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

Part 7:
Thermal mass-flow controllers

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

Partie 7: Régulateurs thermiques de débit massique

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 158, *Analysis of gases*.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

This third edition cancels and replaces the second edition (ISO 6145-7:2009), which has been technically revised. The main changes compared to the previous edition are as follows:

- correction of some errors in the formulae in Annexes A and C;
- minor editorial corrections.

A list of all parts in the ISO 6145 series can be found on the ISO website.

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

Part 7:
Thermal mass-flow controllers

1 Scope

ISO 6145 is a series of documents dealing with various dynamic methods used for the preparation of calibration gas mixtures. This document specifies a method for continuous preparation of calibration gas mixtures, from nominally pure gases or gas mixtures by use of thermal mass-flow controllers. 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 in the thermal mass-flow controller or the ancillary equipment.

If this method is employed for preparation of calibration gas mixtures the optimum performance is as follows: the relative expanded measurement uncertainty U, obtained by multiplying the 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 calibration 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.

NOTE 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 documents are referred to in the text in such a way that some or all of their content constitutes requirements 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*

ISO 7504, *Gas analysis — Vocabulary*

ISO 12963, *Gas analysis — Comparison methods for the determination of the composition of gas mixtures based on one- and two-point calibration*

ISO 19229, *Gas analysis — Purity analysis and the treatment of purity data*

3 Terms and definitions

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

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at: http://www.electropedia.org/

4 Symbols

C_p	Heat capacity (at constant pressure)
i,k	Indices for components in a gas or gas mixture
j	Index for a parent gas
m	Mass
p	Pressure
q	Number of components in the gas mixture
q_m	Mass flow rate
q_V	Volume flow rate
T	Temperature
V	Volume
Φ	Heat flux
ϕ	Volume fraction of a component in a parent gas
φ	Volume fraction of a component in a gas mixture
ρ	Density

5 Principle

The continuous preparation of calibration gas mixtures from nominally pure gases or other gas mixtures by the use of commercially available thermal mass-flow controllers is described. By adjustment of the set-points on the mass 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 matrix gas can be varied by a factor of 1 000.

6 Set-up

6.1 General

To prepare a gas mixture, each gaseous component is passed through a calibrated thermal mass flow controller (TMC) at a known and controlled flow rate and at constant pressure. Accurate flow meters are used to measure the relevant flow rates in order to achieve an acceptable level of uncertainty regardless of the setting of the mass flow controller (see also ISO 6145-1).

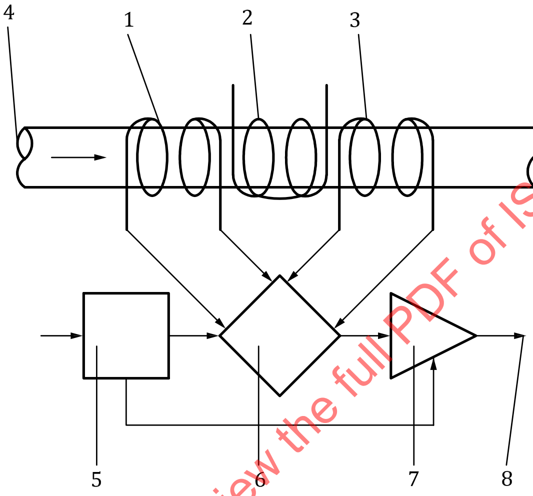
A TMC consists of a measuring unit for mass flow and a proportioning valve which is controlled by an electronic unit (see also Reference [1] and [2]).

6.2 Thermal mass-flow controller using a constant current supply

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

Figure 1 shows the working principle of a TMC and its key parts: heater, temperature sensors and associated circuitry. The two temperature sensors, one upstream and one downstream from the heater form two arms 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 Formula (1):

$$\Phi = C_p \Delta T q_m \tag{1}$$



Key

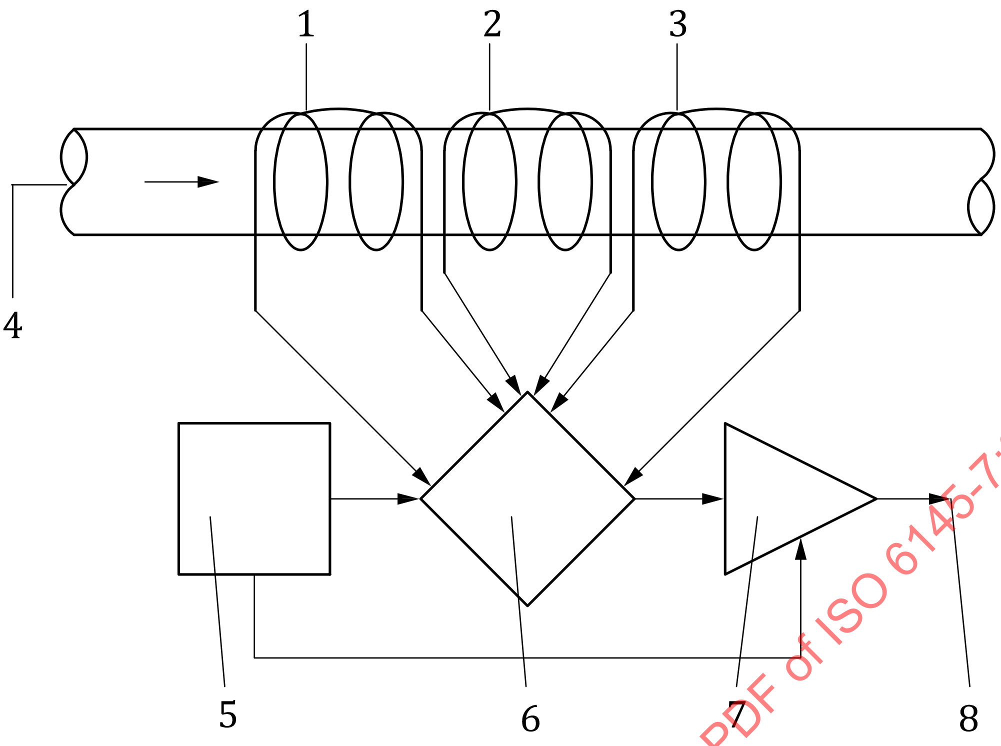
1	temperature sensor 1	5	current supply
2	heater	6	wheatstone bridge
3	temperature sensor 2	7	differential amplifier
4	gas supply	8	signal readout

Figure 1 — Principle of a thermal mass-flow controller with constant current supply

The difference in temperature between sensors results in a potential difference across the Wheatstone bridge circuit and thus a signal. The 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.

6.3 Thermal mass-flow controller under constant temperature control

In the system, shown in Figure 2, the parent gas passes through three heaters in sequence, each of which is connected into an arm 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 uniformly maintained. 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 flow rate.



Key

1	heater 1	5	current supply
2	heater 2	6	wheatstone bridge
3	heater 3	7	differential amplifier
4	gas supply	8	signal readout

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

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

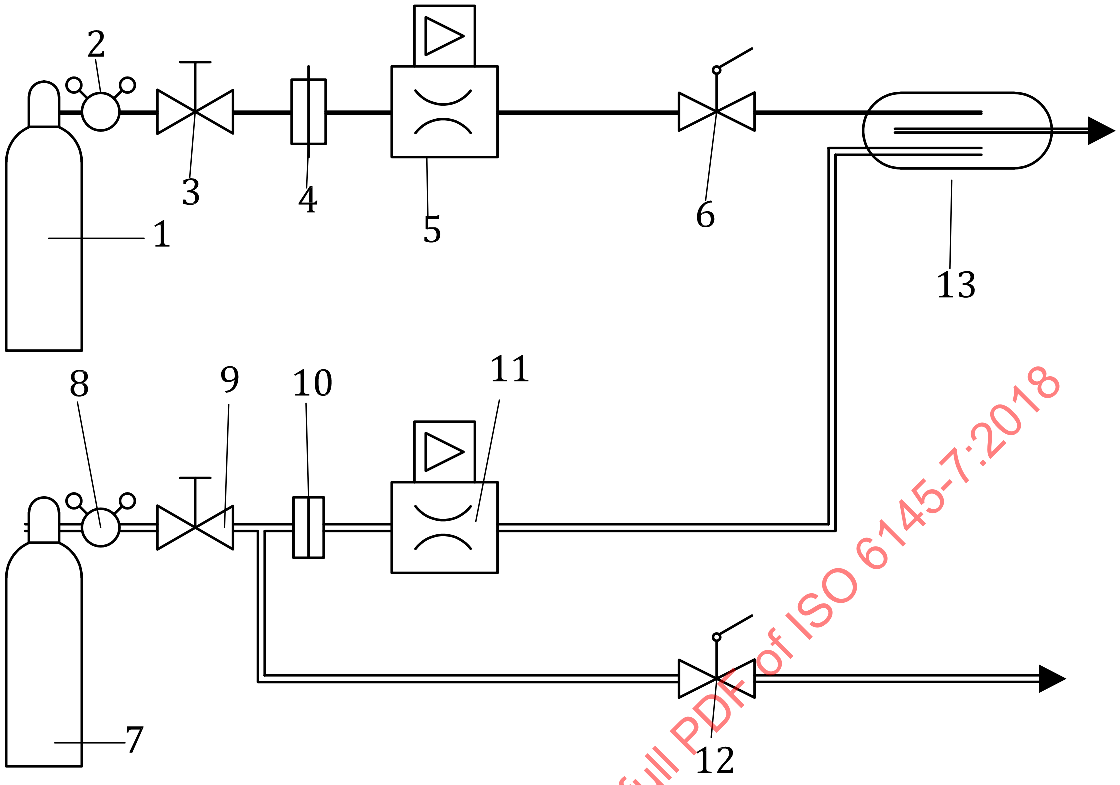
7 Preparation of gas mixtures

7.1 Description of the experimental procedure

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

The pressure and temperature at the time of the calibration shall be recorded. Depending on the gases to be mixed and their departure from ideality, the volume fraction can be somewhat influenced by the ambient pressure and temperature. The pressure and temperature at the time of calibration of the analyser should be as near as possible to those prevalent at the time the TMCs were checked by the comparison method ISO 6143 or ISO 12963 (see 7.3).

Compositions of calibration gas mixtures are normally expressed by volume fractions but manufacturers' accuracy specifications for thermal mass-flow controllers are usually expressed in terms of percentage of the full scale of the instrument. The relative expanded uncertainty of 2 %, which is quoted in the Scope of this document, is 2 % of the volume fraction of the calibration component of the mixture. This value assumes optimum use of each TMC in the system, which means that each is operated at, or very near to, its maximum flow rate. Thus, if a TMC is operated at 10 % of full scale, the expanded uncertainty expressed as percentage of maximum flow (as distinct from relative expanded uncertainty) can be ±1 %, but if expressed instead as a percentage of the actual flow rate the relative expanded uncertainty becomes 10 %.



Key

Matrix 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

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 preparation of binary gas mixtures by means of thermal mass-flow controllers

A binary mixture containing the calibration component at volume fraction 1:11 could be prepared by use of two TMCs each of full scale 1 000 mL/min by operating one at 100 mL/min and the other at 1 000 mL/min. However, the expanded uncertainty associated with the flow rate of the former would be ±10 % of flow rate and the relative expanded uncertainty in the volume fraction would be ±9 %. Use one TMC with a full scale range of 100 ml/min and a second one with a full scale range of 1 000 ml/min, both being operated very close to full scale, so that the mixture has a volume fraction with a relative expanded uncertainty of 2 %.

The same requirement shall be observed relative to preparation of multi component mixtures.

A method for which there is no requirement for calibration against external standards of gas flow rate or volume fraction is described briefly in Annex B, and the reference to the publication which provides the complete description is given in the bibliography.

As shown in Figure 3, gas cylinders (1) and (7)containing the matrix gas and the component of interest 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 (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 (e.g. the 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 flow rates 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 10 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.

Although for most applications the gas mixture will be transmitted at the prevailing ambient atmospheric pressure, this method may 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 density of the gaseous components with pressure in order to assess the validity of this procedure.

7.2 Range of validity

As stated in the scope, this 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 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 6.1.

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

7.3 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 is paid to the materials used in the construction of the flow system. Only materials of low porosity that do not cause adsorption of any of the components in the gases or gas mixture are suitable. The tubing 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.

8 Calculations

8.1 Volume fraction

Determine the volume fraction using any of the methods of calibration for the flow rates described in ISO 6145-1. Due consideration shall be given to the uncertainty associated with the method selected.

Calibration of the TMC will define the mass flow rate, or the volume flow rate, dependent on the method used.

$$q_m = \frac{\Phi}{C_p \Delta T} \tag{2}$$

$$q_V = \frac{\Phi}{C_p \rho \Delta T} \tag{3}$$

The following calculation of the volume fractions is only valid if high-purity gases are used with impurity fractions that are sufficiently low. The purity of the gases shall be evaluated in accordance with ISO 19229 and the purity data shall be prepared accordingly. If impurity levels are too high to be neglected in the calculation of the composition, an alternative calculation shall be used. One possibility is given in Annex A.

The amount of substance fraction is calculated as:

$$x_A = \frac{\dfrac{(q_m)_A}{M_A}}{\left[\dfrac{(q_m)_A}{M_A} + \dfrac{(q_m)_B}{M_B}\right]} \tag{4}$$

where

M_A and M_B	are the molar masses of components A and B respectively;
$(q_m)_A$ and $(q_m)_B$	denote the values of mass flow rate, for components A and B respectively.

The corresponding volume fraction is:

$$\varphi_A = \frac{(q_V)_A}{(q_V)_A + (q_V)_B} \tag{5}$$

8.2 Sources of uncertainty

Commercially available thermal mass flow controllers indicate the gas flow rate usually in volume units as an analogue or digital display. Typical claims for accuracy are ±1 % of full scale, provided that the ambient temperature is maintained within ±5 °C of the temperature at which the instrument was calibrated. The corresponding claims for set point repeatability are ±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 Formulae (2) and (3):

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

$$\frac{u(q_V)}{q_V}=\left[\frac{u^2(\varPhi)}{\varPhi^2}+\frac{u^2(\varDelta T)}{\varDelta T^2}+\frac{u^2(\rho)}{\rho^2}+\frac{u^2(C_p)}{C_p^2}\right]^{\frac{1}{2}} \tag{7}$$

NOTE The expressions for relative combined uncertainty given in Formulae (6) and (7) are provided for information only. They have been given to identify the parameters which contribute to $u_{\mathrm{rel}}(q_m)$ and $u_{\mathrm{rel}}(q_V)$. $\varPhi$ and ΔT are functions of the mass flow controller and the uncertainties are covered by the uncertainty quoted by the manufacturer described in Annex C.

The following is a typical example of the relative change in C_p with temperature and pressure. These values show that the effects of pressure and temperature changes are negligible in comparison with the uncertainty inherent in the controller itself.

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 (1 bar) to 200 kPa (2 bar) is approximately 0,001.

8.3 Uncertainty of measurement

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

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

The relative expanded uncertainty in φ_{A} is then given by the Formula (8):

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

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

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

As necessary, the effect of impurities in the gases mixed on the measurement uncertainty shall be evaluated accordingly (see also Annex A).

This estimate of the relative uncertainty in the composition depends entirely on the uncertainties in measurements of flow rates. The other factor to be taken into account is the efficiency of mixing. To check if a mixing system actually provides a homogeneous calibration gas mixture, mixtures shall be prepared as specified in Clause 7, the compositions shall be checked using the methods given in ISO 6143 or ISO 12963, and the ambient pressure and temperature shall be recorded.

This procedure also identifies bias from other sources and establishes traceability against standard gas mixtures.

Annex A
(informative)

Pre-mixed gases for the preparation of mixtures of high dilution

A.1 Calculation of the 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 (see also Reference [3]):

The volume fraction of component A in a gas mixture with matrix gas B is given by the Formula (A.1):

$$\varphi_\mathrm{A} = \frac{\varphi'_\mathrm{A}\left(q_V\right)_\mathrm{M} + \varphi''_\mathrm{A}\left(q_V\right)_\mathrm{B}}{\left(q_V\right)_\mathrm{M} + \left(q_V\right)_\mathrm{B}} = \frac{\varphi'_\mathrm{A}\left(q_V\right)_\mathrm{M} + \varphi''_\mathrm{A}\left(q_V\right)_\mathrm{B}}{\left(q_V\right)_\varphi} \tag{A.1}$$

where

φ'_A is volume fraction of A in the pre-mixed gas;

φ''_A is volume fraction of A in the matrix gas, B (this will normally be zero);

$(q_V)_\mathrm{M}$ is volume flow rate of the pre-mixed gas, M;

$(q_V)_\mathrm{B}$ is volume flow rate of the matrix gas B;

$(q_V)_\varphi$ is volume flow rate of the calibration gas.

NOTE $(q_V)_\varphi = (q_V)_\mathrm{M} + (q_V)_\mathrm{B}$ 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 flow rates and the standard uncertainties of the volume fractions of the component in the pre-mixed gas and also in the matrix gas (if relevant). Normally the matrix gas will not contain the component of interest.

For the case in which the matrix gas does not contain the component A, see Formula (A.2):

$$\varphi_\mathrm{A} = \frac{\varphi'_\mathrm{A}\left(q_V\right)_\mathrm{M}}{\left(q_V\right)_\mathrm{M} + \left(q_V\right)_\mathrm{B}} \tag{A.2}$$

and the relative standard uncertainty in the volume fraction φ_A is given by the Formula (A.3):

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

This formula is derived from C.2.

Annex B
(informative)

Practical hints

B.1 Equipment

The complete flow system should be clean and free from 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.

NOTE The requirement that the thermal mass-flow controllers are to be operated near to full scale is given in 6.1.

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

All dimensions of the flow paths and the materials of construction should be carefully selected so that interaction with the gaseous components is minimised. In particular, pressure regulators should be suitable for the gases which they are to convey. GC-quality stainless steel should be used to convey reactive components. It is permissible for non-reactive matrix 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 component of interest and 4,0 mm to 6,0 mm for the matrix gas.

B.2 Operation

Before use of the calibration gases, ensure that the pipework for the component of interest 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 (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 analyser.

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 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.

B.3 Calibration and precision

A high-accuracy gas flow dilution system using mass-flow controllers, but not restricted to thermal mass-flow controllers, has been developed and is described in Reference [4]. To gain an appreciation of the method, which has been employed to provide a variety of volume fractions to a typical uncertainty of ±0,4 % of volume fraction, the original paper should be read. The paper details the uncertainty analysis on the basis of the flow rates of the calibration component and the emergent calibration gas and the method has been verified experimentally against gravimetric methods.

An additional paper[5] describes an improved approach to calculating the uncertainties of thermal mass-flow controllers. The paper provides a review of the mathematical basis for a general least-squares solution to the determination of best-fit calibration curves, and separates the systematic contribution to the uncertainty which results from the calibration of the flow system from the random uncertainty incurred each time the system is operated. In an appendix to the paper, the experimental and mathematical procedures are illustrated with reference to the gas flow dilution system which is the subject of References [4], but it is equally applicable in principle to the method of preparation of binary gas mixtures described in this document. Twenty-five literature references are provided.

Annex C
(informative)

Calculation of uncertainties

C.1 Relative standard uncertainty of φ_a in case of nominally pure gases

The symbols are those given in 7.3 and Annex A.

The volume fraction of component A in a mixture of pure gas A and pure gas B is given by:

$$\varphi_\mathrm{A} = \frac{(q_V)_\mathrm{A}}{(q_V)_\mathrm{A} + (q_V)_\mathrm{B}} \tag{C.1}$$

The uncertainty in φ_A is:

$$u(\varphi_\mathrm{A}) = \left\{ \left[\frac{\partial \varphi_\mathrm{A}}{\partial (q_\mathrm{V})_\mathrm{A}} \right]^2 u^2\left[(q_\mathrm{V})_\mathrm{A}\right] + \left[\frac{\partial \varphi_\mathrm{A}}{\partial (q_\mathrm{V})_\mathrm{B}} \right]^2 u^2\left[(q_V)_\mathrm{B}\right] \right\}^{\frac{1}{2}} \tag{C.2}$$

By differentiation of Formula (C.1):

$$\frac{\partial \varphi_\mathrm{A}}{\partial (q_V)_\mathrm{A}} = \frac{(q_V)_\mathrm{B}}{\left[(q_V)_\mathrm{A} + (q_V)_\mathrm{B}\right]^2}$$

$$\frac{\partial \varphi_\mathrm{A}}{\partial (q_V)_\mathrm{B}} = \frac{-(q_V)_\mathrm{A}}{\left[(q_V)_\mathrm{A} + (q_V)_\mathrm{B}\right]^2}$$

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

$$\frac{u(\varphi_\mathrm{A})}{\varphi_\mathrm{A}} = \frac{(q_V)_\mathrm{A} + (q_V)_\mathrm{B}}{(q_V)_\mathrm{A}} \left\{ \frac{1}{\left[(q_V)_\mathrm{A} + (q_V)_\mathrm{B}\right]^2} \right\} \left\{ \left\{ (q_V)_\mathrm{B}^2\, u^2\left[(q_V)_\mathrm{A}\right] \right\} + \left\{ (q_V)_\mathrm{A}^2\, u^2\left[(q_V)_\mathrm{B}\right] \right\} \right\}^{\frac{1}{2}}$$

$$= \frac{(q_V)_\mathrm{A}(q_V)_\mathrm{B}}{(q_V)_\mathrm{A}\left[(q_V)_\mathrm{A} + (q_V)_\mathrm{B}\right]} \left\{ \frac{u^2\left[(q_V)_\mathrm{A}\right]}{(q_V)_\mathrm{A}^2} + \frac{u^2\left[(q_V)_\mathrm{B}\right]}{(q_V)_\mathrm{B}^2} \right\}^{\frac{1}{2}}$$

$$= \frac{(q_V)_\mathrm{B}}{(q_V)_\mathrm{A} + (q_V)_\mathrm{B}} \left\{ \frac{u^2\left[(q_V)_\mathrm{A}\right]}{(q_V)_\mathrm{A}^2} + \frac{u^2\left[(q_V)_\mathrm{B}\right]}{(q_V)_\mathrm{B}^2} \right\}^{\frac{1}{2}}$$

The coverage factor “2” is applied in 7.3 to give 95 % coverage probability.

C.2 Relative standard uncertainty of φ_a in case of diluting a gas mixture

The symbols are those given in 7.3 and Annex A.