methods involved in the preparation of gas mixtures by dynamic volumetric techniques. It also gives a brief presentation of a non-exhaustive list of examples of dynamic volumetric techniques which are described in more detail in other parts of ISO 6145.

2 References

ISO 6142, *Gas analysis — Preparation of calibration gas mixtures — Weighing methods*.

ISO 6143, *Gas analysis — Determination of composition of calibration gas mixtures — Comparison methods*.

ISO 6147, *Gas analysis — Preparation of calibration gas mixtures — Saturation method*.

ISO 6349, *Gas analysis — Preparation of calibration gas mixtures — Permeation method*.

²⁾ In this International Standard, the term "concentration" designates a concentration a mass ratio, a volume ratio, a molar ratio or a ratio of pressures.

ISO 7395, *Gas analysis — Preparation of calibration gas mixtures — Mass dynamic method*.

ISO 6145, *Gas analysis — Preparation of calibration gas mixtures — Dynamic volumetric methods*

— *Part 2: Volumetric pumps*³⁾.

— *Part 3: Periodic injections into a flowing gas stream*.

— *Part 4: Continuous injection method*.

— *Part 5: Capillary calibration devices*³⁾.

— *Part 6: Sonic orifices*.

— *Part 7: Mass flow controllers*³⁾.

— *Part 8: Diffusion*³⁾.

ISO 8959-2, *Gas flow rate measurement — Volumetric method — Part 2: Bell prover*³⁾.

3 Calibration methods

3.1 General

The accuracy and precision of the concentration C_{IM} of a component I of a calibration mixture M depends at any time on the accuracy and precision of the calibration method, the frequency with which it is applied, and the stability of the regulation devices involved in the dynamic preparation technique.

To assess the instantaneous accuracy of the whole procedure, account has to be taken of the time required for the calibration method and the instantaneous possible variation of the principal parameters of the technique as well as any possible drift of these parameters during the calibration procedure.

According to the preparation technique for the gas mixtures used, calibration can be carried out by one of the following methods:

a) measurement of flow rate (mass or volume);

b) comparison method;

c) tracer method;

d) direct chemical analysis.

Table 1 shows the applicability of each calibration method to the different preparation techniques.

In general, the principles of the methods fall into two categories, as follows:

a) those in which the flow rates of component gases are measured either by volume or by mass and in which the concentration in the final mixture is calculated from the flow rate. Different techniques may be used for the individual components of a mixture and these may be calibrated by different methods. The principle of measurements of individual flow rates, however, remains;

b) those which operate directly on the final mixtures.

Since different principles are involved, they are given separately under each individual method.

Since the calibration methods have different principles and the equipment used for the realization of the gas flow rates is different, different units can be used to express the concentrations.

For calibrations using the comparison method, the concentration is expressed in mole fractions because most of the calibration gas mixtures used for the comparison will if possible be described in this way. Using techniques based on volume flow rate leads in the first instance to volume ratios or percent volume. Recalculation of these data to mole fractions is possible but leads to an increase in the uncertainty because of the uncertainty of the density and molar-volume data. In this case the expression in volume fractions is preferred.

Table 1 — Calibration methods applicable to the preparation techniques

Preparation techniques	Calibration methods			
	Comparison (ISO 6143)	Flow rate measurement	Tracer	Direct analysis
Volumetric pumps	+	+	+	May be applicable; depends on nature of components
Periodic injection	+		+	
Continuous injection	+		+	
Capillary	+	+	+	
Sonic orifice	+	+	+	
Mass flow controllers	+	+	+	
Diffusion	+			
Permeation	+			

³⁾ In preparation.

Calibration with the gravimetric method gives mass fractions for the concentrations of components in gas mixtures. These can be recalculated to mole fractions by using the atomic weights. Expression in mole fraction is therefore preferred.

3.2 Measurement of individual flow rates

3.2.1 General

Under some circumstances the total flow rate cannot be taken as the sum of two individual flow rates q_A and q_B which have been measured separately. These problems of non-additivity can be caused by deviations from the laws of ideal gas behaviour or by changes in conditions such as back-pressure or viscosity resulting from the blending of the two flow rates. Deviations from ideal behaviour can be predicted with reasonable accuracy and other non-additivity errors can be minimized by careful attention to apparatus design.

Flow rate measurement is normally carried out using one of the following:

- a) soap-film flowmeter;
- b) mercury-sealed piston flowmeter;
- c) wet gas meter;
- d) variable area flowmeter;
- e) thermal mass flow sensor.

The soap-film and mercury-sealed piston flowmeters share a common principle, i.e. that of timing the travel of a soap bubble or piston between carefully defined points. The wet gas meter is an integrating device which indicates the total volume of gas that has been passed through it (the dry gas meter, familiar from the domestic environment, has a similar integrating property but has not been included because it is less accurate). The variable area flowmeter ("rotameter") is a continuously indicating device. The thermal mass flow sensor measures mass flow rate as a function of heat flux.

Calibration of these flow rate measuring devices is carried out using one of the following methods:

- f) bell prover;
- g) gravimetric method;
- h) weighing the volume of water.

The bell prover is a device for creating a constant and defined flow rate of gas, acting as a mechanically driven gas holder. The gravimetric method measures the mass of gas which has flowed at a constant rate for a defined time through the device to be calibrated. The volume of water equivalent to the measuring volume of a soap-film or mercury-sealed piston flowmeter can be accurately weighed under carefully controlled conditions.

The bell prover and the gravimetric method can be used directly, where appropriate, to calibrate the various preparation techniques, but the information is more commonly transferred via one of the flow rate measurement devices.

3.2.2 Description of flow measurement devices

3.2.2.1 Soap-film flowmeter

3.2.2.1.1 Principle

A special soap-film flowmeter is used for this measurement. The size of the tube is chosen to be much larger than normal so that the volume and time measurements can both be made with greater accuracy. The measuring tube (see Figure 1) is installed vertically in an insulated box, inside which air is continuously circulated at a controlled temperature in the range 23,3 to 23,5 °C with a variation of $\pm 0,02$ °C. The temperature is controlled by thermometers which are calibrated to 0,1 °C and which can be read to 0,01 °C.

The gas to be measured is saturated with water vapour at the temperature of the measuring tube by passing it through three successive wash bottles, each of which contains a sintered bubbler. It is then introduced into the measuring tube by the side-arm at the top. The solution used to produce the soap-film is introduced dropwise through the centre tube at the top. This solution consists of demineralized water containing 0,005 mol/l of sulfuric acid, 4 ml/l of a non-ionic surface-active agent⁴⁾ and 1 ml/l of a colouring agent (e.g. mixed indicator) for better light absorption. When a drop of solution arrives at the narrow section at the top of the tube, a film forms across the tube and is carried down it by the gas flow. Photoelectric cells and lights are located at each side of the tube, positioned in such a way that they cannot move. As the soap-film passes the photoelectric cells, it first starts and then stops an accurate electronic timer. At the outlet of the tube the film bursts in a syphon, and the gas passes out of the system. The pressure in the measuring tube is measured by a U-tube manometer filled with water and connected to the outlet. Before a measurement is made, several bubbles should be formed and passed along the tube to ensure that the walls are thoroughly wetted.

3.2.2.1.2 Influence of temperature variation

The values measured are all recorded in the temperature band between 23,3 and 23,5 °C. The measuring tube is made of borosilicate glass having a coefficient of linear expansion of $3,3 \times 10^{-6} \text{ K}^{-1}$. The result is that, taking into account the control of temperature to $\pm 0,02 \text{ °C}$, there is a maximum variation in the volume of the measuring tube of approximately 2×10^{-7} and a maximum variation in the volume of gas of 7×10^{-5} .

3.2.2.1.3 Influence of the pressure drop

The pressure in the soap-film flowmeter will not vary from atmospheric by more than 1 mbar at any value of flow rate and this can be measured to 0,1 mbar, giving an error of 10^{-4} .

3.2.2.1.4 Diffusion across the film

Diffusion of the gas across the soap-film will not occur since the composition is identical on each side.

3.2.2.1.5 Influence of film thickness

The thickness of the soap-film layer and of the volume of liquid contained in the measuring tube can be determined accurately with a burette. Two drops per measurement are enough to produce a bubble which traverses the measuring volume without bursting. The thickness of the film varies the volume. The volume of a drop of liquid is 0,03 ml compared with a tube volume of 1 356 ml, i.e. an error of 2×10^{-5} and with a reproducibility of $\pm 20 \%$ on two drops.

3.2.2.1.6 Differences in humidity

The saturator is of high efficiency, such that a variation of 1 % relative humidity between one gas and another corresponds to a variation in the volume of the gas of

$$\frac{21,5}{760} \times \frac{1}{100}$$

i.e. 3×10^{-4}

3.2.2.1.7 Solubility of gases in water

Typical values for solubility in 1 ml of water at ambient temperature are 0,02 ml of hydrogen, 0,03 ml of oxygen and 0,87 ml of carbon dioxide.

Even if the water is pure the error in the volume resulting from the carbon dioxide dissolved in 0,6 ml of the liquid just introduced into the measuring tube amounts only to 0,05 ml per 1 356 ml, i.e. an error of 4×10^{-5} .

Variations in solubility over the temperature range likely to be used for this measurement will not significantly affect the likely error.

3.2.2.1.8 Reduction in vapour pressure of water

The reduction in the partial pressure of water caused by the surface active agent or the indicator can only be about 1 % relative. This should remain the same between calibration and measurement and so the errors are represented by the variation in this reduction, according to the degree of saturation (see 3.2.2.1.6). If the variation is 10 % relative, this is 10 % of 3×10^{-4} , i.e. 3×10^{-5} .

⁴⁾ A suitable product, available commercially, is Nekanil C. This information is given for the convenience of the user of this International Standard and does not constitute an endorsement of this product by ISO.