INTERNATIONAL STANDARD

ISO 6145-6

Third edition
2017-07

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

Part 6: Critical flow orifices

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

Partie 6: Orifices de débit critiques

Reference number
ISO 6145-6:2017(E)

ISO copyright office
Ch. de Blandonnet 8 • CP 401
CH-1214 Vernier, Geneva, Switzerland
Tel. +41 22 749 01 11
Fax +41 22 749 09 47
copyright@iso.org
www.iso.org

Contents

Page

Foreword ... **iv**

1 Scope ... **1**

2 Normative references ... **1**

3 Terms and definitions ... **1**

4 Symbols ... **4**

5 Principle ... **5**

6 Calculation of mass flow rate and volume flow rate ... **6**
6.1 General ... 6
6.2 Calculation under ideal conditions ... 7
6.2.1 Calculation of mass flow rate ... 7
6.2.2 Calculation of volume flow rates ... 7
6.3 Calculation of mass flow rate using flow calibration with pure nitrogen ... 8
6.4 Flow rate uncertainty calculation ... 9
6.4.1 General ... 9
6.4.2 Sources of uncertainty ... 9
6.4.3 Uncertainty estimation ... 10

7 Calculation of amount of substance fraction and volume fraction and associated uncertainty evaluation ... **10**
7.1 General ... 10
7.2 Amount of substance fraction calculation and associated uncertainty ... 10
7.2.1 Case of gases with purity ≥ 99,99 % ... 10
7.2.2 Case of pre-mixtures ... 13
7.3 Remarks about uncertainty for the amount fraction ... 15

8 Application to the preparation of gas mixtures ... **15**
8.1 Example of a mixing system ... 15
8.2 Conditions of operation ... 16

9 Calibration and verification ... **17**
9.1 General ... 17
9.2 Calibration of the mixing system in the flow rate ... 17
9.3 Calibration of the mixing system with gas mixtures for a specific gas and concentration ... 17
9.4 Verification of the mixing system ... 17

Annex A (informative) **Example of calculation of isentropic coefficient, viscosity and critical flow coefficient** ... **19**

Annex B (informative) **Calculation of mass and volume flow rates under real conditions** ... **21**

Annex C (informative) **Example of flow calculation for toroidal critical flow orifices under ideal and real conditions** ... **23**

Annex D (informative) **Calculation of mass flow rate using flow calibration with pure nitrogen: examples** ... **25**

Bibliography ... **27**

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, on 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, *Analysis of gases*.

This third edition cancels and replaces the second edition (ISO 6145-6:2003) which has been technically revised.

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

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

Part 6: Critical flow orifices

1 Scope

This document specifies a method for the dynamic preparation of calibration gas mixtures containing at least two gases (usually one of them is a complementary gas) from pure gases or gas pre-mixtures using critical flow orifices systems.

The method applies principally to the preparation of mixtures of non-reactive gases that do not react with any of the materials forming the gas circuit inside the critical flow orifices system or auxiliary equipment. 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.

By selecting appropriate combinations of critical flow orifices, a dilution ratio of 1×10^4 is achievable.

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 will need to be at least two times higher than downstream pressure.

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

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 9300, *Measurement of gas flow by means of critical flow Venturi nozzles*

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

ISO 16664, *Gas analysis — Handling of calibration gases and gas mixtures — Guidelines*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 9300, ISO 7504 and the following apply.

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

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

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

3.1
critical flow orifice
orifice for which the geometrical configuration and conditions of use are such that the flow rate at the throat is *critical* (3.12)

3.2
wall pressure tap
orifice pierced in a pipework wall in such a way that the orifice edge on the inside pipework wall is flattened off

Note 1 to entry: This pressure tap is set up so that the pressure in the orifice equals the static pressure at this point of the circuit pipework.

3.3
static pressure
actual pressure of a gas stream, which can be measured by connecting a pressure gauge to a wall pressure tap

Note 1 to entry: This document uses only absolute pressure values.

3.4
stagnation pressure
pressure that would be found in a gas if the flowing gas stream was isentropically slowed down to zero velocity

Note 1 to entry: This document uses only absolute pressure values.

3.5
stagnation temperature
temperature that would be found in a gas if the flowing gas stream was isentropically slowed down to zero velocity

Note 1 to entry: This document only uses absolute temperature values.

3.6
mass flow rate
q_m
mass of gas per unit of time passing through the orifice

3.7
molar flow rate
q_n
amount of substance of gas per unit of time passing through the orifice

3.8
volume flow rate
q_V
volume of gas per unit of time passing through the orifice

3.9
throat Reynolds number
Re
dimensionless parameter calculated from the gas flow rate and dynamic viscosity under critical flow orifice inlet stagnation conditions

Note 1 to entry: The characteristic dimension is taken as the throat diameter at stagnation conditions. The throat Reynolds number is given by the formula:

$$Re = \frac{4\left(q_m\right)}{\pi \eta_0 d_N}$$

3.10
isentropic coefficient
γ
ratio of the relative variation in pressure to the corresponding relative variation in density under elementary reversible adiabatic (isentropic) transformation conditions

Note 1 to entry: In real gases, the forces exerted between molecules as well as the volume occupied by the molecules have a significant effect on the gas behaviour. In an ideal gas, intermolecular forces and the volume occupied by the molecules can be considered as negligible.

3.11
discharge coefficient
c
dimensionless ratio of the actual flow rate to the ideal flow rate of a non-viscous gas that would be obtained with one-dimensional isentropic flow for the same upstream stagnation conditions

Note 1 to entry: This coefficient corrects for viscous and flow field curvature effects. For each type of critical flow orifice design and installation conditions specified in this document, this coefficient is solely a function of the throat Reynolds number.

3.12
critical flow rate
maximum flow rate through a given orifice under the given upstream conditions

Note 1 to entry: At critical flow, the throat velocity is equal to the local value of the speed of sound (acoustic velocity), the velocity at which small pressure disturbances propagate.

3.13
critical flow function
C_*
dimensionless function which characterizes the thermodynamic flow properties of an isentropic one-dimensional flow between the inlet and the throat of a orifice

Note 1 to entry: It is a function of the nature of the gas and of the *stagnation pressure* (3.4) and *stagnation temperature* (3.5).

3.14
critical flow coefficient of a real gas
C_R
alternative form of the critical flow function, more convenient for gas mixtures

Note 1 to entry: This coefficient can be deduced from critical flow function via the formula:

$$C_R = C_* \sqrt{z_0}$$

3.15
critical pressure ratio
r^*
ratio of the static pressure at the critical flow orifice throat to the stagnation pressure for which the gas mass flow rate through the critical flow orifice is maximal

Note 1 to entry: This ratio is calculated according to the formula given in Clause 5.

$$r^* = \left(\frac{p_{out}}{p_{in}}\right)_{crit} = \left(\frac{2}{\gamma+1}\right)^{\frac{\gamma}{\gamma-1}}$$

3.16
compressibility factor
Z_0
correction factor numerically expressing the fact that the behaviour of a real gas deviates from the ideal gas law at stagnation pressure and temperature

Note 1 to entry: It is defined by the following formula:

$$Z_0 = \frac{p_0 M}{\rho_0 R T_0}$$

where R, the universal gas constant, equals 8, 314 4621 J/(mol·K)

4 Symbols

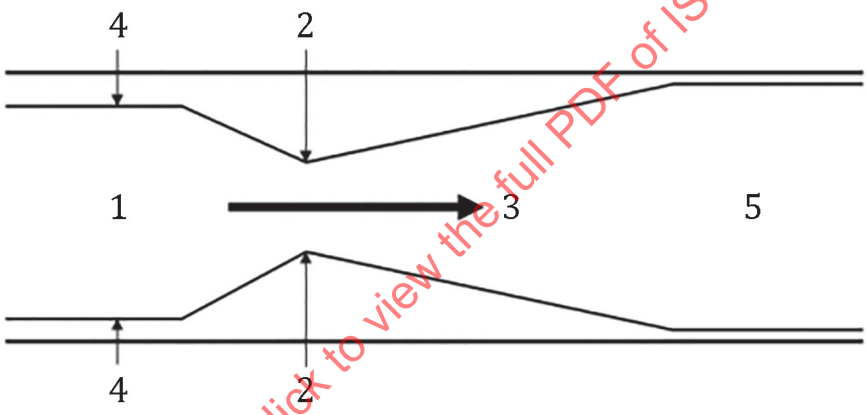
Symbol	Definition	SI unit
A	critical flow orifice throat area	m^2
a,b	coefficients of the discharge coefficient equation	—
C	discharge coefficient calculated for the critical flow orifice	—
C^*_i	critical flow function for the gas under ideal conditions dependent on p and T	—
C_i	sensitivity coefficient	—
C_R	critical flow coefficient for the gas under real conditions dependent on p and T	—
C_p	molar specific heat capacity of the gas at constant pressure	J/(mol·K)
C_V	molar specific heat capacity of the gas at constant volume	J/(mol·K)
d_N	critical flow orifice throat diameter	M
d_t	conduit diameter upstream of the critical flow orifice	M
M	molar mass of the gas	kg/mol
n	coefficient n of the critical flow orifice discharge coefficient equation	—
p_{in}	absolute static pressure measured upstream of the critical flow orifice	Pa
p_n	absolute pressure under normal conditions (101,325 kPa)	Pa
p_{out}	absolute static pressure measured downstream of the critical flow orifice	
p_0	absolute stagnation pressure dependent on p_{in}, T_{in} and q_m	
q_m	mass flow rate	kg/s
q_n	molar flow rate	mol/s
q_V	volume flow rate	m^3/s
r^*	critical pressure ratio	—
R	universal gas constant	J/(mol.K)
Re	critical flow orifices throat Reynolds number	—
T_{in}	temperature measured upstream of the critical flow orifice	K
T_n	temperature under normal conditions (273,15 K)	K
T_0	absolute stagnation temperature dependent on P_{in}, T_{in} and q_m	K
v_g	speed of gas through the critical flow orifices	m/s
v_s	velocity of sound at the throat	m/s
Z_n	compressibility factor under normal conditions (T_n, P_n)	—

Symbol	Definition	SI unit
Z_0	compressibility factor at P_0, T_0	—
γ	isentropic coefficient dependent on P and T	—
η_0	dynamic viscosity calculated for the gas at P_0 and T_0	Pa.s
ρ_{in}	gas density upstream of the critical flow orifice	kg/m^3
ρ_n	gas density at the critical flow orifices throat	kg/m^3
ρ_0	gas density at stagnation condition	kg/m^3

5 Principle

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}.

An example of a critical flow orifice is illustrated in Figure 1.



Key

1 inlet
2 critical flow orifice throat diameter (d_N)
3 direction of flow
4 conduit diameter upstream of the critical flow orifice (d_t)
5 outlet

NOTE 1 The temperature T_{in} and the pressure p_{in} are measured in point 4 and the pressure p_{out} in point 5.

NOTE 2 The temperature T_0 and the pressure p_0 are calculated in point 2 (see 5.2).

Figure 1 — Example of a critical flow orifice

For a given gas at constant temperature, the critical pressure ratio, (r^*), is:

$$r^* = \left(\frac{p_{out}}{p_{in}} \right)_{crit} = \left(\frac{2}{\gamma + 1} \right)^{\frac{\gamma}{\gamma - 1}} \quad (1)$$

Different methods for calculating the isentropic coefficient γ are described in A.1.

For monatomic, diatomic and triatomic gases, this critical pressure ratio will be around 0,5, but it is dependent on pressure and temperature conditions as shown in Table 1.

Table 1 — Influence of the pressure and type of gas on the critical pressure ratio

Gas	Temperature T_{in} °C	Pressure p_{in} bar	Pressure p_{out} bar	$\gamma = C_p/C_V$	Critical pressure ratio r^*
Argon	20,0	2,1	1,0	1,669 7	0,49
	20,0	10,3	5,0	1,681 7	0,49
	20,0	20,7	10	1,696 9	0,49
Nitrogen	20,0	1,9	1,0	1,401 4	0,53
	20,0	9,5	5,0	1,408 6	0,53
	20,0	19,0	10	1,417 7	0,53
Carbon dioxide	20,0	1,8	1,0	1,296 7	0,55
	20,0	9,2	5,0	1,322 2	0,54
	20,0	18,7	10	1,358 9	0,54
NOTE The γ values were calculated for $p = p_{out}$ using the data from the NIST REFPROP V 9.0 database.					

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.

This method is not absolute, as each critical flow orifice system should be calibrated for each gas used, to obtain optimal accuracy with minimal uncertainty (traceable flow calibration or analytical comparison). This is because the formula for the volume flow rate of a gas includes its molar mass. If a different calibration gas is used, a correction factor shall be applied and allowance shall be only made for its associated uncertainty.

The temperatures of all critical flow orifices shall be the same in order to avoid any effects on the flow rates.

To obtain a flow rate below 10 l/min, the throat diameter should be less than 0,2 mm.

6 Calculation of mass flow rate and volume flow rate

6.1 General

Mass and volume flow rates in critical flow orifices are directly proportional to stagnation pressure upstream of critical flow orifices and inversely proportional to the square root of absolute stagnation temperature.

The flow rates through a critical flow orifice running at sonic conditions (below critical pressure ratio) can be calculated under ideal and real conditions using ISO 9300. The flow rate in real conditions is given in Annex B and examples of the calculation of the flow rates under ideal and real conditions in Annex C.

To calculate mass flow rate under real conditions, additional parameters shall be taken into account (viscosity, surface roughness, flow field curvature, installation conditions). Due to the complexity for calculating the flow rate in real conditions, this document presents the flow rate calculation in ideal conditions only.

The calculation using ideal and real conditions can result in flow rates which could be different. This could influence the accuracy of the generated gas mixtures. By calibrating the device with each used gas, this effect will become negligible.

The conversion of mass flow rate to volume flow rate is presented in 6.2.2.

6.2 Calculation under ideal conditions

6.2.1 Calculation of mass flow rate

The mass flow rate of a gas through a critical flow orifice under ideal conditions is given by Formula (2):

$$q_m = \frac{AC_{*i}p_0}{\sqrt{\frac{T_0 R}{M}}} \tag{2}$$

where

q_m is the mass flow rate;

A is the critical orifice throat area;

C_{*i} is the critical flow function for the gas, calculated as follows:

$$C_{*i} = \sqrt{\gamma\left(\frac{2}{\gamma+1}\right)^{\frac{\gamma+1}{\gamma-1}}} \tag{3}$$

R is the universal gas constant;

M is the molar mass of the gas.

NOTE 1 The critical flow orifice throat area is dependent on the critical flow orifice thermal expansion coefficient. It is consequently advisable to use the critical flow orifice within the manufacturer's stated temperature range.

NOTE 2 At under a millimetre, getting a dimensional measurement of the throat diameter becomes particularly difficult. This makes it difficult to obtain an accurate throat area figure.

γ is the isentropic coefficient which can be calculated using different methods described in Annex A:

p_0 is the absolute stagnation pressure, in these conditions:

$$p_0 = p_{in} \tag{4}$$

T_0 is the absolute stagnation temperature, in these conditions:

$$T_0 = T_{in} \tag{5}$$

6.2.2 Calculation of volume flow rates

Dividing mass flow rate by density $\rho_n = \frac{p_n \times M}{R \times T_n}$ gives the volume flow rate:

$$q_V = \frac{q_m}{\rho_n} = A \times C_{*i} \times \frac{p_0 \times T_n}{p_n} \times \sqrt{\frac{R}{M \times T_0}} \tag{6}$$

6.3 Calculation of mass flow rate using flow calibration with pure nitrogen

For practical use, the flow calibration of the device is usually done with pure nitrogen. For the use of the devices with another gas G, it is necessary to calculate a ratio K between the other gas G and nitrogen N_2. These calculations are accurate if the temperature of all critical flow orifices is homogeneous. In this case, calibration could be performed at any temperature. For simplification, the following formula is used under ideal conditions:

$$K = \frac{(q_m)_{\mathrm{G}}}{(q_m)_{\mathrm{N2}}} \tag{7}$$

where

$(q_m)_{\mathrm{G}}$ is the mass flow of gas G;

$(q_m)_{\mathrm{N2}}$ is the mass flow of nitrogen.

$$(q_m)_{\mathrm{N2}} = \frac{A \times C_{*\mathrm{in2}} \times p_{\mathrm{in}\,(\mathrm{N2})}}{\sqrt{\frac{T_{\mathrm{in}\,(\mathrm{N2})} \times R}{M_{\mathrm{N2}}}}} \tag{8}$$

$$(q_m)_{\mathrm{G}} = \frac{A \times C_{*i\mathrm{G}} \times p_{\mathrm{in}\ (\mathrm{G})}}{\sqrt{\frac{T_{\mathrm{in}\,(\mathrm{G})} \times R}{M_{\mathrm{G}}}}} \tag{9}$$

Assuming that T_0 and p_0 are the same for both gases and A and R are constant, Formula (7) becomes:

$$K = \frac{C_{*i\mathrm{G}} \times \sqrt{M_{\mathrm{G}}}}{C_{*i\ \mathrm{N2}} \times \sqrt{M_{\mathrm{N2}}}} \tag{10}$$

The calculation of $C_{*\mathrm{G}}$ and $C_{*\mathrm{N2}}$ is done using the following formulae:

$$C_{*\mathrm{G}} = \sqrt{\gamma_{\mathrm{G}} \times \left(\frac{2}{\gamma_{\mathrm{G}}+1}\right)^{\frac{\gamma_{\mathrm{G}}+1}{\gamma_{\mathrm{G}}-1}}} \tag{11}$$

$$C^*_{N2} = \sqrt{\gamma_{N2} \times \left(\frac{2}{\gamma_{N2}+1}\right)^{\frac{\gamma_{N2}+1}{\gamma_{N2}-1}}} \tag{12}$$

with

$$\gamma_{N2} = \frac{Cp_{N2}}{Cv_{N2}}$$

and

$$\gamma_G = \frac{Cp_G}{Cv_G}$$

Finally, the ratio K between the gas G and nitrogen is given by:

$$K = \frac{\sqrt{M_G \times \gamma_G \times \left(\frac{2}{\gamma_G+1}\right)^{\frac{\gamma_G+1}{\gamma_G-1}}}}{\sqrt{M_{N2} \times \gamma_{N2} \times \left(\frac{2}{\gamma_{N2}+1}\right)^{\frac{\gamma_{N2}+1}{\gamma_{N2}-1}}}} \tag{13}$$

As this ratio is calculated under ideal conditions and not in real conditions, this could affect the accuracy of the flow rate calculation. By calibrating the device with each used gas, this effect will become negligible. An example of calculation is given in Annex D.

6.4 Flow rate uncertainty calculation

6.4.1 General

The uncertainty can be calculated by applying the propagation law, defined by the GUM,[4] on mass flow rate Formula (2) and volume flow rate Formula (6).

6.4.2 Sources of uncertainty

6.4.2.1 Critical flow orifice temperature

To an excellent approximation, temperature fluctuations will lead to only negligible variations in flow rate ratios, provided that temperatures are identical at each critical flow orifice throat.

6.4.2.2 Upstream pressure

The gas volume flow rate through a critical flow orifice depends on the pressure upstream of the critical flow orifices. Therefore, it is essential to use stable gas-pressure regulators in order to ensure that upstream pressure is kept constant. Repeatability for the upstream pressure should be less than 0,2 % for achieving an amount fraction relative expanded uncertainty of 0,5 %.

6.4.2.3 Orifice parameters

The uncertainty of the critical flow orifice throat area A and discharge coefficient c is difficult to evaluate due to the small size of the critical flow orifice throat diameter d_N.

6.4.2.4 Downstream pressure

There is no influence of this parameter if the flow rate through the orifice is critical.

6.4.2.5 Temperature differential on the different gas mixture components

A critical flow orifice mixing system should be designed so that temperature is identical at each critical flow orifice. However, if there is a temperature differential between the two component gases in a binary mixture, the volume flow rate needs to be corrected by applying a gas thermal expansion coefficient. For an ideal gas, the coefficient is 0,003 661 per Kelvin. This value can be applied for real gases to an excellent approximation if working with small temperature differentials (2 K for example) between the gas components.

6.4.3 Uncertainty estimation

Due to the complexity of the evaluation of standard uncertainties for each parameter in Formulae (2) and (6), another approach can be used based on calibration of flow rates of the device.

The uncertainty given in the calibration certificate can be used for flow rate uncertainty. Usually, this relative standard uncertainty is between 0,2 % and 0,3 %.

7 Calculation of amount of substance fraction and volume fraction and associated uncertainty evaluation

7.1 General

To prepare calibration gas mixtures, the gas flowing out of a critical flow orifice (gas 1) and the complementary gas flowing out of another critical flow orifice (gas 2) are mixed. The generated mixture is homogenized in a mixing chamber. The purity of both gases shall be taken into account in order to calculate the volume or amount fractions. The accurate calculation of the amount fraction and uncertainty of each component in the generated gas mixture depends on the determination of the impurities contained in each pure gas used in this preparation. For purity and uncertainty calculation, see ISO 19229.

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.

7.2 Amount of substance fraction calculation and associated uncertainty

7.2.1 Case of gases with purity ≥ 99,99 %

This case can be modelled as:

$$y_1 = \frac{\frac{(q_m)_1}{M_1}}{\frac{(q_m)_1}{M_1} + \frac{(q_m)_2}{M_2}} \tag{14}$$

where

$(q_m)_1$ denotes the mass flow of gas 1;

$(q_m)_2$ is the mass flow of gas 2 (the complementary gas);

M_1 is the molar mass of gas 1;

M_2 is the molar mass of gas 2.

NOTE If the purity data (see 6.1) are to be taken into account, the expression for pre-mixtures can be used instead (see 6.2.2).

Formula (14) can be modified by introducing the flow on a molar basis, and by substituting q_{M1} for q_{mi}/M_i which leads to:

$$y_1 = \frac{(q_n)_1}{(q_n)_1 + (q_n)_2} \tag{15}$$

Derivating Formula (15) gives dq:

$$\mathrm{d}y_1 = \frac{\partial y_1}{\partial (q_n)_1}\mathrm{d}(q_n)_1 + \frac{\partial y_1}{\partial (q_n)_2}\mathrm{d}(q_n)_2 \tag{16}$$

After developing Formula (16):

$$\mathrm{d}y_1 = \left(\frac{1}{(q_n)_1 + (q_n)_2} + \frac{-(q_n)_1}{\left((q_n)_1 + (q_n)_2\right)^2}\right)\mathrm{d}(q_n)_1 + \frac{-(q_n)_1}{\left((q_n)_1 + (q_n)_2\right)^2}\mathrm{d}(q_n)_2 \tag{17}$$

Substitution of Formula (15) into Formula (17) yields:

$$\mathrm{d}y_1 = \left(\frac{y_1}{(q_n)_1} + \frac{-y_1}{(q_n)_1 + (q_n)_2}\right)\mathrm{d}(q_n)_1 + \frac{-y_1}{(q_n)_1 + (q_n)_2}\mathrm{d}(q_n)_2 \tag{18}$$

Using the relationship $(q_n)i = (q_m)_i / M_i$, the partial derivatives with respect to $(q_m)_i$ and M_i gives:

$$\mathrm{d}(q_n)_1 = \frac{1}{M_i}\mathrm{d}(q_m)_i + \frac{-(q_m)_i}{M_i^2}\mathrm{d}M_i$$

Substitution of this expression into Formula (18) yields:

$$\begin{aligned}\mathrm{d}y_1 = {} & \left(\frac{y_1}{(q_n)_1} + \frac{-y_1}{(q_n)_1 + (q_n)_2}\right)\frac{1}{M_1}\mathrm{d}(q_m)_1 + \left(\frac{y_1}{(q_n)_1} + \frac{-y_1}{(q_n)_1 + (q_n)_2}\right)\frac{-(q_m)_1}{M_1^2}\mathrm{d}M_1 \\ & + \frac{-y_1}{(q_n)_1 + (q_n)_2}\frac{1}{M_2}\mathrm{d}(q_m)_2 + \frac{-y_1}{(q_n)_1 + (q_n)_2}\frac{-(q_m)_2}{M_2^2}\mathrm{d}M_2\end{aligned} \tag{19}$$

Formula (19) contains all necessary expressions for the sensitivity coefficients:

$$\frac{\partial y_1}{\partial q_{m1}} = \left(\frac{y_1}{(q_n)_1} + \frac{-y_1}{(q_n)_1 + (q_n)_2}\right)\frac{1}{M_1}$$

$$\frac{\partial y_1}{\partial M_1} = \left(\frac{y_1}{(q_n)_1} + \frac{-y_1}{(q_n)_1 + (q_n)_2} \right) \frac{(q_m)_1}{M_1^2}$$

$$\frac{\partial y_1}{\partial (q_m)_2} = -\frac{y_1}{(q_n)_1 + (q_n)_2} \frac{1}{M_2}$$

$$\frac{\partial y_1}{\partial M_2} = \frac{y_1}{(q_n)_1 + (q_n)_2} \frac{(q_m)_2}{M_2^2}$$

The above expressions can be used as usual to evaluate the uncertainty associated with y_1 using the law of propagation of uncertainty of the GUM[4].

In the following example, it is assumed that two mass flows are mixed (see Table 2). The relative standard uncertainty associated with the mass flows is 2,1 %. The first gas is methane, the second is nitrogen. It is assumed that the gases are totally pure. The molar masses are calculated using the IUPAC[8] atomic weights of 2007.

Table 2 — Sample calculation for a mixture of methane in nitrogen

Quantity	Value	u_i	C_i[a]	$C_i u_i$
$(q_m)_1$	10,00 g/min	0,02 g/min	$1,27\ 10^{-2}$ min/g	$2,53\ 10^{-4}$
$(q_m)_2$	100,0 g/ min	0,2 g/min	$-7,89\ 10^{-3}$ min/g	$-1,58\ 10^{-3}$
M_1	16,042 46 g/mol	0,000 49 g/mol	$-1,27\ 10^{-3}$ mol/g	$-6,20\ 10^{-7}$
M_2	28,013 40 g/mol	0,000 23 g/mol	$4,52\ 10^{-3}$ mol/g	$1,04\ 10^{-6}$
y_1	0,148 661 mol/ mol			0,001 598[b]

[a] Sensitivity coefficient.

[b] Combined standard uncertainty for y_1.

The impact of the purity of the gases can be modelled as follows. The amount–of–substance fraction of the main component is the correction factor that needs be applied to q_{M1}. Supposing that in the previous example the methane is 99,9 % pure and the nitrogen 99,99 % (both on a molar basis). The bias by not correcting for the purity is in terms of the amount–of–substance fractions respectively 0,001 mol/mol and 0,000 1 mol/mol. The correction should be applied as a factor (x=0,999 for methane and x=0,999 9 for nitrogen) to $(q_M)_1$ and $(q_M)_2$ respectively.

The bias (10^{-3} and10^{-4} respectively) is combined with the standard uncertainty associated with $(q_m)_1$ and $(q_m)_2$ respectively:

$$u_i(m_1) = \sqrt{0,2^2 + \left[\left(\frac{10^{-3}}{0,999}\right)\right]^2} = 0,022\ 36$$

$$u_i(m_2) = \sqrt{0,2^2 + \left[\left(\frac{10^{-4}}{0,9999}\right) \times 100\right]^2} = 0,200\ 2$$

The uncertainty evaluation including the purity of the methane and nitrogen is shown in Table 3.

Table 3 — Sample calculation for a mixture of methane in nitrogen including a correction for purity

Quantity	Value	u_i	C_i[a]	$C_i u_i$
$(q_m)_1$	10,00 g/min	0,022 36 g/min	1,27 10^{-2} min/g	2,83 10^{-4}
$(q_m)_2$	100,0 g/min	0,200 2 g/min	−7,89 10^{-3} min/g	−1,58 10^{-3}
M_1	16,042 46 g/mol	0,000 49 g/mol	−1,27 10^{-3} mol/g	−6,20 10^{-7}
M_2	28,013 40 g/mol	0,000 23 g/mol	4,52 10^{-3} mol/g	1,04 10^{-6}
y_1	0,148 661 mol/mol			0,001 605[b]

[a] Sensitivity coefficient.

[b] Combined standard uncertainty for y_1.

The relative expanded uncertainty for the amount fraction with a coverage factor of 2 is 2,2 %, for the current state of the art of flow calibration.

7.2.2 Case of pre-mixtures

If parent gas 1 is a pre-mixture with component i and parent gas 2 is the complementary gas with component i (for example as impurity), the measurement formula for calculating the amount of substance fraction of a component i in the prepared gas mixture is:

$$y_i = \frac{(q_m)_1 \cdot x_{i1} / \bar{M}_1 + (q_m)_2 \cdot x_{i2} / \bar{M}_2}{(q_m)_1 / \bar{M}_1 + (q_m)_2 / \bar{M}_2} \tag{20}$$

where

$\overline{M}_1$ denotes the molecular mass of parent 1;

$\overline{M}_2$ denotes the molecular mass of parent 2;

x_{i1} denotes the amount of substance fractions of component i in parent 1;

x_{i2} denotes the amount of substance fractions of component i in parent 2.

The molecular mass of a gas mixture is defined as:

$$\bar{M}_j = \sum_{k=1}^{n} x_{jk} \cdot M_k$$

where

n denotes the number of components in the gas mixture;

M_k denotes the molar mass of component k.

Formula (20) differs from Formula (14) in that the molar mass of a gas mixture is usually calculated from the molar masses of the components and the gas composition expressed in the amount of substance fractions, so that the molar masses of the parents become a function of their composition too. In the following, the generally applicable expressions for the sensitivity coefficients will be derived. The variables in Formula (20) are assumed to be mutually independent, which is generally speaking not the case for (at least) the molar masses.

The measurement Formula (20) can be written as:

$$y_i = \frac{(q_n)_1 \cdot x_{i1} + (q_n)_2 \cdot x_{i,2}}{(q_n)_1 + (q_n)_2} \tag{21}$$

Both formulae are symmetrical with respect to the parent gases, that is, if one derives the expressions for the sensitivity coefficients for parent gas 1, then one has the analogous expressions for parent gas 2.

Based on Formula (21), the following total differentials can be developed:

$$\mathrm{d}y_i = \left(\frac{x_{i1}}{(q_n)_1 + (q_n)_2} - \frac{y_i}{(q_n)_1 + (q_n)_2}\right)\mathrm{d}(q_n)_1 + \frac{(q_n)_1}{(q_n)_1 + (q_n)_2}\mathrm{d}x_{i1} + \left(\frac{x_{i2}}{(q_n)_1 + (q_n)_2} - \frac{y_i}{(q_n)_1 + (q_n)_2}\right)\mathrm{d}(q_n)_2 + \frac{(q_n)_2}{(q_n)_1 + (q_n)_2}\mathrm{d}x_{i2} \tag{22}$$

Using the relationship $(q_n)_{,i} = (q_m)_i/M_i$, the partial derivatives with respect to $(q_m)_i$ and M_i are the following for $(q_n)_1$ and $(q_n)_2$.

$$\mathrm{d}(q_n)_1 = \frac{1}{M_1}\mathrm{d}(q_m)_1 + \frac{-(q_m)_1}{M_1^2}\mathrm{d}M_1$$

$$\mathrm{d}(q_n)_2 = \frac{1}{M_2}\mathrm{d}(q_m)_2 + \frac{-(q_m)_2}{M_2^2}\mathrm{d}M_2$$

Substitution of these expressions into Formula (22) yields:

$$\mathrm{d}y_i = \left(\frac{x_{i1}}{(q_n)_1 + (q_n)_2} - \frac{y_i}{(q_n)_1 + (q_n)_2}\right)\frac{1}{M_1}\mathrm{d}(q_m)_1 + \left(\frac{x_{i1}}{(q_n)_1 + (q_n)_2} - \frac{y_i}{(q_n)_1 + (q_n)_2}\right)\frac{-(q_m)_1}{M_1^2}\mathrm{d}M_1 + \frac{(q_n)_1}{(q_n)_1 + (q_n)_2}\mathrm{d}x_{i1} + \left(\frac{x_{i2}}{(q_n)_1 + (q_n)_2} - \frac{y_i}{(q_n)_1 + (q_n)_2}\right)\frac{1}{M_2}\mathrm{d}(q_m)_2 + \left(\frac{x_{i2}}{(q_n)_1 + (q_n)_2} - \frac{y_i}{(q_n)_1 + (q_n)_2}\right)\frac{-(q_m)_2}{M_2^2}\mathrm{d}M_2 + \frac{(q_n)_2}{(q_n)_1 + (q_n)_2}\mathrm{d}x_{i2} \tag{23}$$

Formula (23) contains all necessary expressions for the sensitivity coefficients:

$$\frac{\partial y_i}{\partial (q_m)_1} = \left(\frac{x_{i1}}{(q_n)_1 + (q_n)_2} - \frac{y_i}{(q_n)_1 + (q_n)_2}\right)\frac{1}{M_1}$$

$$\frac{\partial y_i}{\partial M_1} = \left(\frac{x_{i1}}{(q_n)_1 + (q_n)_2} - \frac{y_i}{(q_n)_1 + (q_n)_2}\right)\frac{-(q_m)_1}{M_1^2}$$

$$\frac{\partial y_i}{\partial x_{i1}} = \frac{(q_n)_1}{(q_n)_1 + (q_n)_2}$$

$$\frac{\partial y_i}{\partial M_2} = \left(\frac{x_{i2}}{(q_n)_1 + (q_n)_2} - \frac{y_i}{(q_n)_1 + (q_n)_2}\right)\frac{-(q_m)_2}{M_2^2}$$

$$\frac{\partial y_i}{\partial (q_m)_2} = \left(\frac{x_{i2}}{(q_n)_1 + (q_n)_2} - \frac{y_i}{(q_n)_1 + (q_n)_2}\right)\frac{1}{M_2}$$

$$\frac{\partial y_i}{\partial x_{i2}} = \frac{(q_n)_2}{(q_n)_1 + (q_n)_2}$$

7.3 Remarks about uncertainty for the amount fraction

The best relative expanded uncertainty for the amount (or mass) fraction that can be obtained for a binary mixture using pure gases (with a coverage factor of 2) is 0,5 %, for the current state of the art of flow calibration (see 6.3).

Another potential source of error comes from inhomogeneity in the generated gas mixture. Mixture homogeneity shall be checked by verifying the amount (or mass) fraction using a comparison method specified in ISO 6143 or ISO 12963.

8 Application to the preparation of gas mixtures

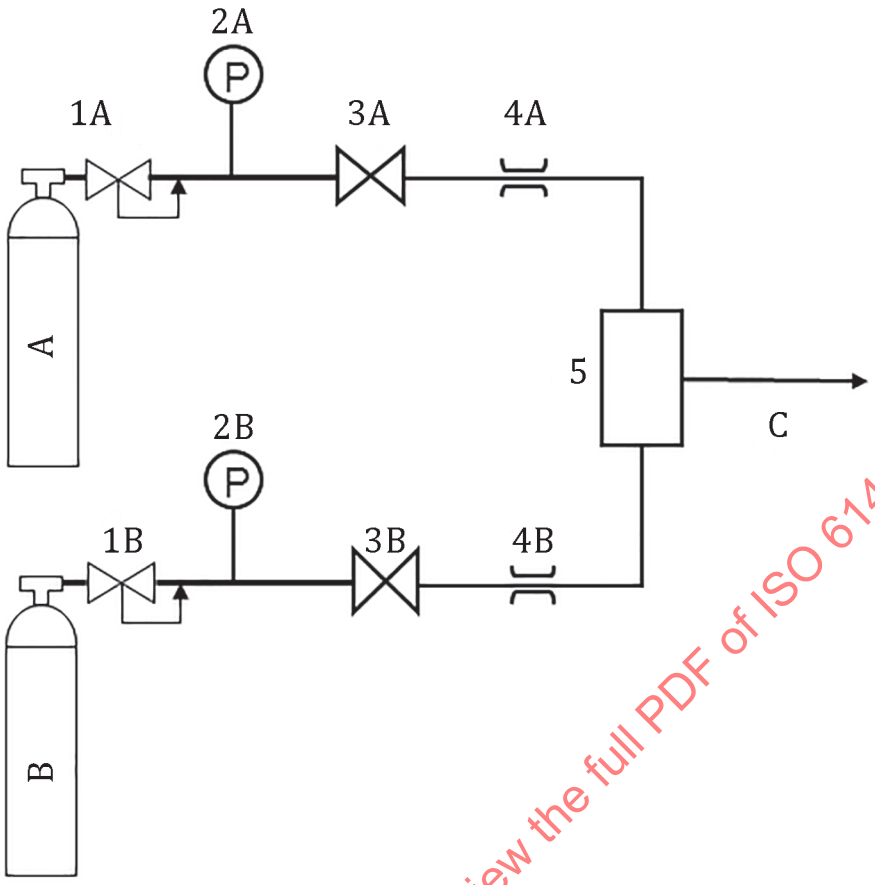
8.1 Example of a mixing system

Figure 2 is a schematic diagram of a system of critical flow orifices for the preparation of a binary mixture of gas A and gas B.

Each gas line is fitted with a pressure regulator and a manometer (1A and 1B). The pressure at the inlet of the orifice 4A and 4B is accurately controlled by pressure-regulating valves (3A and 3B). Both gas flows are mixed in the mixing chamber (5).

To operate the gas mixing system, the gas cylinder valves are opened and the readings on manometers are both adjusted to a value recommended by the manufacturer of the device. The pressure regulators (1A and 1B) are opened to let both gases flow through their respective orifices.

Pressure regulators 1A and 1B are adjusted to set the pressure displayed on the manometers to the values needed to produce the desired flow rates.



Key

A	gas cylinder
B	gas cylinder
C	generated gas mixture
1A,1B	pressure regulator
2A, 2B	pressure sensor
3A, 3B	valve
4A,4B	critical flow orifice
5	mixing chamber

Figure 2 — Preparation of calibration gas mixtures using a critical flow orifices system

This is the simplest representation of a gas mixing system. More sophisticated systems using additional critical orifices can be used to generate more complex mixtures or different dilution ratios.

8.2 Conditions of operation

The general precautions common to all dynamic methods of preparation shall be taken. Special attention shall be made to the materials used in constructing the gas circuit. Only non-adsorbent materials of low porosity are suitable. Pipework shall be clean and all joints correctly fitted.

WARNING — If a corrosive gas is used, special attention shall be given to the materials in contact with the gas and to the implementation of the method. Particular caution is needed when this method is used as a means to prepare gas mixtures containing components that may form potentially explosive mixtures. All necessary measures shall be taken to make sure the apparatus can operate safely. This is of particular importance for this method because

the pressure of the gases in the dilution system is appreciably greater than the atmospheric pressure.

NOTE For further information on safely implementing gas mixtures containing components that can form potentially explosive mixtures, see, for example, the EIGA document 139/10.[6]

9 Calibration and verification

9.1 General

It is mandatory to check the calibration of a mixing system periodically in order to evaluate the possible drift of the system and so to ensure the accuracy of the mixture provided by it. If the drift is negligible, it is not necessary to consider it in the uncertainty budget. If the drift is important, a new calibration is required.

9.2 Calibration of the mixing system in the flow rate

It is necessary to calibrate the mixing system at least once annually in order to obtain the critical flow orifice flow rates together with their uncertainties. This calibration shall be done by a laboratory, specialized in traceable flow measurements and uncertainty calculations. The results obtained provide the parameters required to calculate the concentrations and uncertainties of the mixture prepared using this method. It is recommended that the device be calibrated by an accredited laboratory.

9.3 Calibration of the mixing system with gas mixtures for a specific gas and concentration

It is possible to calibrate a mixing system with its associated gas cylinder(s) at a specific concentration by comparing the concentration of the generated mixture with a reference gas mixture obtained by other methods: traceable gas mixtures in cylinders, dynamically prepared mixtures (see the ISO 6145 series). Extrapolations or interpolations should be done 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.

9.4 Verification of the mixing system

For regular verification of mixing systems between two calibrations, it is possible to compare the component amount fraction in the generated mixture and a respective reference gas mixture obtained by other methods: traceable gas mixtures in cylinders or dynamically prepared mixtures. The values obtained with the mixing system and those obtained with the reference gas mixture are compared using an appropriate gas analyser. The value of D is calculated using ISO 16664.

$$D = \frac{\left| y_0 - y_1 \right|}{\sqrt{u^2\left(y_0\right) + u^2\left(y_1\right)}} \tag{24}$$

where

y_0 is the amount fraction of the generated mixture;

y_1 is the amount fraction of the reference gas mixture;

$u(y_0)$ is the standard uncertainty of the amount fraction of the generated mixture;

$u(y_1)$ is the standard uncertainty of the amount fraction of the reference gas mixture.

If $D \leq 2$, there is no significant difference between the value obtained with the gas blender and that obtained with the reference gas mixture. The gas blender does not drift and complies with its requirements.

If $D > 2$, there is a significant difference between the value obtained with the gas blender and that obtained with the reference gas mixture. The gas blender drifts and does not comply with its requirements. An investigation should be undertaken in order to understand the reasons for this difference. Curative actions, corrective actions and preventive actions should be undertaken in order to avoid this non conformity in the future.

Other verification methods without reference gas mixtures are also possible: use of one linear analyser or two different gas analysers properly calibrated.

Annex A
(informative)

Example of calculation of isentropic coefficient, viscosity and critical flow coefficient

A.1 Example of calculation of the isentropic coefficient

The isentropic coefficient (isentropic expansion factor, isentropic exposent) γ is often defined as the ratio of specific heats of a gas:

$$\gamma = \frac{C_p}{C_V} \tag{A.1}$$

where

C_p is the molar specific heat capacity of the gas at constant pressure;

C_V is the molar specific heat capacity of the gas at constant volume.

For ideal gases the isentropic coefficient does not depend on pressure and temperature and is equal to 5/3 for monatomic gases, 7/5 for diatomic gases and 4/3 for polyatomic gases. For real gases it depends on pressure and temperature. The data for C_p, C_V or directly γ at different temperatures and pressures may be found in many sources. In Table A.1, the isentropic expansion factor and C_p/C_V values, both obtained from NIST REFPROP 9.0 database, for nitrogen, argon and methane are compared. The maximum difference between the two quantities is 0,068 8 for argon.

Table A.1 — Example of calculation of the isentropic expansion factor γ with Refprop V9.0 and Formula (A.1) for nitrogen, argon and methane

Gas	Temperature K	Pressure MPa	Isentropic expansion factor γ (Refprop V9.0)	C_p/C_V (Formula (A.1))
Nitrogen	280	0,1	1,401 2	1,401 7
	300	0,1	1,401 0	1,401 2
	280	2	1,432 6	1,440 3
	300	2	1,431 1	1,433 7
Argon	280	0,1	1,668 6	1,670 0
	300	0,1	1,668 5	1,669 5
	280	2	1,708 3	1,735 4
	300	2	1,705 5	1,724 6
Methane	280	0,1	1,310 9	1,313 7
	300	0,1	1,303 1	1,305 3
	280	2	1,320 5	1,379 6
	300	2	1,313 9	1,358 3

A.2 Example of calculation of the dynamic viscosity

The η can be calculated with the NIST REFPROP V 9.0 database as shown in Table A.2.

Table A.2 — Dynamic viscosity η calculated with Refprop V9.0 for nitrogen, argon and methane

Gas	Temperature K	Pressure MPa	η Pa·s (Refprop V9.0)
Nitrogen	280	0,1	$1{,}695\,5 \times 10^{-5}$
	300	0,1	$1{,}789\,0 \times 10^{-5}$
	280	2	$1{,}726\,0 \times 10^{-5}$
	300	2	$1{,}816\,6 \times 10^{-5}$
Argon	280	0,1	$2{,}146\,2 \times 10^{-5}$
	300	0,1	$2{,}274\,1 \times 10^{-5}$
	280	2	$2{,}185\,6 \times 10^{-5}$
	300	2	$2{,}310\,2 \times 10^{-5}$
Methane	280	0,1	$1{,}048\,2 \times 10^{-5}$
	300	0,1	$1{,}113\,6 \times 10^{-5}$
	280	2	$1{,}078\,6 \times 10^{-5}$
	300	2	$1{,}142\,3 \times 10^{-5}$

A.3 Example of calculation of critical flow coefficient C_R

Two calculations are possible, either from the NIST database or from the formula given in ISO 9300. A comparison of both calculations is given in Table A.3. The maximum difference between these two methods is less than 1×10^{-4}.

Table A.3 — Calculation of the critical flow coefficient C_R with Refprop V9.0 and ISO 9300 for nitrogen, argon and methane

Gas	Temperature K	Pressure MPa	C_R (Refprop V9,0)	C_R (ISO 9300)
Nitrogen	280	0,1	0,685 00	0,685 00
	300	0,1	0,684 95	0,684 92
	280	2	0,690 88	0,690 88
	300	2	0,689 49	0,689 48
Argon	280	0,1	0,726 75	0,726 70
	300	0,1	0,726 63	0,726 6
	280	2	0,736 67	0,736 67
	300	2	0,734 69	0,734 69
Methane	280	0,1	0,671 20	0,671 19
	300	0,1	0,669 93	0,669 92
	280	2	0,686 18	0,686 19
	300	2	0,681 90	0,681 89

Annex B
(informative)

Calculation of mass and volume flow rates under real conditions

B.1 Calculation of the mass flow rate

The mass flow rate of a gas through a critical flow orifice under real conditions is given by the formula:

$$q_m = \frac{A \times c \times C_R \times p_0}{\sqrt{\frac{T_0 \times R}{M}}} \tag{B.1}$$

where

A is the critical flow orifice throat area;

c is the discharge coefficient calculated for the critical flow orifice;

C_R is the critical flow coefficient for the calibration gas under real conditions dependent on P, T;

p_0 is the absolute stagnation pressure dependent on p_{in}, T_{in} and q_m;

T_0 is the absolute stagnation temperature dependent on p_{in}, T_{in} and q_m;

R is the universal gas constant;

M is the molar mass of the calibration gas.

The calculation is performed by serial iterations, as the discharge coefficient is a function of the throat Reynolds number, which is itself a function of mass flow rate. The iteration process is completed once the difference between successive iteration values falls below 1×10^{-8} kg/s.

The critical flow function for the calibration gas is given in A.3 for different gases in the P and T ranges.

The discharge coefficient c calculated for the critical flow orifice is a function of three coefficients a, b and n.

$$c = a - bRe^{-n} \tag{B.2}$$

with the a, b, n coefficients respectively equal to 0,998 5, 3,412 and 0,5 (for toroïdal critical flow orifices described in ISO 9300)

$$Re = \frac{4\left(q_m\right)}{\pi \eta_0 d_N} \tag{B.3}$$

where η_0 is the dynamic viscosity at p_0 and T_0 (see A.2).