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Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods —

Part 1: Methods of calibration

Analyse des gaz — Préparation des mélanges de gaz pour étalonnage à l'aide de méthodes volumétriques dynamiques —

Partie 1: Méthodes d'étalonnage

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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 6145-1 was prepared by Technical Committee ISO/TC 158, *Analysis of gases*.

This second edition cancels and replaces the first edition (ISO 6145-1:1986), in which the estimated uncertainties in the calibration methods and techniques have now been combined in a square-root sum-of-squares manner to form the relative combined standard uncertainty. In comparison with the previous edition the periodic injection has been deleted (limited application).

ISO 6145 consists of the following parts, under the general title *Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods*:

— *Part 1: Methods of calibration*

— *Part 2: Volumetric pumps*

— *Part 4: Continuous injection methods*

— *Part 5: Capillary calibration devices*

— *Part 6: Critical orifices*

— *Part 7: Thermal mass-flow controllers*

— *Part 9: Saturation method*

— *Part 10: Permeation method*

Diffusion will be the subject of a future Part 8 to ISO 6145. Part 3 to ISO 6145, entitled *Periodic injections into a flowing gas*, has been withdrawn.

Introduction

This part of ISO 6145 is one of a series of standards which describes the various dynamic volumetric methods used for the preparation of calibration gas mixtures.

In dynamic volumetric methods a gas, A, is introduced at volume or mass flow rate q_A into a constant flow rate q_B of a complementary gas B. Gas A can be either a pure calibration component, i, or a mixture of i in A.

The volume fraction, $\varphi_{i,M}$ of i in the final calibration gas mixture is given in the following equation:

$$\varphi_{i,M} = \varphi_{i,A}\left(\frac{q_A}{q_A + q_B}\right)$$

where $\varphi_{i,A}$ is the volume or mass fraction of component, i, in the pre-mixed gas A, and is already known from its method of preparation. It is assumed that in this equation, $\varphi_{i,B}$, 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. 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) continuous injection;

c) capillary;

d) critical orifices;

e) thermal mass-flow controllers;

f) diffusion;

g) saturation;

h) permeation;

i) electrochemical generation.

In all cases, and most particularly if very dilute mixtures are concerned, the materials used for the apparatus are 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 operations.

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 part of ISO 6145 emphasizes calibration of the techniques by measurement of the individual flow rates or their ratios, or by determination of the composition of the final mixture.

The uncertainty of the composition of the calibration gas mixture is best determined by comparison with a gas mixture traceable to international standards. Certain of the techniques which may be used to prepare a range of calibration gas mixtures may require several such traceable gas mixtures to verify their performance over that range. The dynamic volumetric technique used has a level of uncertainty associated with it. Information on the final mixture composition depends both on the calibration method and on the preparation technique.

Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods —

Part 1: Methods of calibration

1 Scope

This part of ISO 6145 specifies 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 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 6142, *Gas analysis — Preparation of calibration gas mixtures — Gravimetric method*

ISO 6143, *Gas analysis — Comparison methods for determining and checking the composition of calibration gas mixtures*

ISO 7504, *Gas analysis — Vocabulary*

3 Terms and definitions

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

3.1
uncertainty of measurement
parameter, associated with the result of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the measurand

NOTE 1 Values of the individual statistical uncertainties found in some methods and techniques in this part of ISO 6145 are combined with the values of systematic uncertainties that also occur in a square-root sum-of-squares manner to provide a relative combined uncertainty, or in some cases as a relative expanded uncertainty by application of the coverage factor “2”.

NOTE 2 In keeping with Reference [1] of the Bibliography, the uncertainty of the composition of a mixture is expressed as a relative expanded uncertainty.

4 Calibration methods

4.1 General

4.1.1 The uncertainty in the composition $_{i,}$M of a component i of a calibration mixture M depends at any time on

a) the uncertainty of the calibration method,

b) the frequency with which it is applied,

c) the stability of the control devices involved in the dynamic preparation technique.

To assess the uncertainty of the whole procedure, possible instantaneous variations and drift of the principle parameters of the technique during the calibration procedure shall be considered.

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

— measurement of flow rate (mass or volume);

— comparison method;

— tracer method;

— direct chemical analysis.

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

Table 1 — Calibration methods applicable to the preparation techniques

Preparation techniques	Calibration methods			
	Comparison with ISO 6143 [a]	Flow rate measurement [a]	Tracer [a]	Direct analysis
Volumetric pumps	+	—	+	May be applicable; depends on nature of components
Continuous injection	+	—	+	
Capillary	+	+	+	
Critical orifice	+	+	+	
Thermal mass flow controllers	+	+	+	
Diffusion	+	—	—	
Saturation	+	—	—	
Permeation	+	—	—	

[a] The pluses refer to the measurement of a volume flow. In principle, flow rate measurement can also be performed for continuous injection methods, diffusion methods and permeation methods. Here, mass flows are measured rather than volume flows. For diffusion and permeation tubes the mass flow may be measured continuously using a suspension balance.

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

— Principles 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.

— Principles which operate directly on the final mixtures.

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

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

For calibrations using the comparison method, the content is expressed as a mole fraction or mole concentration because most of the calibration gas mixtures used for the comparison, if possible, are described in this way.

Using techniques based on volume flow rate leads in the first instance to volume fractions. 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.

Calibration by the gravimetric method gives mass fractions for the contents of components in gas mixtures. These can be recalculated to mole fractions by dividing by the respective atomic or molar masses. Expression in mole fraction is therefore preferred.

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 can be caused by deviations from the ideal gas laws or by changes in conditions such as backpressure or viscosity resulting from the blending of the two flow rates. Deviations from ideal behaviour can be predicted with reasonable accuracy and other uncertainties can be minimized by careful attention to apparatus design.

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

a) primary devices, based on absolute principles, for example:

   — gravimetric method;

b) methods which may be considered as potentially primary when the volume of the device is determined by weighing the relevant volume of water, or another suitable liquid of higher density:

   — mercury-sealed piston,

   — bell-prover;

c) many other devices available for the measurement of volume flow, some of which are listed below (calibration of these devices is carried out by using one of the above primary or potentially primary methods):

   — soap-film meter,

   — wet-gas meter,

   — thermal mass flow sensor,

   — variable area flow meter.

The soap-film and mercury-sealed piston flow meters share a common principle, i.e. that of timing the travel of a soap bubble or piston between carefully defined points either electronically or by observation, for example by means of a cathetometer. The volume between these points can be determined by filling with water, which is subsequently weighed (see Annex A).

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 flow meter is a continuously indicating device. The thermal mass flow sensor measures mass flow rate as a function of heat flux.

NOTE These devices are fully described in Annex B.

4.1.4 Calibration of these flow-rate measuring devices is carried out using one of the primary or potentially primary methods:

a) gravimetric method;

b) mercury-sealed piston;

c) bell prover.

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 mercury-sealed piston drives a defined volume of gas over a measured time period into the device to be calibrated. The bell prover is a device for creating a constant and defined flow rate of gas, acting as a mechanically driven gasholder.

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

4.2 Description of primary or potentially primary measuring devices

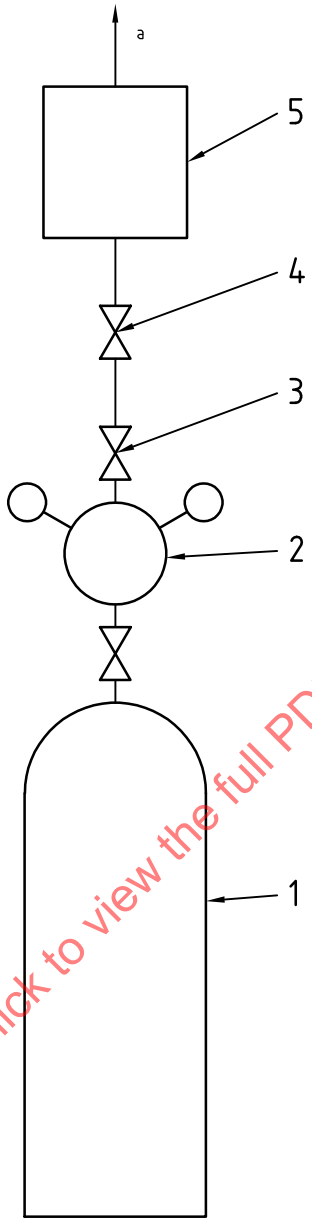
4.2.1 Gravimetric method

4.2.1.1 Principle

Gas from a cylinder flows at a constant rate through the device to be calibrated. This is continued for a sufficiently long period for the loss of mass from the cylinder to be accurately measured. The procedure provides data in terms of mass flow, which can then be converted to molar flow rate or, with assessed uncertainty, to a volume flow rate.

The gas cylinder and flow-rate measuring device are set up as shown in Figure 1. The cylinder (1) is fitted with a pressure regulator (2) on the outlet of which a precision needle valve (3) and shut-off valve (4) lead to the device to calibrated (5). The dead volume between the needle valve outlet and the shutoff valve is minimized by using the smallest size of tubing and fittings commensurate with the desired gas flow rate. The temperature and pressure of the gas are measured at the inlet to the device to be calibrated.

The cylinder valve is opened, the pressure regulator is set to a value of, e.g. 100 kPa (1 bar) gauge, and the needle valve is adjusted to the desired flow rate. When conditions are seen to be steady, the shut-off valve is closed and the pipe-work is disconnected at the outlet of this valve. The cylinder, regulator, needle valve and shut-off valve are weighed as a single unit. The pipe-work is reconnected and the shut-off valve is opened to re-start the flow at the same rate. After the gas has flowed for a period long enough for the mass used to be measured accurately, the shut-off valve is closed and the cylinder, regulator, needle valve and shut-off valve weighed as before. During this period, the gas flow is accurately measured by first calculating the volume of gas from the change in mass, then the flow rate from the volume and the time.



Key

1 cylinder
2 pressure regulator
3 needle valve
4 shut-off valve
5 device to be calibrated

[a] To vent.

Figure 1 — Gravimetric method

4.2.1.2 Uncertainty of measurement

4.2.1.2.1 Uncertainty of weighing

Gravimetric preparation of mixtures is described in ISO 6142. Using the procedures given in ISO 6142, it can be assumed that the mass of gas used in a test can be weighed to a relative standard uncertainty of 2×10^{-4} (i.e. 20 g of gas taken from a 10 kg cylinder whose mass before and after the test can be measured with an uncertainty of 2 mg, giving a relative standard uncertainty of $2\sqrt{2}/20 \times 10^{-3}$, i.e. $1{,}4 \times 10^{-4}$).

4.2.1.2.2 Uncertainty with unstable flows

This uncertainty can be neglected provided the cylinder and its flow-rate control devices are both pressurized with gas to the same degree for both weighings. However, when the gas is shut off before weighing, the pipe-work between the needle valve and the shutoff valve becomes pressurized to the value set on the regulator, and this will cause a surge when the gas flow rate restarts. The uncertainty caused by this surge is the amount of gas required to pressurize the volume between the needle valve and the shut-off valve relative to the amount of gas having flowed. If 2 ml of dead-space is pressurized to 1 bar gauge in a test in which 20 g of methane flows, the standard uncertainty is 7×10^{-5}.

To reduce pressure surge effects which can cause oscillations of flow, stabilize the gas flow before taking any readings. This avoids any uncertainty.

4.2.1.2.3 Uncertainty on conversion of mass to volume

The temperature, pressure, compression (Z) factor and molar mass of the gas, all affect the uncertainty on conversion of mass to volume. Measurement of temperature with an uncertainty of 0,05 °C and pressure to 10 Pa (0,1 mbar) represents relative standard uncertainties of $1{,}7 \times 10^{-4}$ and 10^{-4}, respectively. Compression factors are commonly quoted to four decimal places, which implies an uncertainty of 10^{-4}, and molar masses are known with sufficient accuracy not to contribute significantly. The relative standard uncertainty is therefore not greater than $2{,}2 \times 10^{-4}$.

4.2.1.2.4 Uncertainty due to flow rate variation

If the device to be calibrated measures either instantaneous flow rates or volumes which are small by comparison with the volume taken from the cylinder, then variations in flow rate are a contribution to the uncertainty.

A high quality pressure regulator and needle valve should ensure a flow rate constancy of 0,2 % relative, apart from the initial flow surge (see 4.2.1.2.2), but should be checked for each installation. This level of flow-rate control represents a relative standard uncertainty of 2×10^{-3}.

4.2.1.2.5 Uncertainty of time measurement

The time during which the gas flows from the cylinder can be measured by an electronic timer with a relative standard uncertainty of 2×10^{-4}.

NOTE The uncertainty of the time measurement generally depends on the discharge time. The timer can be very accurate, but if "hand" clocking is used to start and stop the timer the uncertainty in the time measurement is in the order of ± 0,2 s, requiring a 1 000 s discharge time to reach the stated relative uncertainty.

4.2.1.2.6 Relative combined standard uncertainty

The combination of the standard uncertainties described in 4.2.1.2.1 to 4.2.1.2.5 is as follows:

— weighing 2×10^{-4}

— flow transients 7×10^{-5}

— mass to volume $2{,}2 \times 10^{-4}$

— flow rate variation 2×10^{-3}

— timing 2×10^{-4}

— relative combined standard uncertainty $2{,}0 \times 10^{-3}$

4.2.2 Mercury-sealed piston flow meter

4.2.2.1 Principle

A glass measuring tube (see Figure 2) of known diameter and uniformity is set vertically in an insulated box fitted with temperature control. The temperature is maintained constant to within ± 0,02 °C.

The measuring tube is divided into a number of sections by photoelectric cells serving as sensors, and the actual volume between two adjacent photoelectric cells is determined by filling with water and weighing (see Annex A). Greater accuracy is achieved in the calibration if a liquid of higher density is used.

A constant flow moves a frictionless piston with a constant speed upwards. The displaced volume can be estimated from the dimensions of the tube or measured with reference to the water calibration.

The piston, made of plastics (e.g. PVC) or glass contains a horizontal, circular groove, filled with mercury. The purity of the mercury is such as to ensure that the piston does not stick in operation. The use of triple distilled mercury is recommended.

The piston is allowed to attain a constant speed before time measurement is started at Sensor 1.

Depending on the flow rate and the tube size, time measurement is stopped when the piston passes Sensor 2 or Sensor 3. Sensors may be of the reflection type because of the high reflectance of the mercury ring. Because of a high back-pressure caused by the weight of the piston, the measured pressure difference is approximately from 0,1 kPa (1 mbar) up to 1 kPa (10 mbar).

The measuring sequence starts by closing Side A of the 3-way valve (see Figure 2). As soon as the piston passes Sensor 1, time measurement starts; it stops after the piston passes the next sensor. The three-way valve resets its position and the piston falls down on the spring. The flow meter is then ready to restart.

4.2.2.2 Uncertainty of measurement

4.2.2.2.1 Influence of temperature variation

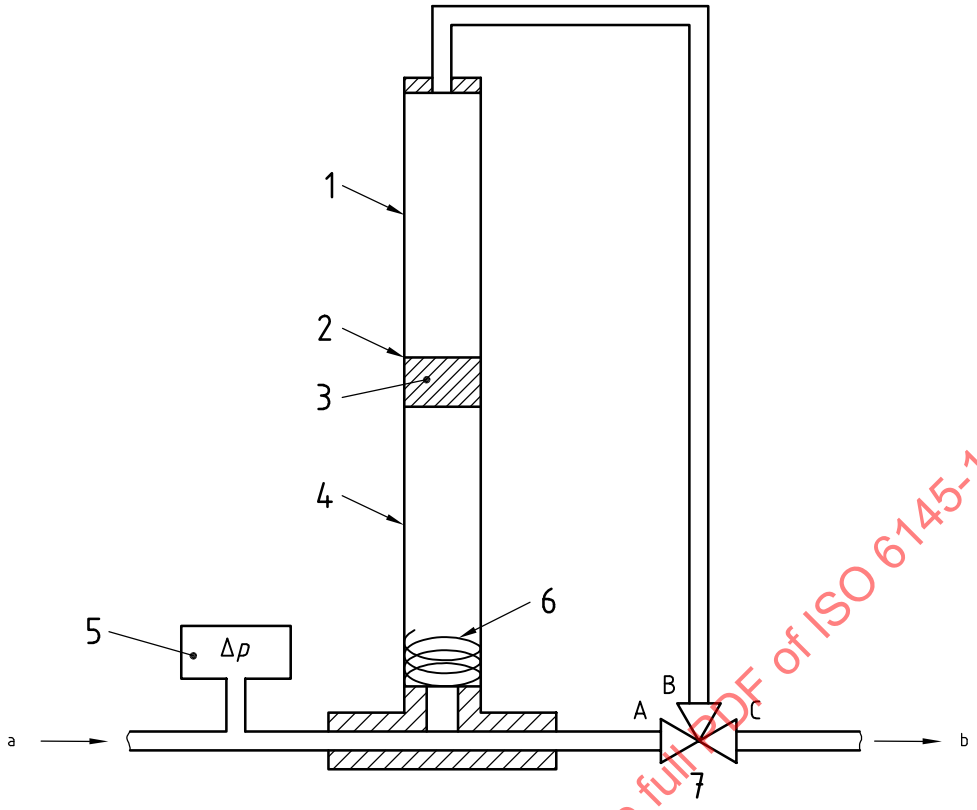
The measuring tube is made of borosilicate glass having a coefficient of linear expansion of $3{,}3 \times 10^{-6}\ K^{-1}$. The result is that, taking into account the control of temperature to ± 0,02 °C, there are relative standard uncertainties in the volume of the tube of approximately 2×10^{-7} and in the volume of gas of 7×10^{-5}.

NOTE The user should be aware that there can be a temperature gradient if flow sensors are heated to operate (e.g. MFCs) in the upstream system. The expansion effects on glass can be neglected.

4.2.2.2.2 Correction for pressure differences and piston pressure

Correction for pressure differences of the flow device between calibration (p_{cal}) and use (p_{use}) is made using the factor $(p_{cal} + p_{piston}) / p_{use}$, in which the piston pressure, p_{piston}, generally takes values between 0,1 kPa and 1 kPa.

Assuming the absolute pressure to be measurable with a relative uncertainty of ± 0,1 %, and the piston pressure to be measurable with an uncertainty of less than ± 10 Pa, then the relative uncertainty of the pressure correction is $1{,}4 \times 10^{-3}$.



Key

1 photoelectric cell Sensor 2 (first volume)
2 photoelectric cell Sensor 3 (second volume)
3 piston
4 photoelectric cell Sensor 1 (start counting)
5 pressure sensor
6 spring
7 3-way valve (Sides A, B, C)

a Flow in.
b To vent.

Figure 2 — Mercury-sealed piston flow meter

4.2.2.2.3 Diffusion across the piston

The construction of the mercury-sealed piston does not provide for the possibility of keeping the same composition of the gas on both sides. Although diffusion along the mercury seal is still possible, the effect is considered negligible in general practice.

4.2.2.2.4 Relative combined standard uncertainty

The combination of the standard uncertainties described in parts 4.2.2.2.1. to 4.2.2.2.3 is as follows:

— temperature 7×10^{-5}
— pressure $1{,}4 \times 10^{-3}$
— diffusion across piston 0
— relative combined standard uncertainty $1{,}4 \times 10^{-3}$

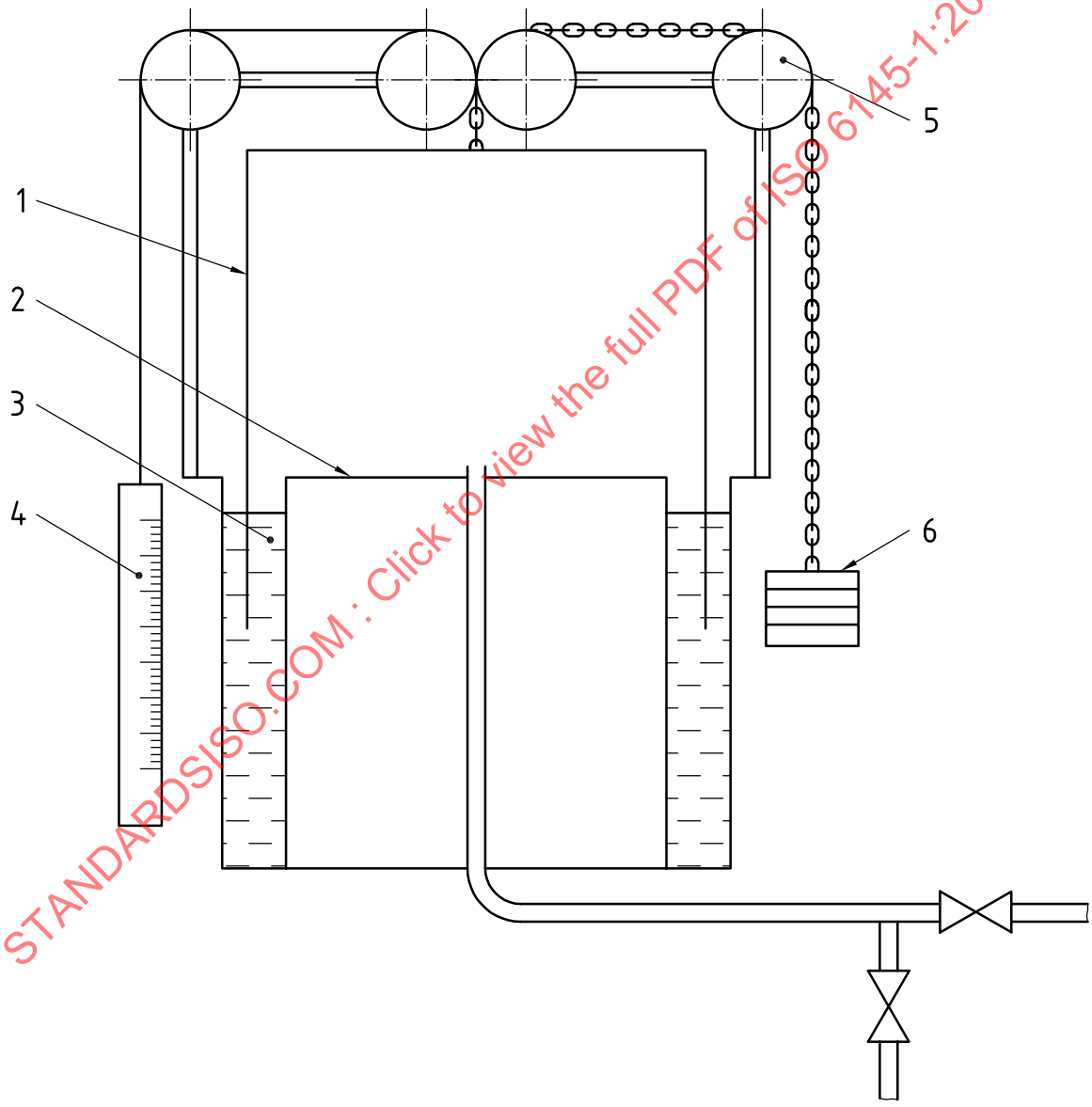
4.2.3 Bell prover

4.2.3.1 General

A gas flow measurement shall be provided by displacing a defined volume of gas at constant flow from the holder of a bell prover within a measured time period.

4.2.3.2 Principle

A schematic diagram of a bell prover is given in Figure 3 and shows the bell (1) in a stationary tank (2) filled with the sealing liquid (3). The measuring scale (4) is used to take readings of the position of the bell, which is supported on a chain passing over rollers (5) and balanced by the counterweight (6).



Key

1	bell	4	measuring scale
2	stationary tank	5	rollers
3	sealing liquid	6	counterweight

Figure 3 — Schematic diagram of a bell prover

The principle of operation is as follows.

a) The bell is raised and filled with air.

b) A definite volume of air is displaced from the prover by lowering the bell (1) into the stationary tank (2) while maintaining constant pressure in the conduits. The time interval over which the air is displaced is measured by a timer. The air flow rate is calculated using the measured values of volume and time interval.

4.2.3.3 Uncertainty of measurement

4.2.3.3.1 Uncertainty on prover capacity

The volume of the bell prover is determined at various points over the usable range and the uncertainty on each volume determination is determined at less than 0,5 cm^3. A best-fit line is drawn through the volume determinations to provide a calibration graph having a relative standard uncertainty of ± 0,05 %. The volume discharged from the bell prover is the difference in volume between the start and finish point, giving an uncertainty of $\sqrt{2}$ times the relative standard uncertainty in calibration, i.e. ± 0,07 %.

4.2.3.3.2 Uncertainties in the use of the measuring scale

The position of the bell prover is determined using a measuring scale which may be read to better than 0,2 mm. Assuming a change in position of 1 m, the relative standard uncertainty would be $\pm (\sqrt{2} \times 0{,}03/\sqrt{3}) / 1\,000 = 0{,}16$ mm in 1 m, or $1{,}6 \times 10^{-4}$.

4.2.3.3.3 Uncertainty on displacement time interval

The time interval may be electronically measured to better than ± 0,001 s. Assuming a discharge time of 40 s, the relative uncertainty is $\pm (\sqrt{2} \times 0{,}001 / \sqrt{3}) / 40 = 2 \times 10^{-5}$.

4.2.3.3.4 Uncertainty on the gas-distributing device

Random variations in the speed of operation of the solenoid valve which starts and stops the gas discharge should not exceed ± 0,03 s. On a discharge time of 40 s, the relative uncertainty is $\pm (\sqrt{2} \times 0{,}03 / \sqrt{3}) / 40 = 6 \times 10^{-4}$.

4.2.3.3.5 Combined uncertainty due to the recalculation of flow rates to reference conditions

These should normally be avoided by carrying out calibrations under the required conditions.

The combination of the standard uncertainties described in 4.2.3.3.1 to 4.2.3.3.4 is as follows:

— capacity 7×10^{-4}

— measuring rule $1{,}6 \times 10^{-4}$

— timing 2×10^{-5}

— distribution 6×10^{-4}

— recalculation 0

— relative combined standard uncertainty $0{,}9 \times 10^{-3}$

This total is the combined uncertainty on the mean flow rate and instability of the flow rate has not been taken into consideration.

4.2.4 Measurement of time

Timing is necessary for some of the flow-rate measuring devices. Photoelectric cells fitted to the soap-film flow meter and mercury-sealed piston flow meter define the upper and lower measuring points between which the film or piston moves. Similarly a photoelectric cell can register the movement of the pointer of a wet-gas meter past a particular point on its scale. The shut-off valve for the gravimetric calibration can be linked to a timer. In all cases, the timer should be an accurate electronic device capable of measuring the time intervals with a relative standard uncertainty of no greater than 2×10^{-4}.

4.2.5 Correction for pressure differences

With the exception of the mercury-sealed piston meter (see 4.2.2.2), a correction for pressure differences between calibration and use of the flow device needs to be applied using a factor p_{cal}/p_{use}. Assuming the absolute pressure to be measurable with a relative uncertainty of $\pm$ 0,1 %, then the relative uncertainty in the correction is $1{,}4 \times 10^{-3}$.

4.2.6 Correction for temperature differences

Correction for temperature differences of the flow device between calibration (T_{cal}) and use (T_{use}) is made using a factor T_{use}/T_{cal}, where T is the absolute temperature of the flowing gas expressed in kelvins. Assuming the temperature measurement to have a relative uncertainty of $\pm$ 0,1 %, then the relative uncertainty in the correction is $1{,}4 \times 10^{-3}$.

4.2.7 Uncertainty calculation

The relative combined standard uncertainties of the primary calibration methods (see 4.2.1.2.6, 4.2.2.2.4 and 4.2.3.3.5) are given in the first column of Table 2. When this method has been used to calibrate one of the secondary methods (see Annex B), the contribution has been added under calibration. Individual standard uncertainties for the measurement and time contributions for each secondary method are included. These have been combined in a square root sum of squares method to provide a combined uncertainty u_c for each method.

The uncertainty contributions depend upon the characteristics of the calibration method and the flow-rate control device. Thus, if a soap-film meter is calibrated by weighing its water content, there are three sources of uncertainty, since the time taken by the soap-film between the graduation marks has to be measured. If, however, the measurement gives a continuous indication (variable area flow meter or thermal mass flow sensor), then once the calibration method flow rate has been established, there is no further need for time measurement and hence no time measurement uncertainty.

The relative combined standard uncertainties listed in Table 2 relate only to the calibration methods described in 4.2 and, when used, the flow-rate measuring devices described in Annex B. When a mixture is prepared using one of the techniques described in subsequent parts of ISO 6145 (see the Bibliography), the relative standard uncertainties associated with the technique should also be taken into account.

Table 2 — Estimated uncertainties of flow-rate measuring methods (see 4.1.3)

Primary calibration method	Source of uncertainty	Secondary flow-rate measuring device[a]			
		Soap film flow meter	Wet-gas meter	Variable area flow meter	Thermal mass flow sensor
Gravimetric $u_{rel} \leqslant 2{,}0 \times 10^{-3}$	Calibration	$2{,}0 \times 10^{-3}$	$2{,}0 \times 10^{-3}$	$2{,}0 \times 10^{-3}$	$2{,}0 \times 10^{-3}$
	Measurement	$3{,}3 \times 10^{-4}$	$5{,}1 \times 10^{-4}$	$2{,}3 \times 10^{-2}$	$1{,}0 \times 10^{-4}$
	Time	$2{,}0 \times 10^{-4}$	$2{,}0 \times 10^{-4}$	0	0
	u_c	$2{,}0 \times 10^{-3}$	$2{,}1 \times 10^{-3}$	$2{,}3 \times 10^{-2}$	$2{,}0 \times 10^{-3}$
Mercury-sealed piston flow meter $u_{rel} \leqslant 1{,}4 \times 10^{-3}$	Calibration	$1{,}4 \times 10^{-3}$	$1{,}4 \times 10^{-3}$	$1{,}4 \times 10^{-3}$	$1{,}4 \times 10^{-3}$
	Measurement	$3{,}3 \times 10^{-4}$	$5{,}1 \times 10^{-4}$	$2{,}3 \times 10^{-2}$	$1{,}0 \times 10^{-4}$
	Time	$2{,}0 \times 10^{-4}$	$2{,}0 \times 10^{-4}$	$2{,}0 \times 10^{-4}$	$2{,}0 \times 10^{-4}$
	u_c	$1{,}5 \times 10^{-3}$	$1{,}5 \times 10^{-3}$	$2{,}3 \times 10^{-2}$	$1{,}4 \times 10^{-3}$
Bell prover $u_{rel} \leqslant 0{,}9 \times 10^{-3}$	Calibration	$0{,}9 \times 10^{-3}$	$0{,}9 \times 10^{-3}$	$0{,}9 \times 10^{-3}$	$0{,}9 \times 10^{-3}$
	Measurement	$3{,}3 \times 10^{-4}$	$5{,}1 \times 10^{-4}$	$2{,}3 \times 10^{-2}$	$1{,}0 \times 10^{-4}$
	Time	$2{,}0 \times 10^{-4}$	$2{,}0 \times 10^{-4}$	$2{,}0 \times 10^{-4}$	$2{,}0 \times 10^{-4}$
	u_c	$1{,}0 \times 10^{-3}$	$1{,}1 \times 10^{-3}$	$2{,}3 \times 10^{-2}$	$0{,}9 \times 10^{-3}$
Weighing of volume of water $u_{rel} \leqslant 7{,}7 \times 10^{-5}$	Calibration	$7{,}7 \times 10^{-5}$	—	—	—
	Measurement	$3{,}3 \times 10^{-4}$	—	—	—
	Time	$2{,}0 \times 10^{-4}$	—	—	—
	u_c	$3{,}9 \times 10^{-4}$	—	—	—

NOTE The combined uncertainties, u_c, for the secondary flow-rate measuring device are those which are the best obtainable under controlled conditions.

[a] See Annex B.

4.3 Measurements on the final mixture

4.3.1 General

This approach eliminates non-additivity uncertainties, e.g. volume changes on mixing of components.

Calibration of the concentration in the final mixture is carried out as described in 4.3.2 to 4.3.3.

4.3.2 Comparison method

Where possible, the content of the prepared gas mixture shall be verified by comparison with a standard prepared or certified by an accredited national or international body. The results provided by this verification shall confirm traceability to that national body within the analytical limits of the comparison method. Use the comparison method described in ISO 6143.

NOTE This verification also yields information about the accuracy of the technique used to prepare the calibration gas mixture.

4.3.3 Measurements on the final mixture

4.3.3.1 General

The measurement on the final mixture shall be performed by one of the two following methods:

a) direct chemical analysis; or

b) tracer methods using comparison or direct chemical analysis.

4.3.3.2 Direct chemical analysis

In some cases, an analytical method exists that should be used to determine the amount of component i in the final mixture without reference to other calibration gas mixtures. The amount of i is determined as the mass or number of moles. The volume of the mixture used in the analytical procedure shall be measured.

4.3.3.3 Tracer methods

The method relies on previous introduction into gas, A, through another preparation method, of a tracer gas, T. The gas, A, then contains:

a) a known volume fraction $\varphi_{T,A}$ of tracer gas T;

b) a known volume fraction $\varphi_{i,A}$ of component i.

The measurement, either by direct chemical analysis or by a comparison method, of the volume fraction φ_{TM} of T in the final mixture M, enables measurement of the dilution ratio $q_A/(q_A + q_B)$ of A in M and hence the concentration i, M in the final mixture, i.e.

$$\varphi_{T,M} = \varphi_{T,A}\left(\frac{q_A}{q_A + q_B}\right) \quad (1)$$

$$\varphi_{i,M} = \varphi_{i,A}\left(\frac{q_A}{q_A + q_B}\right) \quad (2)$$

The tracer gas shall be non-reactive with gases A and B.

This method may be preferred to the comparison method applied to component i, when it is possible to use a tracer gas for which the accuracy and precision of measurement is better at its final volume fraction $\varphi_{T,M}$ than that for the desired component at its final volume fraction $\varphi_{i,M}$. The final volume fraction $\varphi_{i,M}$ may, for example, be lower than that achievable for the desired analytical detection limit.

5 Techniques for preparation of gas mixtures calibrated by the methods described in Clause 4

5.1 General

Several techniques are available and the choice between them should be decided based on the concentration range, the availability of equipment and the required uncertainty. Almost all methods depend upon addition of two flow rates, q_A of gas A and q_B of gas B, with the resultant volume fraction being defined as a first approximation for a direct dilution of pure component A by a gas B, free of gas A:

$$\varphi_A = \frac{q_A}{q_A + q_B} \quad (3)$$

In fact, the general formula is

$$\varphi_{i,\mathrm{M}} = \varphi_{i,\mathrm{A}} \left[\frac{q_\mathrm{A}}{q_\mathrm{A} + q_\mathrm{B}} \right] + \varphi_{i,\mathrm{B}} \left[1 - \frac{q_\mathrm{A}}{q_\mathrm{A} + q_\mathrm{B}} \right] \tag{4}$$

a) when $\varphi_{i,\mathrm{B}}$ the concentration of component i in gas B, is equal to zero:

$$\varphi_{i,\mathrm{M}} = \varphi_{i,\mathrm{A}} \frac{q_\mathrm{A}}{q_\mathrm{A} + q_\mathrm{B}} \tag{5}$$

— for direct dilution of component i, since component i (gas A) is never 100 % pure;

— for dilution of gas A, which contains i at a low concentration, in order to obtain a lower concentration of the component i.

b) when $\varphi_{i,\mathrm{B}}$ is not taken to be equal to zero, for very low concentrations or mass fractions, then generally:

$$\left[\frac{q_\mathrm{A}}{q_\mathrm{A} + q_\mathrm{B}} \right] \ll 1 \tag{6}$$

and

$$\varphi_{i,\mathrm{M}} = \varphi_{i,\mathrm{A}} \left(\frac{q_\mathrm{A}}{q_\mathrm{A} + q_\mathrm{B}} \right) + \varphi_{i,\mathrm{B}} \tag{7}$$

The techniques have different areas of application depending on the concentration range (see Table 3).

The techniques involved are those of mixing gases, which, except for the diffusion and permeation techniques, may themselves be dilute mixtures the compositions of which have been established separately. The range of compositions produced by any technique can thus be considerably extended, and Table 3 gives the range of volume fractions available.

The relative expanded uncertainty defines the ability of the technique to produce a series of consistent mixtures. Variations can be either short-term or long-term with respect to the response time of the system, the long-term variations being more significant.

Table 3 — Dilution ranges for the preparation techniques expressed as mole fraction

Preparation technique	Range of volume fraction (Gas B)	Typical relative expanded uncertainty
Volumetric pumps	10^{-4} to about 1	0,5
Continuous injection	10^{-5} to 10^{-2}	5,0
Capillary	10^{-5} to nominal 1	1,0
Critical orifices	10^{-4} to nominal 1	0,5
Thermal mass flow controllers	10^{-9} to nominal 1	1,0
Diffusion	10^{-9} to 10^{-3}	3,0
Saturation	[a]	1,0
Permeation	10^{-9} to 10^{-6}	2,5

[a] Depends on saturation value of component.

5.2 Volumetric pumps (see ISO 6145-2[3])

Each gas is forwarded separately by a piston pump and is mixed with the other at the outlet. One pump is driven at a constant speed by a synchronous motor and the other at a proportion of this speed by means of gear wheels. Changing the gear wheels changes the composition of the mixture.

The flow rate of each component is described by Equation (8):

$$q = V \times n \tag{8}$$

where

V is the volume capacity of the pump cylinder;

n is the number of strokes per minute.

This method gives repeatable mixtures provided that both of the following conditions are maintained:

a) before use, the motor is allowed to run for at least 30 min to attain thermal equilibrium and to overcome transitory conditions (desorption or dissolution of gas); during this period, the pump draws in a dry gas;

b) any pressure difference equal to or greater than 20 Pa (2×10^{-4} bar) between the two input tubings or of 1 kPa (10^{-2} bar) between the entry and outlet tubings is avoided.

5.3 Continuous injection (see ISO 6145-4[4])

The gaseous or liquid calibration component is injected continuously by means of a mechanically driven syringe at flow rate, q_A, into a continuously flowing complementary gas flow rate, q_B. After mixing in a glass apparatus, the prepared calibration gas mixture is sampled under atmospheric pressure.

5.4 Capillary (see ISO 6145-5[5])

The calibration component, q_A, is passed through a capillary tube under conditions of constant pressure drop into a controlled flow rate of complementary gas q_B. The calibration gas mixture produced may be further diluted, if required at a lower content, through another capillary.

The volume flow rate of a gas A, q_A, passing through the capillary is given by

$$q_A = \frac{\pi r^4 (p_1 - p_2)}{8 \eta L} \tag{9}$$

where

r is the radius of the capillary tube;

L is the length of the capillary tube;

p_1 is the pressure at the inlet of the capillary tube;

p_2 is the pressure at the outlet of the capillary tube;

η is the dynamic viscosity.

5.5 Critical orifices (see ISO 6145-6[6])

When passed through a critical orifice at increasing upstream pressure p_1, the volume flow rate of gas passing through the orifice increases. When the ratio of the gas pressure upstream p_1 and the gas pressure downstream of the orifice p_2 reaches critical value, on further increase of p_1 the volume flow rate of the gas becomes independent with respect to p_2.

Under these conditions, the mass flow rate of gas crossing the nozzle is given by:

$$q_{M,A} = G\left(\frac{p_1}{\sqrt{T_1}}\right) \tag{10}$$

where

G is the defined constant for the gas/orifice pair, determined by calibration for a given gas;

T_1 is the absolute temperature upstream of the nozzle.

The advantage of critical flow is that it is independent of downstream temperature and pressure, provided that the pressure ratio, p_1/p_2 remains > 2.

If ρ_A is the density of gas A, the volume flow rate of A, q_A, is

$$q_A = \frac{q_{M,A}}{\rho_A} \tag{11}$$

This procedure may be extended easily to mixtures comprising any number of constituents.

To use this technique for the preparation of calibration gases, the constituents used should be perfectly free from any solid or liquid impurities.

If a gas mixture is used which contains a component at a content close to saturation, it shall be ensured that there is no condensation of the component as a result of lowering of temperature in the orifice.

5.6 Thermal mass flow controllers (see ISO 6145-7[7])

This technique, using thermal mass flow controllers, allows the control of stable flow rates of one or several gaseous components.

A thermal mass flow sensor (see Annex A) detects the difference of temperature before and after the passage of a gas stream over an electrically heated filament.

Detectors upstream and downstream form part of a Wheatstone bridge that is unbalanced to a degree dependent on the flow rate and a signal is obtained which, after amplification and linearization, indicates the mass flow rate and is used to operate an electrical control valve.

Once a thermal mass flow controller has been calibrated for one gas, calibration for another gas can be approximately calculated from factors supplied. These factors are mainly, but not entirely, based on the heat capacity at constant pressure, c_p, of the gases.

5.7 Diffusion (see ISO 6145-8[8])

This technique is based on the uniform diffusion of a vapour into a stream of complementary gas through a tube connected to a reservoir of the calibration component in its liquid state.

The complementary gas flow rate should not exceed 1 l/min and it is necessary to control the temperature of the diffusion cell to within ± 0,1 °C.

The flow rate of the calibration component A, q_A, is calculated from the following equation:

$$q_A = \frac{AD}{L} \ln\left(\frac{p}{p - p_v}\right) \tag{12}$$

where

A is the area of cross-section of the tube;

L is the length of the tube;

D is the diffusion coefficient;

p is the pressure in the diffusion cell;

p_v is the partial pressure of the diffusing vapour.

Diffusion rates may be measured by weighing the container with the minor component.

5.8 Saturation (see ISO 6145-9[9])

The vapour pressure of a pure substance in equilibrium with its condensed phase depends only on the temperature. If the temperature of the system and the total pressure of the gas mixture are known, the volume fraction of the constituent can be determined.

Complementary gas is passed through a saturator in contact with the condensed phase of the calibration component and the saturation temperature and pressure carefully measured. To ensure complete saturation, it is common to use a pre-saturator.

The volume fraction φ of the component x is, to a good approximation, equal to the ratio between the vapour pressure p_x of the constituent at the temperature T and the total pressure p of the gas mixture in the saturator, i.e.:

$$\varphi_x = \frac{p_x}{p} \tag{13}$$

The value of the relevant partial pressure (vapour pressure) of many components at the temperature T can be found in reference tables or diagrams.

5.9 Permeation (see ISO 6145-10[10])

The calibration component is contained in a sealed tube or container, which consists either wholly or partly of a polymer through which the component can permeate. The component is usually contained as a liquid in equilibrium with its own vapour, but can be contained as a gas. In the former case, the rate of permeation should remain constant while liquid is still present. In the latter case, the rate decays with the pressure of the gas. In either case, the rate of permeation is dependent on the temperature, more significantly when a liquid component is used.

The vessel containing the calibration component is put into a housing, which is purged with the complementary gas. The entire housing is placed in a thermostatted enclosure.

If the permeation rate is constant, it can be measured by weighing the tube at appropriate time intervals. This procedure is described in ISO 6145-10.

If, on the other hand, weighing is difficult or uncertain (owing to tube geometry, very small relative change in mass, significant thermal shocks, filling with diluted component or excessive stabilization time), the comparison method or direct analysis, where appropriate, shall be used to determine the composition.

With this permeation technique, the main uncertainty will result from temperature variation of the thermostatted bath; a variation of 0,15 K can, under practical conditions, produce a 2 % relative standard uncertainty when the tube material is polytetrafluoroethylene (PTFE) or fluorinated ethylene propylene (FEP).

The quality of the complementary, gas is equally very important. It shall be clean, dry and inert with respect to the calibration component.

Annex A
(normative)

Volume measurement by weighing the water content

A.1 Principle

The volume of the device is determined by filling it with water, then weighing the volume of water contained between the upper and lower points where the photoelectric detector cells are sited. This procedure provides a calibration of the volume of the meter. In the case of the soap-film flow meter, this may not necessarily correspond to the volume swept out by the soap bubble. The apparatus shown in Figure A.1 is used for the determination and the sequence of operations for calibration is described below.

The measurement of a volume by weighing the amount of water that it encloses is of very general applicability. The following procedure gives the method for a particular application for determining the volume using the measuring tube of a soap-film meter, which is illustrated in Figure B.1 and is described in B.1.

a) Initially ensure that the volume to be calibrated is carefully cleaned and freed of grease.

b) Fill Burette A, which should have a capacity larger that of the meter, with air-free, triple-distilled water. Ensure that the burette is firmly clamped in position.

c) Weigh a container and cap of sufficient volume to hold the water discharged from the flow meter.

d) With the detector system in operation, slowly open Tap 1 to allow water into the flow-meter system until Detector 1 is activated. Allow 2 cm of water above this level. Close Tap 1.

e) Carefully open Tap 2 to displace air from the tap assembly and then allow water to run to waste until Detector 1 responds to the meniscus level. Immediately close Tap 2.

f) Place the container without its cap under Tap 2.

g) Open Tap 2 and allow water to flow slowly from the flow meter assembly until Detector 2 operates. Immediately close Tap 2 and cap the container to prevent loss of water by evaporation. Check to ensure that drainage in the flow meter raises the level above the set point and re-adjust if necessary.

h) Weigh the capped container on an analytical balance and determine the mass of water.

From the mass of water, the volume is determined according to the following equation:

$$m - \frac{m\rho_a}{\rho_w} = V_{H_2O}\rho_{H_2O} - V_{H_2O}\rho_a \qquad \text{(A.1)}$$

where

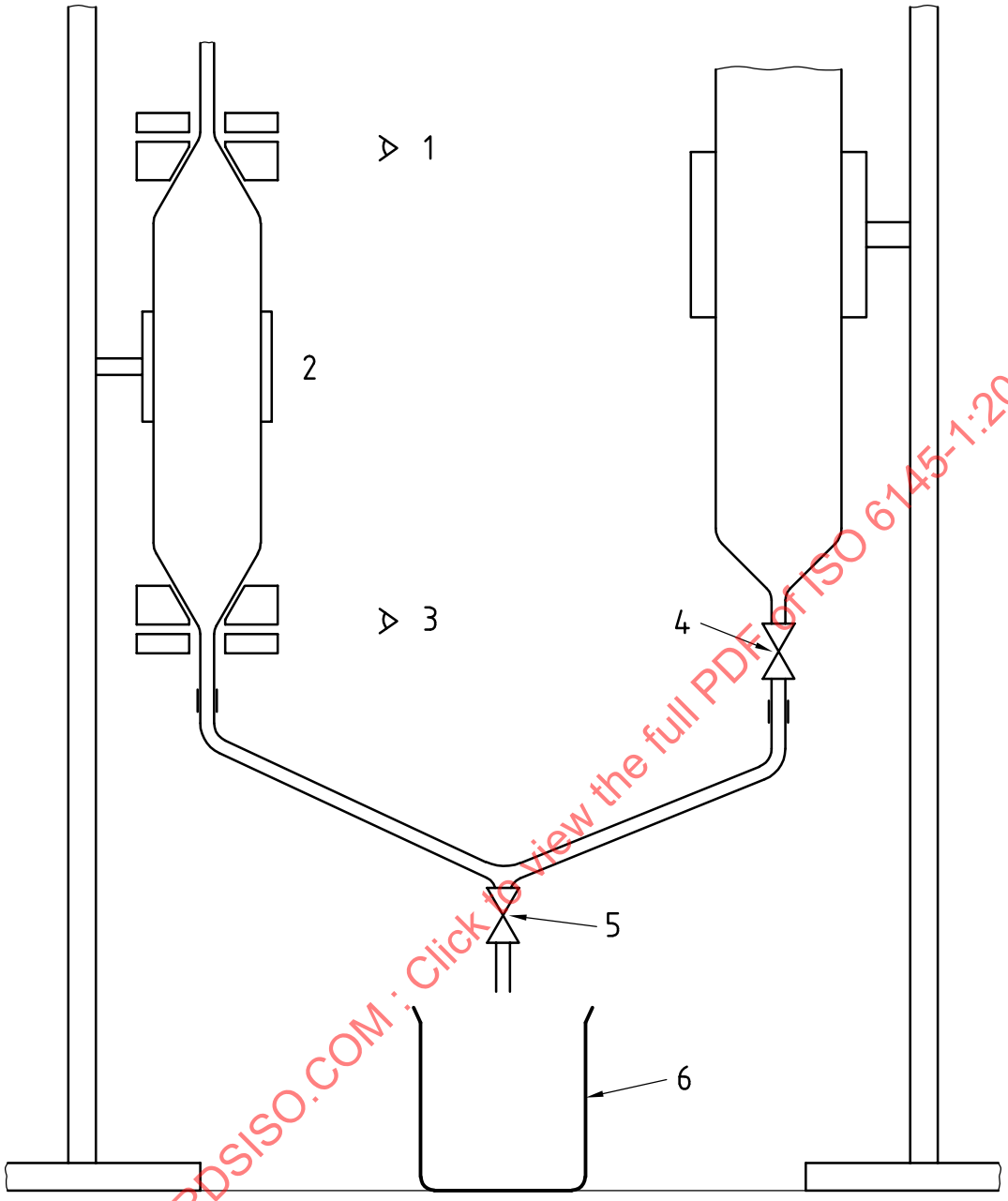
ρ_a is the density of air at the time of weighing;

ρ_{H_2O} is the density of water;

ρ_w is the density of the weights;

m is the mass of water in air (apparent mass);

V_{H_2O} is the volume of water.



Key

1 Detector 1
2 soap-film flow meter
3 Detector 2
4 Tap 1
5 Tap 2
6 weighing vessel

Figure A.1 — Determination of the volume of the soap-film flow meter

The equation may be re-arranged as

$$V_{H_2O} = \frac{m\left(1 - \frac{\rho_a}{\rho_w}\right)}{\rho_{H_2O} - \rho_a} \qquad \text{(A.2)}$$

to calculate the volume of water. If the temperature of the water is the same in the flow meter and at the time of weighing, then the volume of water is the required calibration volume of the assembly. If the temperatures are different, then a correction has to be applied.

If the weighings are carried out by use of an electromagnetic balance, under constant conditions of ambient pressure, temperature and relative humidity, the buoyancy correction, represented by the second term on the right hand side of Equation (A.2), is negligible. However, the balance is calibrated against traceable weights over the regular range of use.

A.2 Uncertainty of response

Assuming an uncertainty of response of 1 mm on a tube of 8 mm diameter, then the uncertainty of the volume is:

$$uV = \frac{2\pi\,(0{,}8)^2}{4} = 0{,}1\,\text{cm}^3$$

And, for example, with a volume of 1 l, would be:

$$\frac{uV}{V} = \frac{0{,}1}{1\,000} = 1{,}0 \times 10^{-4}$$

If the response uncertainty was only 0,1 mm, then the relative uncertainty on the volume is reduced to $1{,}0 \times 10^{-5}$ %.

A.3 Uncertainty of water weighing

The requirement is for an accurate measurement of the difference in mass between the vessel containing water and the vessel only. The accuracy of this determination is dependent on the traceable accuracy of the weights used.

Assuming the uncertainty of the weighing of 1 kg to 2 kg of water to be ± 10 mg, then the relative standard uncertainty on the mass is:

$$\frac{u(m)}{m} = \frac{10}{1 \times 10^6} = 1{,}0 \times 10^{-5}$$

A.4 Uncertainty of ρ_a, the density of air

The uncertainty on the density of air depends on the accuracy of the measurement of the barometric pressure and temperature and relative humidity of air at the time of weighing. It is a buoyancy correction term and as such will have an insignificant effect on the uncertainties of the volume.

NOTE The uncertainty in the air density under controlled conditions of temperature (better than ± 1 K) and relative humidity (40 % to 60 %) is approximately 2×10^{-6} kg·cm^{-3}.

A.5 Uncertainty of ρ_{H_2O}, the density of water

The uncertainty on the density of water has a direct effect on the uncertainty of the volume. The uncertainties on ρ_{H_2O} comes from the state of the water (air-free distilled, de-ionized, etc.) and the measurement of temperature of the water.

Examples of the density of water at different temperatures are given in Table A.1.

Table A.1 — Density of water at different temperatures

Temperature °C	Density of water g/cm^3
15	0,999 13
18	0,998 62
20	0,998 23

Assuming that air-free, freshly distilled water is used, then an uncertainty of 0,1 °C on the measured temperatures gives a relative uncertainty of the water density $u_{rel}(\rho_{H_2O}) = 1 \times 10^{-5}$, which directly translates to a relative uncertainty of the water volume $u_{rel}(V_{H_2O}) = 2 \times 10^{-5}$. This is the major uncertainty.

A.6 Relative combined standard uncertainties

The combination of the uncertainties described in A.2 to A.5 is as follows:

— response $7{,}4 \times 10^{-5}$

— weighing $1{,}0 \times 10^{-5}$

— density of air 0

— density of water $2{,}0 \times 10^{-5}$

— relative combined standard uncertainties $7{,}7 \times 10^{-5}$

The uncertainties are combined in a square-root sum-of-squares manner to form the relative combined standard uncertainty.

Annex B
(informative)

Description of secondary devices which need calibration against primary devices

B.1 Soap-film flow meter

B.1.1 Principle

A special soap-film flow meter 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 be made with greater accuracy. The measuring tube (see Figure B.1) is installed vertically in an insulated box, inside which air is continuously circulated at a controlled temperature in the range of 23,3 °C to 23,5 °C with a variation of ± 0,02 °C. The temperature is controlled by thermostats which are calibrated to 0,1 K with a discrimination of 0,01 K.

The gas to be measured is saturated with water vapour at the temperature of the measuring tube by passage 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 central 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 agent 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 into a siphon, and the gas passes out of the system. The pressure in the measuring tube is measured by a U-shaped 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 the walls are thoroughly wetted.

B.1.2 Influence of temperature variation

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

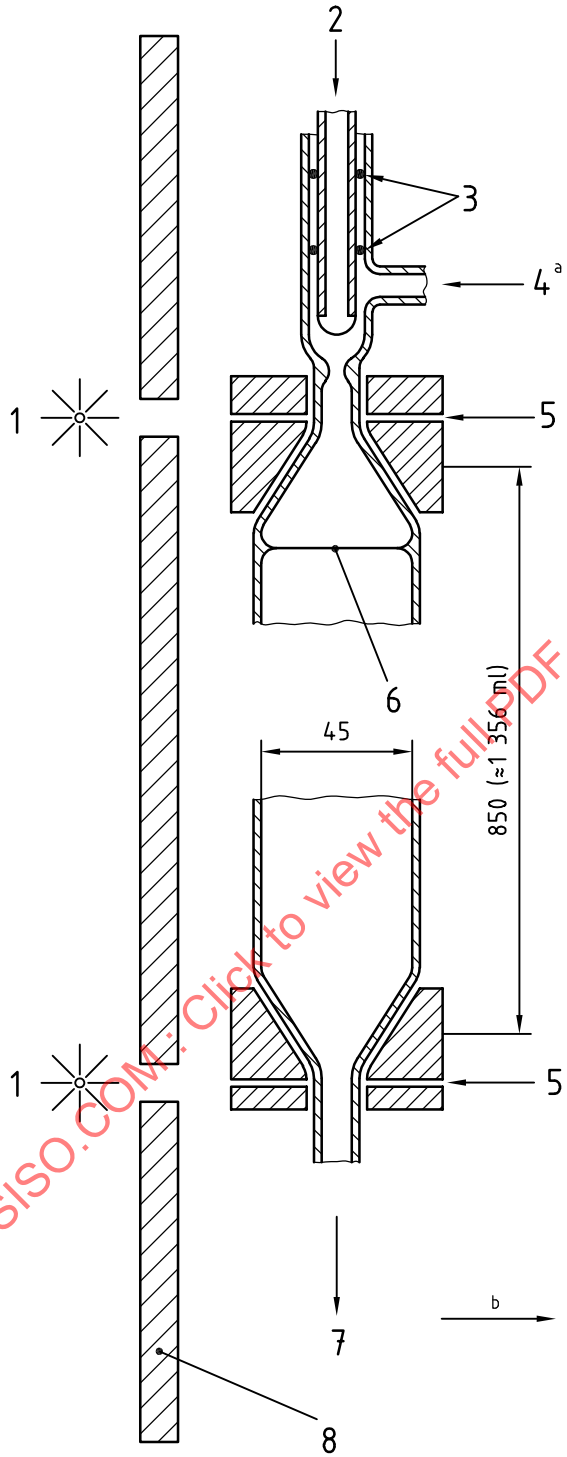
B.1.3 Influence of the pressure drop

The pressure in the soap-film flow meter will not vary from atmospheric by more than 100 Pa (1 mbar) at any value of flow rate and this can be measured to 10 Pa (0,1 mbar), giving a relative standard uncertainty of 10^{-4}.

B.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.

Dimensions in millimetres



Key

1 light source
2 solution producing soap bubbles
3 elasteromeric joint
4 gas inlet
5 photoelectric cell
6 soap bubble
7 syphon
8 surrounding wall

a The gas is saturated with water vapour.

b To gas outlet.

Figure B.1 — Measuring tube of soap-film meter

B.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 using 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. a relative standard uncertainty of 2×10^{-5} and with a repeatability of $\pm$ 20 %.

B.1.6 Differences in humidity

The saturator is of relative high efficiency, such that a variation of 1 % relative humidity, $(\Delta V/V)$ between one gas and another corresponds to a relative variation in the volume of the gas of 3×10^{-4}.

$$\frac{\Delta p}{p} \times \frac{\Delta V}{V} = \frac{21{,}5}{760} \times \frac{1}{100} = 3 \times 10^{-4}$$

where (Δp), 21,5 mm, is the saturated vapour pressure of water at the designated temperature of 23,4 °C.

B.1.7 Solubility of gases in water

Typical values for solubility in 1 ml of water at ambient temperature and pressure 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 uncertainty in the volume resulting from the carbon dioxide dissolved in 0,06 ml of the liquid just introduced into the measuring tube amounts only to 0,05 ml per 1 356 ml, i.e. a relative standard uncertainty of 4×10^{-5}.

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

B.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 be only about 1 % relative. This should remain the same between calibration and measurement and so the uncertainties are represented by the variation in this reduction, according to the degree of saturation (see B.1.6). If the variation is 10 % relative, this is 10 % of 3×10^{-4}, i.e. 3×10^{-5}.

B.1.9 Relative combined standard uncertainties

The combination of the possible uncertainties described in B.1.2 to B.1.8 is as follows:

— temperature 7×10^{-5}

— pressure 1×10^{-4}

— diffusion 0

— film thickness 2×10^{-5}

— humidity 3×10^{-4}

— solubility 4×10^{-5}

— vapour pressure 3×10^{-5}

— total uncertainties $3{,}3 \times 10^{-4}$

B.2 Wet-gas meter

B.2.1 Principle

A wet-gas meter consists of a drum which can rotate about a horizontal axis within an outer case. The drum is divided into four compartments of equal capacity, which are arranged radial about the axis of rotation. Each compartment has an inlet opening at one end and an outlet at the other. The drum rotates in water or oil which is contained in the outer case and the level of which is adjusted to act as a seal so that the compartments fill with, trap and deliver gas in succession. The positions of the inlet and outlet openings are such that at no time are both unsealed by being above the fluid level.

The vanes which separate the compartments dip below the fluid at all times, but are not continued to the spindle, so that fluid is able to pass to and from each compartment as the drum rotates.

Figure B.2 shows the operation of a single compartment of the meter. In Figure B.2 a), the compartment is filled with fluid with both connectors sealed. Rotation of the drum brings it to position Figure B.2 b), where gas can flow into the compartment and by doing so continues to rotate the drum. At position Figure B.2 c), both connectors are sealed once more with a defined volume of gas in the compartment, which is then discharged during further rotation shown in Figure B.2 d).

A pointer attached to the drum spindle rotates against a circular scale on the front of the instrument and a simple mechanical integrator records the number of revolutions.

Meters are generally available in the ranges 0,25 l to 25 l per revolution, suitable for maximum flow rates of 140 l/h to 3 000 l/h. Meters with external water jackets are available for precise temperature control.

If the fluid in the meter is water, the gas entering the meter should be saturated with water vapour at the temperature of the meter. This prevents loss of water from the meter and uncertainty as to the correction for gas volume. If the fluid is oil of low vapour pressure, no such precaution is necessary.

A small amount of pressure is necessary to operate the meter and this is measured by a U-shaped-tube manometer at the meter inlet. Due to slight differences in volume between the compartments, the rate of gas delivery may vary slightly during a complete revolution and so, where possible, only whole numbers of revolutions of the meter should be used. For the same reason, the inlet pressure may vary during a complete revolution and the mean pressure should be estimated.

The meter should be kept level during calibration and use. The level of fluid in the meter is also critical as it defines the volumes of the compartments. This level can be most accurately adjusted with no gas flowing through the meter, after which calibration for each required value of flow rate is necessary. Calibration is independent of the gas used, provided that the fluid is given time to become saturated with the gas in use, and free from any previously used gas.

B.2.2 Temperature variations

Thermal expansion of the meter can be neglected, since the effect on the contained gas volume is much greater. Assuming that the temperature can be read during calibration and analysis to within 0,05 K, and the appropriate correction applied, the maximum variation of 0,07 K (2 readings with 0,05 K uncertainty) represents a relative standard uncertainty of $3{,}4 \times 10^{-4}$.