INTERNATIONAL STANDARD

ISO 6145-4

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

Part 4: Continuous syringe injection method

Analyse des gaz — Préparation des mélanges de gaz pour étalonnage à l'aide de méthodes volumétriques dynamiques —
Partie 4: Méthode continue par seringue d'injection

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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 6145-4 was prepared by Technical Committee ISO/TC 158, *Analysis of gases*.

This second edition cancels and replaces the first edition (ISO 6145-4:1986), which has been technically revised.

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ISO 6145-3, entitled *Periodic injections into a flowing gas*, has been withdrawn.

Introduction

This part of ISO 6145 is one of a series of standards dealing with various dynamic volumetric methods used for the preparation of calibration gas mixtures.

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

Part 4: Continuous syringe injection method

1 Scope

This part of ISO 6145 specifies a method for continuous production of calibration gas mixtures, containing two or more components, from pure gases or other gas mixtures by continuous injection of the calibration component(s) into a complementary gas stream by means of a syringe.

If pre-mixed gases are used instead of pure gases (see Annex A), much lower volume fractions can be obtained. The volume flow rates, from which the volume fractions are determined, can be calculated from the individual flow rates and can be independently measured by a suitable method given in ISO 6145-1.

The merits of the method are that a substantial quantity of the gas mixture can be prepared on a continuous basis and that multi-component mixtures can be prepared almost as readily as binary mixtures if the appropriate number of syringes is utilized, or if the syringe already contains a multi-component mixture of known composition. This method also provides a convenient means for increasing the volume fraction of the calibration component in the mixture in small steps. It is therefore a useful method for evaluation of other characteristics of gas analysers, such as minimum detection limit and dead zone, as well as accuracy. The relative expanded uncertainty in the volume fraction obtainable for a binary mixture (at a coverage factor of 2) is 5 % and the range of applicability is 10^{-5} to 10^{-2}.

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 6145-1, *Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods — Part 1: Methods of calibration*

3 Principle

The calibration component, either in the gaseous or liquid phase, is displaced from a syringe, through a capillary which may be the needle of the syringe, the plunger of which is continuously driven by a suitable variable-speed motor, into a complementary gas stream.

The volume fraction, φ_A of calibration component, A, in a mixture with complementary gas, B, is given by Equation (1):

$$\varphi_A = q_A/(q_A + q_B) \tag{1}$$

where

q_A is the volume flow rate of the calibration component, A;

q_B is the volume flow rate of the complementary gas, B.

If the calibration component is injected in the liquid phase, the flow rate in the gaseous phase on evaporation is given by Equation (2):

$$q_A = (q_{A,\,\mathrm{l}} \times \rho_{A,\mathrm{l}}) / \rho_{A,\,\mathrm{g}} \qquad (2)$$

where

$q_{A,\,\mathrm{l}}$ is the volume flow rate of the injected liquid, in the same units as q_A;

$\rho_{A,\mathrm{l}}$ is the density of the liquid component at the temperature at which the mixture is prepared;

$\rho_{A,\,\mathrm{g}}$ is the density of the component in the gaseous phase, expressed in the same units and at the same temperature as $\rho_{A,\mathrm{l}}$.

Substitution of Equation (2) in Equation (1) then provides the value of φ_A in terms of the parameters listed above.

4 Application to preparation of gas mixtures

4.1 Description of the experimental procedure

4.1.1 Apparatus

Schematic diagrams of examples of apparatus for preparation of binary mixtures are shown in Annex B; Figure B.1 presents the apparatus for filling a syringe with a gaseous calibration component and Figure B.2 shows a mixing system for preparation of the calibration gas mixture.

4.1.2 Selection and calibration of syringe for the calibration component

The flow rate of the calibration component is determined by parallel selection of the cross-sectional area of the syringe barrel and the linear velocity of the plunger. Sometimes, for preparation of a mixture of given volume fraction of the calibration component, it may be preferable to use a syringe of larger cross-section (larger capacity) in combination with a lower plunger velocity, and in other cases a smaller cross-section with higher plunger velocity may provide the better combination (refer for practical hints to Annex C).

Select a suitable combination of linear speed of the syringe drive mechanism and metering syringe of volume appropriate to the volume fraction, and the uncertainty in that volume fraction, of the calibration gas mixture to be prepared.

In order to validate the uniformity of the syringe barrel, since this is a dynamic method, determine the volume of the gas or liquid delivered by the syringe at several graduation marks, and at the temperature at which the gas mixture is prepared. It is necessary, therefore, to allow time for the syringe to return to ambient temperature after it has been warmed, for example by handling, before any measurements are made at any stage. This volume calibration shall be derived from traceable mass measurements of a suitable liquid of known density in the syringe. Since the calibration is to be carried out at several points, i.e. with the syringe partially filled, precautions shall be taken to ensure that the meniscus of the liquid is horizontal when observations of its position are made.

An example of the methodology is presented in Annex C.

4.1.3 Calibration of the syringe driver

Calibrate the syringe driver at the temperature at which the gas mixture is prepared, and against reference equipment which is traceable to international length and time standards. A recommended method for calibration against a digital micrometer and a digital timer is also presented in Annex C.

4.1.4 Preparation of the calibration gas mixture

When the calibration component is in the gaseous phase apparatus, an example of which is shown in Figure B.1, for evacuating, purging and filling the reservoir and filling the syringe shall be used. The procedure is then as follows.

a) Close the shut-off valve on the cylinder of calibration component.

b) Evacuate the entire apparatus until the pressure has been reduced to a value which is sufficiently low, such that any residual gas in the reservoir makes no significant contribution to the volume fraction and has no effect on the stability of the final calibration gas mixture.

   A residual pressure of approximately 100 Pa (1×10^{-3} bar) has been found to be suitable. However, the ultimate vacuum required will depend in practice on the nature and composition of the final gas mixture. Due consideration should therefore be given to the partial pressure of the residual gas when the uncertainty in the volume fraction of the calibration gas mixture is evaluated.

c) Close the shut-off valve between the vacuum pump and the reservoir and fill the reservoir with the calibration component, to a pressure of approximately 110 kPa (1,1 bar). Re-evacuate and refill the reservoir in the same manner. In the final filling operation, adjust the pressure of the calibration component in the reservoir so that the over-pressure is sufficient for the syringe to be filled.

   Make appropriate provision to ensure that hazardous gaseous components are vented safely from the working area.

d) With the plunger pushed fully home, insert the needle of the empty metering syringe through the septum (see Figure B.1) into the reservoir. Raise and lower the plunger several times to ensure that the syringe is thoroughly flushed with the calibration component without any significant contamination.

e) Fill the syringe by fully withdrawing the plunger, then remove the syringe from the septum of the reservoir. With the needle retained in position on the syringe, set the plunger to the first graduation mark and connect the syringe to the mixing system (Figure B.2).

   NOTE A convenient way by which to make the connection is again to use a septum.

   In some cases, it is convenient to introduce the calibration component into the syringe in the liquid phase, then allow it to evaporate after it has issued from the nozzle. The filling procedure is then straightforward but precautions are still required to ensure that no significant amount of air or other contaminants are introduced into the syringe with the liquid.

f) Pass the complementary gas through a pressure regulator and a shut-off valve to a conditioning train, which may consist of a purifier and/or a humidifier and/or a heat exchange unit immersed in a thermostat bath as required. (It may be the case that none of these components is required.)

g) Pass the conditioned gas stream through a calibrated flow meter to a gas-mixing vessel, which may be of any suitable configuration, and at the input of which it meets the calibration component. Inject the calibration component by means of the syringe, filled as described in e), equipped with a mechanically-driven plunger and a variable speed motor, at the predetermined, constant speed.

4.2 Area of validity

The method is applicable to preparation of mixtures of non-reacting species, i.e. those which do not react with any material of construction of the flow path of the complementary gas or that of the calibration component being injected.

Particular care shall be exercised if the method is considered as a means of preparation of gaseous mixtures which contain components that form potentially explosive mixtures in air. Steps shall be taken to ensure that the

apparatus is safe, for example by means of in-line flame arrestors in addition to the items mentioned in 4.1 and listed in Figure B.2.

As is the case for the other dynamic mixing methods presented in ISO 6145, the effectiveness of the mixing system to provide a homogeneous gas mixture shall be checked; it is not satisfactory to rely solely upon the ratio of flow rates as the basis for expression of the gas composition, unless the method has been validated for the gas mixture which is required.

4.3 Operating conditions

The general conditions common to all dynamic techniques of preparation shall be observed. Give careful consideration to materials used in construction of the entire flow system. Use only materials which are of low porosity and which are non-adsorbing. The pipe work shall be clean and all unions secure.

Any flow metering method may be used for the complementary gas provided that the range is appropriate and the materials of construction are compatible with the mixture to be prepared. The complementary gas shall, in any case, be free from particulates. This is especially important if the flow is measured by means of a variable-area flowmeter, where there is no restriction between the float and the interior of the wall of the tube.

The capillary or syringe needle through which the calibration component is delivered shall be of length and cross-section such that there is no measurable backpressure within the syringe at the fastest discharge rate for which it is to be used. This requirement on dimensions applies equally to other parts of the flow paths so that no pressure gradients are caused.

All parts of the apparatus shall be maintained at a uniform temperature.

Practical hints for application of the method are presented in Annex C.

5 Expression of results

5.1 Volume fraction

The volume fraction of calibration component A in complementary gas B is given by Equation (1), or, if the calibration component is in the liquid state, by Equations (1) and (2).

The volume fraction is determined with reference to the methods of calibration described in ISO 6145-1. Due consideration shall be given to the uncertainty associated with the method which is selected.

5.2 Sources of uncertainty

The fundamental sources of uncertainty are in the flow rate of the complementary gas, the determination of the volume of the syringe and the rate of travel of the plunger in the syringe. The precautions presented under 4.3 shall be observed. Errors are introduced if there is backpressure in any part of the flow system, or if the gas streams are not maintained at uniform temperature throughout. In particular, the syringe, during the filling procedure, may have been at a temperature different from that of the rest of the apparatus; in all probability, it will have been warmed by hand-contact. To reiterate the precaution given in 4.1.2, it is necessary to ensure that the temperature of the syringe has returned to that of the rest of the apparatus before the gas mixture is prepared.

If the motor used to drive the syringe is of the variable-frequency stepper type, the flow of gas may be pulsed rather than being at steady, uniform flow. Attention is drawn to this here as a cautionary measure and means of avoidance of this effect are given in Annex C.

Another possible source of uncertainty is inefficient mixing of the calibration component and the complementary gas. The efficiency of mixing is checked by verification of the volume fraction by means of the comparison method (see ISO 6143). This also serves to check the efficiency of vaporization in case of liquid injection. Refer also to 5.3.

5.3 Uncertainty of volume fraction

The uncertainty in the volume fraction of the calibration component in the calibration mixture, at constant temperature and pressure, is estimated from the separate uncertainties in the flow rates of the calibration component and the complementary gas. It is necessary to take into account the sources of uncertainty given in 5.2 relative to individual flow rates.

The volume fraction of component A is given by Equation (1).

The relative expanded uncertainty in φ_A is then given by Equation (3):

$$\frac{U(\varphi_A)}{\varphi_A} = \left[\frac{2q_B}{q_A + q_B}\right] \left\{ \left[\frac{u(q_A)}{q_A}\right]^2 + \left[\frac{u(q_B)}{q_B}\right]^2 \right\}^{\frac{1}{2}} \tag{3}$$

NOTE The derivation of this formula is presented in Annex C of ISO 6145-7:2001[2].

The root mean square (rms) sum of the standard uncertainty contributions is multiplied by the coverage factor $k = 2$ to give a relative expanded uncertainty based on a level of confidence of approximately 95 %.

The standard uncertainty $u(q_B)$ in the flow rate of the complementary gas shall be obtained with reference to ISO 6145-1 for the selected method of flow calibration.

This estimate of the relative uncertainty in the composition rests entirely on the uncertainties in the measurements of flow rates. The other factor to be taken into account is the efficiency of mixing. To check the effectiveness of a mixing system to provide a homogeneous calibration gas mixture, mixtures shall be prepared by the method as described and the compositions shall be checked by the comparison method, specified in ISO 6143. This procedure also identifies bias from other sources and establishes traceability against standard mixtures.