INTERNATIONAL STANDARD

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6145-2

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

Part 2:
Piston pumps

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

Partie 2: Pompes à piston

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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. www.iso.org/directives

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For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information

The committee responsible for this document is ISO/TC 158, *Analysis of gases*.

This second edition cancels and replaces the first edition (ISO 6145-2:2001), which has been technically revised. The main objective of this revision is to extend the first edition for calculating the composition in volume and amount–of–substance fractions from the displacement volumes of piston pumps. Appropriate measurement functions and guidance on uncertainty evaluation are given for the mixing of real gases at unequal operational conditions of the piston pumps.

ISO 6145 consists of the following parts, under the general title *Gas analysis — Preparation of calibration gas mixtures using dynamic 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ISO 6145-3, entitled *Periodic injections into a flowing gas stream*, has been withdrawn.

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

Part 2:
Piston pumps

1 Scope

ISO 6145 comprises a series of International Standards dealing with various dynamic methods used for the preparation of calibration gas mixtures. This part of ISO 6145 describes a method and preparation system using piston pumps. The mixture composition and its associated uncertainty are based on calibration of the piston pumps by dimensional measurements.

The calibration gas mixtures prepared using this method consist of two or more components, prepared from pure gases or other gas mixtures using gas-mixing pumps. Such gas-mixing pumps contain at least two piston pumps, each driven with a defined ratio of strokes, and appropriate accessories for gas feeding and mixture homogenization.

This part of ISO 6145 is applicable only to mixtures of gaseous or totally vaporized components including corrosive gases, as long as these components neither react with each other nor with the wetted surfaces of the mixing pump. The use of gas mixtures as parent gases is covered as well. Multi-component gas mixtures and multi-step dilution procedures are included in this International Standard as they are considered to be special cases of the preparation of two-component mixtures.

This part of ISO 6145 describes a method of preparing calibration gas mixtures whose composition is expressed in volume fractions. The necessary equations and associated uncertainty evaluation to express the gas composition in amount–of–substance fractions are given in Annex A.

With this method, provided that sufficient quality assurance and control measures are taken, calibration gas mixtures can be prepared with a relative expanded uncertainty of 0,5 % (coverage factor $k = 2$) in the volume fraction. Numerical examples showing that under specified conditions smaller uncertainties are attainable are given in Annexes B through D.

Using this method, dilution ratios of 1:10 000 can be achieved in discrete increments. Lower fractions (down to 1×10^{-8}) can be achieved by multi-stage dilution or by the use of gas mixtures as input gases. Final mixture flow rates of 5 l/h to 500 l/h can be realized depending on the equipment used.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 7504, *Gas analysis — Vocabulary*

ISO 14912, *Gas analysis — Conversion of gas mixture composition data*

ISO/IEC Guide 98-3, *Uncertainty of measurement — Part 3: Guide to the expression of uncertainty in measurement (GUM:1995)*

ISO/IEC Guide 99, *International vocabulary of metrology — Basic and general concepts and associated terms (VIM)*

3   Terms and definitions

For the purposes of this document, terms and definitions given in ISO/IEC Guide 99, ISO/IEC Guide 98-3, ISO 14912, ISO 7504, and the following apply.

3.1
operational conditions
pressure and temperature in the piston pumps at which the gas mixture is prepared

3.2
parent gas
pure gas or gas mixture used for preparation of a gas mixture

3.3
piston pump
gas forwarding system comprising cylinder, piston, steering plate, and eccentric driving disk mounted on a common plate

3.4
reduction gear ratio
quotient of the number of strokes and the maximum number of strokes of the piston pump that can be set in distinct steps by the switch gear

3.5
reference conditions
pressure and temperature to which volume fractions refer

3.6
stroke volume
forwarding geometric displacement volume per stroke of a piston pump

4   Symbols

Symbol	Quantity	Unit
B'	second virial coefficient (virial equation–of–state in pressure)	Pa^{-1}
i	index of a component	
k,l	index of a piston pump; index of a parent gas	
L	gear ratio	
N	number of strokes (in a given period of time)	
N_{max}	maximum number of strokes (in a given period of time)	
n	amount–of–substance	mol
n_{mix}	total amount–of–substance of a mixture	mol
p	pressure	Pa
R	ideal gas constant	J mol^{-1} K^{-1}
T	temperature	K
u	standard uncertainty	
V	gas volume	m^3

Symbol	Quantity	Unit
V_{geo}	stroke volume	m^3
x	amount–of–substance fraction (of a component in a parent gas)	1
y	amount–of–substance fraction (of a component in the prepared gas mixture)	1
Z	compressibility	1
ϕ	volume fraction (of a component in the prepared gas mixture)	1
φ	volume fraction (of a component in a parent gas)	1

5 Principle and equipment

5.1 Principle

The principle of the dynamic preparation method described in this part of ISO 6145 is based on the displacement volume of piston pumps forwarding defined gas portions that are continuously merged and homogenized for obtaining the required gas mixture. For pure gases, the volume fraction of component i in the prepared gas mixture is approximately equal to the volume of component i divided by total volume of all components, as given by Formula (1):

$$\varphi_i \approx \frac{N_i \cdot V_{geo,i}}{\sum_k N_k \cdot V_{geo,k}} \tag{1}$$

where ϕ_i denotes the volume fraction of component i at the operational conditions of the piston pumps. These conditions may differ from the conditions at which the calibration gas mixture thus prepared is going to be used.

The calculation of volume fractions is described in Clause 7, in two variants. Method A requires the prepared gas mixture to be used at the operational conditions (7.1), whereas method B covers the expression of the volume fractions at reference conditions (7.2). Depending on the situation, one of these methods shall be used in applications where volume fractions are needed.

In applications, where amount–of–substance fractions are needed, these shall be calculated directly from the displacement volumes. The necessary expressions and associated uncertainty evaluation are given in Annex A.

5.2 Equipment

Calibration gas mixtures with defined composition are prepared using gas-mixing pumps containing two or more piston pumps, pneumatically separated from each other. A common motor drives the piston pumps via separate gear trains and individual switch gears. The number of strokes of the individual piston pumps is defined by preset reduction gear ratios. The gas portions forwarded by each of the piston pumps are quantified by the stroke volume $V_{geo,k}$ and by their individual number of strokes N_k (see Figure 1).
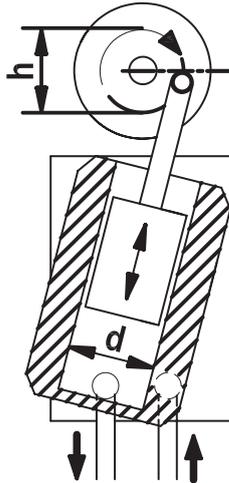
Key

d diameter of cylinder

h height of piston stroke

Figure 1 — Principle of a piston pump

To achieve the required calibration gas mixture, separately forwarded gas portions are merged and homogenized. Since the stroke volume $V_{geo,k}$ is constant, different gas compositions are prepared only by variation of the number of strokes N_k. The use of both quantities is sufficient for the calculation of mixture composition when using pure gases.

The stroke volume of piston pump k is calculated from the diameter of its cylinder and the height of its piston stroke

$$V_{geo,k} = \frac{\pi}{4} \cdot d_k^2 \cdot h_k \qquad (2)$$

The forwarded gas volume is usually given as a whole number times the stroke volume. The number of strokes can be chosen in order to achieve the desired mixing ratio. The gear ratio L_k relates the stroke number to the maximum number of strokes

$$N_k = L_k \cdot N_{\max} \qquad (3)$$

An example of realization of the described method is shown in Figure 2 for a gas-mixing pump comprising two piston pumps 1 and 2 of the same size. Both piston pumps are driven by a common electrical motor, key 8, via defined gear trains with switch gears key 2 and key 4, respectively. Gases 1 and 2 are fed to the piston pumps via gas inlets figure footnotes a and b, respectively. Bubbling vessels (key 5) at the gas inlets are used to control the input pressure to the piston pumps and to adjust a small excess gas flow which is vented at ambient pressure. The temperature of each piston pump can be measured with temperature sensors T_1 and T_2 that shall be integrated into the body of the piston pumps. The gases forwarded by the piston pumps are merged and homogenized in mixing vessel (key 6). The final gas mixture is provided at gas outlet (key 7) to the intended application. Details of the implementation of temperature control of piston pumps and parent gases attaining reduced uncertainties is given in Annex B.

Key
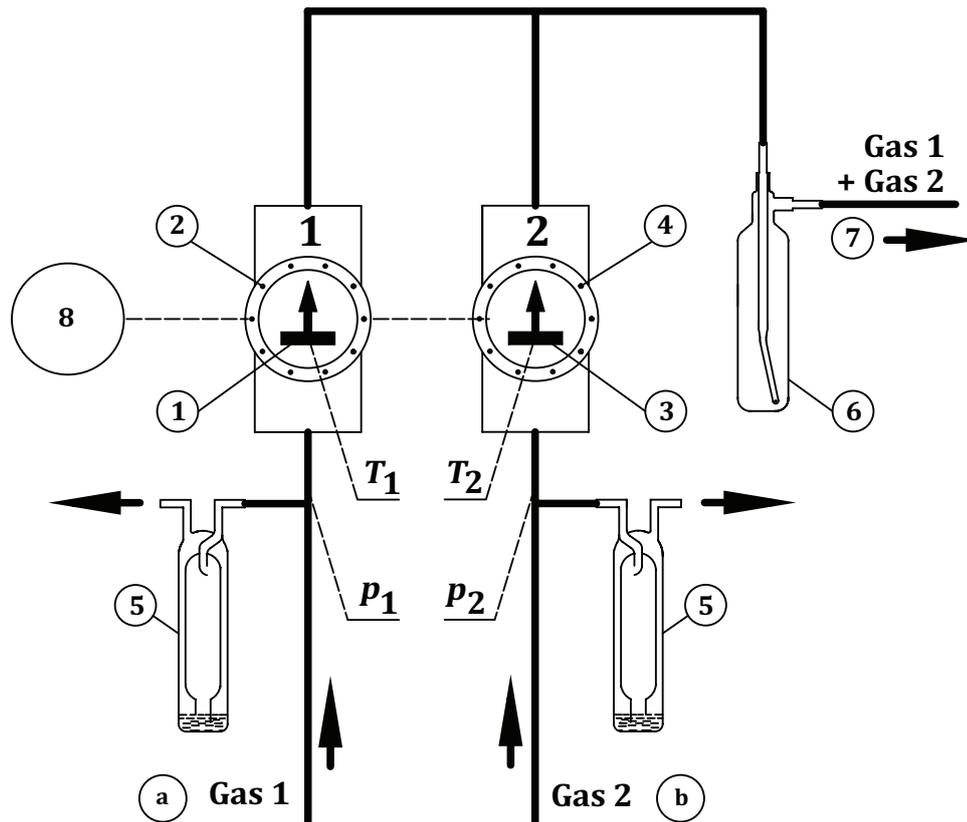
p_1	pressure, piston pump 1	4	switch gears 2
p_2	pressure, piston pump 2	5	bubbling vessel
T_1	temperature sensor, piston pump 1	6	mixing vessel
T_2	temperature sensor, piston pump 2	7	gas outlet for gas mixture
1	piston pump 1	8	drive motor
2	switch gears 1	a	Gas inlet for gas 1.
3	piston pump 2	b	Gas inlet for gas 2.

NOTE   Piston pumps 1 and 2 as shown in Figure 1.

Figure 2 — Example of realization for the dynamic preparation of two-component calibration gas mixtures

6   Calibration gas mixture preparation

6.1   Safety issues

The possibility of dangerous reactions, such as explosions (e.g. mixtures containing flammable gases and oxygen) or strongly exothermic polymerisations (e.g. hydrogen cyanide) and decompositions (e.g. acetylene), shall be excluded for safety reasons. If there is the possibility of formation of hazardous gas mixtures, all appropriate safety precautions shall be applied. Information on dangerous reactions and dangerous combinations that shall be excluded for safety reasons is provided in dangerous goods regulations and in gas supplier handbooks.[1]

Safe discharge of toxic or flammable gases and gas mixtures shall be ensured. Contact with ignition sources shall be avoided, if merging of the parent gases can form flammable mixtures. Short–term concentration peaks can occur when the composition is changed.

Precautions shall be taken during feeding the parent gases to the piston pumps, handling the intermediate gas mixtures and final mixtures. The compliance with applicable safety instructions of the mixing pumps, pressurization pumps, and filling reservoirs shall be confirmed before beginning the preparation.

6.2 Mixture feasibility

The choice of appropriate set-up and suitable procedure for dynamic preparation of gas mixtures can be a complex procedure. At first, all requirements concerning the intended application of the prepared gas mixture shall be defined. Then, the properties of available gases and gas mixtures, possible reactions between gas components and the wetted material of the pumps and peripherals, and the purity and impurities of the mixed gases shall be considered. Further, the characteristics of the applied gas-mixing pumps and the blending method shall be considered.

The following phenomena shall be taken into account when considering the feasibility of preparing the required gas mixture:

a)   reactions between mixture components;

b)   reactions with piston pump, pressurization pump, and container material;

c)   reactions with elastomers and greases (e.g. in the piston pumps, the pressurization pump, the valve seat and seals).

Reactions with elastomers and greases should be prevented by using only materials that are inert to all components of the mixture. If this is not possible, measures should be taken to minimize corrosive attack on the materials with which the gases will make contact such that there is no significant effect on mixture composition and no danger in storage and use.

When choosing a suitable preparation procedure, a number of considerations should be made to ensure that the most appropriate method is used. The following parameters should be considered:

a)   number of components in the final mixture;

b)   range of fractions of each component of the final mixture;

c)   flow rate of the final mixture;

d)   flow rate of the parent gases;

e)   established composition of each parent gas mixture used;

f)   blending method: parallel method — serial method — multiple dilution;

g)   mechanical characteristics of the piston pumps to be used;

h)   performance characteristics of the mixing pump to be used;

i)   pressure to which the final gas mixture has to be delivered;

j)   characteristics of the pressurization pump (if necessary);

k)   possibility of condensation;

l)   requirements on the preparation tolerance.

Using Formula (1), the target composition can be calculated and a preparation procedure selected.

The final mixture composition is calculated using the expressions given in Clause 7 for volume fractions and Annex A for amount–of–substance fractions.

In principle, it is recommended to use gas mixing pumps at those operating conditions where the influence of the sources listed in Table B.1 can be considered not significant. If this is not possible, the

corresponding influences have to be considered by an appropriate uncertainty contribution. Table B.1 and further information about potential sources of uncertainty are listed in Annex B. An example for a set-up with reduced contribution of uncertainty of temperature is given in B.4.

6.3   Preparation system and setting-up of mixture composition

Examples for the setup of a complete system for the dynamic preparation of calibration gas mixtures according to the volumetric method described in this part of ISO 6145 are shown schematically in Figure 2, and in B.4 for high-end applications (i.e. applications with reduced uncertainty).

Gas containing the component(s) of interest and matrix gases shall be fed to piston pumps with slight excess gas flow at a pressure slightly above ambient pressure and at constant temperature (preferably at ambient temperature). The requirement of gas intake at the desired pressure can be met by use of bubblers in a by-pass flow at the gas inlets. This excess gas flow also inhibits the leakage of air into the pump.

Before starting preparation of calibration gas mixtures, the entire flow system external to the mixing pump itself shall be checked for leak tightness and contaminations of gas conduits.

Gas portions forwarded by piston pumps are preset by positioning the reduction gear ratio in a way that the target composition of the calibration gas mixture is obtained as described in Clause 7.

NOTE   Expressions for the calibration gas mixture in terms of amount–of–substance fractions are given in Annex A.

6.4   Input pressure control

Elimination of differences between input pressures of piston pumps is highly relevant for the performance of the method. Pressures at the inputs of the gas-mixing pump shall be maintained as close as possible to the same values for all pistons. For this purpose, the level of sealing liquid in the bubblers shall be the same.

The pressure of gases taken from gas cylinders shall be reduced to the appropriate pressure using 1- or 2-stage pressure reducers. The use of precisely adjustable needle valves or diaphragm pressure reducing valves is recommended to reduce the gas consumption. The regulators shall be directly connected to the gas inputs of the gas-mixing pump. A slight excess of gas is conducted to ambient pressure via a by-pass that is equipped with a bubbling vessel. The use of appropriate bubbling vessels allows reducing pressure difference in the pumps to 10 Pa or less between the gas inlets.

6.5   Temperature control

Elimination of temperature differences between the piston pumps is highly relevant for the performance of the method. The exposure of the mixing pump to all kinds of radiation and air flow shall be avoided.

The Joule-Thomson effect of expanding gases due to pressure reduction or evaporation in case of liquids shall be minimized. If large gas volumes from compressed gas-cylinders are used, reheating of the gases can be necessary.

For optimal performance, it is recommended to measure the temperatures using calibrated temperature sensors using calibrated temperature sensors that are introduced into the sockets integrated into each piston pump and to take temperature differences into account as necessary.

NOTE   The operation of the piston pumps and the gas feed at a constant temperature reduces the uncertainty associated with the composition, an example of its realization is given in B.4.

6.6   Homogenization

The gases forwarded by the piston pumps shall be merged and homogenized in a flow process. For this purpose, the gas mixture is continuously conducted through one or more appropriate mixing vessels.

The design and volume of the mixing vessels shall be adapted to the stroke volume of the piston pumps, their capacities being preferably 10 to 15 times the stroke volume of the largest piston pump.

NOTE   An improvement of gas mixture homogeneity is attained by cascading two or three mixing vessels of the same capacity rather than using only one mixing vessel with increased capacity.

The efficiency of the homogenization equipment, e.g. the mixing vessels, shall be verified by appropriate methods for different gas mixtures and intended applications.

6.7   Stability

Calibration gas mixtures prepared according to this part of ISO 6145 are intended for direct use. If the safety and mixture feasibility conditions are met, no degradation of the mixture composition occurs.

The reproducibility of a gas mixture generated by the preparation system is ensured under the condition that the influencing factors, in particular temperature and pressure, are kept constant.

6.8   Output pressure and flow pulsation

After homogenization, the gas mixtures are available at the gas outlet at approximately ambient pressure. Diameter and length of connecting tubes shall be of appropriate dimensions to avoid an unacceptably high back pressure caused by flow resistance. Tubes with sufficiently wide inner diameter are preferably used. Possible flow restrictions of connected analysers or other devices and apparatus shall be minimized to the extent possible. If so necessary, an outlet pressure above ambient shall be generated separately using suitable compression pumps with appropriate accessories.

Owing to the forwarding principle of piston pumps, the gas flow at the outlet is subject to pulsations in flow. The influence of these pulsations can be minimized by technical means, e.g. appropriate diameter of conduits, reduced flow resistance inside connected units, inserted buffers, or by-pass installations.

6.9   Composition of the parent gases

If pure gases are used, then the volume or amount–of–substance fraction of the main component shall be corrected for the presence of impurities. In case of composition data in terms of amount–of–substance fractions, the amount–of–substance fraction of the main component can be calculated using Formula (4):

$$x_1 = 1 - \sum_{j=2}^{J} x_j \tag{4}$$

The standard uncertainty associated with the amount–of–substance fraction of the main component (x_1) is calculated using Formula (5)

$$u^2(x_1) = \sum_{j=2}^{J} u^2(x_j) \tag{5}$$

If the gas composition data are expressed as volume fractions, the volume fraction of the main component is calculated using Formula (6)

$$\phi_1 = 1 - \sum_{j=2}^{J} \phi_j \tag{6}$$

It is important to verify that the conditions (p and T) at which the volume fractions are given match those at which the gases are mixed and used, respectively. Otherwise, the volume fraction shall be converted from the stated conditions to the required conditions, using, e.g. the method of ISO 14912. More guidance in converting volume fractions is given in 7.2.

The standard uncertainty associated with the volume fraction of the main component (φ_1) is calculated using Formula (7)

$$u^2(\phi_1) = \sum_{j=2}^{J} u^2(\phi_j)$$ (7)

When using gas mixtures as parent gases, the composition (expressed in volume or amount–of–substance fractions) can be used as such, provided that for volume fractions the conditions at which the composition is stated match the operational and reference conditions. If these conditions differ, appropriate correction(s) shall be applied in accordance with ISO 14912.

7 Calculation of volume fractions and associated uncertainty evaluation

7.1 Calculation method A

This calculation method can be used when the calibration gas mixture is used at the same conditions (p and T) as those of the piston pumps. If this is not the case, the method of 7.2 shall be used instead.

The volume fraction of a component i in the calibration gas mixture is computed using Formula (8):

$$\varphi_i = \frac{\sum_k V_k \phi_{ki}}{\sum_k V_k}$$ (8)

or, equivalently, using Formula (1),

$$\varphi_i = \frac{\sum_k N_k \cdot V_{geo,k} \phi_{ki}}{\sum_k N_k \cdot V_{geo,k}}$$ (9)

where φ_{ki} denotes the volume fraction of component i in parent gas k. If the gas composition of the mixture to be diluted is given in amount–of–substance fractions, ISO 14912 shall be applied to convert the amount–of–substance fractions into volume fractions.

If the stroke volumes and the maximum number of strokes of all piston pumps are the same, then the volume fraction can also be computed using the gear ratios in Formula (10):

$$\varphi_i = \frac{\sum\limits_{k} L_k \phi_{ki}}{\sum\limits_{k} L_k} \tag{10}$$

The standard uncertainty associated with ϕ_i is computed using Formula (11)

$$u^2(\varphi_i) = \varphi_i^2 u^2\left(\frac{V_1}{V_2}\right) + \sum\limits_{k}\left(\frac{L_k}{\sum\limits_{l} L_l}\right)^2 u^2(\phi_{ki}) \tag{11}$$

where

$$u^2\left(\frac{V_1}{V_2}\right) = \frac{2u^2(V) + (V_2 - V_1)^2}{V^2} \tag{12}$$

where V_1 and V_2 denote the geometric volumes of the piston pumps P_1 and P_2.

NOTE 1   The expression in Formula (12) accounts for the assumption that the stroke volumes of any two pistons are the same. The formula is also applicable if the nominal volumes are the same, but $V_1 \neq V_2$. If both volumes are exactly equal, Formula (12) reduces to the common expression for the squared standard uncertainty of a ratio of two independent variables, as the second term in the nominator is zero.

NOTE 2   In case of multiple pumps with the same nominal volume, the difference in Formula (12), $(V_2 - V_1)^2$ is to be replaced by $s^2(V)$, where s denotes the standard deviation of the volumes of the pumps.

If not given as volume, the stroke volume shall be computed using Formula (2). The standard uncertainty associated with the stroke volume can be computed using Formula (13)

$$u^2(V_{geo,k}) = \left(\frac{1}{2}\pi h d\right)^2 u^2(d) + \left(\frac{1}{4}\pi d^2\right)^2 u^2(h) + \left(\frac{V_{geo,k}}{p_k}\right)^2 u^2(p_k) + \left(\frac{V_{geo,k}}{T_k}\right)^2 u^2(T_k) \tag{13}$$

In B.3, examples are given for this calculation method, including an uncertainty statement for a gas mixture with 4 components prepared with a gas-mixing pump with 4 piston pumps having different geometric stroke volumes with a ratio of 100: 10: 1 giving a maximum dilution ratio of 1: 1 000.

An example with this calculation method, performing the calibration of a gas analyser for NO measurement in the environmental field with a measuring range 0 ppm[1] to 100 ppm volume fraction is given in Annex D.

7.2   Calculation method B

7.2.1   Calculation of volume fraction

The volume fraction of component i at p_{ref} and T_{ref} is given by Formula (14):

$$\varphi_i = \frac{\sum\limits_{k} V_k p_k T_k^{-1} Z_{ref,k} Z_k^{-1} \phi_{ki}}{\sum\limits_{k} V_k p_k T_k^{-1} Z_{ref,k} Z_k^{-1}} \tag{14}$$

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1)   ppm = parts per million

7.2.2 Calculation of compressibility and associated standard uncertainty

The expression for the volume fraction Formula (14) requires the calculation of the compressibility twice: once at the conditions of mixing (p_k and T_k) and a second time at conditions p_{ref} and T_{ref}. The evaluation of the compressibility can be carried out in different ways, including the use of equations–of–state.[5] Alternatives to the use of equations–of–state include the use of tabulated data.[5] ISO 14912 provides a calculation method based on the virial equation–of–state given by Formula (15):

$$Z(p,T) = 1 + B'(T)p \tag{15}$$

Values for $B'(T)$ are given, among others, in ISO 14912. The calculation of the gas compressibility is described in detail in ISO 14912, including the evaluation of associated measurement uncertainty.

7.2.3 Uncertainty evaluation of the volume fraction

The basis for the uncertainty evaluation is Formula (17). The standard uncertainty associated with the volume fraction of component i can be computed using

$$u^2(\varphi_i) = \sum_k \left(\frac{\partial \varphi_i}{\partial \phi_{ki}}\right)^2 u^2(\phi_{ki}) + \sum_k \left(\frac{\partial \varphi_i}{\partial T_k}\right)^2 u^2(T_k) + \sum_k \left(\frac{\partial \varphi_i}{\partial p_k}\right)^2 u^2(p_k) + \sum_k \left(\frac{\partial \varphi_i}{\partial V_k}\right)^2 u^2(V_k) +$$
$$\sum_k \left(\frac{\partial \varphi_i}{\partial Z_k}\right)^2 u^2(Z_k) + \sum_k \left(\frac{\partial \varphi_i}{\partial Z_{ref,k}}\right)^2 u^2(Z_{ref,k}) \tag{16}$$

The expressions for the sensitivity coefficients in Formula (16) read as follows

$$\frac{\partial \varphi_i}{\partial \phi_{ki}} = \frac{p_k V_k Z_{ref,k}}{T_k Z_k} \frac{1}{W^*}$$

$$\frac{\partial \varphi_i}{\partial T_k} = -\frac{p_k V_k Z_{ref,k}\phi_{ki} + \varphi_i V_k p_k Z_{ref,k}}{T_k^2 Z_k W^*}$$

$$\frac{\partial \varphi_i}{\partial p_k} = \frac{V_k Z_{ref,k}\phi_{ki} - \varphi_i V_k Z_{ref,k}}{T_k Z_k W^*}$$

$$\frac{\partial \varphi_i}{\partial V_k} = \frac{p_k Z_{ref,k}\phi_{ki} - \varphi_i p_k Z_{ref,k}}{T_k Z_k W^*}$$

$$\frac{\partial \varphi_i}{\partial Z_k} = \frac{p_k V_k Z_{ref,k}\phi_{ki} + \varphi_i V_k p_k Z_{ref,k}}{Z_k^2 T_k W^*}$$

$$\frac{\partial \varphi_i}{\partial Z_{ref,k}} = \frac{p_k V_k \phi_{ki} - \varphi_i p_k V_k}{T_k Z_k W^*}$$

where

$$W^* = \sum_k V_k p_k T_k^{-1} Z_{ref,k} Z_k^{-1}$$

The evaluation of the standard uncertainty associated with the pressure, temperature and volume is exemplified in Annex B. Variations in gas temperature and pressure shall be duly incorporated in the values for the respective standard uncertainties.

8 Gas mixture composition verification

Verification of the calculated gas mixture composition prepared by gas-mixing pumps shall be done using one of the following methods:

a) comparison measurements with gas mixtures whose composition is established independently (e.g. using ISO 6143);

b) determination of the gas density with gas density measuring systems (e.g. sink body gauges); this method is only appropriate for binary gas mixtures if used as exclusive verification method; the required minimum difference of density of the respective gases is a further limitation.

c) verification by gas mixtures pair–wise prepared using the gas-mixing pump to be verified comprising the symmetry check performing comparison of two gas mixtures with $x = 0,5$ or $\phi = 0,5$, and verification of linearity performing comparison of two gas mixtures prepared with reduction gear ratios $L_1 = 0,5$; $L_2 = 0,2$ and with $L_1 = 1,0$; $L_2 = 0,4$.

NOTE   More information about these methods is given in Annex C.

The availability of reference gas mixtures with appropriate uncertainty levels for the amount–of–substance fractions shall be established. A recommended scope of a validation procedure is given in Annex D.

If there is no appropriate validation available for the intended range of application with respect to the kind of gases of interest, the mixing ratios, and the forwarded gas volumes, it is necessary to do verification with comparison measurements with 5 (better 7) reference gas mixtures. A recommended scope of validation procedure is given in Annex D.

Annex A
(normative)

Amount-of-substance fractions

A.1 Calibration gas mixture composition

The number of moles (amount–of–substance) forwarded by piston pump *k* is given by Formula (A.1):

$$n_k = \frac{p_k V_k}{R T_k Z_k} \tag{A.1}$$

and shall be directly calculated from the forwarding displacement volumes [see Formula (1)]. Formula (A.1) is based on the equation–of–state for real gases.

For a gas mixture, the expression for the amount–of–substance fraction of component *i* is given by Formula (A.2):

$$y_i = \frac{\sum_k n_k x_{ki}}{\sum_k n_k} \tag{A.2}$$

Apart from n_k, which can be computed using Formula (A.1), the amount–of–substance fractions of the components of the parent gases are required. When mixing a gravimetrically prepared gas mixture with a pure gas, usually the composition is available in amount–of–substance fractions. If other quantities are used, the procedures of ISO 14912 shall be used to convert the gas composition data into amount–of–substance fractions.

When purity data are available, these shall be processed as detailed in 6.9.

A.2 Uncertainty evaluation

The uncertainty evaluation can be carried out as follows. Applying the law of propagation of uncertainty to Formula (A.2) leads to Formula (A.3)

$$u^2(y_i) = \sum_k \left(\frac{\partial y_i}{\partial n_k} \right)^2 u^2(n_k) + \sum_k \left(\frac{\partial y_i}{\partial x_{ki}} \right)^2 u^2(x_{ki}) \tag{A.3}$$

The expressions for the sensitivity coefficients read as

$$\frac{\partial y_i}{\partial n_k} = \frac{x_{ki}}{n_{mix}} - \frac{y_i}{n_{mix}}$$

and

$$\frac{\partial y_i}{\partial x_{ki}} = \frac{n_k}{n_{mix}}$$

where

$$n_{mix} = \sum_k n_k$$

The standard uncertainty associated with n_k is calculated using Formula (A.4):

$$u^2(n_k) = \left(\frac{n_k}{p_k} \right)^2 u^2(p_k) + \left(\frac{n_k}{T_k} \right)^2 u^2(T_k) + \left(\frac{n_k}{V_k} \right)^2 u^2(V_k) + \left(\frac{n_k}{Z_k} \right)^2 u^2(Z_k) \tag{A.4}$$

NOTE   Formula (A.4) is obtained by applying the law of propagation of uncertainty to Formula (A.1).

The evaluation of the standard uncertainty associated with p_k, T_k, V_k, and Z_k is analogous to that in 7.2.3 and exemplified in Annex B.

Annex B
(informative)

Uncertainty evaluation of the gas mixture composition

B.1 Potential sources of uncertainty

All quantities having the potential of influencing the output quantities (i.e. volume or amount–of–substance fractions) should be evaluated as uncertainty components. The list of all potential sources of uncertainty is given in Table B.1. The sources of uncertainty are arranged in three groups, assigned to the piston pumps, the gas components, and the gas mixture, respectively.

Table B.1 — Sources of uncertainty

Category of source	N°	Source of uncertainty	Notes
Sources assigned to the piston pumps	1	Uncertainty of the cylinder diameter	*
	2	Uncertainty of the height of stroke	*
	3	Uncertainty of the number of strokes (stroke ratio)	negligible
	4	Influence of the expansion of cylinder diameter	negligible
	5	Influence of the expansion of the eccentric disk (height of stroke)	negligible
Sources assigned to the gas components	6	Uncertainty of the compressibility	*
	7	Uncertainty of the gas constant R	negligible
	8	Uncertainty of the operational pressure	*
	9	Uncertainty of the operational temperature	*
	10	Uncertainty of the parent gas composition	*
	11	Influence of the flow rate on the flow resistance at the cylinder inlet and outlet	*
	12	Influence of density and viscosity on the flow resistance at the cylinder inlet and outlet	*
	13	Adsorption and desorption of gases inside the piston-pump	*
Sources assigned to the gas mixture	14	Influence of incomplete gas-mixture homogenization (inhomogeneity)	*
	15	Influence of the dynamic pressure at the homogenization unit outlet	*
	16	Loss of gas components due to piston-pump leakage	*
	17	Permeation of air components into the system	*
	18	Influence of intrusion of gas components due to diffusion / leakage	*
	19	Influence of adsorption and desorption of gases inside the homogenization unit and gas ducts	*

*   Uncertainty source to be considered in an uncertainty evaluation of the composition of a calibration gas mixture.

NOTE 1   The number of strokes (line 3) is a count and therefore assumed to have zero uncertainty.

NOTE 2   The expansion of the cylinder and eccentric disk (lines 4 and 5) are by far exceeded by the influence of temperature and pressure on the forwarded gas volume. Hence, these factors can be regarded as negligible.

NOTE 3   The uncertainty associated with the ideal gas constant (line 7) is much smaller than that of other model variables and cancels out in the combination and propagation of uncertainties.

According to the intended application and the required level of uncertainty, the identified sources should be individually assessed and their contribution to the combined uncertainty of composition should be quantified using the numerical procedure for uncertainty calculation given in Clause 7 and Annex A. The individual assessment of the indicated sources of uncertainty is described in B.2.

The uncertainty of input quantities with significant contribution to the combined uncertainty of composition is preferably evaluated as type A, i.e. by statistical analysis of series of measurements on the input quantities. Type B evaluations of uncertainty are acceptable as well.

During the validation for each application the complete system should be assessed for the uncertainty sources listed in Table B.1 marked with an "*" whether these cause a significant influence to the combined uncertainty of the composition of the calibration gas mixture. If possible, this influence should be minimized. In those cases where this is not possible, the remaining contribution should be included in the evaluation of the overall uncertainty.

B.2   Assessment of potential sources and quantification of significant sources of uncertainty

B.2.1   General

All sources of uncertainty listed in Table B.1 should be evaluated, except for those indicated as "negligible". The expressions for propagating the uncertainties are given in Clause 7 and Annex A.

B.2.2   Major sources of uncertainty

The uncertainty sources n° 1 and n° 2 as well as the influencing quantities n° 8 and n° 9 are assessed as major and can be quantified by statistical analysis of different series of measurement (type A analysis) as standard deviation. The measurement values are achieved by using calibrated gauges and measuring instruments. The contribution of these sources of uncertainty to the combined uncertainty of the quantities of composition volume fraction ϕ and amount–of–substance fraction y are calculated separately according to the numerical method given in Clause 7 and Annex A.

Examples of quantity values for $u(E)$ are given in Table B.2. These examples are based on measurements using the commercially available gas-mixing pumps. The examined pumps comprise piston pumps of the same size as mentioned in Clause 6 for calibration gases with fractions of 10×10^{-2} to 90×10^{-2} as well as piston pumps of different size with stroke-volume ratios of 100: 10 for fractions of 1×10^{-2} to 10×10^{-2}.

Table B.2 — Uncertainty contributions expressed in volume fraction

N°	Source of uncertainty E	Uncertainty $u(E)$	Contribution of uncertainty $u(\phi)$	
			$\phi = (1{,}0-10) \times 10^{-2}$	$\phi = (10-90) \times 10^{-2}$
1	Uncertainty of the cylinder diameter	0,001 4 mm	$1{,}0 \times 10^{-5}$	$3{,}6 \times 10^{-5}$
2	Uncertainty of the height of stroke	0,002 mm	$0{,}7 \times 10^{-5}$	$2{,}7 \times 10^{-5}$
8	Uncertainty of the mixture pressure	10 Pa	$0{,}5 \times 10^{-5}$	$2{,}7 \times 10^{-5}$
9	Uncertainty of the mixture temperature	0,04 K	$0{,}7 \times 10^{-5}$	$4{,}5 \times 10^{-5}$
	Combined uncertainty of the component fraction i at 4×10^{-2} and 40×10^{-2} in the calibration gas		$1{,}5 \times 10^{-5}$	$6{,}9 \times 10^{-5}$

The values of uncertainty given in the above table can be expressed as relative standard uncertainty associated with the volume fraction as well. This yields to $u(\phi)$ = 0,04 % for the 0,04 fraction and to $u(\phi)$ = 0,02 % for the 0,4 fraction.

Using the bubblers at the gas inlets of the individual piston pumps as recommended in 5.2, a small excess of gas is dissipated against ambient pressure. Therefore, the pressure at the inlet of the piston

pumps corresponds to the sum of the ambient pressure and the height of the sealing liquid inside the bubblers. The contribution of different values of the ambient pressure to the combined uncertainty of volume or amount–of–substance fractions is negligible. Thus, the uncertainty of pressure (n° 9) is determined by the accuracy of its measurement and fluctuations over time (as appropriate). Regarding the configuration of the equipment, the only component to be added to these is the uncertainty of the opening and flow resistance due to different levels of the sealing liquid in the bubblers. If bubblers of appropriate design are used, this uncertainty is less than 10 Pa (1 mm water column).

The temperature can be measured either with stationary temperature sensors in each piston pump or with one temperature sensor, which measures the temperature of the single piston pumps subsequently. The uncertainty value given in the above table for the temperature (n° 8) is derived from repeated measurements on different commercially available piston pumps with a single Pt100 probe directly connected to the transmitter. The characteristics of the Pt100 resistance with transmitter should be considered as well.

The purity or composition of the parent gases and their impact on the uncertainty (n° 10) should be evaluated as described in 6.9.

B.2.3 Minor sources of uncertainty

The uncertainty sources n° 11 and n° 12 to the flow resistance at the inlet and outlet of the piston pumps usually have a minor influence as shown by a series of measurements on commercially available gas mixing pumps (see Annex D).

The potential adsorption and desorption (n° 13) inside the gas-mixing pump should be checked separately for each gas component, especially for reactive or condensing gases. If necessary, the adsorption/ desorption should be considered by appropriate measures. Most of the gas components are not influenced by this effect. The behaviour of some gases is given in Annex D.

Eventually, occurring contributions of the further uncertainty sources, listed in Table B.1 (n° 14 to n° 19), to the combined uncertainty should be evaluated. If necessary, they should be quantified for the given application and considered by a corresponding uncertainty contribution. Detected leaks of the gas-wetted parts inside and outside of the gas-mixing pump should be removed.

It is strongly recommended to operate the gas-mixing pumps at conditions, which allow the classification of any further sources of uncertainty as not significant.

B.3 Example for calibration gases with 4 components

Examples are outlined in Table B.3 for the evaluation of uncertainty for the composition of calibration gas mixtures with 2 compositions each containing 4 components. The compositions of the parent gases have significant differences in gas quality. The gas-mixing pump used for the dynamic production of these gas mixtures comprises 4 piston pumps driven at equal nominal number of strokes and having distinct stroke volumes graduated in steps of 100: 10: 1.

Table B.3 — Example for calibration gases with 4 components

		Piston pump 1	Piston pump 2	Piston pump 3	Piston pump 4
1	Range of content	$(0,1 - 1,0) \times 10^{-2}$	$(10 - 100) \times 10^{-2}$	$(1,0 - 10) \times 10^{-2}$	$(10 - 100) \times 10^{-2}$
2	$u(d)$ mm	0,001 4	0,001 4	0,001 4	0,001 4
3	$u(h)$ mm	0,002	0,002	0,002	0,002
4	$u(p)$ Pa	10	10	10	10
5	$u(T)$ K	0,04	0,04	0,04	0,04
6	Gas mixture 1				
7	Gas component	C_3H_8	CO_2	H_2	CH_4
8	Reduction gear ratio L	1,0	0,4	0,9	0,5
9	Fraction φ [10^{-2}]	1,000	40,000	9,000	50,000
10	Gas quality / $u(f)$	$2,8/200 \times 10^{-5}$	$2,8/200 \times 10^{-5}$	$2,8/200 \times 10^{-5}$	$2,8/200 \times 10^{-5}$
11	$u(\varphi)$ only $u(f)$	$2,0 \times 10^{-5}$	80×10^{-5}	18×10^{-5}	100×10^{-5}
12	$u(\varphi)$ except $u(f)$	$0,8 \times 10^{-5}$	7×10^{-5}	3×10^{-5}	7×10^{-5}
13	$u(\varphi)$ with $u(f)$	$2,2 \times 10^{-5}$	80×10^{-5}	18×10^{-5}	100×10^{-5}
14	Gas quality / $u(f)$	$4,0/10 \times 10^{-5}$	$4,0/10 \times 10^{-5}$	$4,0/10 \times 10^{-5}$	$4,0/10 \times 10^{-5}$
15	$u(\varphi)$ only $u(f)$	$0,1 \times 10^{-5}$	$4,0 \times 10^{-5}$	$1,0 \times 10^{-5}$	$5,0 \times 10^{-5}$
16	$u(\varphi)$ except $u(f)$	$0,8 \times 10^{-5}$	$6,5 \times 10^{-5}$	$2,9 \times 10^{-5}$	$6,7 \times 10^{-5}$
17	$u(\varphi)$ with $u(f)$	$0,8 \times 10^{-5}$	$7,6 \times 10^{-5}$	$3,1 \times 10^{-5}$	$8,4 \times 10^{-5}$
18	Gas mixture 2				
19	Gas component	C_3H_8	CO_2	H_2	CH_4
20	Reduction gear ratio L	0,2	0,1	0,1	0,9
21	Fraction φ [10^{-2}]	0,198	9,881	0,989	88,933
22	Gas quality / $u(f)$	$2,8/200 \times 10^{-5}$	$2,8/200 \times 10^{-5}$	$2,8/200 \times 10^{-5}$	$2,8/200 \times 10^{-5}$
23	$u(\varphi)$ only $u(f)$	$0,40 \times 10^{-5}$	20×10^{-5}	$2,0 \times 10^{-5}$	180×10^{-5}
24	$u(\varphi)$ except $u(f)$	$0,16 \times 10^{-5}$	3×10^{-5}	$0,4 \times 10^{-5}$	3×10^{-5}
25	$u(\varphi)$ with $u(f)$	$0,43 \times 10^{-5}$	20×10^{-5}	$2,0 \times 10^{-5}$	180×10^{-5}
26	Gas quality / $u(f)$	$4,0/10 \times 10^{-5}$	$4,0/10 \times 10^{-5}$	$4,0/10 \times 10^{-5}$	$4,0/10 \times 10^{-5}$
27	$u(\varphi)$ only $u(f)$	$0,02 \times 10^{-5}$	$0,4 \times 10^{-5}$	$0,1 \times 10^{-5}$	$8,9 \times 10^{-5}$
28	$u(\varphi)$ except $u(f)$	$0,16 \times 10^{-5}$	$2,6 \times 10^{-5}$	$0,4 \times 10^{-5}$	$2,7 \times 10^{-5}$
29	$u(\varphi)$ with $u(f)$	$0,16 \times 10^{-5}$	$2,6 \times 10^{-5}$	$0,4 \times 10^{-5}$	$9,3 \times 10^{-5}$

The individual range of content for each component in the calibration gas mixture corresponds to the forwarding geometrical volume of the affiliated piston pump. The range of content is indicated in line 1 of Table B.3. In lines 8 and 20, the preset reduction gear ratios L of the switch gears are indicated for the composition of the 2 calibration gas mixtures. The target values of composition expressed by the ratio of the forwarded volumes φ_k are shown in lines 9 and 21, their values are calculated by using Formula (1).

The values of the uncertainty of all major sources of uncertainty related to the gas-mixing pump are given in lines 2 through 5. The contribution of these sources of uncertainty to the total uncertainty associated with the volume fraction $u(\phi)$, excluding the contribution of gas quality $u(f)$, is given in lines 12, 16, 24, and 28; they are related only to the employed gas-mixing pump and independent of the gas components and their gas quality.

According to the required level of uncertainty, pure gases of appropriate quality should be selected. Examples using gas qualities of 2,8 and 4,0 are compared in Table B.3. The uncertainty associated with the composition of the parent gases $u(f)$ is evaluated as mentioned in 6.9. The contribution of the purity of the gases is added as square of its fraction in the calibration gas to the sum of squares. This is separately shown in lines 11, 15, 23, and 27.

The comparison of the combined uncertainty of the volume fractions $u(\phi)$ as given in lines 11, 12, 13, and 23, 24, 25 shows that the uncertainty contributions of the gas-mixing pump to the combined uncertainty remains non-significant when using gases with quality grades of 2,8 and less. When using gases with quality grades of 4,0 and higher, the contribution of the gas quality is usually minor, as shown in lines 16, 17, 28, 29.

B.4   Example for set-up with reduced uncertainty

Temperature has the most significant influence to the uncertainty of composition of the prepared gas mixtures. The temperature difference between the piston pumps of a gas-mixing pump is measured and evaluated for uncertainty calculation. The temperature of each individual piston pump is affected by its preset number of strokes, and the temperature of the forwarded gas at the gas inlet and ambient conditions. The impact of these different sources of heat can cause differences of temperature of the piston pumps and thus of the gas inside the piston pump.

The temperature of the piston pumps can be controlled and set to a given reference temperature applying a heat exchanger with cooling coil to the common mounting plate of the piston pumps. The thermostat with circulation pump allows controlling the temperature of the piston pumps to reference temperature and reducing the temperature difference. When passing the parent gases through, the thermostat as well the temperature difference can be reduced to a minimum.

An example for a set-up of a gas-mixing pump with built-in heat exchanger, thermostat with circulation pump, and heat exchanger coils for parent gases introduced into the thermostat is shown in Figure B.1. Controlled temperature difference yields to reduced uncertainty values.

19

Key
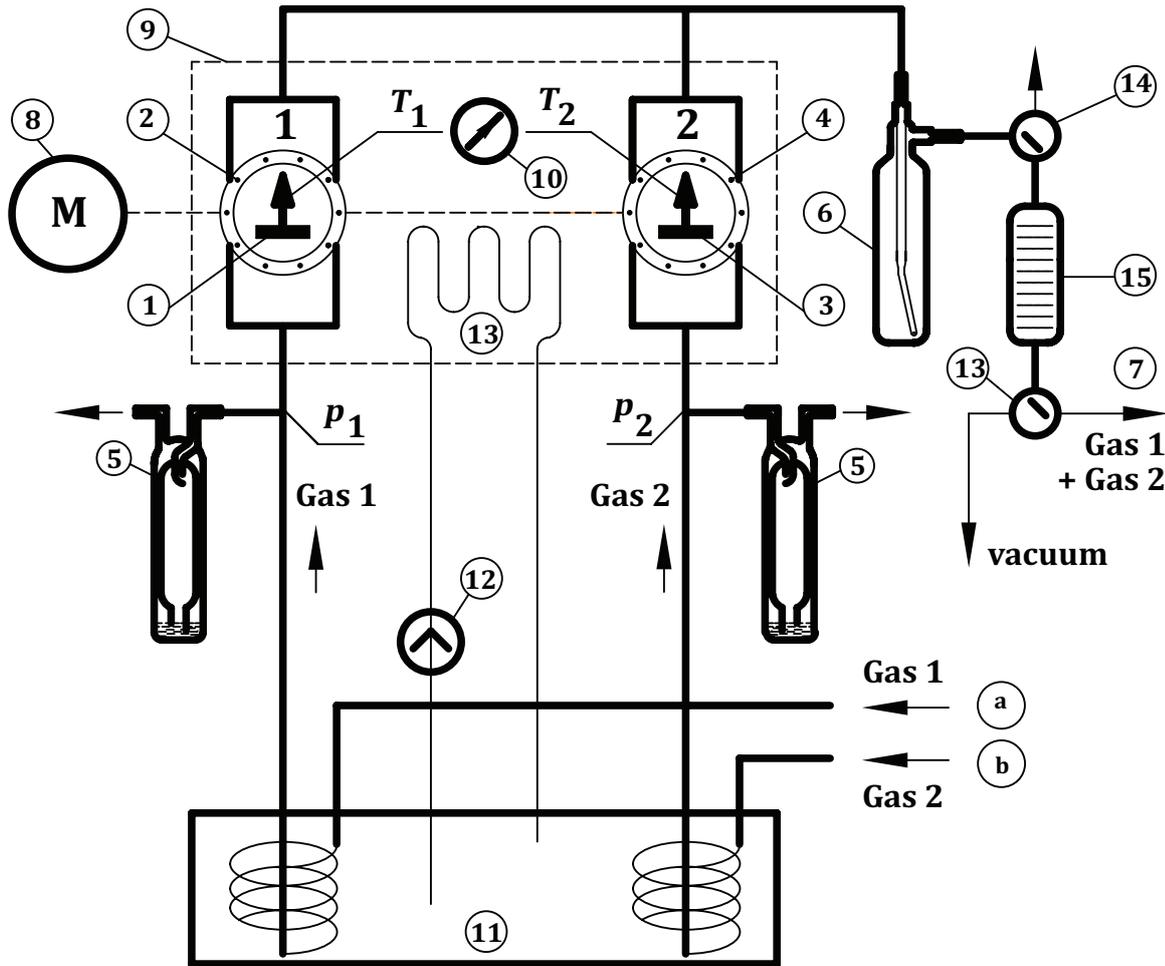
p_1	pressure, piston pump 1	8	drive motor
p_2	pressure, piston pump 1	9	mounting plate
T_1	temperature sensor, piston pump 1	10	thermometer
T_2	temperature sensor, piston pump 2	11	thermostat
1	piston pump 1	12	circulation pump
2	switch gears 1	13	cooling plate
3	piston pump 2	14	cock
4	switch gears 2	15	pulsation damper
5	bubbling vessel	a	Gas inlet for gas 1.
6	mixing vessel	b	Gas inlet for gas 2.
7	gas outlet for gas mixture		

NOTE   Piston pumps 1 and 2 as shown in Figure 1.

Figure B.1 — Set-up with temperature control unit and additional unit for pulsation damping for the dynamic production of two-component calibration gases

Annex C
(informative)

Gas mixture verification

C.1   General

The composition of calibration gas mixtures prepared using gas-mixing pumps as described in this standard is calculated from given measurement functions (see Clause 7). Metrological traceability is established by, among others, dimensional measurements of the cylinder area with diameter d, the height of stroke h of the piston, and the ratio of strokes N of the involved piston pumps. It is assumed that a proportional relation exists between the preset number of strokes and the gas portion forwarded by the respective piston pump (see Clause 5). Thus, it is sufficient to verify a complete range of calculated compositions applying comparison measurements only at one point of the range. The comparison should be done using reference gas mixtures of a composition that has been established independently from the method to be verified.

Comparison measurements are reliably and simply performed for verification using pairs of independent gas mixtures that are sequentially prepared by the one gas-mixing pump to be verified. The complete method consists of two parts; (i) the verification of symmetry and (ii) the verification of linearity. This method can be used with pure gases as well as with gas mixtures. For this method of verification using identical compositions, i.e. identical flow rates of each component, it is not necessary to consider the purity and/or impurities of the parent gases for the comparison measurement.

The analyser used for the comparison measurements serves only as comparator to prove the closeness of agreement of two gas mixtures of the same nominal composition. It is neither necessary to calibrate these analysers nor to know the calibration curve. Analysers having calibration curves that are linear, linearized or curvilinear can be used.

C.2   Comparison with reference gas mixtures

For verification of a range of calibration gas mixtures with calculated quantity values, only one traceable gas mixture is required. The mixture composition preset by the switch gears position is preferably chosen at about 50 % of the operating range of the gas-mixing pump or higher. The composition of the comparison gas mixture should not differ more than ±10 % from the preset composition that is used for the comparison measurement. Comparison gas mixtures can be prepared by dynamic as well as static methods.

A symmetry check and verification of linearity can be performed with pure gases as well as with gas mixtures and thus are applicable in a wide range of intended applications to verify the performance of the gas mixing pump. The measurements should be performed by the manufacturer before the equipment is provided to the user and thereafter periodically by the user. The results should be reported and documented.

An unbroken chain of traceability for the composition of comparison gas mixtures should be established to national or international standards. The purity and relevant impurities of parent gases used for the dynamic preparation of calibration gas mixtures should be considered.

Table C.1 shows a numerical example[4] with amount–of–substance fractions x of O_2 in N_2 wherein a symmetry test is comprised by two measurements with $x = 0,5$.

Table C.1 — Verification by comparison with amount–of–substance fraction O$_2$ in N$_2$

Reference no. of cylinder	Certified reference gas mixture amount fraction y of O$_2$ in N$_2$				Dynamically prepared gas mixture amount fraction x of O$_2$ in N$_2$			
	Reference value %		Analyser indication		calculated value %		Analyser indication	
	y_{O2}	$u(y)$	y_{O2}	$u(y)$	y_{O2}	$u(y)$	y_{O2}	$u(y)$
5073–030 120	20,002	0,002	19,993	0,002	20,001	0,008	19,987	0,002
5016–030 206	50,009	0,002	50,005	0,002	49,918	0,011	49,885	0,002
5016–030 206	50,009	0,002	50,005	0,002	49,943	0,011	49,920	0,002
5064–030 210	79,986	0,003	79,973	0,002	79,849	0,011	79,848	0,002
Measurement conditions:								
— Analyser: Oxygen analyser (paramagnetic);								
— Source: gas mixing pump.								

C.3 Verification with a gas-density gauge (sink-body gauge)

The measurement of only one gas mixture is sufficient for the verification of a range of calculated calibration gas mixtures. The preset mixture composition is preferably chosen at about 50 % of the operating range of the gas mixing pump or higher. The purity and relevant impurities of the parent gases used for the dynamic preparation of calibration gas mixtures should be considered.

The density of the gas mixture measured with the gas density gauge should be converted to amount–of–substance fraction considering the density and the mixing factor of the parent gases. The calculated composition of the gas mixture prepared with the gas-mixing pump should be expressed in amount–of–substance fraction as well.

NOTE   According to ISO 14912, the mixing factor is always unity.

This system is only appropriate for binary gas mixtures if used as exclusive verification method. The required minimum density difference of the gases is a further constraint.

C.4 Symmetry check of gas-mixing pump

For symmetry verification of a gas-mixing pump, the number of strokes of the piston pumps is preset so that the calculated values of the forwarded gas portions are equal. The final gas mixture made of two equal gas portions contains calculated fractions of ϕ = 0,5 and y = 0,5 for each of the two components.

A second gas mixture with calculated fractions of ϕ = 0,5/y = 0,5 is prepared when the gas intakes are changed from one gas component to the other. Each of these two gas mixtures is completely independent of the other. Thus, the symmetry (equivalence) of the forwarded gas portions of the respective piston pumps is proven, if the indications of the analyser for the two gas mixtures are within the expected tolerances.

Table C.2 shows a typical example of verification of a gas-mixing pump comprising two piston pumps with identical maximum stroke volume and nominal number of strokes. Oxygen (O$_2$) and nitrogen (N$_2$) are fed alternatively to piston pumps P$_1$ and P$_2$, yielding to two independent gas mixtures with nominal composition of 50 %. For the calculation of volume fractions at reference conditions (see 7.2), operational temperatures T_1 and T_2 of piston pumps P$_1$ and P$_2$ are measured respectively.

For assessment of symmetry, the quantity value of oxygen in the gas mixture is calculated from the measurement function considering the measured temperature of each piston pump. The calculated values of a set of gas mixtures are compared among each other and with their corresponding indicated

quantity values. Gas mixtures n° 1, n° 2, and n° 3 form a set as do n° 4 and n° 5, n° 6 and n° 7, and n° 8 and n° 9.

Table C.2 — Verification by symmetry check with volume fraction of O_2 in N_2

Piston pump L_1 = 0,5 and L_2 = 0,5		Temperature °C		% volume fraction ϕ		
P_1	P_2	T_1	T_2	Preset	Indicated	calculated
O_2	N_2	24,98	25,17	50,000	50,018	50,016
N_2	O_2	24,98	25,17	50,000	49,986	49,984
O_2	N_2	24,98	25,17	50,000	50,022	50,016
N_2	O_2	28,12	28,39	50,000	49,964	49,978
O_2	N_2	28,12	28,39	50,000	50,014	50,022
O_2	N_2	26,30	26,43	50,000	50,010	50,015
N_2	O_2	26,30	26,43	50,000	49,982	49,985
N_2	O_2	26,75	26,89	50,000	49,983	49,984
O_2	N_2	26,75	26,89	50,000	50,012	50,012
Measurement conditions:						
— Analyser: Oxygen analyser (paramagnetic);						
— Source: gas mixing pump.						

C.5   Verification of linearity

For verification of linearity of a gas-mixing pump, a pair of gas mixtures is prepared with preset equal ratio of strokes but different number of strokes, in a way that the resulting calculated content of each component is equal in both gas mixtures. The number of strokes of the piston pump, of which the linearity is to be verified, is preferably set at 50 % and 100 % of the setting range. The number of strokes of the second piston pump is set at 20 % and 40 % of the setting range, respectively.

For the first gas-mixture, the piston pump 1 is preset to L_1 = 0,5 and the second piston pump 2 to L_2 = 0,2, respectively. For the second gas-mixture, the settings are L_1 = 1,0 and L_2 = 0,4. The composition of both mixtures can be calculated in volume fractions using the method described in 7.1 yielding to equal values of volume fractions using Formula (C.1):

$$\varphi_1 = \frac{L_1 \cdot p_1 \cdot T_2}{L_1 \cdot p_1 \cdot T_2 + L_2 \cdot p_2 \cdot T_1} \tag{C.1}$$

The gas mixtures obtained with settings of 0,50: 0,20 and 1,00: 0,40, respectively, are completely independent of each other. Hence, the linearity of the gas portions forwarded by the piston pump is confirmed if the indications of the analyser for the two gas mixtures are within the expected tolerances.

This method can be applied with pure gases as well as with gas mixtures as parent gas. It is not necessary to consider the purity or relevant impurities of the employed gases. If very pure gases without relevant impurities are used, the volume fraction of gas component 1 is ϕ_1 = 0,714 29 in both mixtures and ϕ_2 = 0,285 71 for gas component 2.

Table C.3 shows a typical example of verification of a gas-mixing pump comprising two piston pumps with identical nominal stroke volume and maximum number of strokes. Oxygen (O_2) and nitrogen (N_2) are fed to the piston pumps P_1 and P_2, yielding to two independent gas mixtures. For the method B calculation of composition (7.2), the temperature T_1 and T_2 of piston pump P_1 and P_2 are measured.

For assessment of linearity, the quantity value of oxygen in the gas mixtures is calculated from the measurement function considering the measured temperature of each piston pump and the compression

factor of each mixed gas. The calculated values of a pair of gas mixtures are compared among each other and with their corresponding indicated quantity values. Gas mixtures n° 1 and n° 2 form a set for linearity assessment of piston pump P_2, n° 3, n° 4, and n° 5 form a set for linearity of piston pump P_1, respectively.

Table C.3 — Verification of linearity with volume fraction of O_2 in N_2

Piston pump		Temperature °C		% volume fraction ϕ		
P_1	P_2	T_1	T_2	Preset	Indicated	Calculated
N_2	O_2	25,10	25,36	71,428	71,372	71,397
N_2	O_2	26,19	27,53	71,428	71,329	71,337
O_2	N_2	27,68	27,16	71,428	71,401	71,393
O_2	N_2	27,24	27,30	71,428	71,417	71,433
O_2	N_2	28,50	27,74	71,428	71,365	71,377
Measurement conditions:						
— Analyser: Oxygen analyser;						
— Source: gas mixing pump.						

Annex D
(informative)

Numerical example

D.1 Requirements for validation

The validation of a gas-mixing pump for a defined application or a range of applications is concerned to the technical execution of the gas-mixing pump itself with appropriate peripheral accessories, the employed gases and/or gas mixtures, the range of dilution ratios, flow rate of the final gas mixture, stability, and homogenization.

In a first step, the evaluation of feasibility as outlined in 6.2 and process parameters is effected and their contribution to the uncertainty of the final gas mixture is considered. Important process parameters include accuracy, repeatability, reproducibility, operation limits, robustness, drift, homogeneity, and stability.

In a second step, the uncertainty budget is established concerning all sources of uncertainty as described in Clause 7, Annex A, and Annex B.

In a third step, an uncertainty statement is made up.

All data employed for the determination of process parameters should be recorded and filed for a defined period by the user of the mixing pump after the last application of the corresponding process. A respective release note should be added as well.

Table D.1 — Examples for validation of binary mixtures

Analyte amount fraction x_i %				Matrix
0,1	1	10	99,9	
He				N_2, O_2, CH_4
N_2				He, O_2, CO_2, CH_4
O_2				He, N_2, CO_2
Ar				CH_4
CO_2				N_2, O_2, CH_4
N_2O				N_2
CO				N_2
CH_4				N_2
C_2H_6				N_2
	SF_6			He, N_2

Alternatively to a validation, verification for an intended application range can be effected using 5 or 7 comparison gases, respectively. The composition of the comparison gases are spread equally over the whole range. For the use of 5 comparison gases, its values should be approximately 10 %, 25 %, 50 %, 75 %, and 90 %, and for the use of 7 comparative gases its values should be 5 %, 20 %, 33 %, 50 %, 66 %, 80 %, and 95 % of the application range.

Detailed experimental data within the production of binary mixtures as shown in Table D.1 are given in Reference [4].

D.2 Numerical example with amount–of–substance fraction of CO_2 in N_2

In this example,[4] pure carbon dioxide (CO_2) is diluted with pure nitrogen (N_2) to provide gas mixtures in the range of amount–of–substance fraction from 0 % to 10 % CO_2.

Table D.2 — Validation with amount–of–substance fraction of CO_2 in N_2[a]

Calculated amount fraction CO_2 %	Coefficient of variation of mean value %	Indication of analyser CO_2 %	Relative deviation between calculated amount fraction and analyser indication %
10,072	0,010	10,068	-0,04
8,344	0,018	8,338	-0,07
7,486	0,014	7,481	-0,07
6,610	0,022	6,604	-0,09
5,720	0,020	5,726	-0,10
4,813	0,011	4,817	0,08
3,888	0,017	3,891	0,08
2,944	0,021	2,947	0,10
1,983	0,021	1,984	0,05
1,001	0,016	1,001	0,00

[a]   Measurement conditions:

—   Analyser: GC (two channel system) with a stream selection valve for four streams and two gas sampling valves;

—   Carrier gas: helium;

—   Columns: column system with two packed columns (6 ft x 1/8" Porapak R, 80/100 mesh);

—   Oven temperature: 75 °C;

—   Detector: µ-TCD.

The spike gas mixtures given in Table D.3 are prepared with a relative expanded uncertainty, *U*, (coverage factor *k* = 2) smaller than 0,1 %.

Table D.3 — Identification of spike gases

Spike gas mixture	Certified value CO_2 %	Indication of analyser CO_2 %
1	0,980	0,980
2	2,424	2,422
3	6,410	6,405
4	10,072	10,072
5	12,481	12,492
Spike gases 1 and 4 are used for calibration of CO_2 analyser.		

D.3 Numerical example with NO and N_2 in gas mixtures

In this example, a gas standard containing φ = 1,000 1 % nitric oxide in nitrogen is diluted with nitrogen to provide gas mixtures in the range of volume fraction from 0 ppm to 100 ppm of NO in N_2

Table D.4 shows the information produced by feeding the gas mixtures generated from the volumetric pump into a NO analyser.

Table D.4 — Analytical data provided by the NO analyser calibrated with a volumetric mixing pump[a]

Dilution factor (x 10²)	Volume fraction ppm	Direct reading from the NO ana- lyser[b]	New curve value[c]	Relative point-by-point dif- ferences[d] of current curve %	Relative point-by-point dif- ferences[e] of new curve %	Relative point-by-point dif- ferences on FSR[f] of cur- rent curve %	Relative point-by-point dif- ferences on FSR[f] of new curve %
0,989 5	98,96	97,43	98,96	−1,55	0,00	−1,53	0,00
0,891 4	89,15	87,73	89,11	−1,59	−0,04	−1,42	−0,03
0,793 2	79,33	78,11	79,34	−1,53	0,02	−1,22	0,01
0,694 7	69,48	68,34	69,42	−1,64	−0,09	−1,14	−0,06
0,596 1	59,62	58,73	59,65	−1,49	0,06	−0,89	0,04
0,497 2	49,72	48,74	49,51	−1,98	−0,44	−0,99	−0,22
0,398 2	39,82	39,08	39,70	−1,87	−0,32	−0,74	−0,13
0,298 9	29,89	29,30	29,76	−1,97	−0,43	−0,59	−0,13
0,199 5	19,95	19,56	19,87	−1,96	−0,42	−0,39	−0,08
0,099 8	9,98	9,81	9,96	−1,72	−0,18	−0,17	−0,02
0,000 0	0,00	0,01	0,01	0,00	0,00	0,01	0,01

[a]   Measurement conditions:

—   Analyser: chemiluminescence;

—   Date: 2006-11-10;

—   Component: NO in nitrogen;

—   Source: Volumetric mixing pump;

—   Full scale range: 100 ppm.

—   Calibration gas:

—   Sample gas flow rate: 670 ml/min.

[b]   Values generated from those held in memory from the previous calibration curve.

[c]   Date of the new calibration is 2006–11–10.

[d]   Relative point-by-point differences between the gas-volume fraction value and the value generated from the current curve.

[e]   Relative point-by-point differences between the gas-volume fraction value and the value generated from the new curve.

[f]   FSR is full-scale range.

Calibration is carried out by feeding primary reference gas mixtures as span gas and pure nitrogen as zero gas into the gas analyser and calculating the results using the generated curve obtained by using the volumetric pump. Primary reference gas mixtures are fed into the analyser to spike the generated curve. In general, only two spike gases are required, one at <25 % and the other at >75 % of the range measured in order to confirm individual points on the curve.

The results of the calibration process are given in Table D.5 below. The variations between current and new coefficients are given in Table D.5 and the spike gases employed are defined in Table D.6. The values obtained for the spike gas mixtures are shown in Table D.7.

Table D.5 — Comparison of curve values with spike gas mixtures

Spike gas	Volume fraction ppm	Direct reading from the NO analyser[a]	New curve value[b]	Relative point-by-point differences[c] of current curve %	Relative point-by-point differences[d] of new curve %	Relative point-by-point differences on FSR[e] of current curve %	Relative point-by-point differences on FSR[e] of new curve %
1	100,09	98,20	100,09	−1,89	0,00	−1,89	0,00
2	53,01	51,94	52,94	−2,04	−0,15	−1,08	−0,08
3	31,10	30,50	31,09	−1,91	−0,02	−0,59	−0,01
4	19,99	19,56	19,94	−2,15	−0,26	−0,43	−0,05

[a] Values generated from those held in memory form the previous calibration.

[b] Date of the new calibration is 2006–11–10.

[c] Relative point-by-point differences between the gas-volume fraction value and the value generated from the current curve.

[d] Relative point-by-point differences between the gas-volume fraction value and the value generated from the new curve.

[e] FSR is full-scale range.

NOTE   The comparison shows that the new curve generated in Table D.5 and that generated using spike gas mixtures agree within ±0,5 %.

Table D.6 — Comparison of curve coefficients

Curve coefficients	Current	New
a	0,984 04	1,000 45
b	−0,076 1	−0,007 6

Table D.7 — Identification of spike gases

Spike gas mixture	Certified value φ ppm	Cylinder no.
1	100,09	ME0529
2	53,01	ME5408
3	31,00	ME5397
4	19,99	ME6272

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