International Standard ISO 6145/6

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Gas analysis — Preparation of calibration gas mixtures — Dynamic volumetric methods — Part 6 : Sonic orifices

Analyse des gaz — Préparation des mélanges de gaz pour étalonnage — Méthodes volumétriques dynamiques — Partie 6: Orifices avec écoulement sonique

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ISO 6145/6-1986 (E)

Foreword

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Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 6145/6 was prepared by Technical Committee ISO/TC 158, *Analysis of gases.*

Users should note that all International Standards undergo revision from time to time and that any reference made herein to any other International Standard implies its latest edition, unless otherwise stated.

Gas analysis — Preparation of calibration gas mixtures — Dynamic volumetric methods — Part 6 : Sonic orifices

1 Scope and field of application

This International Standard constitutes part 6 of ISO 6145, dealing with the various dynamic volumetric techniques used for the preparation of calibration gas mixtures.

It describes the method of preparation, using orifices with sonic flow, of calibration gas mixtures with one or more components, with a volume ratio equal to or greater than 0,1 %, the repeatability of which on the concentration of each of the components is approximately 0,5 % in relative value.

2 References

ISO 6142, *Gas analysis — Preparation of calibration gas mixtures — Weighing methods.*

ISO 6145/1, *Gas analysis — Preparation of calibration gas mixtures — Dynamic volumetric methods — Part 1 : Methods of calibration*

3 Principle of the method

3.1 General

The method consists of adding, to a mixing chamber, constant mass flow rates of gas obtained by sonic flow of gas at a constant pressure through appropriate channels.

3.2 Operating principle of an orifice with sonic or critical flow

For a given upstream pressure p_1, the mass flow rate of a pressure-difference device (orifice plate or nozzle) increases when the downstream pressure p_2 decreases, to tend towards a limit value . If the ratio p_1/p_2 exceeds a value in the region of 2 (critical point), the flow rate remains constant; moreover, it is also necessary that the ratio d/D of the diameter of the pressure difference device d to the diameter of the upstream pipe D remains below 0,2 so that the variations in dynamic pressure can be disregarded.

3.3 Expression of sonic mass flow rate

The theoretical mass flow rate, q_m, of a gas expanding isotropically through a sonic orifice can be expressed in the form

$$q_m = A_c \cdot C_d \cdot \frac{p_1}{\sqrt{T_1}} \cdot \sqrt{\frac{M}{R} \cdot \gamma \left(\frac{2}{\gamma+1}\right)^{\frac{\gamma+1}{\gamma-1}}}$$

where

A_c is the section area of the neck of the orifice;

C_d is the contraction coefficient of the gas jet (also called discharge coefficient);

p_1 is the absolute pressure upstream;

T_1 is the temperature of the gas upstream;

M is the molar mass of the gas;

γ is the ratio of the mass thermal capacities c_p/c_V of the gas (c_p is the mass thermal capacity at constant pressure and c_V is the mass thermal capacity at constant volume);

R is the molar gas constant.

The term beneath the root sign is currently designated by C^*, hence the simplified expression

$$q_m = A_c \cdot C_d \cdot C^* \cdot \frac{p_1}{\sqrt{T_1}} \qquad \ldots (1)$$

The product $A_c \cdot C_d$ represents the area of the section of the sonic gas jet, the contraction coefficient C_d being generally between 0,6 (circular orifice) and 1 (shaped nozzle).

The mass flow rate for a given nozzle and gas depends solely on the pressure and upstream temperature, and is independent of the downstream pressure.

3.4 Area of validity

Pressure and temperature have a complicated influence on the flow rate of a sonic nozzle, as they act directly by p_1 and $1/\sqrt{T_1}$ and indirectly through the γ factor. The latter influence becomes more significant as the behaviour of the gas moves further from that of a perfect gas.

Examples of relative variations of C^* for a temperature deviation ΔT_1 of 10 K and a pressure deviation Δp_1 of 8 bar[1)] are given in the table.

Table — Relative variations of C^*

Gas	T_1 = 30 °C, Δp_1 = 8 bar	p_1 = 5 bar, ΔT_1 = 10 K
	$\dfrac{C^*\text{ (2 bar)} - C^*\text{ (10 bar)}}{C^*\text{ (2 bar)}}$ %	$\dfrac{C^*\text{ (5 bar – 30 °C)} - C^*\text{ (5 bar – 40 °C)}}{C^*\text{ (5 bar – 30 °C)}}$ %
He	−0,02	+1,6
H_2	−0,02	+1,6
O_2	−0,4	+1,6
CH_4	−0,5	+1,8
C_2H_6	−1,7	+1,9
CO_2	−1,3	+1,8

It thus appears that, for the required accuracy, C^* cannot be considered as constant when the upstream conditions vary appreciably.

Moreover, the contraction coefficient C_d depends basically on the geometry of the nozzle and, through the Reynolds number, on the nature of the gas.

This means that, in practice, calibration of the nozzle under conditions close to those of its use is necessary. Knowledge of the theoretical variations of C^*, which are themselves calculated from variations in γ, is subject to a certain inaccuracy. In addition, there is also a deviation due to the fact that the expansion is not completely isentropic, with the result that forecasts of C^* prove difficult.

3.5 Principle of calculation

The molar ratio of component A, X_A, is defined by

$$X_A = \frac{\dfrac{q_{mA}}{M_A}}{\dfrac{q_{mA}}{M_A} + \dfrac{q_{mB}}{M_B} + \dfrac{q_{mC}}{M_C} + \dots}$$

where

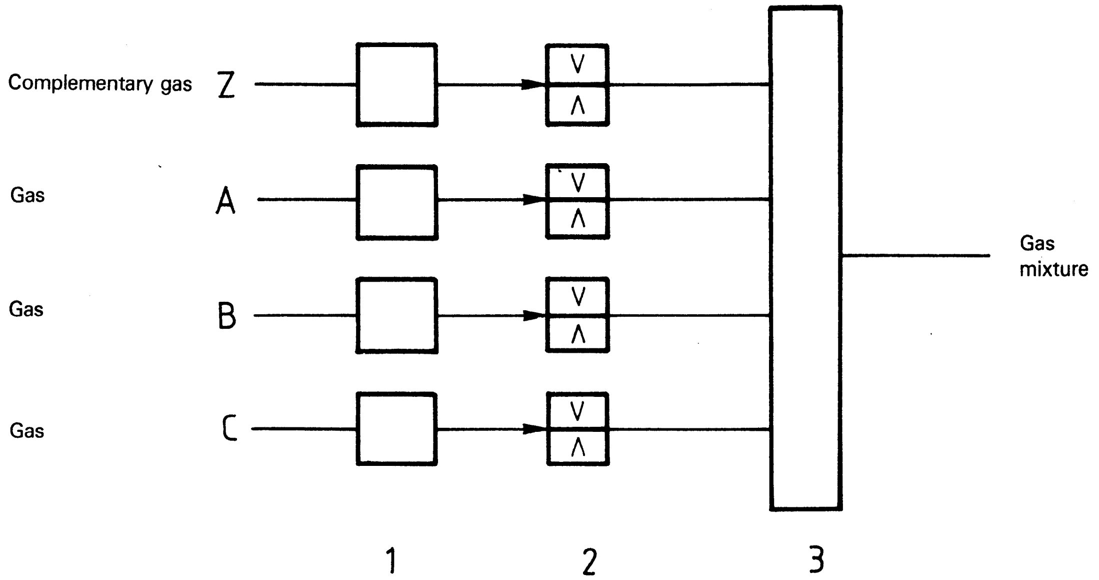
$q_{mA}, q_{mB}, q_{mC}, \dots$ are the mass flow rates of components A, B, C, ...;

$M_A, M_B, M_C, \dots$ are the respective molar masses.

1) 1 bar = 10^5 Pa

4 Practical examples

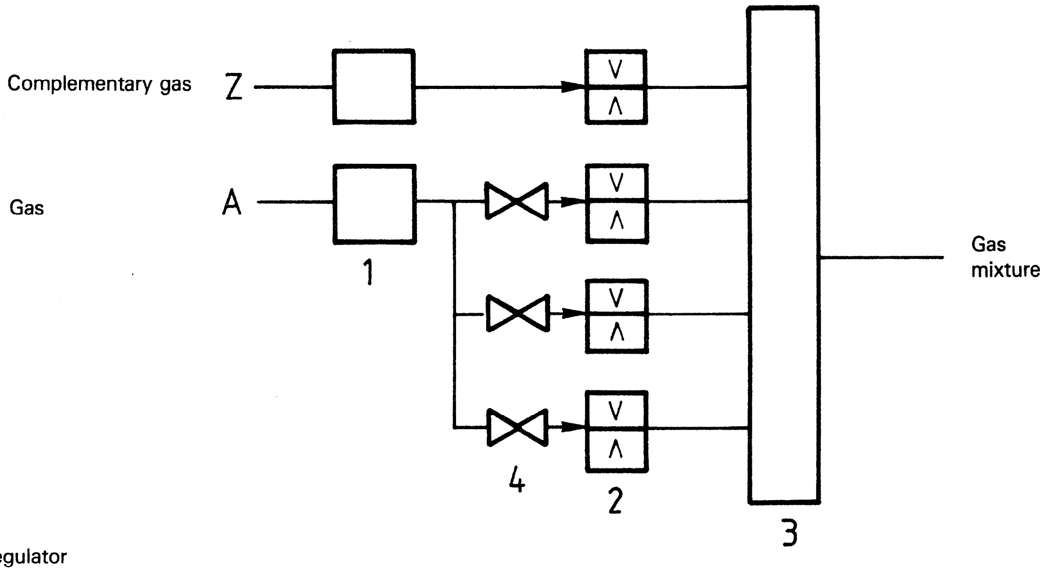
A gas mixer with sonic nozzles comes in the form of high-stability pressure regulator units and sonic nozzles discharging into a mixing chamber. A schematic example is shown in figure 1.



1 = Pressure regulator
2 = Sonic nozzle } temperature controlled
3 = Mixing chamber

Figure 1 — Gas mixer with sonic nozzles discharging into mixing chamber (schematic)

Another possibility consists of several sonic nozzles per component; the mixer thus gives a series of concentrations in a known ratio, according to the combination of sonic nozzles in service. A schematic example is shown in figure 2.



1 = Pressure regulator
2 = Sonic nozzle } temperature controlled
3 = Mixing chamber
4 = Check valve

Figure 2 — Gas mixer with several sonic nozzles per component (schematic)

5 Operating conditions

5.1 Pressures

The absolute upstream pressure p_1 of the sonic nozzles is between 3 and 6 bar. This pressure range enables a variation in the downstream back-pressures of the sonic nozzles of 250 mbar to be achieved, without affecting the value of the concentrations of the mixture.

Only the supply pressure p_1 of the sonic nozzles shall satisfy precise conditions in order to attain levels of repeatability for the concentration proportions stipulated in clause 1.

The stability of this pressure p_1 shall be greater than 5×10^{-4} in relative value.

5.2 Flow rates

In practice, the minimum flow rates are 5 cm^3/min at ambient pressure and temperature.

5.3 Filtration

Filtration of the components and the complementary gas is applied in relation to the section of the passage in the mixer components.

5.4 Temperatures

A simultaneous variation of the absolute temperatures of the components and of the complementary gas does not introduce any variation in the concentration of the mixture.

In the case of a variation in temperature of one component in relation to another component of the mixture, the concentration is modified and this modification can be calculated.

6 Experimental determination of concentrations and examination of sources of error

6.1 General

Any of the calibration methods described in clause 3 of ISO 6145/1 can be used.

The example of calibration given below involves the gravimetric method (sub-clause 3.2.3.2 of ISO 6145/1), the calculation of the effect of variation of temperature and pressure controllers.

6.2 Presentation of the method

$$q'_m = \frac{m}{t} \qquad \ldots (2)$$

The coefficient $A_c \cdot C_d \cdot C^*$ is obtained from equation (3):

$$A_c \cdot C_d \cdot C^* = \left(\frac{m}{t}\right) \cdot \frac{\sqrt{\bar{T}'_1}}{\bar{p}'_1} \qquad \ldots (3)$$

where

$\bar{T}'_1$ is the mean temperature upstream of the nozzle;

t is the time;

$\bar{p}'_1$ is the mean pressure upstream of the nozzle.

The sources of error of the method arise from the following:

a) weighing, refer to ISO 6142 (4.2.1) for the procedure and error calculation;

b) variations in pressure and temperature linked to the quality of the regulators used, and, where applicable, uncertainties in the measurement of these parameters;

c) gas losses arising from compression and decompression in the transfer lines.

By differentiating equation (3):

$$\frac{d(A_c \cdot C_d \cdot C^*)}{A_c \cdot C_d \cdot C^*} = \frac{dm}{m} - \frac{dt}{t} + \frac{1}{2} \cdot \frac{d\bar{T}'_1}{\bar{T}'_1} - \frac{d\bar{p}'_1}{\bar{p}'_1}$$

An evaluation is obtained of the uncertainty on the determination of $A_c \cdot C_d \cdot C^*$ by

$$\frac{\Delta(A_c \cdot C_d \cdot C^*)}{A_c \cdot C_d \cdot C^*} < \frac{\Delta m}{m} + \frac{\Delta t}{t} + \frac{1}{2} \cdot \frac{\Delta\bar{T}'_1}{\bar{T}'_1} + \frac{\Delta\bar{p}'_1}{\bar{p}'_1} \qquad \ldots (4)$$

When the nozzle which has been calibrated in this way is used, with the service pressure and temperature p_1 and T_1 being as close as possible to the values used during calibration, the mass flow rate is given by equation (1):

$$q_m = A_c \cdot C_d \cdot C^* \cdot \frac{p_1}{\sqrt{T_1}}$$

If the values of p_1 and T_1 are subject to measurable fluctuations, mean values should then be taken and q_m becomes a mean flow rate.

By differentiating equation (1):

$$\frac{dq_m}{q_m} = \frac{d(A_c \cdot C_d \cdot C^*)}{A_c \cdot C_d \cdot C^*} + \frac{dp_1}{p_1} - \frac{1}{2} \cdot \frac{dT_1}{T_1}$$

The uncertainty in the determination of q_m is evaluated using the equation

$$\frac{\Delta q_m}{q_m} < \frac{\Delta(A_c \cdot C_d \cdot C^*)}{A_c \cdot C_d \cdot C^*} + \frac{\Delta p_1}{p_1} + \frac{1}{2} \cdot \frac{\Delta T_1}{T_1} \qquad \ldots (5)$$

$$< \Delta \mathrm{Cal} + \Delta \mathrm{f}$$

The calibration error, ΔCal, is calculated by

$$\Delta \mathrm{Cal} = \frac{\Delta(A_c \cdot C_d \cdot C^*)}{A_c \cdot C_d \cdot C^*}$$

The precision error, Δf, depending upon the random variations of the parameters pressure and temperature both during one operation and from one operation to another, is given by

$$\Delta f = \frac{\Delta p_1}{p_1} + \frac{1}{2} \cdot \frac{\Delta T_1}{T_1}$$

6.3 Numerical example — Determination of the molar ratio of a binary mixture CO_2 and N_2

In this example of a calculation, it will be assumed that the pressures and temperatures were measured with the same instruments during calibration and use, and that fluctuations in these parameters were negligible during the period of time t.

6.3.1 Calibration of the "nitrogen" nozzle

$$m = 0{,}264\,97 \pm 10^{-5}\ \text{kg} \qquad \frac{\Delta m}{m} = 3{,}8 \times 10^{-5}$$

$$\bar{p}'_1 = 8{,}048\,3 \times 10^5 \pm 250\ \text{Pa} \qquad \frac{\Delta \bar{p}'_1}{\bar{p}'_1} = 3{,}1 \times 10^{-4}$$

$$\bar{T}'_1 = 309{,}3 \pm 0{,}1\ \text{K} \qquad \frac{\Delta \bar{T}'_1}{\bar{T}'_1} = 3{,}2 \times 10^{-4}$$

$$t = 252{,}2 \pm 0{,}1\ \text{s} \qquad \frac{\Delta t}{t} = 4{,}0 \times 10^{-4}$$

$$A_c \cdot C_d \cdot C^* = \left(\frac{m}{t}\right) \cdot \frac{\sqrt{\bar{T}'_1}}{\bar{p}'_1}$$

$$A_c \cdot C_d \cdot C^* = \frac{0{,}264\,97}{252{,}2} \times \frac{\sqrt{309{,}3}}{8{,}048\,3 \times 10^5}$$

$$= 2{,}295\,81 \times 10^{-8}$$

$$\frac{\Delta(A_c \cdot C_d \cdot C^*)}{A_c \cdot C_d \cdot C^*} < \frac{\Delta m}{m} + \frac{\Delta t}{t} + \frac{1}{2} \cdot \frac{\Delta \bar{T}'_1}{\bar{T}'_1} + \frac{\Delta \bar{p}'_1}{\bar{p}'_1}$$

$$< 3{,}8 \times 10^{-5} + 4 \times 10^{-4} +$$

$$+ \frac{3{,}2}{2} \times 10^{-4} + 3{,}1 \times 10^{-4}$$

Therefore, the calibration error estimated for q_{N_2} is:

$$\Delta Cal_{N_2} < 9{,}1 \times 10^{-4}$$

6.3.2 Calculation of the mass flow rate of nitrogen

$$p_1 = 8{,}048\,5 \times 10^5 \pm 250\ \text{Pa} \qquad \frac{\Delta p_1}{p_1} = 3{,}1 \times 10^{-4}$$

$$T_1 = 309{,}1 \pm 0{,}1\ \text{K} \qquad \frac{\Delta T_1}{T_1} = 3{,}2 \times 10^{-4}$$

The precision error is estimated by

$$\Delta f_{N_2} < (3{,}1 + 1{,}6) \times 10^{-4}$$

$$< 4{,}7 \times 10^{-4}$$

$$q_{N_2} = A_c \cdot C_d \cdot C^* \cdot \frac{p_1}{\sqrt{T_1}}$$

$$= 2{,}295\,82 \times 10^{-8} \times \frac{8{,}048\,5 \times 10^5}{\sqrt{309{,}1}}$$

$$= 1{,}051\,0 \times 10^{-3}\ \text{kg/s}$$

$$\frac{\Delta q_{N_2}}{q_{N_2}} < \Delta Cal_{N_2} + \Delta f_{N_2}$$

$$< 9{,}1 \times 10^{-4} + 4{,}7 \times 10^{-4}$$

$$< 1{,}4 \times 10^{-3}$$

Therefore:

$$\boxed{q_{N_2} = 1{,}051 \times 10^{-3} \pm 1{,}5 \times 10^{-6}\ \text{kg/s}}$$

6.3.3 Calibration of the "carbon dioxide" nozzle

$$m = 0{,}296\,18 \pm 10^{-5}\ \text{kg} \qquad \frac{\Delta m}{m} = 3{,}4 \times 10^{-5}$$

$$\bar{p}'_1 = 5{,}293\,7 \times 10^5 \pm 160\ \text{Pa} \qquad \frac{\Delta \bar{p}'_1}{\bar{p}'_1} = 3{,}0 \times 10^{-4}$$

$$\bar{T}'_1 = 307{,}8 \pm 0{,}1\ \text{K} \qquad \frac{\Delta \bar{T}'_1}{\bar{T}'_1} = 3{,}2 \times 10^{-4}$$

$$t = 1\,607{,}9 \pm 0{,}1\ \text{s} \qquad \frac{\Delta t}{t} = 6{,}2 \times 10^{-5}$$

$$A_c \cdot C_d \cdot C^* = \left(\frac{m}{t}\right) \cdot \frac{\sqrt{\bar{T}'_1}}{\bar{p}'_1}$$

$$= 6{,}104\,80 \times 10^{-9}$$

$$\frac{\Delta(A_c \cdot C_d \cdot C^*)}{A_c \cdot C_d \cdot C^*} < \frac{\Delta m}{m} + \frac{\Delta t}{t} + \frac{1}{2} \cdot \frac{\Delta \bar{T}'_1}{\bar{T}'_1} + \frac{\Delta \bar{p}'_1}{\bar{p}'_1}$$

Which means a calibration error for CO_2 of

$$\Delta Cal_{CO_2} < 5{,}6 \times 10^{-4}$$

$$\boxed{A_c \cdot C_d \cdot C^* = 6{,}104\,80 \times 10^{-9} \pm 3{,}4 \times 10^{-12}}$$

6.3.4 Calculation of mass flow rate of carbon dioxide

$$p_1 = 5{,}293\,5 \times 10^5 \pm 160 \text{ Pa} \qquad \frac{\Delta p_1}{p_1} = 3{,}0 \times 10^{-4}$$

$$T_1 = 307{,}9 \pm 0{,}1 \text{ K} \qquad \frac{\Delta T_1}{T_1} = 3{,}2 \times 10^{-4}$$

The precision error is estimated by

$$\Delta f_{CO_2} < 3 \times 10^{-4} + 1{,}6 \times 10^{-4}$$

$$< 4{,}6 \times 10^{-4}$$

$$q_{CO_2} = A_c \cdot C_d \cdot C^* \cdot \frac{p_1}{\sqrt{T_1}}$$

$$= 1{,}841\,7 \times 10^{-4} \text{ kg/s}$$

$$\frac{\Delta q_{CO_2}}{q_{CO_2}} < \Delta Cal_{CO_2} + \Delta f_{CO_2}$$

$$< 5{,}6 \times 10^{-4} + 4{,}6 \times 10^{-4}$$

$$< 10{,}2 \times 10^{-4}$$

$$< 1{,}0 \times 10^{-3}$$

$$\boxed{q_{CO_2} = 1{,}841\,7 \times 10^{-4} \pm 1{,}8 \times 10^{-7} \text{ kg/s}}$$

6.3.5 Calculation of the molar ratio of carbon dioxide in the nitrogen

$$C_{CO_2} = \frac{\dfrac{q_{CO_2}}{M_{CO_2}}}{\dfrac{q_{CO_2}}{M_{CO_2}} + \dfrac{q_{N_2}}{M_{N_2}}}$$

$$= \frac{q_{MCO_2}}{q_{MCO_2} + q_{MN_2}}$$

$$= \frac{q_{MCO_2}}{q_M}$$

where

M_{CO_2} and M_{N_2} are the molar masses of carbon dioxide and nitrogen;

q_{MCO_2} and q_{MN_2} are the molar flow rates of CO_2 and N_2;

q_M is the total molar mass of the mixture produced.

Disregarding the uncertainties on the molar masses, the relative uncertainty on the molar ratio of CO_2 is evaluated as follows:

$$\frac{\Delta C_{CO_2}}{C_{CO_2}} < \left(\frac{\Delta q_{MCO_2}}{q_{MCO_2}}\right)\left(1 - \frac{q_{MCO_2}}{q_M}\right) + \left(\frac{\Delta q_{MN_2}}{q_{MN_2}}\right)\left(\frac{q_{MN_2}}{q_M}\right)$$

$$< \left(\frac{\Delta q_{CO_2}}{q_{CO_2}}\right)\left(1 - C_{CO_2}\right) + \left(\frac{\Delta q_{N_2}}{q_{N_2}}\right) \cdot C_{N_2}$$

$$< \left(\frac{\Delta q_{CO_2}}{q_{CO_2}} + \frac{\Delta q_{N_2}}{q_{N_2}}\right) \cdot C_{N_2}$$

$$C_{CO_2} = 100{,}35 \text{ mmol/mol}$$

$$\frac{\Delta C_{CO_2}}{C_{CO_2}} < (1 + 1{,}4) \times 10^{-3} \times 0{,}9$$

$$< 2{,}2 \times 10^{-3}$$

or, when isolating the components coming from the calibration and from the precision on the two flow rates,

$$\frac{\Delta C_{CO_2}}{C_{CO_2}} < \left(\Delta Cal_{CO_2} + \Delta Cal_{N_2}\right) \cdot C_{N_2} + \left(\Delta f_{CO_2} + \Delta f_{N_2}\right) \cdot C_{N_2}$$

$$< \Delta Cal_{C_{CO_2}} + \Delta f_{C_{CO_2}}$$

where

$\Delta Cal_{C_{CO_2}}$ is from the calibration errors on the two flow rates;

$\Delta f_{C_{CO_2}}$ is from the precision errors on the two flow rates.

$$\Delta Cal_{C_{CO_2}} < (5{,}6 + 9{,}1) \times 10^{-4} \times 0{,}9$$

$$< 13{,}23 \times 10^{-4}$$

$$< 1{,}4 \times 10^{-3}$$

$$\Delta f_{C_{CO_2}} < (4{,}6 + 4{,}7) \times 10^{-4} \times 0{,}9$$

$$< 8{,}4 \times 10^{-4}$$

$$< 0{,}9 \times 10^{-3}$$

$$\boxed{C_{CO_2} = 100{,}35 \pm 0{,}23 \text{ mmol/mol}}$$