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

Part 1: General aspects

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

Partie 1: Aspects généraux

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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.

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

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

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

This document was prepared by Technical Committee ISO/TC 158, *Gas analysis*.

This third edition cancels and replaces the second edition (ISO 6145-1:2003), which has been technically revised. The main changes compared to the previous edition are as follows.

— The techniques for the preparation of gas mixtures are described in an abbreviated manner since there is no need to repeat the text and formulae from each of the different parts of the ISO 6145 series. However, a summary table (Table 1) presenting the advantages and limitations of each method has been introduced.

— Recommendations regarding the handling of the dynamic mixing systems and quality considerations have been added.

— The methods and instruments to calibrate a dynamic system have changed and are better described.

— The calculations to obtain composition and uncertainties are more detailed, and the different ways of mixing gases (volume flow rates or mass flow rates) have been taken into account.

— Clauses on certificates (7.4) and verification (Clause 10) have been added.

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

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

Introduction

This document is one of a series of standards which describes the various dynamic methods for the preparation of calibration gas mixtures.

Several techniques are available and the choice between them is decided based on the desired gas composition range, the consistency of equipment with the application and the required level of uncertainty. This document aids with making an informed choice by listing all the advantages and limitations of the methods.

The main techniques used for the preparation of gas mixtures are:

a) piston pumps;

b) continuous injection;

c) capillary;

d) critical orifices;

e) thermal mass-flow controllers;

f) diffusion;

g) saturation;

h) permeation;

i) electrochemical generation.

In dynamic methods, a gas A is introduced at a known constant volume or mass flow rate into a known constant flow rate of a complementary gas B. Gases A and B can be either pure gases or gas mixtures. The preparation process can be continuous (such as mass flow controllers, permeation tube) or pseudo-continuous (such as piston pump).

The dynamic preparation techniques produce a continuous flow of calibration gas mixtures into the analyser but do not generally allow the build-up of a reserve by storage under pressure.

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

Part 1: General aspects

1 Scope

This document gives a brief overview of each of the dynamic techniques which are described in detail in the subsequent parts of ISO 6145. This document provides basic information to support an informed choice for one or another method for the preparation of calibration gas mixtures. It also describes how these methods can be linked to national measurement standards to establish metrological traceability for the composition of the prepared gas mixtures.

Since all techniques are dynamic and rely on flow rates, this document describes the calibration process by measurement of each individual flow rate generated by the device.

Methods are also provided for assessing the composition of the generated gas mixtures by comparison with an already validated calibration gas mixture.

This document provides general requirements for the use and operation of dynamic methods for gas mixture preparation. It also includes the necessary expressions for calculating the calibration gas composition and its associated uncertainty.

Gas mixtures obtained by these dynamic methods can be used to calibrate or control gas analysers.

The storage of dynamically prepared gas mixtures into bags or cylinders is beyond the scope of this document.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

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

ISO 7504, *Gas analysis — Vocabulary*

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

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

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

3 Terms and definitions

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

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

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

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

3.1
mass flow rate
q_m
mass of gas per unit of time

3.2
volume flow rate
q_v
volume of gas per unit of time

4 Symbols

Symbol	Definition
i, k	Indices for components in a gas or gas mixture
j	Index for a parent gas
K	Conversion factor between two gases
m	Mass of a component
M	Molar mass of a component
p	Pressure
q	Number of components in the gas mixture
q_m	Mass flow rate
q_n	Amount-of-substance flow rate
R	Ideal gas constant
r	Number of parent gases
T	Temperature
V	Volume
q_v	Volume flow rate
$u(x)$	Standard uncertainty of a quantity x
v	Mass fraction of a component in a parent gas
w	Mass fraction of a component in a gas mixture
x	Amount-of-substance fraction of a component in a parent gas
y	Amount-of-substance fraction of a component in a gas mixture
Z	Compressibility factor
φ	Volume fraction of a component in a parent gas
ϕ	Volume fraction of a component in a gas mixture

5 Principle

5.1 General

All preparation techniques described in ISO 6145 (all parts) are based on the combination of gas flows. These flow rates can be measured on a volume or mass basis. The composition is calculated from the flow rate data and the composition of the parent gases.

It is applicable only to

— pure gases,

— gas mixtures, or

— totally vaporized components at ambient pressure,

which do not react with each other or with any surfaces of the mixing device.

For the calculation of the composition, it is essential to appreciate the composition of the parent gases used for preparing the calibration gas mixture. Even if such gases are considered "pure", their purity shall be verified in accordance with ISO 19229. The corresponding compositional data of these parent gases shall be used in the calculation of the composition, as described in Clause 7.

Practically, all preparation systems are furthermore sensitive to changes or fluctuations in the conditions under which the calibration gas mixture is prepared. These conditions typically include the pressure and temperature of the gases, as well as the dynamic effects of combining flows and homogenization of the calibration gas mixture, among others. In the subsequent parts of ISO 6145, attention is drawn to these effects, and care shall be taken to follow these instructions.

Several techniques are available and the choice between them should be decided based on the desired composition range, the availability of equipment and the required uncertainty.

The principles of gas mixing systems are described in each part of ISO 6145.

Depending on its principle, each dynamic method will generate gas mixtures of composition based on either volume fraction, mass fraction, amount-of-substance fraction or mass concentration. The calibration procedure will also affect the expression of gas mixture composition (mass, volume or amount-of-substance fraction). The final fraction and its associated uncertainty depend both on the calibration method and on the preparation technique.

5.2 Suitability of the method to the application

Before preparing a gas mixture, it is necessary to consider the suitability of the dynamic system to the application. Pressure and flow rates should be consistent with the analyser to which the dynamic system will be linked.

Users shall comply with the manufacturers' recommendations. Check if the dynamic method is sensitive to external parameters, such as temperature or atmospheric pressure, and follow the recommendations given in each part of ISO 6145.

Depending on the principle used by the dynamic system, the achievable range of concentration in the final mixture will differ. In order to compare the capabilities of each method, a dilution ratio is estimated as follows:

— use of pure components as parent components (for example: in cylinders, or permeation tubes or by syringe injection);

— only one step dilution is considered.

This dilution ratio could be extended for some dynamic systems by two step dilution.

When choosing the type of the dynamic method, the user shall take into consideration the advantages and limitations of each method.

5.3 Piston pumps

ISO 6145-2 specifies a volumetric method for the dynamic preparation of calibration gas mixture using piston pumps. Two or more piston pumps, combined in a gas-mixing pump, are driven with a defined ratio of strokes. The stroke volume of each piston pump is individually determined by the geometry (cross-section) of the cylinder and the height of stroke of the piston. The composition is rapidly changed by the mechanical changing of the ratio of strokes. Suitable peripherals for gas feeding and homogenization of the final mixture are recommended.

The calibration of the stroke volume is made by dimensional measurements in the SI base unit of length. Uncertainty evaluation of the gas mixture composition and an assessment of potential sources with quantification of significant sources of uncertainty are out lined in detail in ISO 6145-2.

The merits of the method are that the composition and the associated uncertainty of the calibration gas mixture are calculated from the geometric stroke volume and the ratio of strokes of the piston pumps. The content of each component is directly expressed in volume fractions and in amount-of-substance fractions.

Final mixture flow rates from 5 l/h to 500 l/h can be prepared depending on the equipment used.

Using this method, dilution ratios from 1:1 up to $1:10^4$ can be prepared from initial amount-of-substance fraction. Higher dilution ratios can be prepared by a two-stage dilution.

5.4 Continuous (syringe) injection

ISO 6145-4 specifies a method for preparation of calibration gas mixtures using continuous injection.

The calibration component, either in the gaseous or liquid phase, is displaced from a reservoir through a capillary into a complementary inert gas stream. The system may contain a syringe, whose plunger is continuously driven by a suitable variable-speed motor. Alternatively, the component may be forced through the capillary by controlled pressurization of the reservoir.

This method applies also to multi-component mixtures of known composition. In the case of liquids, the calibration component is vaporized while mixing with the complementary gas.

The flow rate of the calibration component is determined by the geometry (cross-section) of the syringe and the linear velocity of the plunger or by the continuous weighing of the reservoir.

Using this method, dilution ratios from $1:10^4$ up to $1:10^7$ can be prepared from initial amount-of-substance fraction.

5.5 Capillary

ISO 6145-5 specifies a method for the continuous preparation of calibration gas mixtures from pure gases or gas mixtures using capillary tubes in single or multiple combinations.

A constant flow of gas from a capillary tube under conditions of constant pressure drop is added to a controlled flow of complementary gas. The complementary gas may be derived from another capillary tube.

This application is used in industrial gas mixing panels for the production of specific gas atmospheres. Gas dividers can be used to divide gas mixtures prepared from pure gases or gas mixtures into controlled proportions by volume.

Using this method, dilution ratios from 1:1 up to $1:10^4$ can be prepared from initial amount-of-substance fraction.

5.6 Critical flow orifices

ISO 6145-6 specifies a method for the continuous preparation of calibration gas mixtures by use of critical flow orifice systems.

When passed through a critical orifice at increasing upstream pressure P_{in}, the volume flow rate of gas passing through the orifice will increase. When the ratio of the gas pressure downstream P_{out} and the gas pressure upstream P_{in} of the orifice has reached the critical value, the volume flow rate of the gas becomes independent with respect to P_{out} and is proportional to P_{in}.

To prepare calibration gas mixtures, the gas blender mixes the complementary gas flowing at a known rate out of one or several critical flow orifice(s) and the gas to be diluted flowing out of one or several critical flow orifice(s). The resulting mixture is generally homogenized in a mixing chamber.

Although it is more particularly applicable to the preparation of gas mixtures at atmospheric pressure, the method also offers the possibility of preparing calibration gas mixtures at pressures greater than atmospheric. The upstream pressure should be at least two times higher than the downstream pressure. The range of flow rates covered by this document extends from 1 ml/min to 10 l/min.

It has the merit of allowing multi-component mixtures to be prepared as readily as binary mixtures if an appropriate number of critical flow orifices are used.

Using this method, dilution ratios from 1:1 up to $1:10^4$ can be prepared from initial amount-of-substance fraction. Higher dilution ratios can be prepared by a two-stage dilution.

5.7 Thermal mass flow controller

ISO 6145-7 specifies a method for continuous preparation of calibration gas mixtures using thermal mass flow controllers. By adjustment of the set-points on the flow controllers, it is possible to change the composition of the gas mixture rapidly and in a continuously variable manner.

The range of flow rates covered by this document extends from 1 ml/min to 10 l/min.

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

Using this method, dilution ratios from 1:1 up to $1:10^4$ can be prepared from initial amount-of-substance fraction. Higher dilution ratio can be prepared by two stage dilution.

5.8 Diffusion

ISO 6145-8 describes a method, which applies to components that are liquids or solids that can produce a vapour. The vapour of the pure component migrates by diffusion through a diffusion cell of suitable dimensions (length, diameter) into a flow of a complementary gas. The rate of diffusion should remain constant, if the system is kept at constant temperature and the pure component is still present as liquid or solid.

The substance, of a known high purity, is contained in a reservoir that acts as the source of the component vapour. The reservoir is provided with a vertically placed diffusion cell. This assembly (the diffusion cell) is placed in a temperature-controlled enclosure that is purged at a constant flow rate by a high-purity and inert complementary gas. The diffusion rate is measured by periodic weighing of the diffusion cell.

Using this method, dilution ratios from 1:10 up to $1:10^3$ can be prepared from initial amount-of-substance fraction.

5.9 Saturation

ISO 6145-9 specifies a method for the dynamic preparation of calibration gas mixture based upon the vapour saturation pressure of liquid and solid substances. The complementary gas flow is passed through a temperature-controlled saturator in which the vapour of the calibration component is maintained in equilibrium with their liquid or solid phases.

The amount-of-substance fraction of the calibration component in the gas flow is approximately equal to the ratio of the vapour pressure of the component and the total pressure of the mixture at that temperature. The saturation pressure values for very many components as a function of temperature are given in reference books.

This method applies to all pure components that are in a stable equilibrium with their vaporized and liquid phase. The vapour pressure in equilibrium with its condensate phase depends only on temperature. Variation of volume fraction is achieved by variation of temperature and pressure in the saturator.

Two procedures are described for the application of this method. Calculation of composition and uncertainty evaluation are given based on vapour pressure data.

The merits of the method are that calibration gases with condensable components can be dynamically prepared and used at ambient conditions near the individual component condensation point. In combination with other volumetric dynamic methods a small flow of saturated calibration gas can be easily diluted by a large flow of complementary gas to very small volume fractions.

Using this method, dilution ratios from $1:10^3$ up to $1:10^6$ can be prepared from initial amount-of-substance fraction .

5.10 Permeation method

ISO 6145-10 describes a method in which the calibration component is contained in a sealed tube or container, which consists either wholly or partly of a polymer through which the component can permeate. The component is usually contained as a liquid or solid in equilibrium with its own vapour but can be contained as a gas. In the former case, the rate of permeation should remain constant while the liquid is still present. In the latter case, the rate decays with the pressure of the gas. In either case, the rate of permeation is dependent on temperature.

The vessel containing the calibration component is put into an enclosure. The diluent gas is passed through the enclosure at a fixed flow rate. The entire housing is placed in a temperature-controlled chamber.

The permeation rate can be measured by weighing the tube periodically. This procedure is described in ISO 6145-10.

Using this method, gas mixtures of dilution ratios from 1:10 up to $1:10^3$ can be prepared from the permeation rate.

5.11 Electrochemical generation

ISO 6145-11 describes a method based on electrochemical generation of one pure component which is diluted in a complementary gas. The composition of the gas mixture is controlled by the magnitude of the electrical charge passed through the electrolyte in the cell and by the flowrate of the complementary gas and is dependent on the efficiency of the cell.

An advantage of the method is that a stable gas mixture can be established rapidly within a few minutes. However, in ISO 6145-11, a list indicates that the number of different gases that can be produced by electrochemical generation is limited to those which follow: oxygen, nitrogen, hydrogen, hydrogen cyanide, hydrogen sulphide, chlorine, bromine, chlorine dioxide, ammonia, phosphine, arsine, nitric oxide, carbon dioxide and ozone.

Using this method, dilution ratios from $1:10^4$ up to $1:10^7$ can be prepared from initial amount-of-substance fraction.

5.12 Summary

Table 1 gives a summary of the preparation techniques.

Table 1 — Preparation techniques — Summary

Preparation technique	Range of dilution ratio in one-step	Advantages	Limitations
ISO 6145-2: Piston pumps	1:1 to 1:10^4	Two-step dilution possible, down to 1:10^8	— Outlet flow stability — Atmospheric pressure
ISO 6145-4: Continuous injection	1:10^4 to 1:10^7	Starting from a liquid or a gas	Stability of the flow of gas A and duration limitation due to the syringe volume
ISO 6145-5: Capillary	1:1 to 1:10^4	Two-step dilution possible	— High sensitivity to pressure and temperature — Calibration for each gas or use of conversion factor
ISO 6145-6: Critical flow orifices	1:1 to 1:10^4	Two-step dilution possible, down to 1:10^8	Calibration for each gas or use of conversion factor
ISO 6145-7: Thermal mass flow controllers	1:1 to 1:10^4	Two-step dilution possible, down to 1:10^8	Calibration of MFC according to each gas or use of conversion factor
ISO 6145-8: Diffusion	1:10 to 1:10^3	Large range of components available (gas, liquid or solid)	High sensitivity to pressure and temperature
ISO 6145-9: Saturation	1:10^3 to 1:10^6	Large range of components available (gas, liquid or solid)	High sensitivity to pressure and temperature
ISO 6145-10: Permeation	1:10 to 1:10^3	Large range of components available (gas, liquid or solid)	— High sensitivity to pressure and temperature — Not recommended above 10 µmol/mol
ISO 6145-11: Electrochemical generation	1:10^4 to 1:10^7	Stable gas mixtures can be established within a few minutes	Restricted to 14 gases at present

6 Recommendations for handling the dynamic system

6.1 Safety considerations

6.1.1 Reactions between mixture components

Before preparing a gas mixture, it is necessary to consider possible chemical reactions between the components of the mixture. The method cannot be used to prepare mixtures:

- containing potentially chemically interactive substances (such as hydrochloric acid and ammonia);
- producing other possible dangerous reactions including explosions (such as mixtures containing flammable gases and oxygen);
- producing strong exothermic polymerizations (such as high concentrations of hydrogen cyanide); and
- containing gases which can decompose (such as acetylene).

A comprehensive compilation of reactive combinations is not available. Therefore, chemical expertise is required to assess the possible hazards or stability of a gas mixture.

For dangerous reactions and dangerous combinations, to be excluded for safety reasons, some information can be found in regulations on dangerous goods and in gas supplier handbooks.

6.1.2 Reactions with dynamic system materials

Before preparing a gas mixture, it is necessary to consider possible chemical reactions of mixture components with materials of the dynamic system. Special consideration shall be given to adsorption and attack by corrosive gases with metals or elastomers used in the dynamic systems. Such reactions should be prevented by using only materials that are inert to all components of the mixture. If this is not possible, measures shall be taken to minimize corrosive attack on the materials with which the gases make contact to prevent any significant effect on mixture composition.

Information on the compatibility of gases with container materials is given in gas sampling guidelines, in ISO 16664, ISO 11114-1 and ISO 11114-2, corrosion tables and gas supplier handbooks.

6.2 Quality considerations

6.2.1 Purity of parent gas standards or "zero" gas

The accuracy of the final concentration will depend significantly on the purity of the parent gases and the zero gas used for the preparation of the calibration gas mixture. Impurities in the parent gases are often one of the most critical contributors to the uncertainty of the final mixture composition. The uncertainty contributions depend on the amount of impurities present in the pure, parent gases and upon the accuracy with which these impurities have been measured. In many cases, the purity of the complementary gas is of most importance. This is especially true when the amount-of-substance fraction of the minor component is low, and this component is likely to be an impurity in the complementary gas. It is also important to evaluate critical impurities that may react with the minor component (for example, oxygen present in pure nitrogen will react with NO to form NO_2). The result of purity analysis of parent gases shall be incorporated into a purity table containing the amount (or mass) fractions of all components with accompanying uncertainties derived from analysis.

A gas generator can be used as a source of a complementary gas. A gas generator refers to a device that produces pure gases from air purification (N_2, O_2, or air) or by water electrolysis (H_2). When a gas generator is used, special attention should be drawn to the purity of the gas delivered. For instance, a nitrogen generator can concentrate argon and hydrocarbons to a significant amount.

ISO 19229 describes the process to follow for performing a purity analysis.

6.2.2 Gas handling

In all cases, and most particularly if very dilute mixtures are concerned, the materials used for the apparatus are chosen as a function of their resistance to corrosion and low adsorption capacity.

The pressure regulators and the pipework shall be purged before use.

It should be pointed out that the surface adsorption phenomena have a lower impact for dynamic methods than for static methods.

ISO 16664 gives recommendations for good practice in gas handling.

7 Calibration methods of a dynamic system

7.1 Generalities on the calibration

Any dynamic system should be calibrated either by flow rate or by concentration before the first use.

There are two approaches to calibrate a dynamic system.

— Considering each element of the dynamic system and calibrating each of them; in that case, the flow rates of each element are calibrated either by volume or by mass. The concentration in the generated mixture is obtained by calculation, using flow rates.

— Considering the dynamic system as a global entity and calibrating the generated gas mixture by comparison with reference gas mixtures or direct chemical analysis. The calibration will be valid for the considered operating conditions.

Since the calibration methods rely upon different principles and the equipment used for the realization of the gas flow rates is different, different units can be used to express the contents.

7.2 Calibration of each element

7.2.1 General

The dynamic system shall be calibrated with metrologically traceable equipment, for example a flowmeter having a calibration certificate with stated metrological traceability. This calibration could be performed by the user, the manufacturer or by an external calibration laboratory.

Using techniques based on volume or mass flow rate leads to a composition expressed as volume fractions, mass fractions or mass concentrations. Recalculation of these data to amount-of-substance fractions is possible (see ISO 14912) but leads to an increase of the uncertainty due to the density and molar-volume data uncertainties.

The major calibration will be a flow rate calibration, but for some preparation techniques, other physical parameters can also be used for calibration. In these cases, the system shall be calibrated by some physical parameters in addition to flow rate. Table 2 lists calibrations applicable to the preparation techniques.

Table 2 — Calibrations applicable to the preparation techniques

Preparation techniques	Quantities
ISO 6145-2 Piston pumps	Flow rate or diameter of cylinder and height of piston stroke
ISO 6145-4 Continuous injection	Flow rate and diameter of the syringe and velocity of the syringe driver if a syringe is used
ISO 6145-5 Capillary	Flow rate
ISO 6145-6 Critical flow orifices	Flow rate
ISO 6145-7 Thermal mass flow controllers	Flow rate
ISO 6145-8 Diffusion	Flow rate and mass loss over time
ISO 6145-9 Saturation	Temperature and pressure
ISO 6145-10 Permeation	Flow rate and temperature and mass loss over time
ISO 6145-11 Electrochemical generation	Flow rate and electric current

The calibration of equipment measuring these quantities shall follow the requirements described in different parts of ISO 6145.

Flow rate calibration is normally carried out using one of the following devices:

— balance and chronometer;

— piston prover;

— thermal mass flowmeter;

— laminar flow element.

7.2.2 Calibration devices for flow rate: Principle and uncertainty

7.2.2.1 General

Calibration devices shall be traceable to SI units. The calibration uncertainties of these calibration devices shall be taken into account in the final uncertainty budget of the dynamically prepared mixtures composition.

Most of the time, the uncertainties are provided by external calibration laboratory or manufacturer.

7.2.2.2 Balance and chronometer

Gas from a cylinder, standing on a balance, flows at a constant flow rate through the device to be calibrated. This is performed for a sufficiently long period to measure accurately the loss of mass from the cylinder and the time. Mass flow rate can be calculated by the ratio of the loss of mass over the time of the observation.

Mass flow rates should be sufficiently stable. If the mass flow rates are unstable, the measurement will not be representative.

Calibration by the gravimetric method gives mass fractions for the contents of components in gas mixtures.

The sources of uncertainty are coming from the weighing and the time measurement.

The traceability to SI units is ensured if traceable balance (mass pieces) and traceable chronometer are used.

7.2.2.3 Piston prover

A glass measuring tube of known diameter and uniformity is set vertically in an insulated box fitted with temperature control. The measuring tube is divided into a number of sections by optical cells serving as sensors.

A constant flow moves a frictionless piston upwards. The piston is allowed to attain a constant speed before time measurement is started at Sensor 1.

The measuring sequence starts by closing a 3-way valve. As soon as the piston passes Sensor 1, chronometer starts; the chronometer is stopped when the piston passes the second sensor. Time measurement depends on the flow rate and the tube size. The three-way valve resets its position and the piston falls down on the spring. The flowmeter is then ready to restart.

The flow rate is calculated by dividing the volume between the two sensors by the time the piston takes to move from one sensor to the second.

The choice of flowmeter shall be adapted to the flow rate to be measured.

Commercial systems available provide flow measurements from 5 ml/min to 100 l/min.

The traceability and the uncertainties of the flow rate are given by the calibration certificate of the piston prover issued by a competent laboratory.

Influence factors for such system are temperature and pressure. The piston prover shall include a temperature sensor and a pressure sensor (preferably in the gas flow) in order to take into account the influence of these two factors.

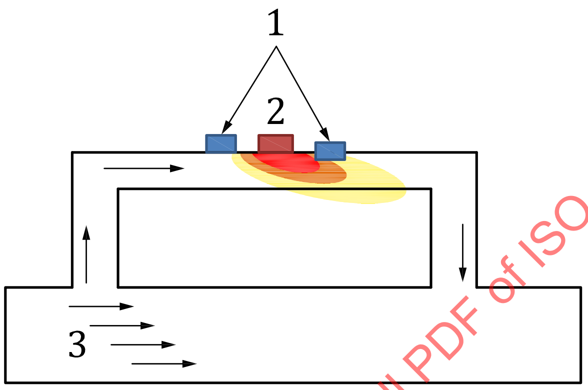
7.2.2.4 Thermal mass flowmeter (MFM)

There are two types of thermal mass flowmeters:

— Capillary-tube type: a small fraction of the flowing gas is diverted in a capillary tube, in which the temperature sensors and the heating element are located (see Figure 1);

— CMOS type: the entire flowing gas passes directly on the temperature sensors and the heating element (see Figure 2).

The principle is based on the thermal conductivity of the gas. Both types use 2 temperature sensors and a heating element arranged/placed such as described below.



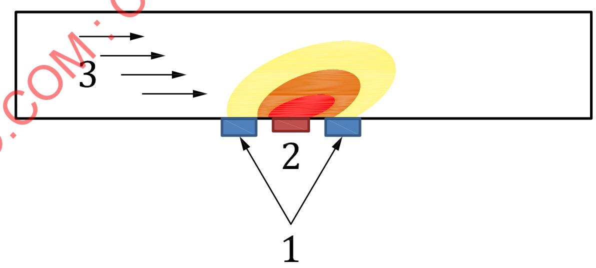
Key

1 temperature sensor

2 heating element

3 gas

Figure 1 — MFM with capillary tube



Key

1 temperature sensor

2 heating element

3 gas

Figure 2 — MFM with CMOS

The gas passes over the first temperature sensor, then over a heating element, and then reaches a second temperature sensor. When the gas flows, the upstream sensor is cooled by the passage of the gas, and the downstream sensor is heated by the passage of the gas, which produces a temperature difference. The temperature difference is directly proportional to the mass flow of the gas.

Depending on the gas type and its physical properties, the response of the sensor changes.

The traceability and the uncertainties are given in flow rate by the calibration certificate of the MFM manufacturer or by an accredited laboratory. The sources of uncertainty are coming from the temperature variation, the pressure variation and the heat flow variation.

7.2.2.5 Laminar flow element (LFE)

Laminar flow is a requirement for the function of the LFE, which operates on differential pressure measurement, in order to characterize the flow of fluid in a pipe. Indeed, in a laminar regime, this kind of flowmeter introduces a constriction in the pipe that creates a pressure drop. When the flow rate increases, a greater pressure drop is created: the pressure drop is linear relative to the flow rate (Poiseuille law).

Laminar flow requires a Reynolds number lower than 2 300, which depends on viscosity, flow rate and also on the geometry of the pipe. To reach laminar flow inside the LFE, large flows shall be divided in a number of capillaries.

This flow rate is either a mass flow rate or a volume flow rate according to its own calibration protocol.

LFE is generally calibrated with nitrogen. If another gas is used, the flow rate of this gas shall be corrected with the internal correction factor implemented in the LFE. For best accuracy or gases not having an internal correction factor, it is necessary to calibrate LFE with that specific gas.

The traceability and the uncertainties are given in flow rate by the calibration certificate of the LFE manufacturer or by an external laboratory. The sources of uncertainty are coming from the temperature, the pressure and the viscosity of the gas. Pressure accuracy shall be controlled regularly, and the pressure shall be adjusted if required.

7.2.2.6 Flow calibration measurement designs

Each part of a dynamic system that handles flow rate shall be calibrated independently. The calibration measurement design shall comply with the use of the dynamic system. The calibration points shall be chosen to span the relevant range of flow rates. Each flow rate shall be measured at least 3 times. The number of calibration points depends on the working range, the interpolation model and the expected uncertainty.

Both the dynamic system and calibration gases should be at working conditions (temperature and pressure) before calibration. If it is not possible, correction factors shall be applied with their related uncertainty.

After introducing calibration gases in the dynamic system, the stability of the flow rate shall be obtained before any valid readings are taken from the data acquisition system.

The data may be inspected for outliers by using a suitable outlier test. If outliers are found, the data should be investigated; outliers should be rejected only if there are sound technical reasons for doing so.

To achieve the best uncertainty, the dynamic system should be calibrated with the same parent gases as those used for generating the mixture.

For practical use, the flow calibration of the device is done with a reference gas (usually pure nitrogen or air). For the use of the devices with another gas *G*, it is necessary to calculate a ratio *K*, called conversion factor or K factor, between the mass flow rate of the other gas *G*, q_{mG}, and the mass flow rate of the reference gas G_{ref}, q_{mGref}, according to Formula (1):

$$K = \frac{q_{mG}}{q_{mGref}} \tag{1}$$

In this case, the uncertainty of the generated mixture should take into account the uncertainty of the conversion factor.

The manufacturers of dynamic systems generally establish a list of *K* factors for common gases.

7.3 Single point calibration of a dynamic system by comparison with reference gas mixtures

A comparison method is always applicable for all dynamic preparation techniques.

It is possible to calibrate a specific concentration of a dynamic technique by comparing the concentration of the generated mixture with a reference gas mixture obtained by other methods: traceable gas mixtures in cylinders or dynamically prepared mixtures (see ISO 6145 series). Extrapolations or interpolations should be carried out with extreme care, based on the technology used. It is necessary to take into account the uncertainties of the traceable gas mixtures used in order to calculate the combined uncertainty of the specific concentration.

For calibrations by the comparison method, the content is expressed as an amount-of-substance fraction because most of the calibration gas mixtures used for the comparison are certified in this way.

If there is no calibration gas mixture with the correct components and necessary composition available, the dilution ratio may be calibrated with other gas mixtures or dynamic techniques. In this case, the uncertainty of the generated mixture should take into account the uncertainty of this calibration. This uncertainty could be higher than the one obtained by flow calibration.

The reference gas mixture used for calibration shall be traceable to SI units and within its certified stability period.

The calibration of the dynamic system by comparison shall refer to ISO 6143 or ISO 12963.

7.4 Calibration certificate

The calibration certificate provides the results of the calibration of the dynamic system. It should, at least, contain:

— the results;

— the uncertainties;

— the methods and equipment used;

— the date of calibration;

— the calibration primary or transfer standards used (if applicable).

8 Calculation of the composition and its uncertainty

8.1 General

The expressions given in this clause are given in a form such that they are valid for the use of pure gases as well as gas mixtures and parent gases. In the case of pure gases, the purity shall be evaluated in accordance with ISO 19229. Depending on the subsequent calculations, it can be convenient to express the composition of the parent gases in amount-of-substance fractions, mass fractions, or volume fractions.

When the composition of the prepared gas mixture is required in quantities other than the ones covered in this clause, one of the specified calculation methods shall be used, followed by converting the composition to the desired quantity using ISO 14912.

Where applicable, the compressibility factor of a parent gas shall be computed in accordance with ISO 14912, or by another suitable method. Such methods include, among others, the use of tabulated data, an equation-of-state, or some empirical correlation of the compressibility factor as a function of the temperature, pressure, and gas composition.

For the use of most calculation methods, the composition of the parent gas should be available in amount-of-substance fractions.

The molar masses of the components and their uncertainties are required for the conversion of mass fraction to amount-of-substance fraction. The values of the atomic weights used to calculate molar masses shall be taken from the most recent publication of the commission on atomic weights and isotopic abundances of the International Union of Pure and Applied Chemistry (IUPAC). A practical approach for the interpretation of the standard atomic weights is given in Annex B.

These are general calculations. More detailed calculations can be found in each part of ISO 6145.

8.2 Calculations for volumetric methods

8.2.1 General

The different techniques using volumetric methods are listed below:

— piston pumps;

— continuous injection;

— capillary;

— saturation.

The detailed formulae related to these techniques can be found in the different parts of ISO 6145 series.

8.2.2 Formulae

Almost all the previous quoted methods are based on addition of several flow rates q_{vj}, containing volume fractions of component k, φ_{jk}, with the resultant volume fraction ϕ_k, defined as Formula (2):

$$\phi_k = \frac{\sum_{j=1}^{r} q_{v\,j} \varphi_{j,k}}{\sum_{j=1}^{r} q_{v\,j}} \tag{2}$$

The uncertainty is calculated by applying the propagation law as shown in Formula (3).

$$u^2(\phi_k) = \sum_{j=1}^{r} \left(\frac{\partial \phi_k}{\partial \varphi_{j,k}} \right)^2 u^2(\varphi_{j,k}) + \sum_{j=1}^{r} \left(\frac{\partial \phi_k}{\partial q_{v,j}} \right)^2 u^2(q_{v\,j}) \tag{3}$$

The detailed calculations can be found in Annex A.

8.2.2.1 Example for 2 gases

When applied to 2 pure gases containing a component k (gas 1 and gas 2), the previous formula is as shown in Formula (4):

$$\Phi_k = \frac{q_{v,1} \cdot \varphi_{1,k} + q_{v,2} \cdot \varphi_{2,k}}{q_{v1} + q_{v2}} \tag{4}$$

8.3 Calculations for gravimetric methods

8.3.1 General

The different parts using gravimetric methods are listed below:

— critical flow orifices;

— thermal mass flow controllers;

— permeation;

— diffusion.

8.3.2 Formula

The previous methods are based on addition of several mass flow rates $q_{m,j}$, containing mass fractions of component k, v_{jk}, with the resultant mass fraction w_k, defined in Formula (5):

$$w_k = \frac{\sum_{j=1}^{r} q_{m\,j} v_{j,k}}{\sum_{j=1}^{r} q_{m\,j}} \tag{5}$$

The uncertainty is calculated by applying the propagation law, as shown in Formula (6):

$$u^2(w_k) = \sum_{j=1}^{r} \left(\frac{\partial w_k}{\partial v_{j,k}} \right)^2 u^2(v_{j,k}) + \sum_{j=1}^{r} \left(\frac{\partial w_k}{\partial q_{m\,j}} \right)^2 u^2(q_{m\,j}) \tag{6}$$

More details for these calculations can be found in Annex A.

Most of the time, the permeation/diffusion rate of the calibration component is expressed as a mass flow rate, while the total flow rate of the complementary gas plus the flow rate of the calibration component is expressed as a volume flow rate. It then gives the final result as mass concentration which is dependent on the pressure and temperature conditions.

EXAMPLE for two gases

When applied to two pure gases (gas 1 and gas 2), the previous formula is as shown in Formula (7):

$$w_k = \frac{q_{m,1} \cdot v_{1,k} + q_{m,2} \cdot v_{2,k}}{q_{m1} + q_{m2}} \tag{7}$$

9 Sources of uncertainty and uncertainty of the final mixture

The concentration in the generated mixture is obtained by calculation, using flow rates.

The uncertainty in the content of a component of a calibration mixture depends at any time on:

a) the uncertainty of calibration of the dynamic system;

b) the uncertainty of the parent gases composition (cylinder gas mixture, gas or liquid in permeation and diffusion tubes).

Depending on the two approaches to calibrate a dynamic system, the sources of uncertainty are different.

Considering each element of the dynamic system and calibrating each of them, the sources are flow rates and other quantities listed in Table 2.

Considering the dynamic system as a global entity and calibrating the generated gas mixture by comparison with reference gas mixtures, the sources come from the uncertainty of the comparison method.

10 Verification

10.1 Principle

Whenever possible, the composition of the prepared gas mixture shall be verified by comparison with a measurement standard (for example, a certified reference material or a calibrated analyser). Use one of the comparison methods described in ISO 6143 and ISO 12963.

In some cases, depending on the component, a direct chemical analysis method exists, such as titration, to determine the amount-of-substance fraction of component *k* in the final mixture with or without reference to other calibration gas mixtures. Pay special attention to gas trapping into liquid.

10.2 Verification criteria

A periodical verification should be carried out in order to quantify drifts and to ensure the accuracy of the mixture provided by the dynamic system.

For regular verification of mixing systems between two calibrations, it is possible to compare the amount-of-substance fraction assigned to the generated mixture according to preparation procedure, y_0, with the amount-of-substance fraction y_1 determined by comparison of the generated mixture with the reference gas mixture(s), i.e. traceable gas mixtures in cylinders or dynamically prepared mixtures obtained by other methods, using an analyser. The difference, D, between these values is calculated with Formula (8), taking in account their respective uncertainties. In case of use of gas cylinders, the reference gas mixture should be within its expiry date.

$$D = \frac{|y_0 - y_1|}{\sqrt{u^2(y_0) + u^2(y_1)}} \quad (8)$$

If $D \leq 2$ there is no significant difference between the value obtained according to preparation procedure and that obtained by comparison with the reference gas mixture. The dynamic system does not drift and complies with its requirements.

If $D > 2$, there is a significant difference between the value obtained according to preparation procedure and that obtained by comparison with the reference gas mixture. The dynamic system probably drifts and thus may not comply with its requirements. An investigation should be undertaken in order to understand the reasons for this difference. It can come from the reference gas mixture, or from the material compatibility between the dynamic system and the gas used, or from the analyser (matrix effect in case of different balance gases).

Curative and corrective actions should be undertaken in order to avoid this non-conformity in the future.

10.3 Recalibration criteria

The dynamic system shall be recalibrated following corrective action (such as cleaning or repair, etc.) which may change or affect the initial calibration parameters or if the periodic verification acceptance criteria have not been met.

Annex A
(normative)

Calculation details

A.1 Volumetric methods

A.1.1 Volume fractions and associated uncertainty

The volume fraction of component k at p_{ref} and T_{ref} is computed as Formula (A.1):

$$\phi_k = \frac{\sum_{j=1}^{r} V_j p_j T_j^{-1} Z_{\text{ref},j} Z_j^{-1} \varphi_{j,k}}{\sum_{j=1}^{r} V_j p_j T_j^{-1} Z_{\text{ref},j} Z_j^{-1}} \tag{A.1}$$

The basis for the uncertainty evaluation is Formula (A.1). The standard uncertainty associated with the volume fraction of component k shall be computed using Formula (A.2)

$$u^2(\phi_k) = \sum_{j=1}^{r} \left(\frac{\partial \phi_k}{\partial \varphi_{j,k}}\right)^2 u^2(\varphi_{j,k}) + \sum_{j=1}^{r} \left(\frac{\partial \phi_k}{\partial T_j}\right)^2 u^2(T_j) + \sum_{j=1}^{r} \left(\frac{\partial \phi_k}{\partial p_j}\right)^2 u^2(p_j) + \sum_{j=1}^{r} \left(\frac{\partial \phi_k}{\partial V_j}\right)^2 u^2(V_j) + \sum_{j=1}^{r} \left(\frac{\partial \phi_k}{\partial Z_j}\right)^2 u^2(Z_j) + \sum_{j=1}^{r} \left(\frac{\partial \phi_k}{\partial Z_{\text{ref},j}}\right)^2 u^2(Z_{\text{ref},j}) \tag{A.2}$$

The expressions for the sensitivity coefficients in Formula (2) read as follows [see Formulae (A.3) to (A.8)]:

$$\frac{\partial \phi_k}{\partial \varphi_{j,k}} = \frac{p_j V_j Z_{\text{ref},j}}{T_j Z_j} \frac{1}{W^*} \tag{A.3}$$

$$\frac{\partial \phi_k}{\partial T_j} = -\frac{p_j V_j Z_{\text{ref},j} \varphi_{j,k} + \phi_k V_j p_j Z_{\text{ref},j}}{T_j^2 Z_j W^*} \tag{A.4}$$

$$\frac{\partial \phi_k}{\partial p_j} = \frac{V_j Z_{\text{ref},j} \varphi_{j,k} - \phi_k V_j Z_{\text{ref},j}}{T_j Z_j W^*} \tag{A.5}$$

$$\frac{\partial \phi_k}{\partial V_j} = \frac{p_j Z_{\text{ref},j} \varphi_{j,k} - \phi_k p_j Z_{\text{ref},j}}{T_j Z_j W^*} \tag{A.6}$$

$$\frac{\partial \phi_k}{\partial Z_j} = \frac{p_j V_j Z_{\text{ref},j} \varphi_{j,k} + \phi_k V_j p_j Z_{\text{ref},j}}{Z_j^2 T_j W^*} \tag{A.7}$$

$$\frac{\partial \phi_k}{\partial Z_{\text{ref},j}} = \frac{p_j V_j \varphi_{j,k} - \phi_k p_j V_j}{T_j Z_j W^*} \quad \text{(A.8)}$$

where

$$W^* = \sum_{l=1}^{r} V_l p_l T_l^{-1} Z_{\text{ref},l} Z_l^{-1}$$

A.1.2 Amount-of-substance fractions and associated uncertainty

The amount-of-substance fraction of a component k in a gas mixture shall be computed as follows. First, calculate the amount-of-substance flow rate as shown in Formula (A.9)

$$q_{n\,j} = \frac{p_j q_{V\,j}}{RT_j Z_j} \quad \text{(A.9)}$$

directly from the volume flow rate, and pressure and temperature.

For the prepared gas mixture, the expression for the amount–of–substance fraction of component k is given by Formula (A.10)

$$y_k = \frac{\sum_{j=1}^{r} q_{n\,j} x_{k,j}}{\sum_{j=1}^{r} q_{n\,j}} \quad \text{(A.10)}$$

The uncertainty evaluation can be carried out as follows. Applying the law of propagation of uncertainty to Formula (A.10) leads to Formula (A.11)

$$u^2(y_k) = \sum_{j=1}^{r} \left(\frac{\partial y_k}{\partial q_{n\,j}} \right)^2 u^2(q_{n\,j}) + \sum_{j=1}^{r} \left(\frac{\partial y_k}{\partial x_{k,j}} \right)^2 u^2(x_{k,j}) \quad \text{(A.11)}$$

The expressions for the sensitivity coefficients read as Formula (A.12) and (13):

$$\frac{\partial y_k}{\partial q_{n\,j}} = \frac{x_{jk}}{q_{n,\text{mix}}} - \frac{y_k}{q_{n,\text{mix}}} \quad \text{(A.12)}$$

and

$$\frac{\partial y_k}{\partial x_{j,k}} = \frac{q_{n\,j}}{q_{n,\text{mix}}} \quad \text{(A.13)}$$

where

$$q_{n,mix} = \sum_{j=1}^{r} q_{n\,j}$$

The standard uncertainty associated with q_{nk} is calculated using Formula (A.14)

$$u^2(q_{n\,j}) = \left(\frac{q_{n\,j}}{p_j} \right)^2 u^2(p_j) + \left(\frac{q_{n\,j}}{T_j} \right)^2 u^2(T_j) + \left(\frac{q_{n\,j}}{V_j} \right)^2 u^2(V_j) + \left(\frac{q_{n\,j}}{Z_j} \right)^2 u^2(Z_j) \quad \text{(A.14)}$$

