
गैस विश्लेषण — गत्यात्मक आयतनी
पद्धतियों के प्रयोग द्वारा अंशशोधन
गैस मिश्रण तैयार करना

भाग 8 विसरण पद्धति

**Gas Analysis — Preparation of
Calibration Gas Mixtures Using
Dynamic Volumetric Methods**

Part 8 Diffusion Method

ICS 71.040.40

© BIS 2015



BUREAU OF INDIAN STANDARDS
मानक भवन, 9 बहादुरशाह ज़फर मार्ग, नई दिल्ली-110002
MANAK BHAVAN, 9 BAHADUR SHAH ZAFAR MARG
NEW DELHI-110002

www.bis.org.in www.standardsbis.in

NATIONAL FOREWORD

This Indian Standard (Part 8) which is identical with ISO 6145-8 : 2005 'Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods — Part 8: Diffusion method' issued by the International Organization for Standardization (ISO) was adopted by the Bureau of Indian Standards on the recommendation of the Industrial Gases Sectional Committee and approval of the Chemical Division Council.

This standard is being published in various parts. Other parts of this standard are as follows:

- Part 1 Methods of calibration
- Part 2 Volumetric pumps
- Part 4 Continuous syringe injection method
- Part 5 Capillary calibration devices
- Part 6 Critical orifices
- Part 7 Thermal mass-flow controllers
- Part 9 Saturation method
- Part 10 Permeation method
- Part 11 Electrochemical generation

The text of ISO Standard has been approved as suitable for publication as an Indian Standard without deviations. Certain conventions and terminologies are, however, not identical to those used in Indian Standards. Attention is particularly drawn to the following:

- a) Wherever the words 'International Standard' appear referring to this standard, they should be read as 'Indian Standard'.
- b) Comma (,) has been used as a decimal marker while in Indian Standards, the current practice is to use a point (.) as the decimal marker.

In this adopted standard, reference appears to the following International Standard for which Indian Standard also exists. The corresponding Indian Standard, which is to be substituted in its place, is listed below along with its degree of equivalence for the edition indicated:

<i>International Standard</i>	<i>Corresponding Indian Standard</i>	<i>Degree of Equivalence</i>
ISO 6145-7 Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods — Part 7: Thermal mass-flow controllers	IS 16249 (Part 7) : 2015 Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods : Part 7 Thermal mass-flow controllers	Identical with ISO 6145-7 : 2009

In reporting the result of a test or analysis made in accordance with this standard, if the final value observed or calculated, is to be rounded off, it shall be done in accordance with IS 2 : 1960 'Rules for rounding off numerical values (*revised*)'.

Indian Standard

GAS ANALYSIS — PREPARATION OF CALIBRATION GAS MIXTURES USING DYNAMIC VOLUMETRIC METHODS

PART 8 DIFFUSION METHOD

1 Scope

This part of ISO 6145 specifies a dynamic method using diffusion for the preparation of calibration gas mixtures containing component mole fractions ranging from 10^{-9} to 10^{-3} . A relative expanded uncertainty of measurement, U , obtained by multiplying the relative combined standard uncertainty by a coverage factor $k = 2$, of not greater than $\pm 2\%$ can be achieved by using this method.

By keeping the path between the diffusion source and place of use as short as possible, the method can be applied for the generation of low-concentration calibration gases of organic components that are liquid at room temperature, with boiling points ranging from about 40 °C to 160 °C.

This part of ISO 6145 is applicable not only for the generation of calibration gas mixtures of a wide range of hydrocarbons at ambient and indoor air concentration levels, but also for the generation of low-concentration gas mixtures of water.

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 6145-7, *Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods — Part 7: Thermal mass-flow controllers*

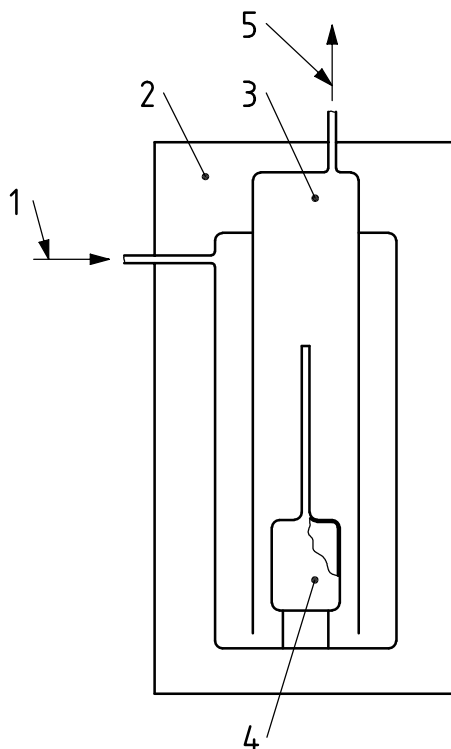
3 Principle

The calibration component migrates by diffusion through a diffusion tube of suitable dimensions (length, diameter) into a flow of a complementary gas, i.e. the complementary gas of the mixture prepared. The liquid calibration component, of a known high purity, is contained in a reservoir that acts as the source of the component vapour. The reservoir is provided with a vertically placed diffusion tube. This assembly (the diffusion cell) is placed in a temperature-controlled containment that is purged at a known and constant flow rate by a high-purity complementary gas (see Figure 1). The composition of the mixture is determined from the diffusion mass flow of the calibration component and the flow rate of the complementary gas.

The diffusion mass flow rate of the calibration component in principle depends on

- its diffusion coefficient in the complementary gas,
- its vapour pressure at the temperature of the containment,
- the dimensions of the diffusion tube.

Accurate determination of the mass flow rate is achieved by either continuous weighing, after mounting the tube in a suspension microbalance, or by periodic weighing. The method of determination affects the uncertainty of the (momentary) mass flow of the calibration component (see 7.2).



Key

- 1 complementary gas inlet
- 2 containment
- 3 diffusion tube
- 4 liquid reservoir
- 5 calibration gas outlet

Figure 1 — Schematic of diffusion apparatus

4 Reagents and materials

4.1 Liquid substances to be used as calibration component, of the highest possible purity so as to avoid any effects on the diffusion mass flow.

If possible, the nature and quantities of the impurities should be known and allowance made for their effects.

4.2 Complementary gas, of known purity, established by appropriate analytical techniques, e.g. Fourier-transform infrared spectrometry or gas chromatography.

The nature of the complementary gas shall be adapted to the substance to be used as the calibration component. For example, air shall not be used as complementary gas for the preparation by diffusion of calibration gas mixtures of oxidizable substances.

5 Apparatus

5.1 Diffusion apparatus

5.1.1 Materials

The materials of the diffusion apparatus shall be chosen so as to avoid effects of physical or chemical sorption or desorption on the content of the calibration component. The smaller the desired content, the greater the effect of sorption/desorption phenomena.

Diffusion reservoirs and tubes, as well as temperature containments and blending apparatus, should preferably be manufactured out of borosilicate glass. Choose chemically inert, flexible tube materials for the supply of complementary gas and transport of calibration gas mixture. Pay special attention to all junctions as possible sources of leaks.

5.1.2 Complementary gas flow configuration

Before the complementary gas reaches the diffusion cell, it is essential that its temperature be controlled to that of the diffusion cell containment. In order to achieve the uncertainty stated in Clause 1, the temperature in the containment should be controlled to within $\pm 0,15$ K.

The minimum flow rate of the complementary gas should be sufficient to remove all component vapour without saturation. The maximum allowable rate should be low enough to avoid convective transport of the calibration component vapour inside the diffusion tube. This maximum flow rate is dependent upon the geometry of the diffusion apparatus. It is recommended to keep the Reynolds number of the complementary gas flow in the diffusion cell below 100. At a temperature of 25 °C, the following condition should approximately be fulfilled:

$$v \cdot d < 1,6 \times 10^{-3}$$

where

v is the average linear velocity of the complementary gas, in metres per second;

d is the diameter, in metres, of the tubing through which the complementary gas flows.

5.1.3 Choice of temperature

The choice of temperature depends on the diffusion cell characteristics and the diffusion mass flow rate required. To carry out temperature control, establish thermal equilibrium within the diffusion cell at a value close to ambient temperature or at a temperature sufficiently above ambient so as to avoid effects of ambient conditions on temperature control. The use of a temperature slightly above ambient has two advantages:

- accurate control of temperature can more easily be achieved near ambient temperature,
- the temperature of the complementary gas can more easily be controlled.

5.2 Diffusion cells, consisting of a borosilicate glass reservoir capable of holding a sufficiently large quantity of the liquid calibration component, fitted with a diffusion tube. Several design examples are given in Reference [1].

In principle, Equation (1) can be applied for the prediction of diffusion volume flow rates ^[1] and, conversely, for the calculation of approximate dimensions and temperatures of diffusion tubes and containments necessary for the generation of a given mass flow rate of the calibration component.

$$q_V(A) = \frac{A}{L} D \cdot \ln \left(\frac{p}{p - p_v} \right) \quad (1)$$

where

- $q_V(A)$ is the volume flow rate of component A, in cubic metres per second;
- A is the cross-sectional area of the diffusion tube, in square metres;
- L is the length of the diffusion tube, in metres;
- D is the diffusion coefficient, in square metres per second;
- p is the pressure in the diffusion cell, in pascals or kilopascals;
- p_V is the partial pressure of the calibration component, in pascals or kilopascals.

If no data for the diffusion coefficients exist, methods for their calculation are given in the literature. The method of Fuller, Schettler and Giddings [2] is the most successful, but errors of up to 25 % can easily occur. Data for the atomic and structural volume increments applicable to calibration component and complementary gases and vapours are given in Reference [4].

To achieve the best performance, diffusion tubes should remain within the following dimensional ranges:

- $L > 0,03$ m;
- ratio of L to diameter of diffusion tube > 3 ;
- diameter: 0,001 m to 0,02 m.

NOTE Units which operate on the diffusion principle are commercially available and provide calibration gas mixtures containing highly adsorptive vapours. An example of one such unit for the preparation of reference standards of humidity in volume fractions of 10^{-9} and its performance details are given in Annex A.

6 Procedure

6.1 Preliminary checks and operating conditions

Before assembling or filling a diffusion cell, the purity of the substance to be used as calibration component is to be assessed using an appropriate analytical technique (e.g. Fourier-transform infrared spectrometry or gas chromatography) so as to quantify any likely major contaminants.

Periodically check the diffusion mass flow at a known, fixed temperature and complementary gas flow rate as an indication of stability of the calibration compound in the reservoir. If the diffusion mass flow drifts by more than 1 % per month, this may be an indication of the presence of impurities. In that case, the contents of the diffusion cell should be replaced.

When first placing the diffusion cell in its containment, allow the system to equilibrate before performing the first weighing so as to ensure constancy of the diffusion mass flow. Generally, a period of 24 h is sufficient.

To change the content of the calibration gas mixture, adjust the complementary gas flow rate. Alternatively, the calibration gas mixture can be further diluted, and its contents adjusted, by application of a secondary flow of a diluent gas. Changing the temperature of the diffusion-cell containment for adjustment of the content of the calibration gas mixture is not recommended.

During the period of use, maintain the diffusion cell at constant temperature in order to avoid delay due to the time needed to restore equilibrium.

6.2 Determination of mass loss

6.2.1 Handling the diffusion cell

Ensure that all weighing is performed with extreme cleanliness and avoid direct contact of the diffusion cell with hands. Use gloves and clean pliers or tweezers. If appropriate, depending on the type used, close the diffusion cell before weighing.

6.2.2 Periodic-weighing mode

The temperature and relative humidity in the weighing room should be controlled and kept constant during successive readings. The cell is periodically removed from the enclosure, weighed, and returned immediately to the enclosure. In a given time interval, the diffusion cell will decrease in mass. The measurement of this change in mass will have an associated measurement uncertainty. Therefore, the choice of the time interval over which the weighings are made depends on the required uncertainty. Choose the time interval such that the weighing uncertainty is a small fraction (e.g. < 1%) of the mass loss of the diffusion cell during this interval. Determine the diffusion rate by calculation of the mass difference between the periodic weighings and the time interval between them.

Because of the dependence of the diffusion mass flow rate on ambient pressure, a correction to standard pressure (usually 101,325 kPa) may be applied as follows

$$\bar{q}_m(A) = \frac{\Delta m}{\Delta t} \frac{\bar{p}}{p_0} \quad (2)$$

where

$\bar{q}_m(A)$ is the average mass flow rate of component A from the diffusion cell over time period Δt , in grams per minute;

Δm is the mass difference, in grams, between consecutive weighings;

Δt is the time interval, in minutes, between consecutive weighings;

\bar{p} is the average air pressure, in kilopascals, over the interval between weighings;

p_0 is the standard pressure for correction (usually 101,325 kPa).

The actual momentary mass flow is then calculated from $q_m(A)$ by applying a reverse correction for actual pressure

$$q_m(A) = \bar{q}_m(A) \frac{p_0}{p} \quad (3)$$

where p is the actual air pressure, in kilopascals.

NOTE An example of the mass flows of diffusion cells for toluene and for trichloromethane as a function of time is given in Annex B.

6.2.3 Continuous-weighing mode

The diffusion cell is weighed continuously on a load cell that transmits its readings to a computer (acquisition analysis diagnostics). Choose the frequency at which weighings are to be recorded to be as close as possible to the value obtained by dividing the diffusion rate by the accuracy of the weighing system. This will indicate systematic deviations from a constant mass-loss rate.

EXAMPLE A diffusion rate of $2,0 \times 10^{-6} \text{ g}\cdot\text{min}^{-1}$ and a weighing system accuracy of $1 \times 10^{-6} \text{ g}$ would suggest a sampling rate of 2 min^{-1} .

7 Expression of results

7.1 Calculation

The mass concentration of the calibration component A in the resulting gas mixture, $\beta(A)$, is given by:

$$\beta(A) = \frac{q_m(A)}{q_V} \quad (4)$$

where

$q_m(A)$ is the diffusion rate (mass flow) of the calibration component A having dimensions $\text{M}\cdot\text{T}^{-1}$ and, for example, expressed in micrograms per minute ($\mu\text{g}\cdot\text{min}^{-1}$);

q_V is the total volume flow rate of the complementary gas plus the flow rate of the component gas, having dimensions $\text{L}^3\cdot\text{T}^{-1}$ and expressed, for example, in litres per minute ($\text{l}\cdot\text{min}^{-1}$).

For practical purposes, the flow rate q_V of the component can be neglected. In the case of a two-stage dilution procedure the flow rate q_V is the sum of the flow rates of the complementary gas and the diluent gas.

The above calculation then gives the mass concentration of the gas mixture, $\beta(A)$, in dimensions of $\text{M}\cdot\text{L}^{-3}$, in units for example of micrograms per cubic metre ($\mu\text{g}\cdot\text{m}^{-3}$). Note that in this case the concentration is dependent on the pressure and temperature conditions.

The calculated concentration can be converted into a mole fraction, $x(A)$, by taking into account the molar mass, $M(A)$, of the component gas and the molar mass, M_{tot} , of the sum of the gases under measurement conditions. The mass flow rate of the mixture can be calculated from the multiplication of volume flow rate, $q_{V,\text{tot}}$, and the density, ρ_{tot} , of the mixture under measurement conditions; the molar mass flow rate is then obtained by dividing ($q_{V,\text{tot}} \times \rho_{\text{tot}}$) by M_{tot} . For practical purposes the density and the molar mass of the complementary gas under measurement conditions can be used:

$$x(A) = \frac{q_m(A)}{M(A)} \times \frac{M_{\text{tot}}}{q_{V,\text{tot}} \cdot \rho_{\text{tot}}} \quad (5)$$

Combination of Equations (4) and (5) gives:

$$x(A) = \frac{\beta(A)}{M(A)} \times \frac{M_{\text{tot}}}{\rho_{\text{tot}}} \quad (6)$$

Alternatively, if the complementary gas flow is measured as a mass flow of gas, $q_{m,\text{cg}}$, the mole fraction of the resulting gas mixture can be calculated by taking into account the molar mass of the component gas, $M(A)$, and that of the complementary gas, M_{cg} . The component gas flow can usually be neglected in the sum of the mass flow so that:

$$x(A) = \frac{q_m(A)}{M(A)} \times \frac{M_{\text{cg}}}{q_{m,\text{cg}}} \quad (7)$$

The results may be expressed in any appropriate units.

NOTE Equations (4), (6) and (7) are related by constants which have a negligible uncertainty associated with them (the typical relative uncertainty in a molar mass is $\pm 1 \times 10^{-5}$). Therefore, the relative uncertainty associated with the mole fraction is the same as that associated with the mass concentration.

7.2 Sources of uncertainty

7.2.1 General

There are several sources of uncertainty, the principal ones of which are identified below:

- a) measurement of mass flow from diffusion cell:
 - balance,
 - buoyancy effects,
 - purity of calibration component,
 - stability of calibration component,
 - effects of sorption or desorption;
- b) short-term fluctuations in mass flow of the calibration component;
- c) measurement of time;
- d) measurement of flow rate of complementary gas and optional diluent gas:
 - flow meter,
 - purity of complementary gas and optional diluent gas;
- e) short-term fluctuations in complementary and diluent gas flows.

An example of an uncertainty evaluation of the generation of a calibration gas mixture by diffusion, based on periodic weighing, is given in Annex C.

7.2.2 Measurement of the mass flow from the diffusion cell

7.2.2.1 Balance

Uncertainties in the mass measurement usually result from deficiencies in the calibration of the weighing device and/or from the limited sensitivity of the balance. Weighing devices shall be traceably calibrated. The intervals between subsequent weighings shall be sufficiently large so as to minimize the contribution of balance resolution to the combined uncertainty.

7.2.2.2 Buoyancy effects

The mass of air displaced by the diffusion cell during weighing affects the apparent mass. Compensation for this can be made by calculation of the magnitude of this buoyancy change. The true mass loss, Δm , of the diffusion cell is calculated according to Equation (8):

$$\Delta m = m_1 - m_2 + (\rho_1 - \rho_2)V \quad (8)$$

where

m_1 is the apparent mass of the diffusion cell at the time of the first weighing;

m_2 is the apparent mass of the diffusion cell at the time of the second weighing;

ρ_1 is the density of air at the time of the first weighing;

ρ_2 is the density of air at the time of the second weighing;

V is the volume of the diffusion cell.

In the case in which the atmospheric conditions (temperature, pressure and humidity) remain constant in the interval between the first and second weighings, the buoyancy will remain constant and the determination of mass loss, given by the difference between the initial and final weighings, will not be subject to a buoyancy correction.

If a two-pan balance configuration is used, this buoyancy effect can be eliminated by employing a tare mass having the same volume as the diffusion cell.

If a single-pan balance configuration is used, then the buoyancy effect can be eliminated by performing relative weighings against the same tare mass having a volume equal to that of the diffusion cell.

Alternatively, if no correction for buoyancy is applied, then the uncertainty due to buoyancy effects shall be fully taken into account.

7.2.2.3 Purity of the calibration component

As discussed above in 3.1, before using a diffusion cell for the preparation of gas mixtures, any impurities in the calibration component shall be identified and quantified, or upper limits placed on their relative concentrations. Appropriate analytical techniques shall be used for this purpose. Frequent (e.g. weekly) checks on the diffusion mass flow rate at a fixed temperature and complementary gas flow rate are a good means of verifying that a single component is diffusing (see 6.1).

7.2.2.4 Stability of calibration component

Some substances may undergo polymerization or may react, either with other compounds present or with diffusion cell materials. This will have the effect of reducing the true concentration of the final gas mixture, and account shall be taken of this effect in determination of the total uncertainty.

7.2.2.5 Effects of sorption or desorption

The apparatus shall be allowed to reach equilibrium before use. The establishment of equilibrium can be checked by measuring the calibration component content as a function of time.

7.2.3 Short-term fluctuations in calibration component mass flow

In addition to the uncertainty arising from the contributions described above, the momentary mass flow that is used for the calculation of actual concentration values is governed by short-term fluctuations. In general, the uncertainties related to these short-term fluctuations add to the average mass flow as

$$q_m(A) = \bar{q}_m(A) + \Sigma \delta q_m(A) \quad (9)$$

in which $\Sigma \delta q_m(A)$ represents the sum of contributions of sources of short-term variation in $q_m(A)$.

Starting from Equation (2), applying Maxwell's and Antoine's equations to express D and p_v as functions of temperature and air pressure, $\Sigma \delta q_m(A)$ can be expressed as follows:

$$\Sigma \delta q_m(A) = (c_1 + c_2) \delta p + c_3 \delta T \quad (10)$$

where δp and δT represent short-term fluctuations in air pressure and diffusion cell temperature, and c_1 , c_2 and c_3 are sensitivity coefficients derived from characteristics of the diffusion cell, the calibration component and external conditions.

Application of Equation (10) for the derivation of uncertainty contributions shows that, in practice, when diffusion cell temperature is controlled to within $\pm 0,15$ K, normal fluctuations in air pressure will lead to relative uncertainties in $q_m(A)$ of about 0,4 % to 0,6 %. These are due mainly to uncertainties of the components' vapour pressures due to temperature variations.

7.2.4 Measurement of time

The measurement of the time interval between weighings may be incorrect due to errors in the time measurement. This is minimized by regular traceable calibration of the measuring device. The calibration uncertainty shall be considered in the overall uncertainty analysis.

7.2.5 Measurement of the flow rate of the complementary and diluent gases

7.2.5.1 Flow meter

The measurement of the flow rate of the complementary and diluent gases contributes to the final uncertainty in the composition of the calibration gas mixture. This is minimized by regular traceable calibration of the flow meter. Uncertainties for various flow meters shall be estimated as specified in ISO 6145-1.

7.2.5.2 Impurities of complementary and diluent gases

Any impurities in the complementary gases shall be identified and quantified, or upper limits placed on their relative concentrations. Appropriate analytical techniques shall be used for this purpose.

7.2.6 Short-term fluctuations in complementary and diluent gas flow rates

Short-term variations in complementary and diluent gas flow rates shall be checked by repeated measurement of flow rates. In general, the relative uncertainty associated with these fluctuations is estimated to be $< 0,4$ %.

7.2.7 Possibility of leaks

The presence of a leak within the diffusion apparatus has an effect on the measurement uncertainty of the gas mixture. If there is a leak immediately after the complementary gas has swept over the diffusion cell then the concentration of the prepared gas mixture is lower than the value calculated using Equation (2). A thorough leak test of the diffusion apparatus should be conducted before measurements are made using the system, and an upper limit placed on the magnitude of leaks present.

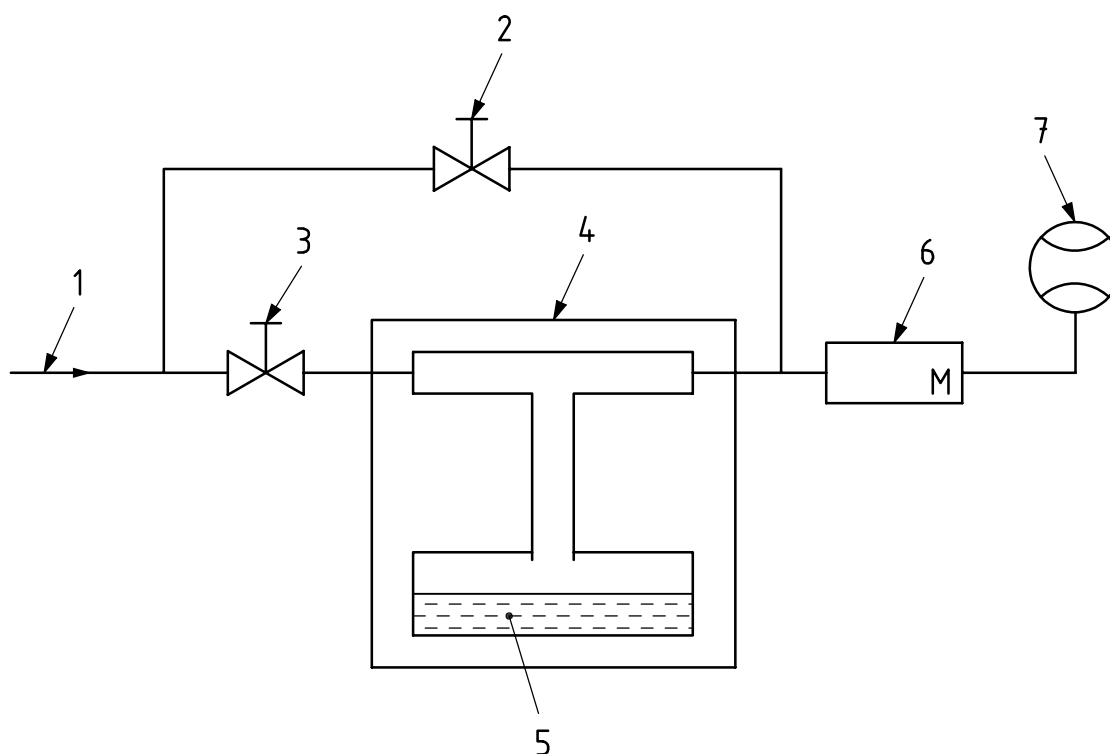
Annex A (informative)

Practical example of a diffusion cell calibrator configured for evaluating speed of response in a hygrometer

A.1 General background

The diffusion method has been applied to moisture generation for a number of years and approved for use on non-reactive gases including methane. The schematic setup is essentially similar to that described in Clause 5 and given in Figure A.1, with adequate monitoring and/or control of the significant variables outlined under earlier sections.

The significance and convenience of this method is that it permits the fundamental performance assessment and intercomparison of different cells, engineered to produce the same results, using mass as the prime intercomparison unit. Concentration ranges from 5×10^{-9} to 10^{-3} have been achieved with good repeatability.



Key

- 1 dry air
- 2 flow control valve V2
- 3 flow control valve V1
- 4 temperature-controlled chamber
- 5 water
- 6 hygrometer
- 7 flow meter

Figure A.1 — Example of a diffusion cell calibrator

Data collected over several years showed that basic uncertainties increased to $\pm 2\%$ in the 10^{-9} region. Mass generation data is initially determined for each cell and then intercomparison studies are carried out between other cells. This methodology forms a convenient basis for an ongoing control in any particular location. The use of a fast responding moisture comparator can be used to indicate the short-term stability of moisture generation thus precluding time dependent averages.

The method is of particular relevance for the determination of time of response, and in the calibration of individual moisture sensors.

Historically, a statement of errors has usually been ascribed to a unit being calibrated once equilibrium conditions have been reached. This does take a variable amount of time, depending upon the response of the device itself and that of the calibration system. The device response can now be accurately assessed and a dynamic calibration carried out, with a statement of errors related to the lapsed time following any moisture change. This can be of particular value in enabling end users to modify their operational methods so as to obtain readings of significance related to the available sampling time within a process measurement.

A.2 Example

In the following example, the diffusion calibrator has been used to carry out comparative speed of response tests between several hygrometers undergoing evaluation. All the hygrometers were found to be accurate within their manufacturer's tolerance, but not all gave repeatable data after short exposure to high moisture levels within the sampling time required by the end user. Such a configuration as described below enabled the user to establish the performance characteristics of each hygrometer under dynamic and realistic operating conditions.

Air from heat-reactivated driers was considered adequately dry for the application, and fed into the calibrator (see Figure A.1). The flow control valve V1 is set to purge at a constant flow rate through the diffusion cell, raising the moisture content entering the hygrometer.

A typical diffusion cell used for calibration of commercial hygrometers may have a flow rate of 400 ml/min, generating a moisture content of 12 ml/m³. Because variations in flow rate within the range 100 ml/min to 500 ml/min will not change the mass of water diffused per unit time into the dry air stream, constant flow rate monitoring through V1 is not required.

Flow control valve V2 determines the flow rate of dry air injected into the sample line. Altering the valve setting will instantly change the 10^{-9} level sampled by the hygrometer so that the true instrument response speed may be assessed. In the above example, the 10^{-9} level (L , expressed in millilitres per cubic metre) of the hygrometer sample gas may be determined by the following formula:

$$L = \frac{12 \times 400}{\sum q} \quad (\text{B.1})$$

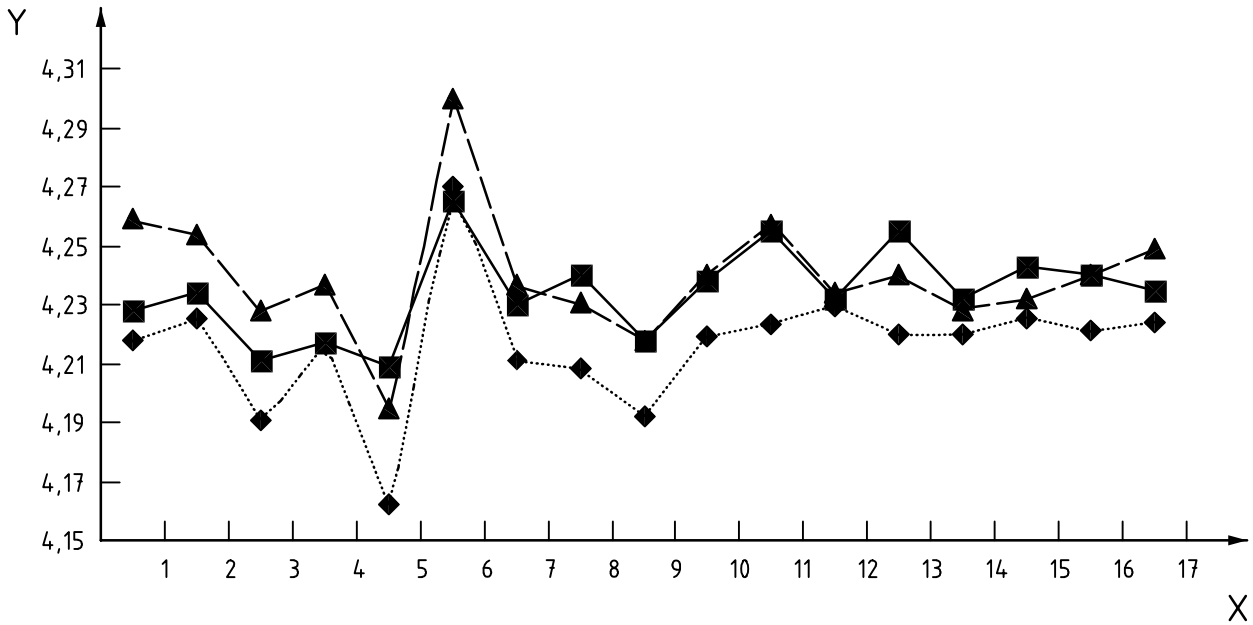
Here $\sum q$ represents the total flow rate, in millilitres per minute, of the gas mixture to the hygrometer, and a volume fraction of 12 ml/m³ at 400 ml/min provides a diffusion rate.

Cells with different values of diameter and length of diffusion tube can be supplied giving humidity ranges corresponding to frost points less than $-70\text{ }^{\circ}\text{C}$.

A.3 Stability of diffusion cell output

An example of the output from an accredited system is given in Figure A.2. It can be seen that the actual data derived from three such cells (indicated as TC 16, TC 17 and TC 18), under strictly controlled conditions, correlated with each other to within 0,5%. This corresponds to a moisture variation of less than $\pm 0,05\text{ ml/m}^3$ at the 10 ml/m^3 level. It therefore provides a low initial base of uncertainty to which any additional

uncertainties, associated with individual configurations, would be added and still provide acceptable practical interchangeability of data around the world in various locations.



Key

X time, days

Y output, mg/day

-◆..... TC 16
- TC 17
- ▲— TC 18

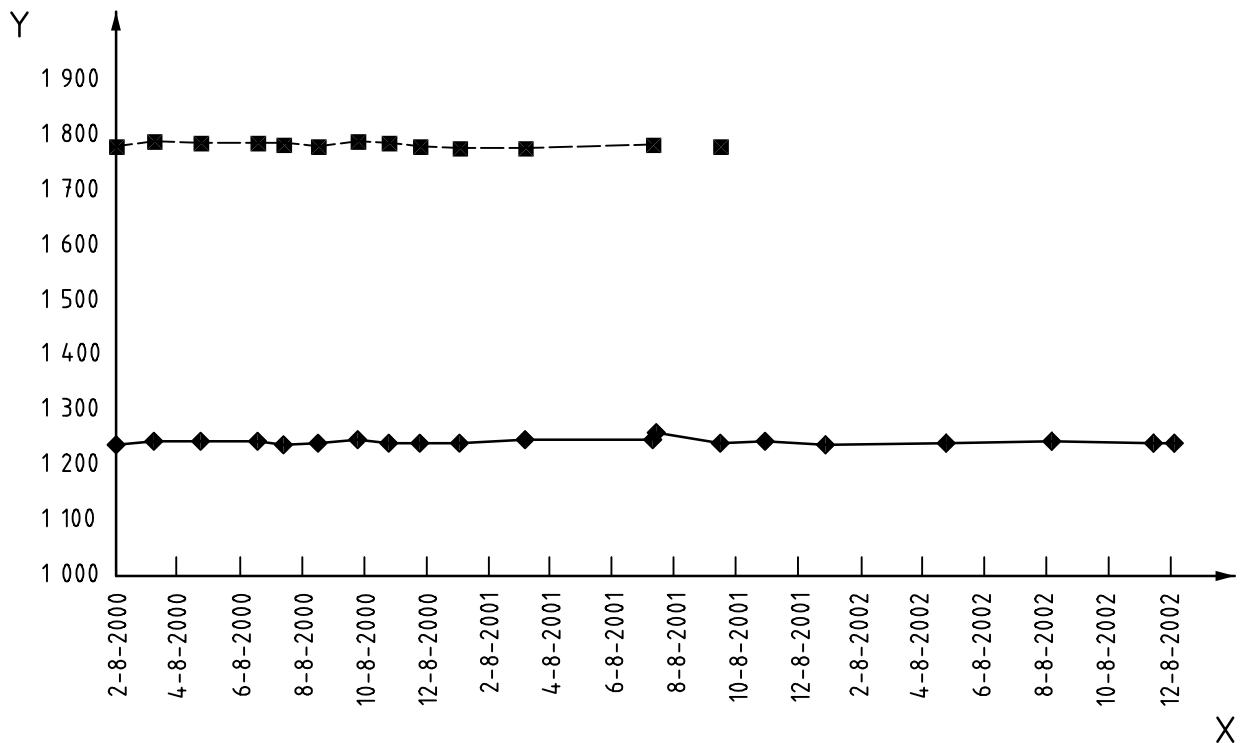
NOTE Data, corrected for pressure and time-lapse, provided by MCM Thorpe Arch, Budgate, UK.

Figure A.2 — Stability of moisture generation

Annex B
 (informative)

Example of performances of diffusion cells for toluene and trichloromethane

In Figure B.1, an example of the output (in 10^{-9} g/min) of a diffusion cell for both toluene and trichloromethane is given. The data are listed in Table B.1.



Key

X date

Y mass flow rate, mg/min

—◆— toluene

- -■- - trichloromethane

Figure B.1 — Examples of performance of diffusion cells

Table B.1 — Diffusion cell mass flow rate

Toluene 10 ⁻⁹ g/min		Trichloromethane 10 ⁻⁹ g/min	
1 237	1 249	1 782	1 777
1 244	1 259	1 790	1 779
1 244	1 242	1 788	1 785
1 245	1 244	1 786	1 782
1 237	1 238	1 784	
1 241	1 242	1 780	
1 249	1 244	1 791	
1 243	1 240	1 786	
1 243	1 243	1 780	
1 242	mean: 1 244		mean: 1 784
1 247	std: 5		std: 4

Annex C (informative)

Example of uncertainty calculations for a periodic weighing system

C.1 General

This example is based on the application of a 10 cm³ diffusion cell with benzene, with a nominal mass flow rate of 5,0 µg·min⁻¹ that is weighed every 4 weeks (nominal mass difference between weighings = 201,6 mg).

C.2 Measurement of mass flow from diffusion cell

C.2.1 Balance

The uncertainty u in the mass difference derived from subsequent weighings is expressed as $\sqrt{2}$ times the uncertainty of a single weighing. This uncertainty is derived from calibration of the balance. In the current example the uncertainty of a single weighing is ± 50 µg. Hence the uncertainty contribution from the balance equals:

$$u(m_1 - m_2) = \pm \sqrt{2} \times 50 = \pm 70 \text{ µg}$$

C.2.2 Buoyancy

The uncertainty due to buoyancy effects is calculated from the volume of the diffusion tube (10 cm³) and knowledge of extremes of temperature, pressure and relative humidity (RH) at individual weighings. Extreme combinations of pressure, temperature and humidity are 98,6 kPa/292,9 K/60 % RH and 103,7 kPa/292,5 K/40 % RH, leading to extremes in air density of 1 166,5 µg·cm⁻³ to 1 231,7 µg·cm⁻³ [5]. The resulting uncertainty in the air density, assuming a triangular distribution, is

$$u(\rho) = \frac{(1231,7 - 1166,5)}{2\sqrt{3}} = 15,7 \text{ µg} \cdot \text{cm}^{-3}$$

For an average diffusion cell with a volume of 10 cm³, the uncertainty becomes:

$$u(\text{buoyancy}) = \pm 10 \times 15,7 = \pm 157 \text{ µg}$$

The total uncertainty due to the weighing then is

$$u(\Delta m) = \pm 172 \text{ µg}$$

For a diffusion cell with a nominal mass flow rate of 5,0 µg min⁻¹ and a 4-week weighing interval, the relative uncertainty due to balance effects becomes

$$\frac{u(\Delta m)}{\Delta m} = \pm 172/201600 = 0,00085 = 0,09 \%$$

C.2.3 Substance purity

The purity stated by the manufacturer ($\geq 99,8\%$) is used for further uncertainty evaluation; assuming a rectangular distribution with no correction applied for impurity, the relative uncertainty contribution is:

$$u(\text{purity}) = \pm \frac{0,2}{\sqrt{3}} = \pm 0,12\%$$

C.2.4 Time measurement

The time interval between subsequent weighings can be determined with an uncertainty < 1 min. The uncertainty of time measurement of an interval of 40 320 min is negligible.

C.2.5 Pressure corrections

Equations (2) and (3) are used to correct for influences of pressure on the diffusion mass flow. For application of Equation (2), knowledge is required of the average pressure between weighings. When pressure is measured by continuous logging of short-term pressure measurements, the uncertainty in the average pressure over a 4-week period reduces to the uncertainty in the calibration of the barometer used. Usually, the relative uncertainty is $\pm 0,1\%$ or better. For this case, the following is assumed:

$$u(\bar{p}) = \pm 0,1\%$$

For back-correction to actual pressure conditions, knowledge of actual pressure p is required. If a single pressure measurement is used, the uncertainty is built up of the calibration uncertainty plus the uncertainty of a single pressure reading. For the barometer used, the latter uncertainty is $\pm 0,05$ kPa, leading to a total relative uncertainty of $\pm 0,11\%$.

The total relative uncertainty due to pressure correction is therefore:

$$u(p, \text{cor}) = \pm \sqrt{2} \times 0,1 = \pm 0,15\%$$

C.2.6 Stability and sorption effects

Stability is not expected to be a problem when benzene is used. By proper choice of materials and equilibration time, sorption effects are assumed to be negligible.

C.2.7 Short-term fluctuations

For benzene, calculated as described previously in 7.2.3, a relative uncertainty of $\pm 0,5\%$ may be expected:

$$u(q_m, \text{short-term}) = \pm 0,5\%$$

C.2.8 Combined uncertainty in mass flow

By combination of the above uncertainty sources, a combined relative uncertainty in the momentary (actual) mass flow rate from a diffusion cell, under the above assumptions, is estimated to be

$$u(c, q) = \pm \sqrt{\frac{u^2(\Delta m)}{(\Delta m)^2} + u^2(\text{purity}) + u^2(p, \text{cor}) + u^2(\text{short-term})} = \pm 0,5\%$$

C.3 Flow rate of the complementary gas

C.3.1 Flow meter

The uncertainty in the reading of the mercury-sealed piston meter used is derived from the uncertainty in the calibration of the volume between timing sensors; the relative uncertainty is:

$$u(\text{flowmeter}) = \pm 0,1\%$$

C.3.2 Flow measurement

The uncertainty in the actual flow measurement is calculated from the standard deviation of three successive flow measurements. Typical relative standard deviations are $< \pm 0,05\%$.

$$u(q_{V,\text{meas}}) = \pm \frac{0,05}{\sqrt{3}} = \pm 0,03\%$$

C.3.3 Corrections for pressure and temperature

The measured complementary flow rate is converted to standard pressure and temperature (101,325 kPa; 293,15 K) and corrected to actual conditions of pressure and temperature on application of the calibration gas mixture:

$$q_{V,\text{cor}} = q_{V,\text{meas}} \frac{101,325}{p_{\text{meas}}} \times \frac{t_{\text{meas}}}{293,15} \quad (\text{C.1})$$

$$q_{V,\text{act}} = q_{V,\text{cor}} \frac{101,325}{p_{\text{act}}} \times \frac{t_{\text{act}}}{293,15} \quad (\text{C.2})$$

The combined corrections involve two measurements of pressure and temperature, each with a relative uncertainty (calibration plus reading) of $\pm 0,11\%$. The combined relative uncertainty for the corrections to and from standard pressure and temperature is

$$u(pT,\text{cor}) = \pm 2 \times 0,11 = \pm 0,22\%$$

C.3.4 Impurities in the complementary gas

By applying appropriate gas purification, for example by using a combination of molecular sieve drying and subsequent filtration over silica gel and active charcoal (possibly also in combination with catalytic conversion of hydrocarbons), benzene concentrations in the complementary gas of $< 0,5 \times 10^{-9} \text{ g}\cdot\text{m}^{-3}$ are feasible. The associated uncertainty is

$$u(\text{cg,purity}) = \pm \frac{0,5 \times 10^{-9}}{\sqrt{3}} = \pm 0,3 \times 10^{-9} \text{ g}\cdot\text{m}^{-3}$$

This uncertainty becomes relevant for calibration gas contents of $< 60 \times 10^{-9} \text{ g}\cdot\text{m}^{-3}$.

C.3.5 Short-term fluctuations in complementary gas flow rate

Since a flow rate correction is applied to actual temperature conditions, only the temperature-independent part of the short-term fluctuations is taken into account. For the mass-flow rate controller used, these are determined by measurement to be $\pm 0,1\%$ relative.

The relative uncertainty used is

$$u(q_{cg, \text{short-term}}) = \pm 0,1 \%$$

C.3.6 Combined uncertainty in complementary gas flow rate

By combination of the above uncertainty sources, a combined relative uncertainty in the momentary (actual) complementary gas flow rate, under the above conditions, is estimated to be:

$$u(cg, q_V) = \pm \sqrt{u^2(\text{flowmeter}) + u^2(\text{meas}) + u^2(\text{cg, purity}) + u^2(pT, \text{cor}) + U^2(\text{cg, short-term})} = \pm 0,26 \%$$

C.4 Combined uncertainty of calibration component content

By combining the uncertainties in the calibration component mass flowrate and the complementary gas volume flow rate, the relative uncertainty in the calibration component content is estimated to be:

$$u(\rho) = \pm \sqrt{u^2(c, q_m) + u^2(cg, q_V)} = \pm 0,6 \%$$

C.5 Expanded uncertainty of calibration component content

By using a coverage factor of 2, representing a confidence interval of approximately 95 %, the expanded relative uncertainty of the calibration component content is

$$U(\rho) = \pm 1,2 \%$$

Bibliography

- [1] G.O. NELSON, *Gas Mixtures. Preparation and Control*, Lewis Publishers, Chelsea MI, 1992
- [2] E.N. FULLER, P.D. SCHETTLER and J.C. GIDDINGS, A New Method for Prediction of Binary Gas Phase Diffusion Coefficients, *Ind. Eng. Chem.*, 5 (1966) pp. 19-27
- [3] REID, PRAUSNITZ and SHERWOOD. *Controlled Test Atmospheres — Principles and Techniques*, Ann Arbor Science Publishers Inc., Ann Arbor, Michigan, USA 1971. p. 147, 3rd ed
- [4] R. SCHWARTZ, *Guide to Mass Determination with High Accuracy*, PTB-Bericht MA-40, 1995, p. 26
- [5] ISO 6143, *Gas analysis — Comparison methods for determining and checking the composition of calibration gas mixtures*
- [6] ISO 6145-1, *Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods — Part 1: Methods of calibration*
- [7] ISO 6145-6, *Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods — Part 6: Critical orifices*

Bureau of Indian Standards

BIS is a statutory institution established under the *Bureau of Indian Standards Act, 1986* to promote harmonious development of the activities of standardization, marking and quality certification of goods and attending to connected matters in the country.

Copyright

BIS has the copyright of all its publications. No part of these publications may be reproduced in any form without the prior permission in writing of BIS. This does not preclude the free use, in course of implementing the standard, of necessary details, such as symbols and sizes, type or grade designations. Enquiries relating to copyright be addressed to the Director (Publications), BIS.

Review of Indian Standards

Amendments are issued to standards as the need arises on the basis of comments. Standards are also reviewed periodically; a standard along with amendments is reaffirmed when such review indicates that no changes are needed; if the review indicates that changes are needed, it is taken up for revision. Users of Indian Standards should ascertain that they are in possession of the latest amendments or edition by referring to the latest issue of 'BIS Catalogue' and 'Standards: Monthly Additions'.

This Indian Standard has been developed from Doc No.: CHD 06 (1720).

Amendments Issued Since Publication

Amendment No.	Date of Issue	Text Affected

BUREAU OF INDIAN STANDARDS

Headquarters:

Manak Bhavan, 9 Bahadur Shah Zafar Marg, New Delhi 110002

Telephones: 2323 0131, 2323 3375, 2323 9402

Website: www.bis.org.in

Regional Offices:

Telephones

Central	: Manak Bhavan, 9 Bahadur Shah Zafar Marg NEW DELHI 110002	{ 2323 7617 2323 3841
Eastern	: 1/14, C.I.T. Scheme VII M, V.I.P. Road, Kankurgachi KOLKATA 700054	{ 2337 8499, 2337 8561 2337 8626, 2337 9120
Northern	: SCO 335-336, Sector 34-A, CHANDIGARH 160022	{ 260 3843 260 9285
Southern	: C.I.T. Campus, IV Cross Road, CHENNAI 600113	{ 2254 1216, 2254 1442 2254 2519, 2254 2315
Western	: Manakalaya, E9 MIDC, Marol, Andheri (East) MUMBAI 400093	{ 2832 9295, 2832 7858 2832 7891, 2832 7892

Branches: AHMEDABAD. BANGALORE. BHOPAL. BHUBANESHWAR. COIMBATORE. DEHRADUN. FARIDABAD. GHAZIABAD. GUWAHATI. HYDERABAD. JAIPUR. KOCHI. LUCKNOW. NAGPUR. PARWANOO. PATNA. PUNE. RAJKOT. VISAKHAPATNAM.