International Standard ISO 6349

Gas analysis — Preparation of calibration gas mixtures — Permeation method

Analyse des gaz — Préparation des mélanges de gaz pour étalonnage — Méthode par perméation

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FOREWORD

ISO (the International Organization for Standardization) is a worldwide federation of national standards institutes (ISO member bodies). The work of developing International Standards is carried out through ISO technical committees. Every member body interested in a subject for which a technical committee has been set up 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.

Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council.

International Standard ISO 6349 was developed by Technical Committee ISO/TC 158, *Analysis of gases*, and was circulated to the member bodies in June 1978.

It has been approved by the member bodies of the following countries :

Belgium	Korea, Rep. of	United Kingdom
Bulgaria	Mexico	USA
Czechoslovakia	Netherlands	USSR
France	Philippines	Yugoslavia
Germany, F.R.	South Africa, Rep. of	
Ireland	Turkey	

No member body expressed disapproval of the document.

Gas analysis — Preparation of calibration gas mixtures — Permeation method

1 SCOPE AND FIELD OF APPLICATION

This International Standard describes the principles of the permeation method, which is a continuous dynamic method, for the preparation of calibration gas mixtures in which the components that it is desired to use generally have a concentration between 10^{-9} and 10^{-5} (by volume), with an achievable accuracy of 2 % of the concentration of the component. (In practice, concentrations may also be expressed in micrograms per cubic metre). In the concentration range considered, it is difficult to maintain the gas mixtures in a stable state; it is therefore necessary to prepare the calibration gas just prior to its use, and to transfer it by the shortest path possible to the place where it is to be used.

2 PRINCIPLE

The principle of the method relies on the permeation of the component which is to be used (SO_2, NO_2, NH_3, etc.) through an appropriate membrane into a flow of carrier gas which constitutes the complementary gas of the mixture obtained. The constituent, in a pure state, is contained in a tube[1] (see clause 3), which is totally or partially swept at a known and controlled flow rate by the complementary gas, which is completely clean, purified and, in particular, free from any trace of the component, and thus becomes charged with molecules having diffused. The complementary gas shall be chosen so as to avoid any interaction with the materials constituting the permeation tube.

The diffusion rate of the substance through the membrane depends upon the substance itself, the nature, constitution and area of the membrane, and the temperature and differences between the partial pressure of the gas inside and outside the tube. These factors can be kept constant by proper operation of the tube.

In the present state of knowledge, no formula is available to describe this phenomenon exactly.

If the diffusion rate is maintained constant, it may be determined by simple weighings at convenient time intervals (methods other than weighing have been proposed in recent literature, mentioned in the bibliography, but are not dealt with in this International Standard). To allow this operation to be carried out, taking account of the various parameters affecting the diffusion rate, it is necessary that the following requirements be fulfilled for a given tube containing a known substance :

— the tube shall be maintained at a temperature as constant as possible between two weighings;

— the outside of the tube shall be permanently swept by the carrier gas in order to maintain the partial pressure of the constituent under consideration outside the tube at a negligible value;

— the gas pressure inside the tube shall be maintained constant between two weighings, i.e. either the substance shall be partly in the liquid phase or the quantity of the substance in the tube shall be large compared to the mass lost by permeation.

The concentration C of the calibration gas mixture so prepared is a function of the diffusion rate of the tube and the flow rate of the complementary gas. It is given by the formula

$$C = \frac{q_m}{q_V}$$

where

q_m is the permeation rate (mass flow rate) of the calibration component under given conditions;

q_V is the complementary gas flow rate (in appropriate units).

3 EXAMPLE OF APPLYING THE METHOD

3.1 Examples of permeation tubes (see figure 1)

The tube contains a liquid phase and a gaseous phase; the membrane through which the diffusion takes place may be in contact with the liquid phase only, or with the gaseous phase only, or with both. However, unless it has been ascertained that the phase in contact has no effect on the permeation rate, the tube shall be used with the phase in contact identical to that used for the determination of the permeation rate.

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1) The word "tube" is used whatever the shape of the vessel. It is also understood (except in 3.3.4) to include the tube contents.

3.2 Examples of permeation apparatus (see figures 2 and 3)

It is recommended that, before use, the permeation tube be kept in an anhydrous atmosphere, in an airtight container in a cold place (at approximately 5 °C, for example in the bottom of a refrigerator) in order to reduce the diffusion rate, and hence the substance loss, to a minimum and to avoid any condensation on the tube.

During use, the tube is placed in a flow system which enables the exterior of the permeation membrane to be swept by the carrier gas (for example pure nitrogen from a cylinder). The whole device is placed in a temperature controlled bath (gaseous or, preferably, liquid).

The constant flow rate of the carrier gas may be achieved by a controlling system and monitored by a flowmeter. The value of the flow rate is determined by means of a gas meter.

The existence of an outlet for surplus gas enables the analyser to take the gas flow rate necessary for its calibration or control.

For special applications, it is possible to place in the same temperature-controlled bath, several permeation tubes respectively filled with different substances, provided that any interaction risk is avoided.

3.3 Operating precautions

3.3.1 Use of the permeation tube

When first used, it is necessary to allow the system to reach a state of equilibrium over approximately 48 h before carrying out the first weighing, in order to ensure that the permeation rate is well stabilized.

It is essential to control the temperature of the bath to within 0,1 K because the tube diffusion rate may for example double for an increase in temperature of approximately 7 K.

NOTE — Under certain circumstances, in which the diffusing gas is highly soluble in the membrane polymer, an increase in temperature may reduce the permeation rate.

The time interval between two weighings (of the order of several days) depends upon the required accuracy. It is recommended that the tube be weighed regularly (especially towards the end of its life) in order to ensure that its diffusion rate is constant. Weighing intervals shall be chosen so that the measured mass loss is normally at least 10 mg.

The weighing should be made preferably under the same environmental conditions in which the tube is operated. Thermal shocks and adsorption of water during the weighing procedure must be avoided.

During the period of use, it is preferable to leave the tube always at the same temperature, principally to avoid the delay, sometimes very lengthy, which is necessary to restore equilibrium. Thermal shocks should be avoided as far as possible.

3.3.2 Sweeping of the tube by the carrier gas

According to the permeation tubes used, it is sometimes desirable to use perfectly pure and anhydrous carrier gases.

Before it reaches the tube, it is essential that the temperature of the carrier gas be controlled at the chosen value; any system which enables the carrier gas to remain in the temperature-controlled bath for a sufficient period of time is satisfactory (beads, baffles, etc.) (see figure 2).

The dilution system may have one stage only (see figure 2) or two stages; in this latter case, the tube can always be swept at a constant flow rate.

In order to alter the concentration of the mixture obtained, it is recommended that this be achieved by adjustment of the carrier gas flow rate (avoiding any change of the tube diffusion rate by changing the temperature); in this case, equilibrium is rapidly obtained.

3.3.3 Choice of temperature

The choice of temperature depends on the tube characteristics and the permeation rate required; in practice, temperature control should be carried out as follows :

a) If control is effected only by heating, the temperature shall be sufficiently high for the ambient temperature variations not to affect it, for example 40 °C.

b) If control is also effected by cooling, a temperature closer to, or even below, ambient temperature may be suitable.

The choice of a temperature close to the ambient temperature has two advantages :

1) significant variations in the tube temperature are avoided during weighings,

2) the temperature of the carrier gas may be more easily controlled.

3.3.4 Choice of materials

3.3.4.1 PERMEATION TUBE

A number of polymers having sufficient chemical and mechanical resistance may be used for the permeation membrane. In general, polytetrafluoroethylene (PTFE), polyethylene, polypropylene or a copolymer of tetrafluoroethylene and hexafluoropropylene (FEP) is used.

Account should be taken of the variations of the material characteristics with change of temperature.

3.3.4.2 PERMEATION APPARATUS

The materials used for the permeation apparatus shall be chosen so as to avoid any alteration of the concentration of the calibration component by sorption (chemical or physical). The smaller the desired final concentration, the greater is the effect of the adsorption phenomena until establishment of a constant concentration.

If possible, glass shall be used. Flexible tube materials and metals shall be chosen in relation to the constituent for calibration, especially with regard to the transfer of the gas between the permeation apparatus and the analyser.[1]

3.3.5 *Choice of permeating substances*

The permeating substances shall be of the highest purity in order to avoid any effect of impurities on the permeation rate; if this is not possible, the nature and quantities of the impurities shall be known and allowance made for their effect.

4 ACCURACY

4.1 Sources of error

A number of fundamental sources of error may be cited :

— the known laws apply to quasi-ideal conditions, which implies in particular a perfect thermodynamic equilibrium of the fluids contained in the tube;

— the phenomenon of back-diffusion tends to decrease the diffusion;

— the gases used are not ideal;

— certain substances may polymerize or combine (vinyl chloride is an example of a material which may polymerize).

This explains why it is stated in clause 2 that no formula is available at present to describe the phenomenon exactly.

4.2 Calculation of concentration

The following example is for a calibration gas for the determination of sulphur dioxide (SO_2).

If

q_m is the SO_2 diffusion rate, in micrograms per minute, and

q_V is the sweeping flow rate, in cubic metres per minute,

then the concentration C, in micrograms per cubic meter, of SO_2 in the calibration gas is given by the formula

$$C = \frac{q_m}{q_V}$$

To express the concentration C as a volume ratio, it is necessary to take account of the molar volume of SO_2, and the relationship is therefore

$$C = 0{,}38 \times 10^{-9} \frac{q_m}{q_V}$$

In the case of an analyser with a flow rate of 18 l/h, and with a permeation tube having an SO_2 diffusion rate equal to 1 µg/min, this analyser may be calibrated up to a concentration of approximately 10^{-6} in volume ratio.

4.3 Diffusion rate

For a given tube, knowledge of the average diffusion rate depends on the accuracy of the balance and the time interval between two weighings (the error arising in the duration of the weighing is negligible).

Consider the example of a tube with a diffusion rate of 1 µg/min and where the time interval between two weighings is equal to 10 000 min (approximately 7 days). The tube mass loss will therefore be equal to 10 mg. If the balance accuracy is $\pm$ 0,1 mg, the error due to the balance (for this time interval) will be 2 %.

The effect of the accuracy of temperature control on the short-term constancy of the diffusion rate can only be vaguely estimated : for example, for the same tube with the diffusion rate of 1 µg/min, suppose that this rate doubles for a temperature increase of 7 K; if the temperature control is made at $\pm$ 0,1 K, it implies an error of approximately 1 %.

The instantaneous diffusion rate is therefore in this case determined within 3 % (2 % + 1 %) as a maximum.

4.4 Complementary gas flow rate

The accuracy of this flow rate may be estimated at about 1 to 2 % according to the devices used. The error is smaller in the case of a one-stage dilution.

4.5 Accuracy

The accuracy obtained depends on the knowledge of two parameters : the diffusion rate of the permeation tube and the flow rate of the complementary gas.

For the example given above, the accuracy on the instantaneous concentration may be evaluated as $\pm$ 5 % (3 % found in 4.3 and 2 % assessed in 4.4).

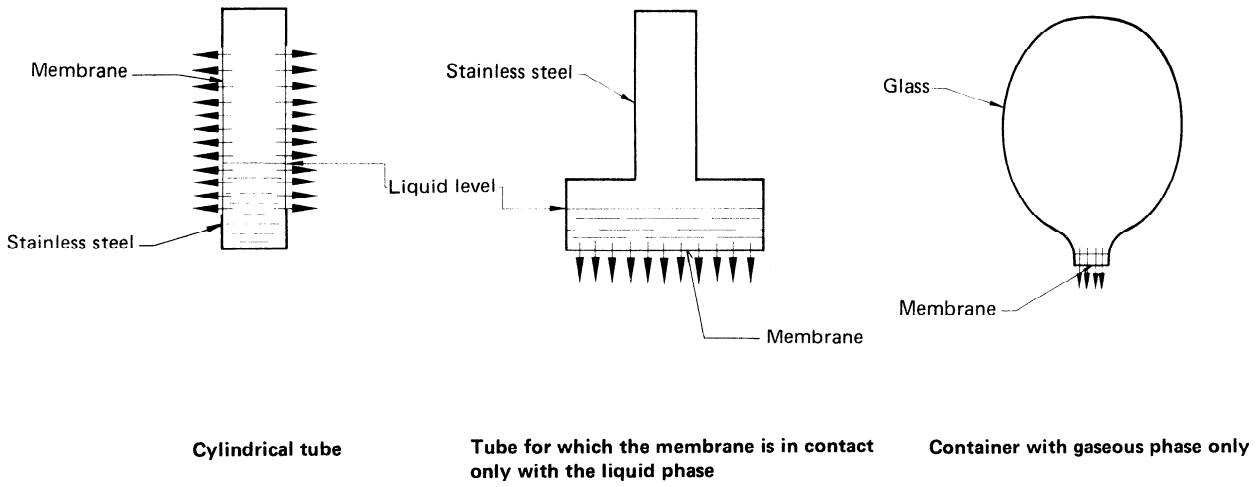1) An International Standard for sampling and transfer lines is in preparation.

FIGURE 1 — Examples of permeation tubes
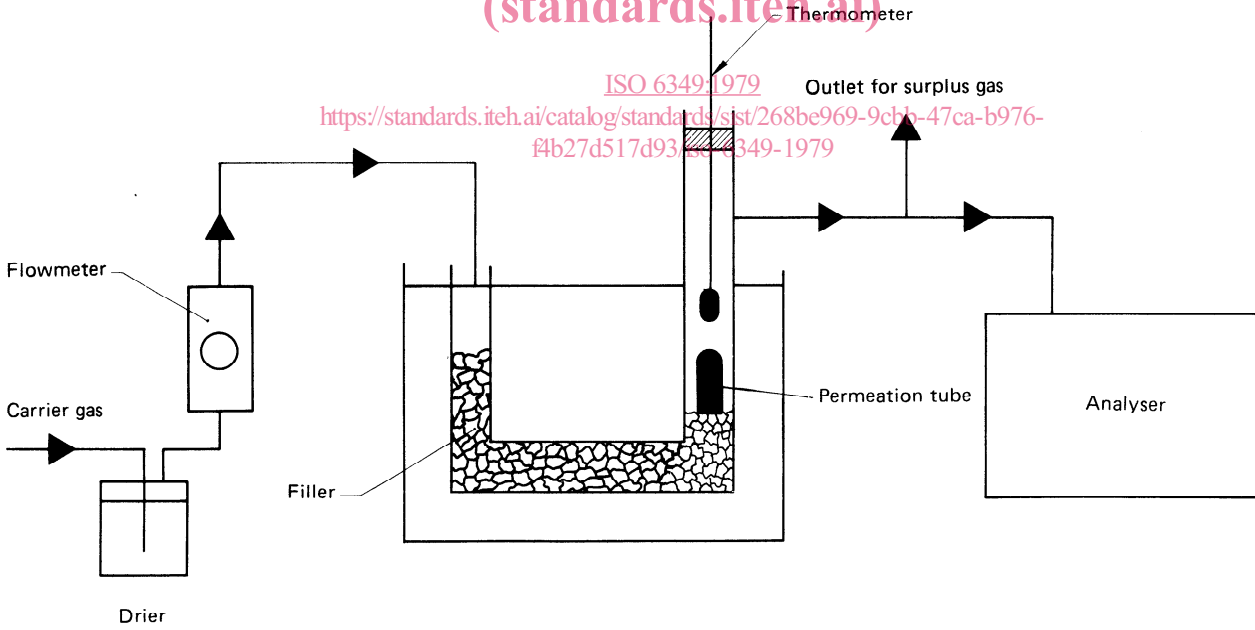
FIGURE 2 — Example of a permeation apparatus
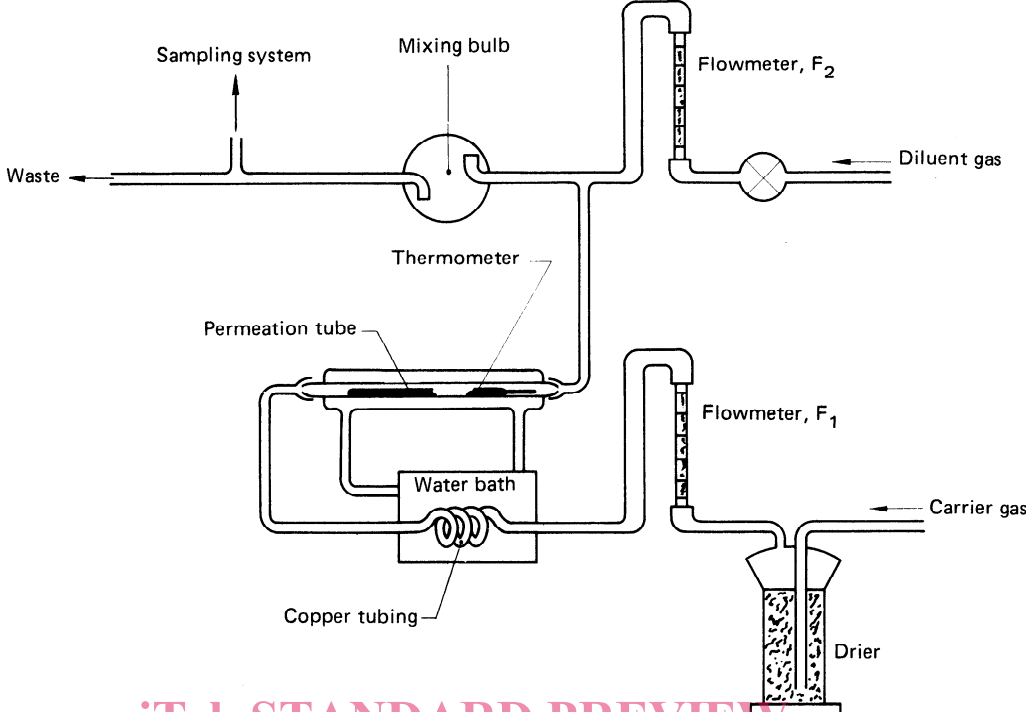
FIGURE 3 — Further example of permeation apparatus

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BIBLIOGRAPHY

This bibliography gives, for reference purposes only, a few literature references dealing with permeation tubes. The list is not exhaustive and does not form part of this International Standard.

Volumetric displacement procedure

SALTZMAN, B.E., FELDMANN, C.R., and O' KEEFFE, A.E., *Environ. Sci. Technol.* **3**, 1275 (1969).

SALTZMAN, B.E., BURG, W.R., and RAMASWAMY, G., *Environ. Sci. Technol.* **5**, 1121 (1971).

Differential pressure measurement procedure

MC KINLEY, J.J., *A calibration system for trace analyzers,* 16th National Symposium, Instrument Society of America, Pittsburg, Pa, (May 1970).

DIETZ, R.N., COTE, E.A., and SMITH, J.D., *Anal. Chem.* **46**, No. 2, 315 (1974).