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ISO 6145-5

Second edition
2009-11-01

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

Part 5:
Capillary calibration devices

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

Partie 5: Dispositifs d'étalonnage par capillaires

Reference number
ISO 6145-5:2009(E)

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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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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.

ISO 6145-5 was prepared by Technical Committee ISO/TC 158, *Analysis of gases*.

This second edition cancels and replaces the first edition (ISO 6145-5:2001), which has been technically revised. Some subclauses (such as Procedure and Calculations) have been detached from other closely related clauses and readability has been improved by bringing these subclauses closer together. The principle and verification parts have been clarified and separated, the uncertainty section has been checked and slightly updated and Annex A has been revised. An informative derivation of the relative combined standard uncertainty calculation has been added as Annex B.

ISO 6145 consists of the following parts, under the general title *Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods*:

- *Part 1: Methods of calibration*
- *Part 2: Volumetric pumps*
- *Part 4: Continuous syringe injection method*
- *Part 5: Capillary calibration devices*
- *Part 6: Critical orifices*
- *Part 7: Thermal mass-flow controllers*
- *Part 8: Diffusion method*
- *Part 9: Saturation method*
- *Part 10: Permeation method*
- *Part 11: Electrochemical generation*

ISO 6145-3, entitled *Periodic injections into a flowing gas stream*, has been withdrawn.

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

Partie 5: Capillary calibration devices

1 Scope

This part of ISO 6145 is one of a series of International Standards dealing with the various dynamic volumetric techniques used for the preparation of calibration gas mixtures. This part specifies a method for the continuous production of calibration gas mixtures from pure gases or gas mixtures using capillary calibration devices in single or multiple combinations (gas dividers).

Single capillary systems can be used to provide gas mixtures where the minor component is in the range of volume fractions from 10^{-8} to 0,5.

The relative expanded uncertainty of this technique is less than ±2 % ($k = 2$) relative. 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 gases or gas mixtures into controlled proportions by volume. These devices are capable of dilutions in the range of volume fractions from 0,000 5 to 0,9 of the primary gas concentration with a relative repeatability of better than 0,5 %.

Traceability of the gas mixtures produced by a gas divider is achieved by comparison of a mixture with gas mixtures related to national or international gas standards. An example is given in Annex A.

2 Normative references

The following referenced documents are indispensable for the application 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 6145-1, *Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods — Part 1: Methods of calibration*

3 Principle

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 flow may also be derived from another capillary tube.

The appropriate capillaries are selected to give the required flows of gases into the mixing manifold. If an appropriate capillary is selected, the required flow is obtained by adjusting the pressure drop across the capillary.

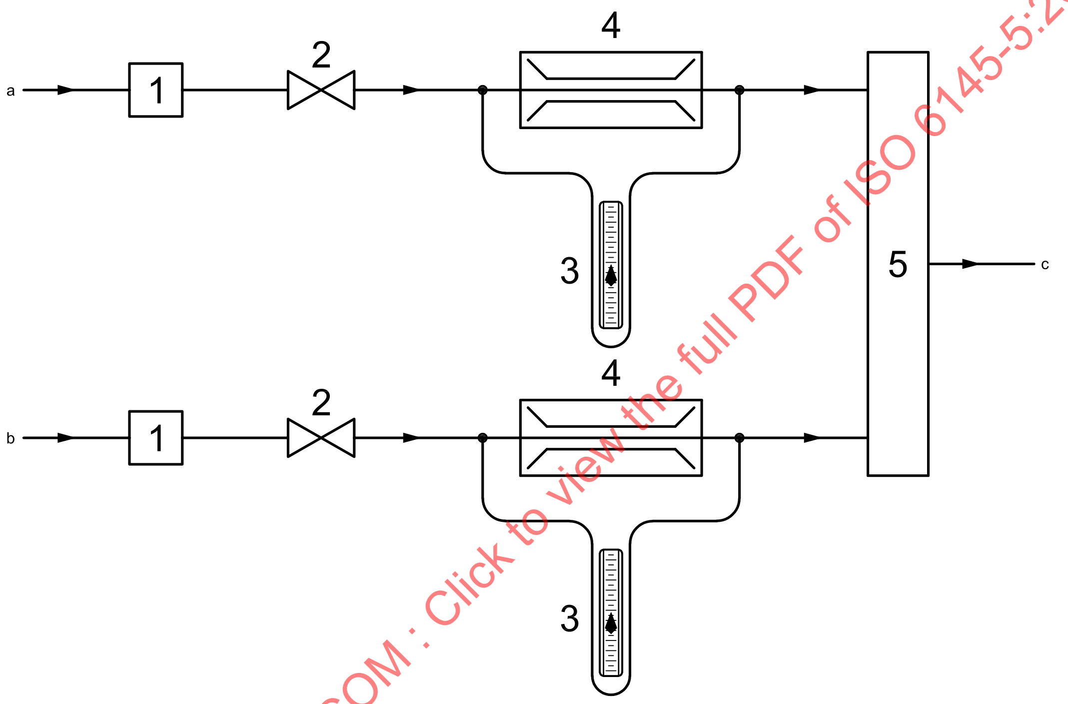
Commercially available units consisting of several capillary tubes are called gas dividers. Such gas dividers containing combinations of capillaries may be used to dilute pure gases or further dilute calibration gas mixtures with complementary gas, thus generating further calibration standards.

4 Apparatus

4.1 Two-capillary blending system

4.1.1 Set-up

Figure 1 shows a possible set-up of a gas mixing system using two capillary tubes, i.e. a two-capillary system.



Key

1 two-stage pressure regulator
2 fine adjustment valve
3 pressure differential manometer
4 capillary
5 mixing manifold

[a] Gas A.
[b] Complementary gas.
[c] Gas mixture.

Figure 1 — Two-capillary blending system

4.1.2 Apparatus

4.1.2.1 **Capillaries**, each supplied with gas from a cylinder fitted with a two-stage pressure regulator, gas filter and a fine adjustment valve.

4.1.2.2 **Two-stage pressure regulator**, equipped with fine adjustment valves.

4.1.2.3 **Differential manometer**, capable of measuring the pressure drop across the capillary.

4.1.2.4 Gas manifold, fed by the flow from each capillary where mixing occurs to produce the calibration gas mixture at the outlet.

4.1.2.5 Gas filters, to filter the component gases, so as to prevent blockage of the capillaries.

4.1.2.6 Thermostatic controller (optional), to maintain the temperature of the capillaries constant. Variations in temperature can cause a significant change in the viscosity of the component gas passing through the capillary. For high accuracy, it is necessary to provide thermostatic control of the capillaries. With thermostatic control of a water-jacket to ±1 °C, the volume fraction of the final mixture will not vary by more than ±2 %.

4.1.3 Procedure

4.1.3.1 Operation

Open the gas supply cylinders and adjust the two-stage pressure regulators to approximately 200 kPa gauge outlet pressure. Open the fine adjustment valves to give the pressure drop across the capillaries required for the desired flows. The required pressure drop can be estimated using a modification of Equation (1), given in 4.1.3.2.

The accuracy of the mixture produced at any moment is principally affected by the constancy of the flow rates of each component. These can be estimated by observations of the variation in the pressure differential manometers applied across each capillary.

4.1.3.2 Determination of the capillary flow rate

The volume flow rate q_A of a gas A emerging from a capillary is approximately expressed as:

$$q_A = \frac{\pi r^4 (p_1 - p_2)}{8\eta L} \tag{1}$$

where

r is the radius of the capillary tube;

p_1 is the inlet pressure to the capillary;

p_2 is the outlet pressure of the capillary;

η is the dynamic viscosity of the gas at the temperature of usage;

L is the length of the capillary tube.

For a given capillary, Equation (1) can be simplified by the use of an individual calibration factor. For its determination, the gas flow from one capillary is passed into a flowmeter with known accuracy. Additionally, readings are taken of the differential pressures required to provide a range of flows. A calibration curve is constructed by plotting pressure differences $(p_1 - p_2)$ against flow rates. The gradient of this line will be the individual calibration factor K for the specified gas.

$$\begin{aligned} q_A &= K_A (p_1 - p_2)_A \\ q_A &= K_A \Delta p_A \end{aligned} \tag{2}$$

where

K_A is an individual factor for gas A;

Δp_A is equal to $(p_1 - p_2)$ across the capillary.

In practice, the determination of the flow by the use of a calibration factor is advisable because several influences, for example, viscosity of the gases and temperature changes, can be recognized.

4.2 Multiple capillary devices using gas dividers

4.2.1 Set-up of a gas divider

For gas dividers, multiple capillary tubes are combined. Such combinations shall be realized according to the system in Figure 1 or according to the systems in Figures 2 and 3. While, in the first set-up, the pressure difference is controlled individually for each capillary, the pressure differences in the latter realizations are equal for all capillaries.

Gas dividers in the context of this part of ISO 6145 are systems with an equal pressure difference for all included capillary tubes. Generally, such gas dividers can be divided into two groups:

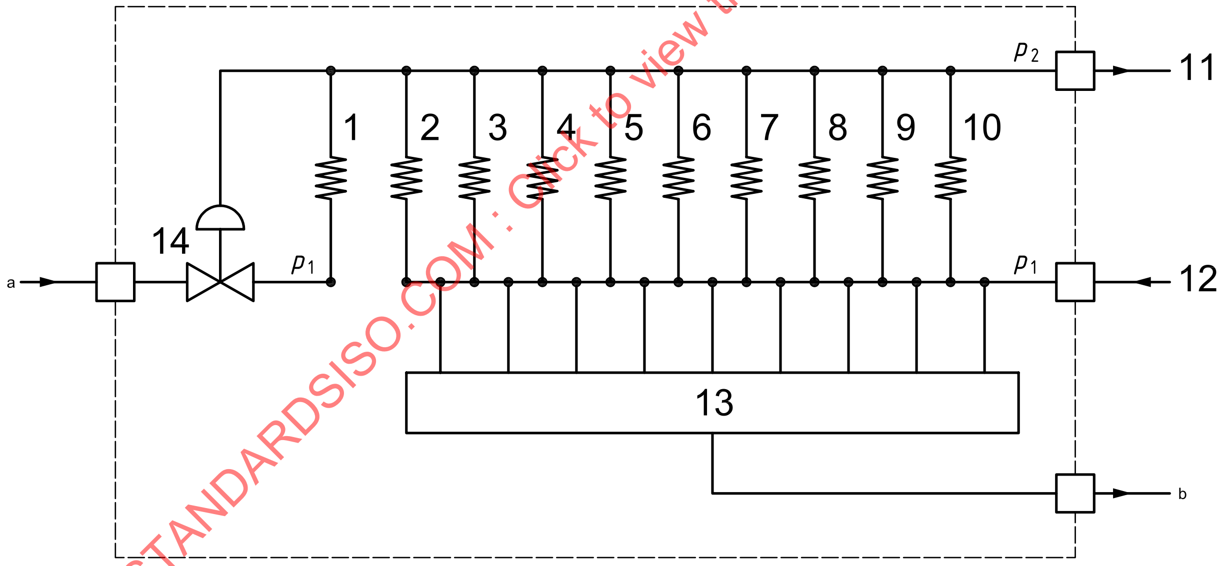
a) gas dividers with a combination of non-identical capillaries (4.2.2);

b) gas dividers with a combination of identical capillaries (4.2.3).

4.2.2 Gas dividers with a combination of non-identical capillaries

The gas dividers with non-identical capillaries are combinations of more than two capillaries of different lengths and diameters and thus provide different flow rates (see Figure 2). Usually, one capillary is used for the dilution gas (capillary tube 1 in Figure 2) while the component gas is flowing through one (capillary tube 2 in Figure 2) or a combination of the other capillaries.

During operation, the gas pressures of the component and dilution gas shall be adjusted by external regulators.



Key

1	dilution-gas capillaries
2-10	component-gas capillaries
11	generated gas
12	component gas, volume fraction, φ_0
13	division-switching valve
14	pressure regulator

[a] Dilution gas.

[b] Exhaust gas.

Figure 2 — Principle of operation

To increase the dilution-factor range, an additional capillary may be installed and switched, when necessary, in parallel with the first one. By selecting the capillaries through which the component gas flows, at least 9 levels of dilution can be obtained when those capillaries are used individually. The use of their combinations can provide dilution-factor values of 10 to 2 000. These “component-gas capillaries” may be equal or different in design.

The individual capillary flow rates are determined according to 4.1.3.2. To determine or to verify the respective dilution factor, it is sufficient to perform a comparison for one mixture obtained by using each capillary.

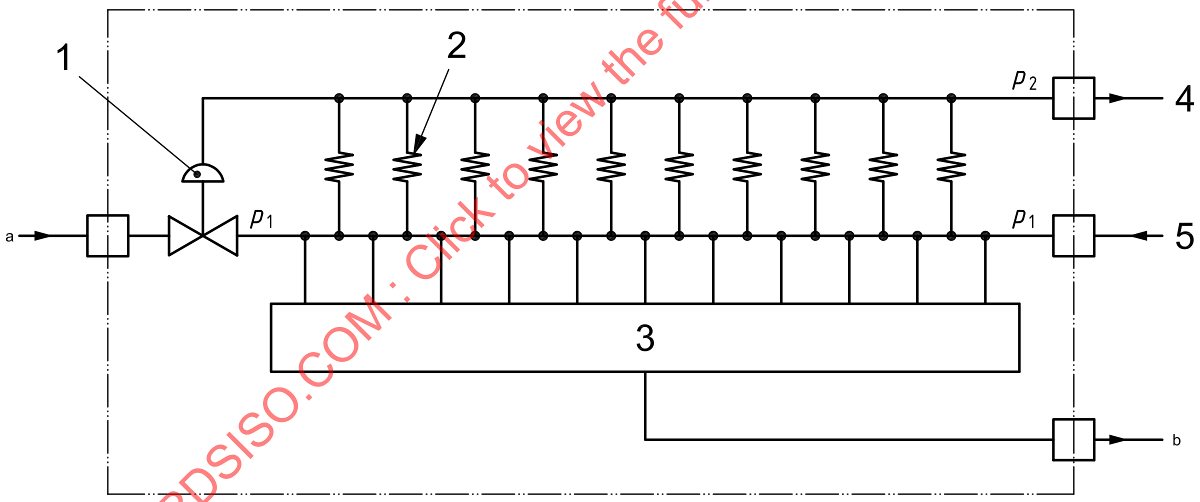
4.2.3 Gas dividers with a combination of identical capillaries

Such a gas divider contains a combination of capillary tubes of exactly the same lengths and diameters. Provided that there is not a large difference in viscosity of the gases employed and the pressure across the capillaries is constant, each tube will possess the same resistance to flow.

Most available gas dividers incorporate a solenoid switching system which enables the selection of different capillaries and different volume fractions of the gas divided.

The flow rates of the component gas and the dilution gas shall be controlled by the capillary tubes and blended to generate the gas which is divided. The volume fraction of the generated gas is determined from the flow rates of the component gas and dilution gas.

In the example illustrated in Figure 3, the gas divider has 10 identical capillaries.



Key

1 pressure regulator

2 capillary

3 division-switching valve

4 generated gas

5 component gas, volume fraction, φ_0

[a] Dilution gas.

[b] Exhaust gas.

Figure 3 — Gas divider with identical capillaries

4.2.4 Operation of a gas divider with identical capillaries

Either the component gas or the dilution gas always flows through the m capillaries (10 capillaries in the examples in Figures 2 and 3). By selecting the total number of capillaries through which the component and dilution gases flow, $(m + 1)$ stages of dilution, varying from 0 to m, can be obtained in the system. As the flow characteristics of the m capillaries are identical, external changes affect them all equally. Consequently the selection of different capillaries controlling the component- and dilution-gas flows to give a required volume fraction are unaffected by changes in temperature and atmospheric pressure changes. During operation, the gas pressures of the component and dilution gas shall be adjusted by external regulators.

4.2.5 Determination of the flow rates

For gas dividers with non-identical capillaries, each capillary shall be calibrated using the method given in 4.1.3.2.

For gas dividers with identical capillaries, the flow through each capillary is determined as the quotient of the overall flow rate and the number of all capillaries of the gas divider.

$$q = \frac{q_{\mathrm{all}}}{m} \tag{3}$$

where

q is the flow rate through each capillary;

m is the number of all capillaries of the gas divider;

q_{all} is the overall flow rate through all capillaries of the gas divider.

The overall flow rate through all capillaries, q_{all}, is determined by:

$$q_{\mathrm{all}} = K \cdot (p_1 - p_2) = K \cdot \Delta p \tag{4}$$

where K is a temperature- and component-dependent calibration factor determined following the procedures described in 4.1.3.2. This implies the individual calibration factors of the capillary tubes and the deviations of the individual capillary from the mean.

The volume flow rate q_{A} of a gas A emerging from the gas divider is approximately expressed as:

$$q_A = n \cdot q \tag{5}$$

where

q_{A} is the gas flow rate of the component gas A;

n is the number of capillaries through which the component gas A flows.

The volume flow rate q_{B} of the complementary gas B is approximately expressed as:

$$q_{\mathrm{B}} = (m - n) \cdot q \tag{6}$$

5 Expression of results

NOTE All uncertainty expressions presented are in line with the ISO/IEC Guide 98-3 (GUM)[1].

5.1 Volume fraction

The volume fraction of component A, φ_{A}, is defined by the equation:

$$\varphi_{\mathrm{A}} = \frac{q_{\mathrm{A}}}{\sum q} \tag{7}$$

where

φ_{A} is the volume fraction of the component gas in the resulting gas mixture;

q are the flow rates of component and complementary gases.

If pre-mixtures were used, this results in:

$$\varphi_{\mathrm{A}} = \frac{q_{\mathrm{A}} \cdot \varphi_{\mathrm{A0}}}{\sum q} \tag{8}$$

where φ_{A0} is the volume fraction of gas A in the component gas before blending.

Equations (7) and (8) may be simplified for the use of a gas divider with identical capillaries, provided that there are only small differences in the viscosity of the gases employed. Then the volume fraction, φ_{A}, is calculated using the following equation:

$$\varphi_{\mathrm{A}} = \frac{n \cdot q}{m \cdot q} = \frac{n}{m}\text{, or} \tag{9}$$

$$\varphi_{\mathrm{A}} = \frac{n}{m} \varphi_{\mathrm{A0}}$$

if a pre-mixture is used where

n is the number of capillaries through which the component gas (gas A) flows;

m is the number of all capillaries ($m = 10$ in Figure 3).

5.2 Sources of uncertainties

5.2.1 Temperature

To eliminate temperature effects, most gas dividers have all the gas flow capillaries mounted on one metal block which acts as a heat sink for the capillaries. Any change in temperature will apply to both complementary and dilution gases and is compensated. Capillaries on separate blocks, whose temperatures vary, shall be thermostatically controlled.

5.2.2 Viscosity

Viscosity effects can have an appreciable effect on the flow rates of gases through the capillaries. This effect varies with the type of gas used and its volume fraction. Viscosity data can be used as a guide for volume fractions over 1 %.

Some gas dividers, which are computer controlled to calibrate instruments, have a built-in correction for viscosity effects on the calibration curves produced from these analysers.

5.2.3 Pressure

Atmospheric pressure variations affect all gas flows equally. For gas dividers, where all capillary tubes are very similar, pressure influences are cancelled out if the pressure differential does not substantially fall (to < 70 %), otherwise the accuracy of the gas divider is affected.

5.2.4 Geometry of the capillary tubes

As can be seen in Equation (1), the geometry of the tubes has an important impact on the quantity of the flow. The unknown effects of the geometry (e.g. inner surface, non-circularity) are recognized if the gas flow through the capillary tube is determined via the use of a calibration factor (see 4.1.3.2).

5.3 Verification of the blending system/gas divider

To achieve the stated uncertainty of this technique, it is necessary to carry out a calibration of the gas blending system/gas divider. Calibration shall be carried out in accordance with ISO 6145-1, by measurement of flow rates through capillaries or by comparison of the final mixtures with the standards in accordance with ISO 6143. The comparison method is necessary when traceability to national or international standards is needed.

For the calibration of a gas divider with identical capillaries, at least two points on the range of volume fractions ($<$ 25 % and $>$ 75 % of the range) have to be calibrated with gas standards traceable to national or international standards.

For gas dividers with non-identical capillaries, comparison of the mixtures produced with each individual component-gas capillary is carried out. To determine (verify) the respective dilution factor, it is enough to perform comparison for one mixture obtained by using each capillary. As the dilution factors of the divider can differ by orders of magnitude, either different gas analysers or pre-mixtures shall be used in comparison.

The uncertainty of this comparison has to be included in the uncertainty budget of the mixture preparation.

An example of this technique is given in Annex A.

5.4 Determination of uncertainties

As can be seen in Equations (1) and (2), changes in the pressure drop will immediately influence the flow through the capillaries. Variations in pressure difference $\Delta p = p_1 - p_2$ are affected by changes in atmospheric pressure acting on the outlet of the mixing manifold.

The relative combined standard uncertainty, $u_\text{c}(q_\text{A})/q_\text{A}$, of q_A is:

$$\frac{u(q_\text{A})}{q_\text{A}} = \sqrt{\left[\frac{u(K_\text{A})}{K_\text{A}}\right]^2 + \left[\frac{u(\Delta p)}{\Delta p}\right]^2} \tag{10}$$

where

$u(K_\text{A})$ is the standard uncertainty of K according to the calibration of the capillary (see its derivation in Annex B);

$u(\Delta p)$ is the standard uncertainty of the pressure differential due to its variability.

Equation 10 is also valid for the use of a gas divider. If a gas divider is used, the uncertainty of the calibration factor K should not only include possible temperature and viscosity effects, but also the geometrical differences of the combined capillary tubes.

For the example of a binary mixture, the uncertainty of the composition is expressed in the form of the relative uncertainty of the volume fraction of component A, as in Equation (7):

$$\frac{U\left(\varphi_{\mathrm{A}}\right)}{\varphi_{\mathrm{A}}} = \frac{2q_{\mathrm{B}}}{q_{\mathrm{A}} + q_{\mathrm{B}}}\sqrt{\left[\frac{u\left(q_{\mathrm{A}}\right)}{q_{\mathrm{A}}}\right]^2 + \left[\frac{u\left(q_{\mathrm{B}}\right)}{q_{\mathrm{B}}}\right]^2} \tag{11}$$

The reported expanded uncertainty of measurement $U\left(\varphi_{\mathrm{A}}\right)$, to be used on the left side of Equation (11), is stated as the standard uncertainty of measurement multiplied by the coverage factor $k = 2$ calculated from a normal distribution to give a coverage probability of approximately 95 %.

Annex A
(informative)

Numerical example

A.1 Calibration of a gas analyser using a gas divider

In this example, a gas standard containing 4,571 % carbon dioxide in nitrogen is diluted with nitrogen to provide gas mixtures in the range 0 % to 4,571 %. The gas divider is computer controlled and feeds an infrared gas analyser. The regression on the results is calculated using a computer programme and is presented in Table A.1.

All gases used for calibration purposes should be analysed before use, to check for the presence of any component gas that may invalidate the concentration of the minor component.

Table A.1 — Analytical data provided by an infrared analyser calibrated with a gas divider

Calibration gas %	Gas concentration	Direct reading analyser	Current generated curve value[a]	New curve value[b]	Percent of point[c], current curve	Percent of point[d], new curve	Percent difference on FSR[e], current curve	Percent difference on FSR, new curve
100	4,571	93,79	4,571	4,569	0,00	−0,04	0,00	−0,03
90	4,113	87,09	4,138	4,135	0,61	0,53	0,50	0,44
80	3,655	79,17	3,659	3,655	0,11	0,00	0,09	0,00
70	3,197	71,07	3,202	3,197	0,16	0,00	0,09	0,01
60	2,740	62,48	2,744	2,739	0,15	−0,03	0,09	0,01
50	2,283	53,47	2,289	2,285	0,26	0,09	0,14	0,04
40	1,826	44,05	1,836	1,833	0,55	0,38	0,22	0,14
30	1,369	33,99	1,375	1,373	0,44	0,29	0,13	0,08
20	0,912	23,41	0,914	0,913	0,22	0,11	0,04	0,01
10	0,457	12,17	0,454	0,454	−0,66	−0,66	−0,06	−0,07
0	0,000	0,00	0,000	0,000	0,00	0,00	0,00	0,00

NOTE The values obtained for the percent of point difference in columns 6 and 7 show an accuracy of better than 1,0 %.

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

[b] 14 July 1994, date of the new calibration.

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

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

[e] FSR: Full scale range.

Table A.1 shows the information produced by feeding the gas mixtures generated from the gas divider into an infrared gas analyser. The measurement conditions are

- System: traceable gas mixtures,
- Analyser: AIA-120[1],
- Component: CO_2,
- Source: gas divider,
- Full scale range: 5,0 %,
- Status: not saved, and
- Calibration gas: 45 000/4/100 794.

A.2 Calibration of a gas divider (assessment of traceability procedure)

Calibration is carried out by feeding traceable standards into the gas analyser and calculating the results using the generated curve obtained by using the gas divider. Primary reference-gas mixtures are fed into the analyser to spike the generated curve. In general, only two spike gases are required for the calibration of the dividers with identical capillaries, one at < 25 % and the other at > 75 % of range, to confirm individual points on the curve.

The results of the calibration process are given in Table A.2. The variations between current and new coefficients are given in Table A.3 and the spike gases employed are defined in Table A.4. The values obtained for the spike gas mixtures (1-5) are shown in Table A.2.

Table A.2 — Comparison of curve values with spike gas mixtures

Spike gas	Gas concentration	Direct reading analyser	Current generated curve value[a]	New curve value[b]	Percent of point[c], current curve	Percent of point[d], new curve	Percent difference on FSR[e], current curve	Percent difference on FSR, new curve
1	4,092	86,20	4,082	4,079	–0,24	–0,32	–0,19	–0,26
2	2,537	58,40	2,535	2,530	–0,07	–0,28	–0,03	–0,13
3	2,520	58,10	2,520	2,515	0,00	–0,20	0,00	–0,09
4	1,993	47,40	1,995	1,991	0,10	–0,10	0,04	–0,04
5	1,083	27,40	1,085	1,083	0,18	0,00	0,04	0,00

NOTE All results are better than 0,32 %. This agreement between the general curve results and the traceable spike gases confirms the generated curve as a valid calibration curve with a traceable accuracy of better than +0,5 %.

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

[b] 14 July 1994, date of the new calibration.

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

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

[e] FSR: full scale range.

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[1] AIA-120 is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.

In columns 4 and 5 of Table A.2, the values are obtained on the spike gas mixtures based on the old calibration and then recalculated from the results of these mixtures. Discrepancies between the values obtained on the spike gas mixtures and those used in the original calibration are given as percents of point comparisons in column 7.

Table A.3 — Comparison of curve coefficients

Curve coefficients	Current	New
a1	+3,511 400e + 002	+3,510 400e + 002
a2	+2,022 700e + 000	+1,987 400e + 000
a3	−1,726 700e − 002	−1,683 700e − 002
a4	+1,192 700e − 004	+1,185 900e − 004

Table A.4 — Identification of spike gases

Spike gas mixture	Identification
1	40 000/4/230 393
2	25 000/4/300 493
3	CAL-726
4	CAL-892
5	10 000/4/270 892

In Table A.4, spike gas mixtures 3 and 4 are provided by a metrological institute. The other spike gases are those prepared by the traceable gas supplier.