SLOVENSKI STANDARD
SIST ISO 6145-4:1995

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Gas analysis -- Preparation of calibration gas mixtures -- Dynamic volumetric methods --
Part 4: Continuous injection method

Analyse des gaz -- Préparation des mélanges de gaz pour étalonnage -- Méthodes
volumétriques dynamiques -- Partie 4: Méthode d'injection continue

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International Standard ISO 6145/4

Gas analysis — Preparation of calibration gas mixtures — Dynamic volumetric methods — Part 4 : Continuous injection method

Analyse des gaz — Préparation des mélanges de gaz pour étalonnage — Méthodes volumétriques dynamiques — Partie 4: Méthode d'injection continue

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ISO 6145/4-1986 (E)

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.

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. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

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

Users should note that all International Standards undergo revision from time to time and that any reference made herein to any other International Standard implies its latest edition, unless otherwise stated.

INTERNATIONAL STANDARD ISO 6145/4-1986 (E)

Gas analysis — Preparation of calibration gas mixtures — Dynamic volumetric methods — Part 4 : Continuous injection method

1 Scope and field of application

This International Standard constitutes part 4 of ISO 6145, which deals with the various dynamic volumetric techniques used for the preparation of calibration gas mixtures.

It describes the production of calibration gas mixtures by continuous mixing of volume flows, whereby the precision of the concentration of each constituent in the range 10 000 to 10 ppm (V/V) amounts to about 5 %.

2 References

ISO 6143, *Gas analysis — Determination of composition of calibration gas mixtures — Comparison methods.*

ISO 6145/1, *Gas analysis — Preparation of calibration gas mixtures — Dynamic volumetric methods — Part 1: Methods of calibration.*

ISO 8221, *Gas analysis — Preparation of calibration gas mixtures containing a condensable component — Gravimetric method.* [1]

3 Principle

The minor component, either gas or liquid, is displaced from a mechanically driven syringe through a capillary tube into a continuously flowing complementary gas stream. After mixing, the mixture can be sampled at atmospheric pressure. Multi-component mixtures can be prepared by using several syringes simultaneously, or by discharging from one syringe a gas or liquid mixture of known composition.

The volume ratio C_A of the calibration component in the mixture is defined as

$$C_A = \frac{q_A}{q_A + q_B}$$

where

q_A is the gas volume flow rate of the injected component;

q_B is the volume flow rate of complementary gas, expressed in the same units as q_A.

In the case where the injected component is a liquid, the gas volume flow rate is given by

$$q_A = \frac{q_{LA} \cdot \varrho_{LA}}{\varrho_{GA}}$$

where

q_{LA} is the liquid volume flow rate of the injected calibration component, expressed in the same units as q_A;

ϱ_{LA} is the density of the liquid component at the temperature of operation;

ϱ_{GA} is the density of the vapour of the injected component at the temperature of operation, expressed in the same units as ϱ_{LA}.

The volume ratio is defined as

$$C_A = \frac{q_{LA} \cdot \varrho_{LA}}{q_{LA} \cdot \varrho_{LA} + q_B \cdot \varrho_{GA}}$$

At lower levels, it may be expressed with sufficient accuracy as

$$C_A = \frac{q_A}{q_B}$$

where the injected component is a gas, or as

$$C_A = \frac{q_{LA} \cdot \varrho_{LA}}{q_B \cdot \varrho_{GA}}$$

where the injected component is a liquid.

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1) In preparation.

1

4 Practical example

The figure shows a possible arrangement.

Complementary gas (1), cleaned (3) or humidified (4) as desired, passes through a coil of tubing (5) and a variable-area flowmeter (6) and then to the mixing train (12). Flow rate is adjusted by a regulator and valve assembly (2). The syringe (9) is connected by a length of capillary tubing (8), which may, for example, be a syringe needle, to the inlet of the mixing train. The syringe is filled with the minor component via a 3-way cock (7), and the plunger (10) is driven by a motor (11) at one of a range of speeds. The mixing tube consists of five 250 ml round vessels connected by short lengths of glass tubing of 30 mm inside diameter.

5 Operating conditions

5.1 Complementary gas flow rate

This can be varied over a wide range by appropriate choice of variable-area flowmeter. Any individual meter has a usable range of about 10:1 but should be chosen so that the float operates in the upper half of the scale. It is essential that the complementary gas be dust-free, in case particles lodge between the float and tube wall, distorting the readings. The regulator and valve assembly should give a flow rate which is sufficiently constant that its variations are not detectable as movements of the float.

5.2 Calibration component flow rate

This can be varied both by adjusting the motor, which usually has a range of set speeds, and by selecting the size of syringe. Gas-tight syringes are available from 10 µl to 50 ml capacity. The capillary or syringe needle should be chosen so that no significant back-pressure develops in the syringe at the highest rate of discharge.

Low levels of vapour from injection of a liquid component can be produced by using a syringe of microlitre capacity, or by diluting the component in a non-interfering solvent and using a syringe of larger capacity.

5.3 Mixing

The motor which drives the syringe plunger is commonly of the stepping type with variable frequency. It can therefore happen that at low rates of plunger travel the component is discharged in discrete quantities rather than continuously. If the time interval between plunger steps approaches the time constant of the mixing train, variations in composition will be seen at the outlet. This can be overcome by using a mixing train of greater volume, or by using a different syringe such that the same rate of discharge can be achieved but with a faster plunger movement (and hence a shorter time between refills of the syringe).

When the calibration component is a liquid, it is possible that the rate of evaporation into the complementary gas stream may be less than the rate of discharge. If a plug of glass wool at the tip of the injection needle does not provide a sufficiently large surface area for complete evaporation, reduce the volume flow rate of the liquid to the point where evaporation is complete and instantaneous.

5.4 Pressure and temperature

There should be no temperature difference between different parts of the apparatus. The tubing and connections are sized so that no significant back-pressure develops in the apparatus at normal levels of flow rate. Typical laboratory variations in ambient temperature and pressure are acceptable.

6 Experimental determination of concentration and examination of sources of error

6.1 General

This technique is calibrated by the comparison method (ISO 6143), by the tracer method (ISO 6145/1, 3.3.4) or by direct chemical analysis where appropriate.

The example given below involves calibration by comparison with a mixture prepared as specified in ISO 8221. Errors associated with this method of calibration are described and also those errors associated with the repeatability of the continuous injection technique.

6.2 Presentation of the method

The requirement is to produce a mixture of about 200 µmol/mol of n-hexane in nitrogen.

The total uncertainty on concentration is given by

$$\frac{\Delta C_A}{C_A} < \Delta Cal + \Delta f$$

where

ΔCal is the calibration uncertainty;

Δf is the precision or repeatability uncertainty.

The concentration is defined by the comparison method as

$$C_A = C_{AE} \cdot r$$

where

C_{AE} is the concentration of n-hexane in the gravimetric standard;

r is the ratio of analytical responses.

2

Hence

$$\Delta \text{Cal} = \frac{\Delta C_{AE}}{C_{AE}} + \frac{\Delta r}{r}$$

Considering those aspects of the technique which affect its repeatability, the concentration can be expressed as

$$C_A = \frac{q_{LA} \cdot \varrho_{LA}}{q_B \cdot \varrho_{GA}} \quad \text{(see clause 3)}$$

The flow rate of liquid component, q_{LA}, is expressed as

$$q_{LA} = \frac{V_s}{t}$$

where

V_s is the volume of the syringe, in cubic centimetres, between two graduation marks;

t is the time, in seconds, to discharge the contents between these marks.

The flow rate of complementary gas through a variable-area flowmeter is expressed as

$$q_B = K_1 \cdot h \left(\frac{\varrho_F - \varrho_{GB}}{\varrho_{GB}} \right)^{0,5}$$

where

K_1 is a constant which includes the coefficient of discharge through the annulus;

h is the height, in millimetres, of the float above the zero position;

ϱ_F is the density of the float, in grams per cubic centimetre;

ϱ_{GB} is the density of the complementary gas, expressed in the same units as ϱ_F.

Since $\varrho_F \gg \varrho_{GB}$, the equation simplifies to

$$q_B = \frac{K_2 \cdot h}{(\varrho_{GB})^{0,5}}$$

where K_2 is a constant which includes K_1 and the density of the float.

Hence

$$C_A = \frac{V_s \cdot \varrho_{LA} \cdot (\varrho_{GB})^{0,5}}{t \cdot \varrho_{GA} \cdot K_2 \cdot h}$$

Assuming that V_s, ϱ_{LA} and K_2 are not influenced by operating conditions so as to change between calibration and use, then

$$C_A = \frac{K_3 \cdot (\varrho_{GB})^{0,5}}{t \cdot \varrho_{GA} \cdot h}$$

Variations in ambient conditions (temperature, pressure) will affect the gas phase density of both components to the same extent, so that

$$C_A = \frac{K_4}{t \cdot h \cdot (\varrho_{GA})^{0,5}}$$

ϱ_{GA} varies directly with pressure, p, and inversely with temperature, T, so that the precision error is

$$\Delta f = \frac{\Delta t}{t} + \frac{\Delta h}{h} + \frac{1}{2} \cdot \frac{\Delta T}{T} + \frac{1}{2} \cdot \frac{\Delta p}{p}$$

NOTE — When the component delivered by syringe is a gas, then

$$C_A = \frac{q_A}{q_B} = \left(\frac{V_s}{t} \right) \left[\frac{(\varrho_{GB})^{0,5}}{K_2 \cdot h} \right]$$

The error terms are of the same order as for the case of a liquid, and so the precision error calculation is unchanged.

6.3 Numerical example

6.3.1 Calibration by the comparison method

A gravimetric standard is used, prepared by the method of ISO 8221.

Mass of hexane, $m_1 = 0,910$ g $\Delta m_1 = 2 \times 10^{-4}$ g
Mass of nitrogen, $m_2 = 1\,478$ g $\Delta m_2 = 0,1$ g
Purity of hexane, $b = 0,99$ $\Delta b = 0,001$

Relative uncertainty of the analytical method used in the pressure test cycles:

$$\frac{\Delta R}{R} = 0,005$$

Concentration of hexane

$$x_1 = \frac{\dfrac{0,910}{86}}{\dfrac{0,910}{86} + \dfrac{1\,478}{28}} \times 0,99 \times 10^6$$

$$= 198,4 \ \mu\text{mol/mol}$$

$$\frac{\Delta x_1}{x_1} = \frac{\Delta m_1}{m_1} (1 - x_1) + \frac{\Delta m_2}{m_2} (1 - x_1) + \frac{\Delta b}{b} + \frac{\Delta R}{R}$$

$$C_{AE} = 198,4 \qquad \frac{\Delta C_{AE}}{C_{AE}} = 0,006\,3$$

The comparison methods (ISO 6143) are used to compare the dynamic volumetric sample with the gravimetric standard using a gas chromatographic method.

Ratio of responses, $r = 1,055$

Standard deviation, $s = 0,004\,2$

Number of comparisons, $n = 3$

3

ISO 6145/4-1986 (E)

Hence

$$\frac{\Delta r}{r} = 0,01$$

Therefore, the concentration of hexane produced by the continuous injection technique is

$$C_A = C_{AE} \cdot r$$

$$= 209,3 \ \mu mol/mol$$

and the uncertainty on calibration is

$$\Delta Cal = \frac{\Delta C_{AE}}{C_{AE}} + \frac{\Delta r}{r}$$

$$= 0,016$$

6.3.2 Precision error

Between calibration and use, errors can be introduced from the following sources:

a) adjustment error of the complementary gas flow rate;

b) adjustment error of the calibration component flow rate;

c) effect of ambient temperature variations;

d) effect of ambient pressure variations.

It can be assumed that the precision with which the height, h, of the float in the variable-area flowmeter can be read, i.e. $\Delta h/h$, should not exceed 2×10^{-2}.

The motor driving the syringe containing the calibration component will be driven by reference to mains frequency, in which case the variations in $\Delta t/t$ should not exceed 5×10^{-3}.

Ambient temperature variations of 3 °C represent a value of $\Delta T/T$ of 1×10^{-2}.

Atmospheric pressure variations of 20 mbar represent a value of $\Delta p/p$ of 2×10^{-2}.

The overall precision error is therefore

$$\Delta f = \frac{\Delta t}{t} + \frac{\Delta h}{h} + \frac{1}{2} \cdot \frac{\Delta T}{T} + \frac{1}{2} \cdot \frac{\Delta p}{p}$$

$$= 4 \times 10^{-2}$$

4