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ISO 6145-7

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

Part 7: Thermal mass-flow controllers

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

Partie 7: Régulateurs thermiques de débit-masse

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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 3.

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 part of ISO 6145 may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

International Standard ISO 6145-7 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 injection method*

— *Part 5: Capillary calibration devices*

— *Part 6: Critical orifices*

— *Part 7: Thermal mass-flow controllers*

— *Part 9: Saturation method*

— *Part 10: Permeation method*

Diffusion will be the subject of a future part 8 to ISO 6145. Part 3 to ISO 6145, entitled *Periodic injections into a flowing stream*, has been withdrawn.

Annexes A, B and C of this part of ISO 6145 are for information only.

Introduction

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.

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

Part 7:
Thermal mass-flow controllers

1 Scope

This part of ISO 6145 specifies a method for the continuous production of calibration gas mixtures, containing two or more components, from pure gases or other gas mixtures by use of commercially available thermal mass-flow controllers. By adjustment of set-points on flow controllers to pre-determined values, it is possible to change the composition of the gas mixture rapidly and in a continuously variable manner. By selection of appropriate combinations of thermal mass-flow controllers and with use of pure gases, the volume fraction of the component of interest in the complementary gas can be varied by a factor of 1 000. The relative expanded uncertainty of measurement, U, obtained by multiplying the relative combined standard uncertainty by a coverage factor, $k = 2$, is not greater than 2 %.

If pre-mixed gases are used instead of pure gases, mole fractions below 10^{-6} can be obtained. The measurement of mass flow is not absolute and the flow controller requires independent calibration.

The merits of the method are that a large quantity of the gas mixture can be prepared on a continuous basis and that multi-component mixtures can be prepared as readily as binary mixtures if the appropriate number of thermal mass-flow controllers is utilized.

Gas blending systems, based upon thermal mass-flow controllers, and some including the facility of computerization and automatic control, are commercially available.

2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this part of ISO 6145. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this part of ISO 6145 are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

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

ISO 6145-1:1986, *Gas analysis — Preparation of calibration gas mixtures — Dynamic volumetric methods — Part 1: Methods of calibration*.

3 Principles

3.1 Thermal mass-flow controller using a constant current supply

To prepare the gas mixture each gaseous component is passed at a known, controlled flowrate, and at a constant pressure, from a calibrated thermal mass-flow controller.

A thermal mass-flow controller consists of a measuring unit for mass flow and a proportioning valve which is controlled by an electronic unit.

The flowing gas is passed through a heater connected to a constant current supply and the temperature is measured upstream and downstream from the heater.

The schema in Figure 1 shows the heater, temperature sensors and associated circuitry. The two temperature sensors, one upstream and one downstream from the heater form two resistors of a Wheatstone bridge circuit, which is balanced to give zero reading when there is no gas flow. When there is a gas flow through the system a temperature difference, ΔT, is established between the two sensors such that the heat flux, Φ, is given by:

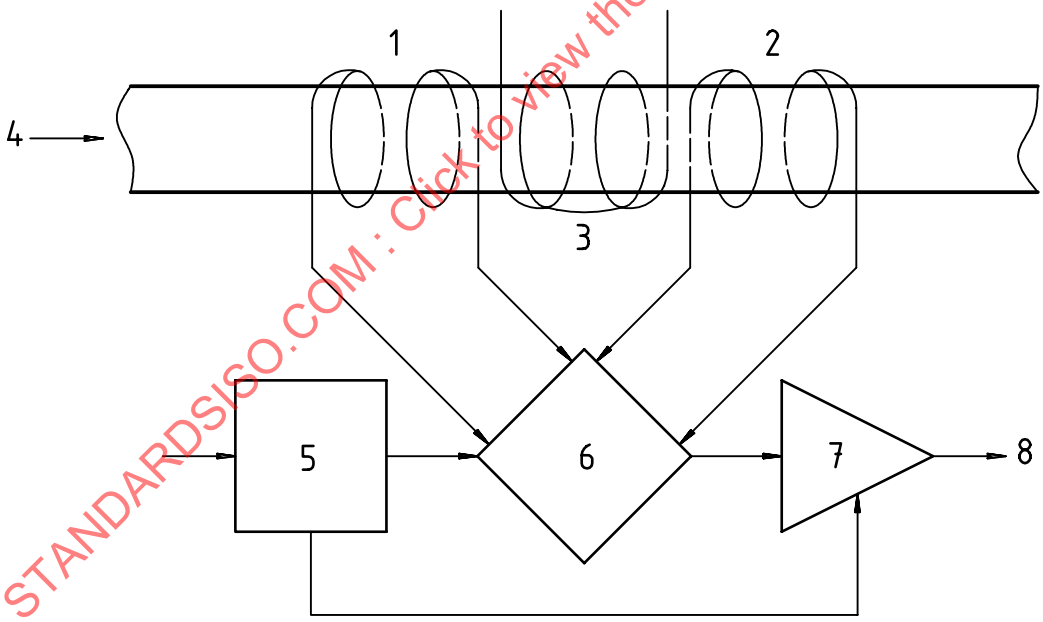
$$\Phi = C_{\mathrm{p}} \Delta T q_m \tag{1}$$

where

C_{p} is the heat capacity per unit mass, or molar heat capacity, of the gas at constant pressure;

q_m is the mass flowrate.

The difference in temperature between sensors results in a potential difference across the Wheatstone bridge circuit and thus a signal. This signal is compared with an adjustable reference voltage in a differential amplifier. The resulting output signal is in turn used for operating a control valve to regulate the flow of gas.



Key

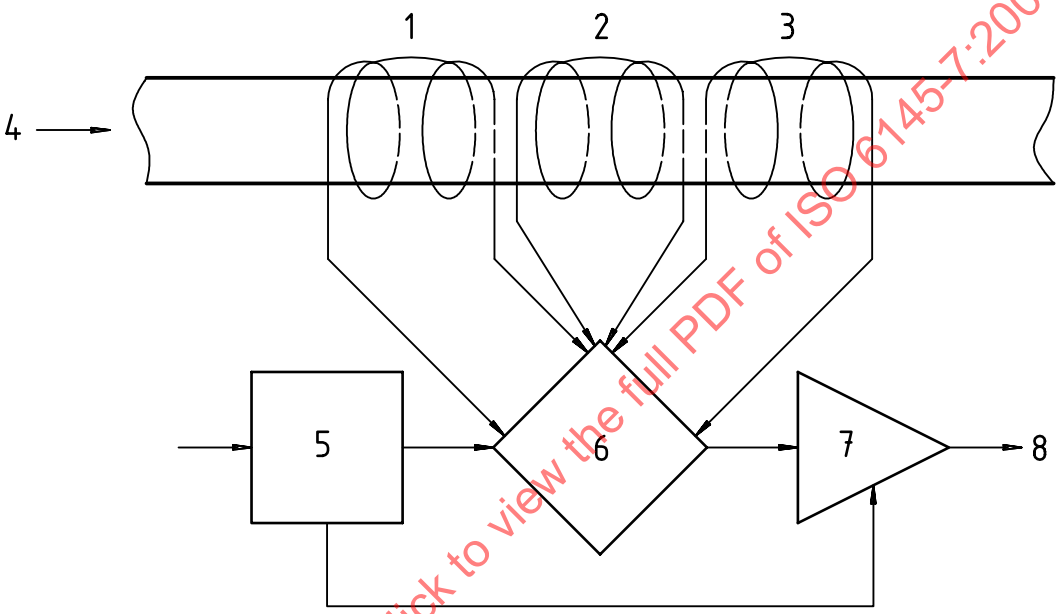
1	Temperature sensor 1
2	Temperature sensor 2
3	Heater
4	Gas supply
5	Current supply
6	Wheatstone bridge
7	Differential amplifier
8	Signal readout

Figure 1 — Thermal mass-flow controller with constant current supply

3.2 Thermal mass-flow controller under constant temperature control

In this system (Figure 2) the gas passes through three heaters in sequence and each of which is connected into an resistor of a self-regulating Wheatstone bridge. Instead of the difference in temperature being measured, the input to each heater is such that the temperature distribution along the flow path is maintained uniform. The Wheatstone bridge current is proportional to the heat loss and therefore proportional also to the mass flow of the gas. The output signal is again used to operate a solenoid valve to control the mass flowrate.

In the preparation of multicomponent mixtures, it is often necessary to use one mass-flow controller for each component. Dual-channel controllers are available and may be used for the preparation of binary mixtures or, for example, for the preparation of mixtures of a given gas in air.



Key

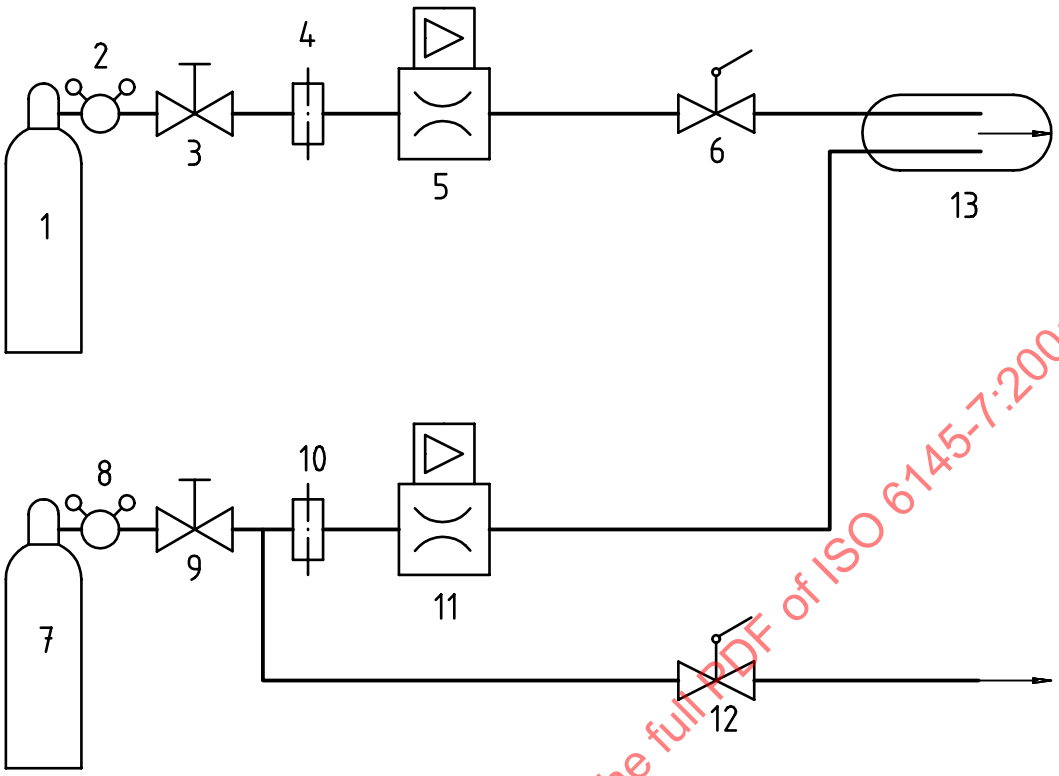
1	Heater 1
2	Heater 2
3	Heater 3
4	Gas supply
5	Current supply
6	Wheatstone bridge
7	Differential amplifier
8	Signal readout

Figure 2 — Thermal mass-flow controller under constant temperature control

4 Preparation of gas mixtures

4.1 Description of the experimental procedure

A schematic diagram of the arrangement for the preparation of binary mixtures is shown in Figure 3.



Key

Complementary gas:

1 Cylinder of pressurized gas
2 Pressure regulator
3 Shut-off valve
4 Filter against contamination
5 Thermal mass-flow controller
6 Shut-off valve (optional)

Calibration component:

7 Cylinder of pressurized gas
8 Pressure regulator
9 Shut-off valve
10 Filter against contamination
11 Thermal mass-flow controller
12 Shut-off valve
13 Mixing vessel

Figure 3 — Mixing apparatus for production of binary gas mixtures by means of thermal mass-flow controllers

Gas cylinders (1) and (7) containing the complementary gas and the calibration component, respectively, are connected to the thermal mass-flow controllers (5) and (11) through pressure regulators (2) and (8) and shut-off valves (3) and (9). The two in-line filters (4) and (10) provide protection against contamination. The gases from the flow controllers enter the mixing vessel (13).

The recommended working range for the pressure regulators is 60 kPa[1)] (0,6 bar) to 600 kPa (6,0 bar). The pressure regulator for the “gaseous component” shall also be suitable for the particular component involved (for example the

1) 1 bar = 100 kPa = 0,1 MPa; 1 Pa = 1 N/m^2

diaphragm shall be of stainless steel or other corrosion-resistant material). Similarly, the thermal mass-flow controllers shall be suitable for use with the gaseous components and for the requirements of the gas mixture.

Set the input pressures appropriate to the controllers using the pressure regulators and open the shut-off valves (3), (6) and (9). Purge the inlet path of the gaseous component through the shut-off valve (12), which shall be of a type which can be operated rapidly.

Adjust the set points of the controllers so as to obtain the respective flowrates in the correct ratio for the desired composition of the binary gas mixture; meanwhile, continue the purging process of the input tube for the component gas by multiple opening and closing of valve (12), until a total volume of gas at least ten times the volume of the flow path has been vented.

When the system has been thoroughly purged, feed the gases via the thermal mass-flow controllers to the mixing vessel (13), constructed from inert materials. Provided that the resistance to flow downstream of the mixing vessel (13) is low in relation to the flow being delivered at the source, the mixture flows at ambient atmospheric pressure to the instrument.

NOTE Although for most applications the gas mixture will be transmitted at the prevailing ambient atmospheric pressure, this method can also conceivably be applied to convey mixtures at elevated exit pressures. However, in this case it would be necessary to give due consideration to changes in C_p and in the density of the gaseous components with respect to pressure in order to assess the validity of this procedure.

4.2 Area of validity

The method is applicable to the preparation of mixtures of non-reacting species, i.e. those which do not react with any material of construction of the flow path in the thermal mass-flow controller or the ancillary equipment. Particular care shall be exercised if the method is considered as a means of preparation of gaseous mixtures which contain components which 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 listed in 4.1.

This method is not absolute and each thermal mass-flow controller shall be calibrated for the particular gas for which it is to be used.

4.3 Operating conditions

The conditions for efficient operation of the sensor system are that there shall be no heat loss or heat gain, other than that which results from the flow of gas, between the region of the heater and that of the downstream sensor, and that there shall be uniform temperature distribution across the gas stream. The assumption that C_p is constant is valid only over a restricted range of temperature. The general precautions common to all dynamic techniques of preparation shall be observed. It is essential that attention be paid to the materials used in the construction of the flow system. Only materials of low porosity, and which are non-adsorbing are suitable. The pipework shall be clean and all unions secure.

Unless independence of the thermal mass-flow controller to its orientation has been established it shall be maintained in the orientation in which it was calibrated. Controllers shall be calibrated for the components in question and it may be necessary to consult the manufacturer of the controller if the type of gas is to be changed; it may be necessary for the sensor to be changed.

5 Calculations

5.1 Volume fraction

The volume fraction can be determined with reference to any of the methods of calibration described in clause 3 of ISO 6145-1:1986. Due consideration shall be given to the uncertainty associated with the method selected.

Calibration of the thermal mass-flow controller will define the mass flowrate, q_m, or the volumetric flowrate, q_V, dependent on the method used.

$$q_m = \frac{\Phi}{C_\mathrm{p}\Delta T} \tag{2}$$

$$q_V = \frac{\Phi}{C_\mathrm{p}\rho\Delta T} \tag{3}$$

where ρ is the density of the component.

The mole fraction is

$$x_\mathrm{A} = \frac{q_{m,\mathrm{A}}}{M_\mathrm{A}} \Big/ \left(\frac{q_{m,\mathrm{A}}}{M_\mathrm{A}} + \frac{q_{m,\mathrm{B}}}{M_\mathrm{B}} \right) \tag{4}$$

where

M_A and M_B are the molar masses of components A and B respectively;

$q_{m,\mathrm{A}}$ and $q_{m,\mathrm{B}}$ are the values of mass flowrate, q_m, for components A and B respectively.

The corresponding volume fraction is:

$$\varphi_\mathrm{A} = q_{V,\mathrm{A}} / \left(q_{V,\mathrm{A}} + q_{V,\mathrm{B}} \right) \tag{5}$$

5.2 Sources of uncertainty

Commercially available thermal mass-flow controllers indicate the gas flowrate usually in volume units as an analogue or digital display. Typical claims for accuracy are $\pm$ 1 % of full scale, provided that the ambient temperature is maintained within $\pm$ 5 °C of the temperature at which the instrument was calibrated. The corresponding claims for set-point repeatability are $\pm$ 0,2 % full scale.

It is assumed that pressures and temperatures respectively are measured with the same instruments during calibration and use, so that the standard uncertainties in these measurements are constant throughout.

From equations (2) and (3):

$$\frac{u\left(q_m\right)}{q_m} = \left\{ \left[\frac{u\left(\Phi\right)}{\Phi} \right]^2 + \left[\frac{u\left(C_\mathrm{p}\right)}{C_\mathrm{p}} \right]^2 + \left[\frac{u\left(\Delta T\right)}{\Delta T} \right]^2 \right\}^{1/2} \tag{6}$$

$$\frac{u\left(q_V\right)}{q_V} = \left\{ \left[\frac{u\left(\Phi\right)}{\Phi} \right]^2 + \left[\frac{u\left(C_\mathrm{p}\right)}{C_\mathrm{p}} \right]^2 + \left[\frac{u\left(\Delta T\right)}{\Delta T} \right]^2 + \left[\frac{u\left(\rho\right)}{\rho} \right]^2 \right\}^{1/2} \tag{7}$$

NOTE The expressions for relative combined uncertainty given in equations (6) and (7) are provided for information only. They have been given in order to identify the parameters which contribute to $u\left(q_m\right)/q_m$ and $u\left(q_V\right)/q_V$. Φ and ΔT are functions of the mass-flow controller and the uncertainties are covered by the uncertainty quoted by the manufacturer.

The following is a typical example of the relative change in C_p with temperature and pressure.

EXAMPLE With reference to effects of pressure and temperature changes, the relative change in C_p for nitrogen, for example, at 100 kPa (1 bar) for a change of 5 K in temperature from 290 K is approximately 0,000 2. The relative change in C_p at 290 K for a change in pressure from 100 kPa $\left(1\ \mathrm{bar}\right)$ to 200 kPa $\left(2\ \mathrm{bar}\right)$ is approximately 0,001.

These values show that the effects of pressure and temperature changes are negligible in comparison with the uncertainty inherent in the controller itself.

5.3 Uncertainty of the volume fraction

The uncertainty of the volume fraction of the component in the calibration mixture, at constant temperature and pressure, can be estimated from the separate uncertainties in the flowrates of the component and the complementary gas.

The volume fraction, φ_{A}, of component A is given by equation (5).

The relative expanded uncertainty in $\varphi_{V,\mathrm{A}}$ is then given by:

$$\frac{U(\varphi_{\mathrm{A}})}{\varphi_{\mathrm{A}}} = \left(\frac{2\,q_{V,\mathrm{B}}}{q_{V,\mathrm{A}} + q_{V,\mathrm{B}}}\right)\left\{\left[\frac{u(q_{V,\mathrm{A}})}{q_{V,\mathrm{A}}}\right]^2 + \left[\frac{u(q_{V,\mathrm{B}})}{q_{V,\mathrm{B}}}\right]^2\right\}^{1/2} \tag{8}$$

The derivation of the above formula is summarized in C.1 of annex C.

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

The uncertainty in the flowrates is estimated by calibration of the thermal mass-flow controllers by one of the methods presented in ISO 6145-1.

This estimate of the relative uncertainty in the composition depends entirely on the uncertainties in measurements of flowrates. 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 described in clause 4 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 gas mixtures.

Annex A
(informative)

Pre-mixed gases for preparation of mixtures of high dilution

A.1 Calculation of volume fraction

If pre-mixed gases are used instead of pure gases mixtures of higher dilution can be prepared. Calculation of volume fraction is then as below.

The volume fraction of component A in the final calibration gas mixture is given by:

$$\varphi_{\mathrm{A}} = \frac{\varphi'_{\mathrm{A}} q_{V,\mathrm{M}} + \varphi''_{\mathrm{A}} q_{V,\mathrm{B}}}{q_{V,\mathrm{M}} + q_{V,\mathrm{B}}} = \frac{\varphi'_{\mathrm{A}} q_{V,\mathrm{M}} + \varphi''_{\mathrm{A}} q_{V,\mathrm{B}}}{q_{\varphi}} \tag{A.1}$$

where

φ'_{A} is volume fraction of A in the pre-mixed gas;

φ''_{A} is volume fraction of A in the complementary gas, B (this will normally be zero);

$q_{V,\mathrm{M}}$ is volume flowrate of the pre-mixed gas, M;

$q_{V,\mathrm{B}}$ is volume flowrate of the complementary gas, B;

q_{φ} is volume flowrate of the calibration gas.

NOTE $q_{\varphi} = q_{V,\mathrm{M}} + q_{V,\mathrm{B}}$ only if there is no volume change on mixing.

A.2 Uncertainty of volume fraction

It is necessary to take into account the standard uncertainties of the volume flowrates and the standard uncertainties of the volume fractions of the calibration component in the pre-mixed gas and also in the complementary gas (if relevant). Normally the complementary gas will not contain the calibration component.

For the case in which the complementary gas does not contain the active component A:

$$\varphi_{\mathrm{A}} = \frac{\varphi'_{\mathrm{A}} q_{V,\mathrm{M}}}{q_{V,\mathrm{M}} + q_{V,\mathrm{B}}} \tag{A.2}$$

and the relative standard uncertainty in the volume fraction φ_{A} is given by:

$$\frac{u(\varphi_{\mathrm{A}})}{\varphi_{\mathrm{A}}} = \frac{q_{V,\mathrm{B}}}{q_{V,\mathrm{B}} + q_{V,\mathrm{M}}} \left\{ \left[\frac{u(q_{V,\mathrm{M}})}{q_{V,\mathrm{M}}}\right]^2 + \left[\frac{u(q_{V,\mathrm{B}})}{q_{V,\mathrm{B}}}\right]^2 + \left(\frac{q_{V,\mathrm{M}} + q_{V,\mathrm{B}}}{q_{V,\mathrm{B}}}\right)^2 \left[\frac{u(\varphi'_{\mathrm{A}})}{\varphi'_{\mathrm{A}}}\right]^2 \right\}^{1/2} \tag{A.3}$$

This equation is derived in C.2.

Annex B
(informative)

Practical hints

The complete flow system should be clean and free of particulates.

Pressure regulators and associated pipework should be dedicated for use with specific gaseous components.

The thermal mass-flow controller should be maintained in the same orientation when it is calibrated and when in use for preparation of gas mixtures.

The operating ranges should be appropriate for the gaseous component, mixing ratio, minimum flowrate and the possible volume fractions. The use of an unsuitable range results in increased uncertainty.

Shut-off valves should be installed between pressure regulators and thermal mass-flow controllers to ensure that there is no leakage from the regulators.

All dimensions of the flow paths and the materials of construction should be carefully selected so as to minimize interaction with the gaseous components. In particular, pressure regulators should be suitable for the gases which they are to convey. GC-quality stainless steel tubing should be used to convey reactive components. It is permissible for non-reactive complementary gases to be conveyed in plastics materials such as polyethylene or polytetrafluorethylene. If there is any risk of adsorption, however, stainless steel should be used.

The nominal inner diameter of the conveyance tubes should be 1,5 mm to 2,0 mm for the active component and 4,0 mm to 6,0 mm for the complementary gas.

Before use of the calibration gases, ensure that the pipework for the active component is sufficiently purged with the component concerned. A short period is satisfactory in the case of the pure gas or pre-mixed gases at higher volume fractions, but several hours are necessary for the more dilute pre-mixed gases (below 10^{-4} by volume).

For calibration of gas analysers at normal atmospheric pressures the calibration gas should be supplied at no excess pressure; suitable by-pass tubes should therefore be provided. The excess depends upon the calibration gas component and the pressure dependence of the analyzer.

In the case of corrosive or toxic gases any excess flow should be safely vented but long runs of venting pipework should be avoided in order to minimize back-pressure effects.

In the event of a short interruption in the analyser calibration procedure, conveyance of the gases should not be arrested and if connecting tubes are removed they should be adequately sealed against contamination.

Annex C
(informative)

Uncertainty of volume fraction — Mathematical derivation

C.1 Derivation of the relative standard uncertainty, u, in φ_A

The symbols are those given in 5.3, except that the suffix "V" (for example in $q_{V,A}$) has been omitted in order to simplify the formulae.

The concentration of component A in a mixture of A and complementary gas B is given by:

$$\varphi_A = \frac{q_A}{q_A + q_B} \tag{C.1}$$

where q_A and q_B are respectively the flowrates of the components A and B.

The uncertainty in φ_A is:

$$u(\varphi_A) = \left\{ \left[\frac{\partial \varphi_A}{\partial q_A}\right]^2 [u(q_A)]^2 + \left(\frac{\partial \varphi_B}{\partial q_B}\right)^2 [u(q_B)]^2 \right\}^{1/2} \tag{C.2}$$

By differentiation of equation (C.1):

$$\left(\frac{\partial \varphi_A}{\partial q_A}\right)^2 = \left[\frac{q_B}{(q_A + q_B)^2}\right]^2$$

$$\left(\frac{\partial \varphi_A}{\partial q_B}\right)^2 = \left[\frac{-q_A}{(q_A + q_B)^2}\right]^2$$

and by substitution in equation (C.2) the relative standard uncertainty is:

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

$$= \frac{q_A q_B}{q_A (q_A + q_B)}\left\{\left[\frac{u(q_A)}{q_A}\right]^2 + \left[\frac{u(q_B)}{q_B}\right]^2\right\}^{1/2}$$

$$= \frac{q_B}{q_A + q_B}\left\{\left[\frac{u(q_A)}{q_A}\right]^2 + \left[\frac{u(q_B)}{q_B}\right]^2\right\}^{1/2}$$

The coverage factor "2" is applied in 5.3 to give 95 % coverage probability.

C.2 Uncertainty of the volume fraction — Mathematical derivation

NOTE This expression has been derived for the mass-flow controller method, but is equally applicable for other methods described in the various parts of ISO 6145.

The symbols are those given in A.1, except that the suffix "V" (for example in $q_{V,M}$) has been omitted in order to simplify the formulae.