INTERNATIONAL STANDARD

ISO 6145-2

Second edition
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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

Reference number
ISO 6145-2:2014(E)

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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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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ISO 6145-3, entitled *Periodic injections into a flowing gas stream*, has been withdrawn.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):

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

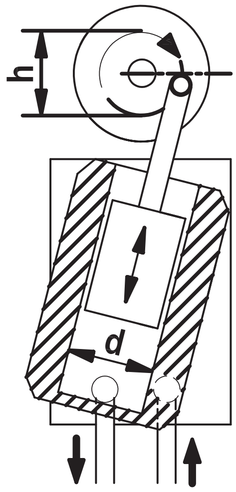
where ϕ_i denotes the volume fraction of component i at the operational conditions of the piston pumps. These conditions may differ from the conditions at which the calibration gas mixture thus prepared is going to be used.

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.

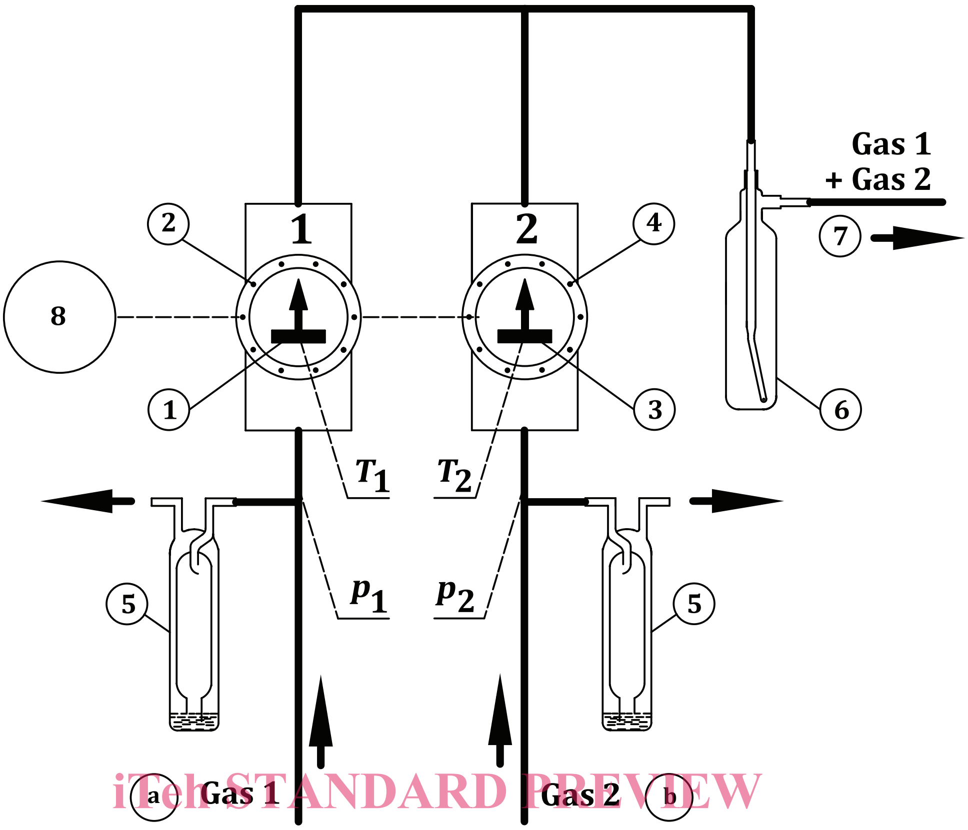
The stroke volume of piston pump k is calculated from the diameter of its cylinder and the height of its piston stroke

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

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

$$N_k = L_k \cdot N_{\max} \tag{3}$$

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.

