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

**Part 9:
Saturation method**

*Analyse des gaz — Préparation des mélanges de gaz pour étalonnage
à l'aide de méthodes volumétriques dynamiques —
Partie 9. Méthode par saturation*

ISO 6145-9:2009

<https://standards.iteh.ai/catalog/standards/sist/e326283a-e2ef-4ed5-9702-ade580adb5a6/iso-6145-9-2009>



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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 6145-9 was prepared by Technical Committee ISO/TC 158, *Analysis of gases*.

This second edition cancels and replaces the first edition (ISO 6145-9:2001) and ISO 6145-9:2001/Cor 1:2002, which have been technically revised. As Annex B is purely informative, and included as a guide to the methods of calculation of the volume fractions, the numerical examples which are presented in it have been carried forward verbatim from ISO 6145-9:2001 to this updated standard. Although some references have been updated in the present bibliography to the most recent editions, the tables in Annex A have also been reproduced verbatim and are based on data from the earlier editions of the relevant publications (References [3], [4] and [7] to [10] in the Bibliography). In the application of this updated standard, it is firmly recommended that the more recent versions of the publications be consulted, even though it is anticipated that any amendments to the earlier versions will be minor ones. For example, the 15th edition of Reference [4] was published in 1999 and the 2nd edition of Reference [8] was published in 1984.

ISO 6145-9 also cancels and replaces ISO 6147, which has the same subject. In comparison with ISO 6147, ISO 6145-9 gives more detailed information on the use of the apparatus and a clause on the uncertainty of measurement has been added. 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.

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*

ISO 6145-3, entitled *Periodic injections into a flowing gas stream*, has been withdrawn.

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

Part 9: Saturation method

1 Scope

This part of ISO 6145 is one of a series of International Standards dealing with various dynamic volumetric methods used for the preparation of calibration gas mixtures. This part specifies a method for continuous production of calibration gas mixtures containing one or more readily condensable components. 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 $\pm 1\%$, can be obtained using this method.

Unlike the methods presented in the other parts of ISO 6145, the method described in this part does not require accurate measurement of flow rates since flow rates do not appear in the equations for calculation of the volume fraction.

Readily condensable gases and vapours commonly become adsorbed on surfaces, and it is therefore difficult to prepare stable calibration gas mixtures of accurately known composition, containing such components, by means of static methods. In addition, these calibration gas mixtures cannot be maintained under a pressure near the saturation limit without the occurrence of condensation. The saturation method can be employed to prepare mixtures of this type.

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

ISO 7504, *Gas analysis — Vocabulary*

ISO 16664, *Gas analysis — Handling of calibration gases and gas mixtures — Guidelines*

3 Terms and definitions

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

4 Principle

The vapour pressure of a pure substance in equilibrium with its condensed phase depends on the temperature only. At pressures close to the prevailing barometric pressure, and in the absence of significant

gas phase interactions, such as occur with hydrocarbon mixtures, the volume fraction of the constituent can be calculated from knowledge of the temperature and pressure of the system.

If a complementary gas is simply brought into contact with the condensed phase of a volatile component at a given temperature with no external agency, the equilibrium (saturation) condition is reached quite slowly. In order to accelerate the process, the complementary gas is passed through the condensed phase at an elevated temperature, T_1 , following which the gas mixture thus obtained is cooled to a lower temperature, T_2 , which is below the dew-point. To ensure that saturation is attained, the difference in temperature ($T_1 - T_2$) should be at least 5 K.

The volume fraction φ_x of the constituent x is, to a good approximation, equal to the ratio of the vapour pressure p_x of the calibration component at temperature T_2 to the total pressure p of the gas mixture at the same temperature in the condenser:

$$\varphi_x = \frac{p_x}{p} \tag{1}$$

The value of the relevant partial pressure (vapour pressure) of the constituent at temperature T_2 can be found in tables or diagrams in References [1] to [4] in the Bibliography.

5 Equipment

5.1 Set up

An overview of the equipment that shall be used for producing calibration gas mixtures by the saturation method is shown in Figure 1.

A continuous flow of complementary gas from the supply (item 1 in Figure 1) is passed firstly through a filter (item 2 in Figure 2) containing quartz fibre material to remove suspended particles.

NOTE Items 11 and 12 in Figure 1 are required only when a recycling system of calibration gas is employed.

The procedure specified in 5.2 to 5.8 shall be followed for the assembly and use of the equipment in order to minimize uncertainty in the volume fraction of the components.

5.2 Gas preparation

Clean and dry the complementary gas before it is introduced into the saturator.

5.3 Compatibility of the apparatus

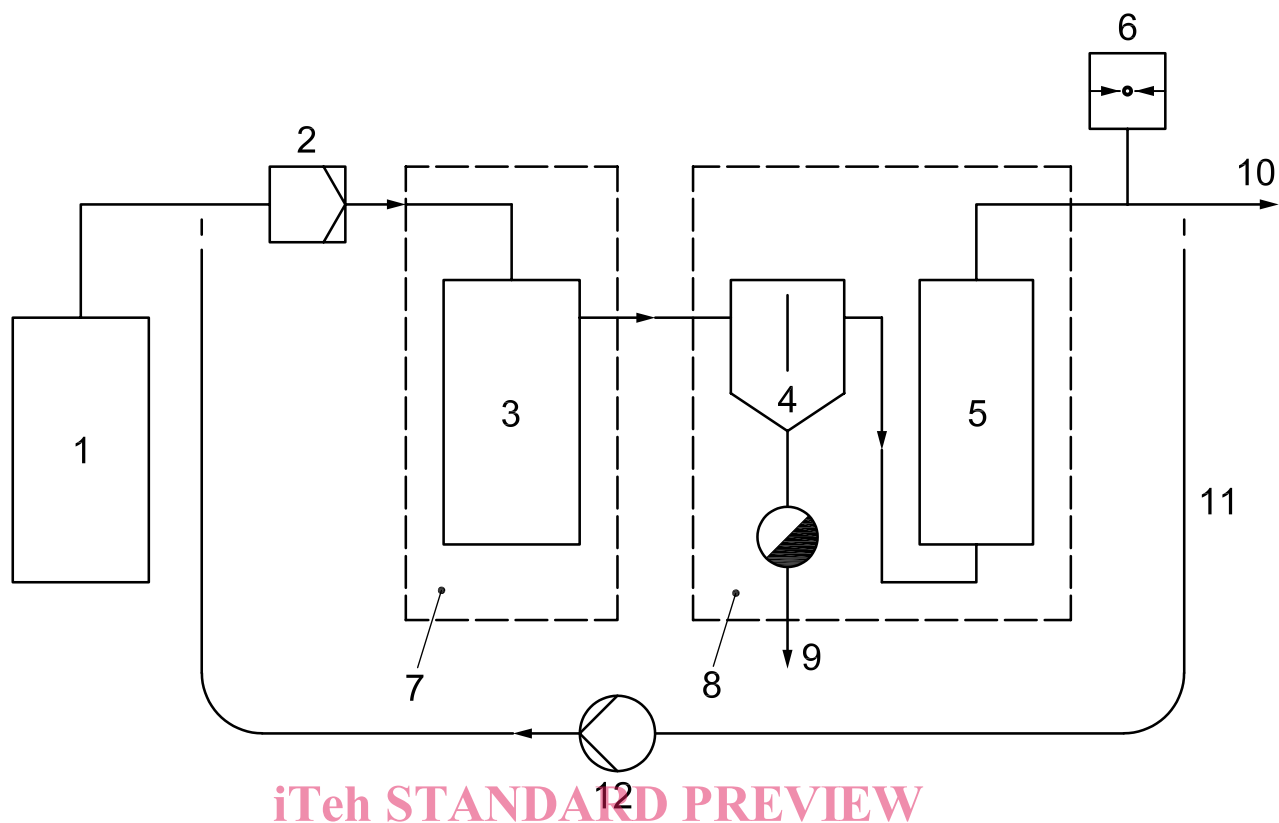
In the apparatus, use components, particularly sample lines, constructed exclusively in materials which are known to exhibit negligible interaction with the components of the calibration gas mixture. Avoid materials which may be permeable to the component gases and/or the gas mixture, or upon which adsorption could take place. If in doubt, the compatibility of sample lines shall be checked before they are used for the preparation of the sample gas mixture.

5.4 Selection of the apparatus

Use sample lines of which the cross-sectional areas are of sufficient magnitude to ensure that the pressure drop resulting from the resistance to flow remains negligibly small.

5.5 Pressure measurement

Measure the total pressure at the outlet of the pressure-equalizing vessel.



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Key

- | | | | |
|---|--|----|--|
| 1 | supply of complementary gas | 7 | constant-temperature control (T_1) |
| 2 | filter for suspended particles | 8 | constant-temperature control (T_2) |
| 3 | saturator | 9 | condensate outlet |
| 4 | condenser, constructed of a material that is of adequate thermal conductivity (e.g. copper or stainless steel) | 10 | calibration-gas-mixture outlet |
| 5 | pressure-equalizing vessel with baffles | 11 | circulation system |
| 6 | pressure gauge | 12 | circulation pump |

Figure 1 — Schema of equipment for producing calibration gas mixtures by the saturation method

5.6 Temperature control

This shall comply with the specification for transfer of calibration gas mixtures in ISO 16664.

Ensure that the temperature of the gas line is sufficiently higher than T_2 so as to prevent condensation; when necessary, a heated connecting line shall be provided.

5.7 Instrumentation

Use exclusively instruments of high accuracy for measurement: thermometers with an error of measurement less than $\pm 0,05$ K, and pressure-measuring devices with an error of measurement less than ± 1 hPa [1mbar]¹⁾.

1) 1 bar = 10^5 N/m² = 0,1 MPa

5.8 Purity

Use exclusively components of purity $\geq 99,99\%$, because certain impurities, if present, affect the vapour pressure.

NOTE It is possible that components of such purity cannot be acquired. If it is desired to apply the method in such cases, attention is drawn to 8.2.5 of ISO 6144:2003^[5] which outlines the additional factors to be considered relative to the estimate of the expanded relative uncertainty.

6 Procedure

6.1 Installation

Arrange the cooling surfaces so as to obtain identical temperatures of the gas and the condenser at the condensate outlet. Place the pressure-equalizing vessel with baffles after the condenser in order to remove aerosols from the gas stream. Maintain the pressure-equalizing vessel at the same temperature as the condenser. Ensure that the temperature of the cooling medium in the vessel, holding the condenser and the pressure-equalizing vessel, remains constant by means of suitable cooling and heating elements via a control circuit.

In addition to the temperature T_2 , maintain the pressure, p , of the gas mixture constant in the condenser and display it. Collect the condensate produced in the condenser in a condensate receiver or remove it continuously by pumping.

6.2 Operation of a direct system

Pass the complementary gas into the calibration component in its liquid phase in the saturator (item 3 in Figure 1) at temperature T_1 . Ensure that the condensation temperature of the calibration component in the flow of complementary gas is higher than the temperature T_2 of the subsequent condenser (item 4 in Figure 1). Cool the gas mixture in the condenser until some of the calibration component condenses. The condensate is discharged through the condensate outlet (item 9 in Figure 1). The calibration gas mixture from the outlet of the condenser passes through a pressure-equalizing vessel (item 5 in Figure 1) in which any liquid droplets which may still be present are separated. Both the condenser (item 4 in Figure 1) and pressure-equalizing vessel (item 5 in Figure 1) are located in a thermostatically controlled container (item 8 in Figure 1) at temperature T_2 . The pressure of the calibration gas mixture emerging at the sampling point (item 10 in Figure 1) is measured by the pressure gauge (item 6 in Figure 1).

6.3 Operation of a closed circulation system

A closed-loop circulation system may also be used. This system operates continuously and, when in use, will eliminate any lengthy delays in the procedures required to attain equilibrium conditions. The calibration gas is circulated around an additional loop (item 11 in Figure 1) by means of a pump (item 12 in Figure 1).

After the gas has been passed around the flow path several times in order to establish equilibrium, the calibration gas mixture can be extracted at the sampling point (item 10 in Figure 1). Gas extracted from the system shall be carefully replaced by introduction of fresh complementary gas from the supply (item 1 in Figure 1), ensuring that there are no pressure changes.

NOTE It is possible to check, by observing the condensate flow, whether saturation is established in the condenser. Since the volume fraction of the gaseous to condensed phases is approximately 1000:1, and only a fraction of the components which pass into the complementary gas is separated out in the condenser as condensate, the volume flow rate through the outlet (item 9 in Figure 1) is very low. A physical dew-point measurement on the outlet gas can be carried out to confirm that equilibrium has been achieved.

7 Uncertainty of measurement

The relative uncertainty depends on the total pressure of the gas in the condenser and on the saturated vapour pressure. Annex A shall be followed for further calculations with vapour pressure data. Whereas the total pressure is known with satisfactory uncertainty, the uncertainty of the vapour pressure value depends on

- the uncertainty of condensate temperature measurement,
- the temperature control (i.e. $\Delta T < 0,05$ K can be measured),
- the uncertainty of the vapour pressure data used, and
- the purity of each component.

The relative expanded uncertainty in the volume fraction of calibration component x shall be estimated with the aid of the determinable individual uncertainties by means of Equation (2).

The relative standard uncertainties of measurement are combined in a square-root sum-of-squares manner to form the overall relative expanded uncertainty as follows:

$$\frac{U(\varphi_x)}{\varphi_x} = 2 \sqrt{\left\{ \left[\frac{u(p_x)}{p_x} \right]_{T_2} \right\}^2 + \left[\frac{u(p)}{p} \right]^2 + \left\{ \left[\frac{T_2}{p_x} \left(\frac{dp_x}{dT} \right)_{T_2} - 1 \right] \times \left[\frac{u(T)}{T} \right]_{T_2} \right\}^2} \quad (2)$$

where

$\frac{U(\varphi_x)}{\varphi_x}$ is the relative expanded uncertainty in the volume fraction of the calibration component;

$\left[\frac{u(p_x)}{p_x} \right]_{T_2}$ is the relative standard uncertainty in the vapour pressure curve at working point T_2 ;

$\frac{u(p)}{p}$ is the relative standard uncertainty in the measurement of the total pressure;

$\left(\frac{dp_x}{dT} \right)_{T_2}$ is the increase in the vapour pressure curve at working point T_2 ;

$\left[\frac{u(T)}{T} \right]_{T_2}$ is the relative standard uncertainty in the temperature measurement of T_2 .

The coverage factor “2” has been applied in order to give a coverage probability of approximately 95 % in the case of normal distribution.

NOTE 1 The method of derivation of the formula for expression of the relative combined standard uncertainty $U(\varphi_x/\varphi_x)$ is presented in Annex C of ISO 6145-7:2009^[6].

NOTE 2 Equation (1) is an approximation and can therefore constitute another source of uncertainty resulting from non-ideal behaviour of gases and vapours. This should be borne in mind in the assessment of the uncertainty in the volume fractions of calibration gas mixtures prepared by this method, particularly because it is used for mixtures in which the calibration component will normally be readily condensible and therefore substantially non-ideal. It is not possible to quantify, in general, this contribution to the uncertainty budget but it is considered to be small enough to be negligible in proportion to the other sources of uncertainty. Experimental work reported in the literature has shown that, for some mixtures, the deviations from additivity of pressures are less than those of volumes, but for others the opposite is true.