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

**Part 1:  
Methods of calibration**

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*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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# Contents

Page

Foreword .....	iv
Introduction .....	v
<b>1</b> <b>Scope</b> .....	<b>1</b>
<b>2</b> <b>Normative references</b> .....	<b>1</b>
<b>3</b> <b>Terms and definitions</b> .....	<b>1</b>
<b>4</b> <b>Calibration methods</b> .....	<b>2</b>
4.1 <b>General</b> .....	<b>2</b>
4.2 <b>Description of primary or potentially primary measuring devices</b> .....	<b>4</b>
4.3 <b>Measurements on the final mixture</b> .....	<b>12</b>
<b>5</b> <b>Techniques for preparation of gas mixtures calibrated by the methods described in Clause 4</b> .....	<b>13</b>
5.1 <b>General</b> .....	<b>13</b>
5.2 <b>Volumetric pumps (see ISO 6145-2<sup>[3]</sup>)</b> .....	<b>15</b>
5.3 <b>Continuous injection (see ISO 6145-4<sup>[4]</sup>)</b> .....	<b>15</b>
5.4 <b>Capillary (see ISO 6145-5<sup>[5]</sup>)</b> .....	<b>15</b>
5.5 <b>Critical orifices (see ISO 6145-6<sup>[6]</sup>)</b> .....	<b>16</b>
5.6 <b>Thermal mass flow controllers (see ISO 6145-7<sup>[7]</sup>)</b> .....	<b>16</b>
5.7 <b>Diffusion (see ISO 6145-8<sup>[8]</sup>)</b> .....	<b>16</b>
5.8 <b>Saturation (see ISO 6145-9<sup>[9]</sup>)</b> .....	<b>17</b>
5.9 <b>Permeation (see ISO 6145-10<sup>[10]</sup>)</b> .....	<b>17</b>
<b>Annex A (normative) Volume measurement by weighing the water content</b> .....	<b>19</b>
<b>Annex B (informative) Description of secondary devices which need calibration against primary devices</b> .....	<b>23</b>
<b>Bibliography</b> .....	<b>32</b>

## 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.

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# 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*

<https://standards.iteh.ai/catalog/standards/sist/e0a4abd5-2757-4844-8719-02ca4b5c79/ISO-6145-1-2003>

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.

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

ISO 6145-1:2003  
**Table 1 — Calibration methods applicable to the preparation techniques**

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

<sup>a</sup> 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**

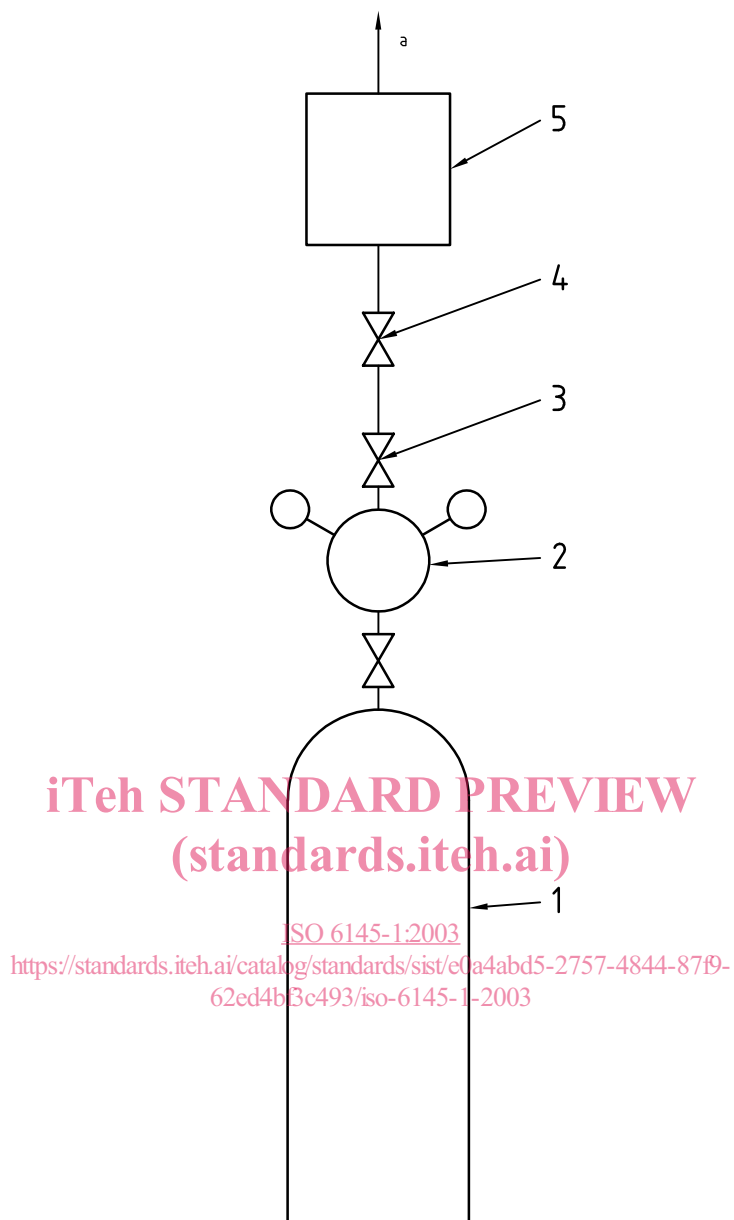
### **4.2.1 Gravimetric method**

#### **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 be calibrated (5). The dead volume between the needle valve outlet and the shut-off 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

<sup>a</sup> 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  $2 \times 10^{-4}$  (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  $7 \times 10^{-5}$ .

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  $2,2 \times 10^{-4}$ .

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**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  $2 \times 10^{-3}$ .

**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  $2 \times 10^{-4}$ .

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  $\pm 0,2$  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  $2 \times 10^{-4}$
- flow transients  $7 \times 10^{-5}$

— mass to volume	$2,2 \times 10^{-4}$
— flow rate variation	$2 \times 10^{-3}$
— timing	$2 \times 10^{-4}$
— 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  $\pm 0,02$  °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<sup>-1</sup>. The result is that, taking into account the control of temperature to  $\pm 0,02$  °C, there are relative standard uncertainties in the volume of the tube of approximately  $2 \times 10^{-7}$  and in the volume of gas of  $7 \times 10^{-5}$ .

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 ( $p_{\text{cal}}$ ) and use ( $p_{\text{use}}$ ) is made using the factor  $(p_{\text{cal}} + p_{\text{piston}}) / p_{\text{use}}$ , in which the piston pressure,  $p_{\text{piston}}$ , generally takes values between 0,1 kPa and 1 kPa.

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