INTERNATIONAL STANDARD

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2004-06-15

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

Reference number
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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.

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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.

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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):

$$\varphi_A = q_A/(q_A + q_B) \quad (1)$$

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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.

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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

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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.

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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.

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Annex A
(informative)

Pre-mixed gases for preparation of mixtures of high dilution

A.1 Calculation of results

If pre-mixed gases are used instead of pure gases, mixtures of higher dilution can be prepared. Calculation of results relative to a binary mixture is then as below:

The volume fraction of component A in the final calibration gas mixture is given by Equation (A.1) (provided there is no volume change on mixing):

$$\varphi_A = \frac{\varphi'_A q_M + \varphi''_A q_B}{q_M + q_B} = \frac{\varphi'_A q_M + \varphi''_A q_B}{q_\varphi} \tag{A.1}$$

where

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

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

q_M is the volume flow rate of the pre-mixed gas;

q_B is the volume flow rate of the complementary gas B;

q_φ is the volume flow rate of the calibration gas mixture.

A.2 Uncertainty of volume fraction

It is necessary to take into account the uncertainties of the volume flow rates and the 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 calibration component, A:

$$\varphi_A = \frac{\varphi'_A q_M}{q_A + q_B} \tag{A.2}$$

and the relative expanded uncertainty in the volume fraction φ_A is given by

$$\frac{U(\varphi_A)}{\varphi_A} = \frac{2q_B}{q_B + q_M} \left\{ \left[\frac{u(q_M)}{q_M} \right]^2 + \left[\frac{u(q_B)}{q_B} \right]^2 + \left(\frac{q_M + q_B}{q_B} \right)^2 \left[\frac{u(\varphi'_A}{\varphi'_A} \right]^2 \right\}^{\frac{1}{2}} \tag{A.3}$$

The derivation of Equation (A.3) is presented in ISO 6145-7:2001, Annex C. The 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 uncertainty in the flow rate of the carrier gas is obtained with reference to ISO 6145-1 for the selected method of flow calibration.

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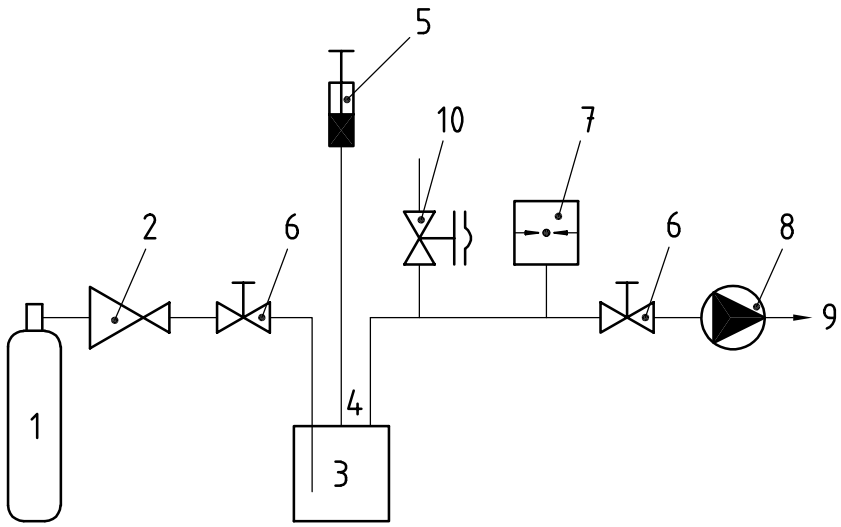
Annex B
(informative)

Example of apparatus for preparation of calibration gas mixtures

A schema of an apparatus for filling a syringe with a gaseous calibration component is given in Figure B.1. The reservoir should be capable of operation up to a pressure of 140 kPa (1,4 bar). A pressure gauge to measure pressures from 10 kPa (0,1 bar) to 200 kPa (2 bar) to an uncertainty of 100 Pa (1 mbar) is suitable. The relief valve should operate at 130 kPa (1,3 bar), and the vacuum pump should be of a type which can generate a vacuum of 5 Pa (0,05 mbar).

Silicone rubber is a suitable material for the septum and the syringe should be of the gas-tight type, e.g. as used in gas chromatography.



Key

1 compressed gas cylinder filled with the calibration component
2 two-stage pressure regulator
3 reservoir
4 septum
5 syringe
6 shut-off valve
7 pressure gauge
8 vacuum pump
9 gas filter
10 relief valve

Figure B.1 — Schema of apparatus for filling a syringe with a gaseous calibration component

A schema of an apparatus for the production of binary calibration gas mixtures by means of continuous syringe injection is given in Figure B.2.

Be careful with placing a flow meter after a humidifier. If the humidity reaches the point of condensation, the condensed liquid may cause significant errors in the system.

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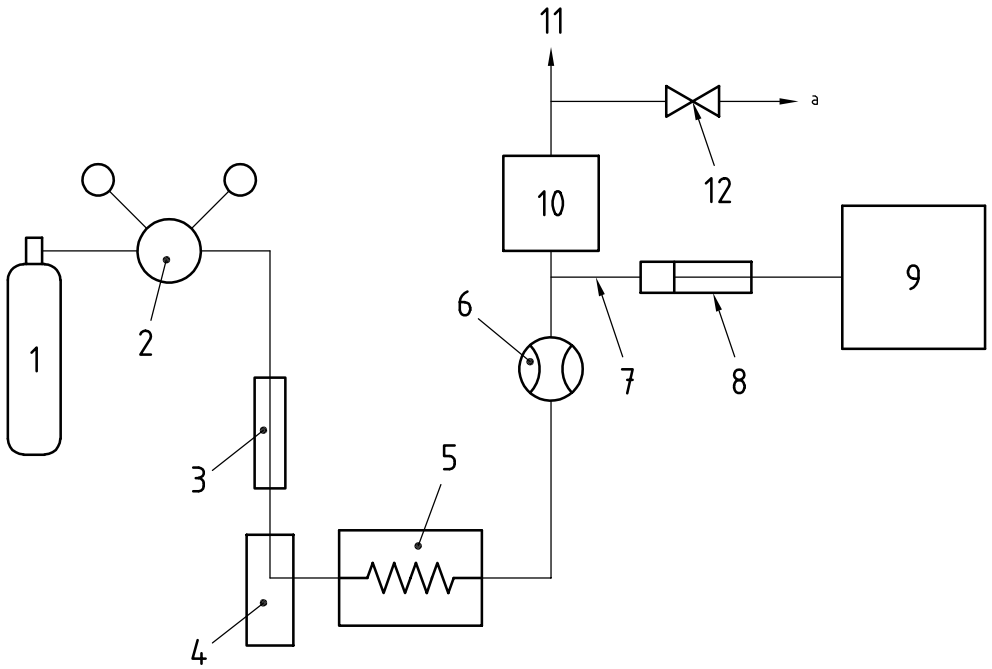

Key

1 compressed gas cylinder filled with the complementary gas
2 two-stage pressure regulator
3 purifier (if applicable)
4 humidifier (if applicable)
5 heat exchanger in thermostat
6 flow meter
7 dosing capillary
8 syringe
9 syringe driver
10 mixing chamber
11 calibration gas
12 shut-off valve to vent

[a] Vent.

Figure B.2 — Schema of apparatus for production of binary calibration gas mixtures by means of continuous syringe injection

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Annex C
(informative)

Practical hints

C.1 General

The entire flow system should be clean and free from particulates.

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

A shut-off valve should be located in the line downstream of the pressure regulator on the cylinder of complementary gas, in order to ensure that there is no leakage past the regulator.

All dimensions of the flow paths and the materials of construction should be carefully selected so that interaction with the gaseous components is minimized. In particular, pressure regulators should be suitable for the gases that they are to convey. The syringe will normally be of glass, but apart from this, GC-quality stainless steel 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.

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

The syringe driver may be a motor of the stepping type and of variable frequency. At low plunger speeds, it is possible that the calibration component will be discharged in discrete aliquots rather than as a continuous flow. If the time interval between the steps of the drive mechanism approximates to the time constant of the mixing train, sinusoidal-type variations in the composition will be observed at the outlet. This effect may be overcome by increasing the volume of the mixing train or by employing a syringe of smaller volume, such that the identical discharge rate can be achieved but at a faster drive.

If the calibration component is a liquid, the rate of evaporation into the complementary gas stream may be lower than the rate of discharge. Introduction of a plug of glass wool at the tip of the injection needle is a means of increasing the surface area at which evaporation occurs. If this still does not provide for complete evaporation, it then becomes necessary to reduce the flow rate of the liquid to a value at which evaporation is rapid and complete. The flow rate of the complementary gas should then be reduced proportionately so that the required composition is maintained, and at the same time it is necessary to observe the evaporation of the liquid to check that it is still complete at the reduced flow rate of complementary gas. It is also recommended that a syringe containing the calibration component in the liquid phase be mounted vertically and with the needle uppermost.

C.2 Example of methodology to determine the characteristics of metering syringes

C.2.1 Determination of volume of the syringe (V)

The volumes of the syringes (data provided by EC Joint Research Centre, Ispra, Italy) were determined by filling with water and deriving volume from the mass of liquid (measured with a Mettler AT 201 balance) contained in the syringe (corrected for water density of 0,998 g/cm^3 at 22 °C). A high-sensitivity balance in the appropriate range (see below) was used for the weighing procedure. Several replicate volume measurements were carried out in a hysteresis cycle and the results are shown in Table C.1.

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Table C.1 — Results for determining the volume of the syringe

Volume of NO syringe V µl					Volume of SO_2 syringe V µl		
Syringe 1	Syringe 2	Syringe 2	Syringe 3	Syringe 4	Syringe 1	Syringe 2	Syringe 3
24,71	39,9	40,0	78,49	99,37	39,72	49,22	69,47
24,80	39,6	39,9	78,40	99,30	39,81	49,28	69,52
24,69	39,6	40,0	78,48	99,50	39,67	49,31	69,42
24,80	39,9	40,0	78,60	99,50	39,76	49,24	69,45
24,77	40,0	40,0	78,58	99,45	39,72	49,20	69,44
24,76	39,9	40,1	78,65	99,43	39,66	49,37	69,36
24,74	39,9	39,9	78,69	99,47	39,74	49,23	69,37
24,76	39,8	40,1	78,63	99,44	39,74	49,32	69,39
24,85	39,9	40,0	78,52	99,33	39,68	49,22	69,43
24,73	39,9	39,9	78,56	99,47	39,72	49,27	69,37
24,73	40,2	39,7	78,60	99,55	39,69	49,28	69,47
24,74	39,9	—	78,58	99,48	39,81	49,24	69,47
24,74	40,1	—	78,65	99,46	39,69	49,27	69,46
24,71	40,0	—	78,79	99,36	39,76	49,25	69,44
24,84	40,1	—	78,63	99,36	39,76	49,18	69,36

C.2.2 Uncertainty of the volume determination

Variations in the measured volume reflected variability in the filling and emptying process and in the performance of the balance. The standard deviations, $u_{V,1}$, of the estimates for the volume, V, listed in Table C.1, are given in Table C.2.

The balance was also subject to a linearity deviation from the true value as $+$ 0,02 mg (equivalent to 0,02 ml) in the range 0 g to 5 g. Assuming a rectangular distribution, the best estimate of the respective standard uncertainty in V, $u_{V,2}$, is also shown in Table C.2.

Table C.2 — Measured volumes of the syringes

Syringe type	Syringe number	Average volume V µl	Uncertainty of filling and emptying syringe for determining V $u_{V,1}$ µl	Uncertainty of the balance for determining V $u_{V,2}$ µl
NO	1	24,71	$4{,}68 \times 10^{-2}$	$1{,}15 \times 10^{-2}$
	2	39,86	$4{,}56 \times 10^{-2}$	$1{,}15 \times 10^{-2}$
	3	78,43	$9{,}44 \times 10^{-2}$	$1{,}15 \times 10^{-2}$
	4	99,23	$7{,}15 \times 10^{-2}$	$1{,}15 \times 10^{-2}$
SO_2	1	39,65	$4{,}56 \times 10^{-2}$	$1{,}15 \times 10^{-2}$
	2	49,16	$4{,}94 \times 10^{-2}$	$1{,}15 \times 10^{-2}$
	3	69,29	$4{,}86 \times 10^{-2}$	$1{,}15 \times 10^{-2}$

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C.3 Example of calibration certificate for a syringe driver

The following data for this were provided by Sira Test and Certification Ltd, UK.

NOTE The following details are entered at the head of the certificate; Name of customer, order number, certificate reference number, date of receipt of instrument, date of calibration, instrument manufacturer, model number and serial number.

The proprietary “syringe pump” (syringe driver) was calibrated against a digital micrometer and a digital timer the calibrations of which are traceable to national standards. The calibration was carried out at 20 °C ± 2 °C. The syringe pump was set up with the following parameters and in accordance with the manufacturer's instructions, but with the digital micrometer in the position, which would normally be occupied by the syringe.

Syringe type: Proprietary plastics syringe, 1 cm^3 (1 ml)

Diameter of syringe: 4,70 mm

Volume of syringe: 0,40 cm^3 (0,40 ml)

The initial position of the syringe plunger is measured from the right hand end stop.

Table C.3 — Results of syringe plunger calibration using digital micrometer

Initial position	Theoretical travel	Plunger travel at a flow rate of 2 ml/h	Plunger travel at a flow rate of 5 ml/h	Plunger travel at a flow rate of 10 ml/h	Plunger travel Mean	Difference between theoretical and experimental travel
mm	mm	mm	mm	mm	mm	% reading
10	23,055	22,99	22,99	23,00	22,99	−0,3
35	23,055	23,01	23,01	22,98	23,00	−0,2
60	23,055	23,02	22,98	22,98	22,99	−0,3

Table C.4 — Results of syringe plunger calibration using timer

Indicated rate	Theoretical run time	Run time: Run 1	Run time: Run 2	Run time: Run 3	Run time: Mean	Difference between theoretical and experimental run time
ml/h	s	s	s	s	s	% reading
2	720,0	720,41	720,38	720,41	720,4	0,1
5	288,0	288,15	288,19	288,25	288,2	0,1
10	144,0	144,12	144,22	144,13	144,2	0,1

The uncertainty of length measurement is estimated to be ± 0,03 mm and the uncertainty of time measurement is estimated to be ± 0,3 s.

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Annex D
(informative)

Example of the determination of the uncertainty in the concentration of a calibration gas mixture prepared by the continuous injection method

D.1 Model equation

To take into account the uncertainty on

a) the volume fraction of calibration component,

b) the volume fraction of the calibration component in the complementary gas,

c) the volume flow rate of the calibration component and of the complementary gas,

d) the uncertainty of the determination of linear velocity of the plunger and the diameter of the syringe, or on the volume of the syringe and on the time rate of travel of the plunger in the syringe;

the following equations are used:

$$\varphi = \frac{\varphi_A q_A + \varphi_B q_B}{q_A + q_B} \tag{D.1}$$

The volume flow rate of the calibration component is in general determined by an internal software of the infusion pump according to the desired flow rate, q, the determined volume of the syringe, V, the operational length of the syringe, L, and the travel of the plunger, l, which is a characteristic of each infusion pump. The describing equation is used:

$$q_A = vS \tag{D.2}$$

with $v = \frac{l}{t}$ and $S = \frac{V}{L}$

The combined uncertainty, u_c, is then:

$$\begin{aligned} u_c^2(\varphi) &= \left(\frac{\partial\varphi}{\partial\varphi_A}\right)^2 u^2(\varphi_A) + \left(\frac{\partial\varphi}{\partial\varphi_B}\right)^2 u^2(\varphi_B) + \left(\frac{\partial\varphi}{\partial q_A}\right)^2 u^2(q_A) + \left(\frac{\partial\varphi}{\partial q_B}\right)^2 u^2(q_B) \\ &= \frac{(\varphi_A - \varphi_B)^2 \left[q_B{}^2 \;\; u^2(q_A) + q_A{}^2 \;\; u^2(q_B)\right]}{(q_A + q_B)^4} + \frac{q_A{}^2 \;\; u^2(\varphi_A) + q_B{}^2 \;\; u^2(\varphi_B)}{(q_A + q_B)^2} \end{aligned} \tag{D.3}$$

with expanded uncertainty: $U(\varphi) = 2 \;\; u_c(\varphi)$.

To compute $u(q_A)$, the following equations are used:

$$u^2(q_A) = v^2 u^2(S) + S^2 u^2(v)$$

with $u^2(v) = \frac{1}{t^2} u^2(l) + \frac{l^2}{t^4} u^2(t)$

and $u^2(S) = \frac{1}{l^2} u^2(V) + \frac{V^2}{l^4} u^2(l)$ (D.4)

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D.2 List of quantities

Quantity	Unit	Description
φ	—	Volume fraction of the calibration gas mixture
φ_A	—	Conventional true volume fraction of the calibration component in the gas supplied as calibration component
q_A	m^3/s	Volume flow rate of calibration component
φ_B	—	Volume fraction of the calibration component in the complementary gas
q_B	m^3/s	Volume flow rate of complementary gas
S	m^2	Cross-sectional area of the syringe
v	m/s	Linear velocity of the plunger
L	m	Operational length of the syringe
l	m	Travel of the plunger
t	s	Duration of travel of the plunger
V	m^3	Volume of the syringe

φ_A The volume fraction of the calibration component and its corresponding uncertainty should be evaluated either by the end-user or provided by an external laboratory accredited for such testing. For the purpose of this example, a lower and an upper limit for the purity are chosen to be 0,995 and 1,000 with maximal probability for the purity equal to 0,997 5 and null probability that the purity is 0,995 or 1,000. The probability distribution is then triangular with 100 % probability that the purity lies within this interval: value: 0,997 5, half-width of distribution: 0,002 5.

q_A Some conditions are supposed to be fulfilled such as: the syringe needle is such that there is no backpressure within the syringe, the syringe is maintained at room temperature, no vibration occurs when the plunger is pushed, the radius of the syringe is constant throughout the travel of the plunger, all precautions are taken to avoid any dead volume in the syringe, no diffusion of gas occurs through the needle or closing valve of the syringe after it has been filled, the calibration gas mixture is prepared from non-reacting species.

φ_B In the case of sulfur dioxide, a volume fraction of less than 1×10^{-9} can be attained. For expression of the standard uncertainty a Type B triangular distribution with half-width of distribution: 1×10^{-9} is chosen.

q_B The volume flow rate of complementary gas, controlled, for example, by using a thermal mass controller for which a common value for expanded uncertainty is 1 %. Example: value: $3{,}33 \times 10^{-5}$ m^3/s, standard uncertainty: $0{,}016\,66 \times 10^{-5}$ m^3/s.

l For travel of the plunger, data from the example of the calibration certificate for a syringe driver are used: value: 0,023 m, half-width of distribution: 0,000 03 m, Type B rectangular distribution.

t For duration of travel of the plunger, the data in C.3, example of calibration certificate for a syringe driver are used: value: 288 s, half-width of distribution: 0,3 s, Type B rectangular distribution.

V The volumes of the syringe used for injection may be determined by filling it with water and deriving volume from the weight of liquid contained in the syringe (corrected for water density of 0,998 g/cm^3 at 22 °C). The uncertainty of the balance should be included in the determination of uncertainty of the volume of syringe. For the volume of the syringe, the data in C.2, example of methodology to determine the characteristics of metering syringes are used: value: $39{,}65 \times 10^{-9}$ m^3, standard uncertainty: $4{,}70 \times 10^{-11}$ m^3.

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D.3 Uncertainty budget

Quantity	Value	Standard uncertainty
φ_A	0,997 5	$1{,}02 \times 10^{-3}$
q_A	$1{,}273 \times 10^{-10}$ m^3/s	$1{,}37 \times 10^{-12}$ m^3/s
v	$7{,}986 \times 10^{-6}$ m/s	$6{,}03 \times 10^{-8}$ m/s
l	$2{,}300 \times 10^{-3}$ m	$1{,}73 \times 10^{-5}$ m
t	288,2 s	0,173 s
S	$1{,}593 \times 10^{-5}$ m^2	$1{,}22 \times 10^{-7}$ m^2
V	$3{,}965 \times 10^{-8}$ m^3	$4{,}70 \times 10^{-11}$ m^3
l	$2{,}300 \times 10^{-3}$ m	$1{,}73 \times 10^{-5}$ m
φ_B	$1{,}000 \times 10^{-9}$	$4{,}08 \times 10^{-10}$
q_B	$3{,}330 \times 10^{-5}$ m^3/s	$1{,}67 \times 10^{-7}$ m^3/s
φ	$3{,}819\,5 \times 10^{-6}$	$4{,}53 \times 10^{-8}$

D.4 Result

Quantity: φ

Value: $3{,}819 \times 10^{-6}$

Relative expanded uncertainty: $\pm$ 2,4 %

Coverage factor: 2

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