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

Part 8:
Diffusion method

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

Partie 8: Méthode par diffusion

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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 6145-8 was prepared by Technical Committee ISO/TC 158, *Analysis of gases*.

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 syringe injection method*

— *Part 5: Capillary calibration devices*

— *Part 6: Critical orifices*

— *Part 7: Thermal mass-flow controllers*

— *Part 8: Diffusion method*

— *Part 9: Saturation method*

— *Part 10: Permeation method*

— *Part 11: Electrochemical generation*

Introduction

This part of ISO 6145 is one of a series of International Standards that present various dynamic volumetric methods used for the preparation of calibration gas mixtures. In the lower part of the mole fraction range considered, it is difficult to prepare and maintain gas mixtures – for example of certain organic or reactive components – in cylinders. This dynamic method has the advantage of a practically unlimited supply of calibration component, whereby adsorption effects can be reduced or even eliminated.

If the complementary gas flow is measured as a gas mass flow, the preparation of calibration gas mixtures using diffusion is a dynamic-gravimetric method which gives contents in mole fractions. Principles for the measurement of the complementary gas flow are given in ISO 6145-1.

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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).
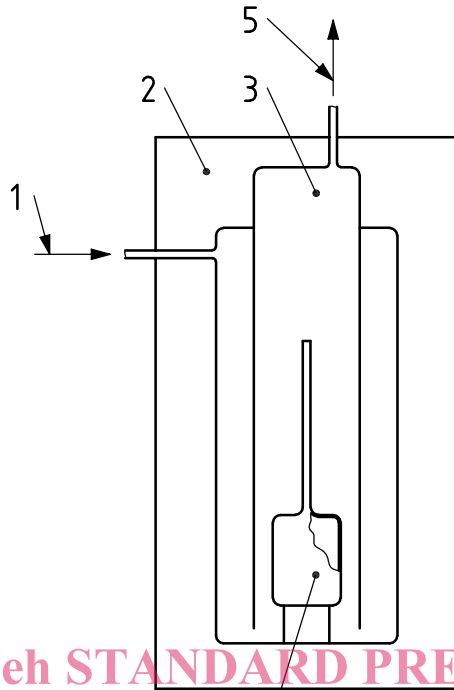
Key

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.

$$q_V(\mathsf{A}) = \frac{A}{L} D \cdot \ln\left(\frac{p}{p - p_\mathsf{v}}\right) \tag{1}$$

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

$$\overline{q}_m(\mathrm{A}) = \frac{\Delta m}{\Delta t}\frac{\overline{p}}{p_0} \tag{2}$$

where

$\overline{q}_m(\mathrm{A})$ 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;

$\overline{p}$ 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 $q_m(\mathrm{A})$ by applying a reverse correction for actual pressure

$$q_m(\mathrm{A}) = \overline{q}_m(\mathrm{A})\frac{p_0}{p} \tag{3}$$

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.