INTERNATIONAL STANDARD

ISO 6145-5

First edition
2001-04-01

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 6145-5:2001(E)

PDF disclaimer

This PDF file may contain embedded typefaces. In accordance with Adobe's licensing policy, this file may be printed or viewed but shall not be edited unless the typefaces which are embedded are licensed to and installed on the computer performing the editing. In downloading this file, parties accept therein the responsibility of not infringing Adobe's licensing policy. The ISO Central Secretariat accepts no liability in this area.

Adobe is a trademark of Adobe Systems Incorporated.

Details of the software products used to create this PDF file can be found in the General Info relative to the file; the PDF-creation parameters were optimized for printing. Every care has been taken to ensure that the file is suitable for use by ISO member bodies. In the unlikely event that a problem relating to it is found, please inform the Central Secretariat at the address given below.

© ISO 2001

All rights reserved. Unless otherwise specified, no part of this publication may be reproduced or utilized in any form or by any means, electronic or mechanical, including photocopying and microfilm, without permission in writing from either ISO at the address below or ISO's member body in the country of the requester.

ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.ch
Web www.iso.ch

Printed in Switzerland

COPYRIGHT International Organization for Standardization
Licensed by Information Handling Services

Contents

Annex

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 3.

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 part of ISO 6145 may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

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

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 injection method*
- *Part 5: Capillary calibration devices*
- *Part 6: Critical orifices*
- *Part 7: Thermal mass-flow controllers*
- *Part 9: Saturation method*
- *Part 10: Permeation method*

Diffusion will be the subject of a future part 8 to ISO 6145. Part 3 to ISO 6145, entitled *Periodic injections into a flowing stream,* has been withdrawn.

Annex A of this part of ISO 6145 is for information only.

Introduction

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.

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

Part 5:
Capillary calibration devices

1 Scope

This part of ISO 6145 specifies a technique for the continuous production of calibration gas mixtures from pure gases or gas mixtures using capillary 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 repeatability of this technique is approximately 2 %. 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 0,1 to 0,9 of the primary gas with a relative repeatability of better than 0,5 %.

Traceability of the gas mixtures produced by a gas divider can be achieved by comparison of a mixture at the higher and lower end of the range with gas mixtures related to national or international gas standards. An example is given in annex A.

2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this part of ISO 6145. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this part of ISO 6145 are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

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

ISO 6145-1:1986, *Gas analysis — Preparation of calibration gas mixtures — Dynamic volumetric methods — Part 1: Methods of calibration.*

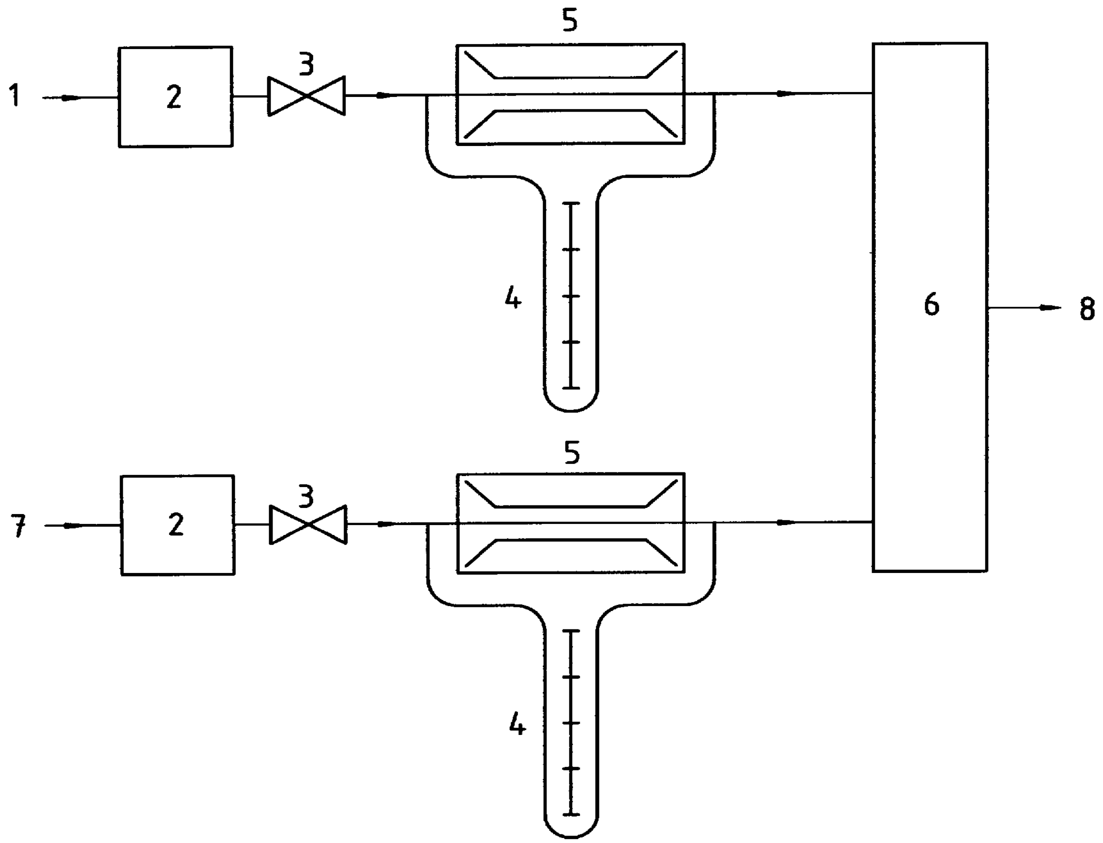
3 Singular or multiple capillary combinations

3.1 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 may be derived from another capillary tube.

3.2 Apparatus

3.2.1 Two-capillary system, as shown in Figure 1 and consisting of the following.



Key

1	Gas A
2	Two-stage pressure regulator
3	Fine adjustment valve
4	Pressure differential manometer
5	Capillary
6	Mixing manifold
7	Complementary gas
8	Gas mixture

Figure 1 — Two-capillary blending system

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

The appropriate capillaries shall be selected to give the required flows of gases A and B into the mixing manifold. These capillaries shall be calibrated using the method described in ISO 6145-1:1986, clause 3. The gas flow from one capillary is passed into a soap-film meter and 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 [see equation (2)]. The results of this calibration will allow a capillary to be selected such that the required flow can be obtained by adjusting the pressure drop across the capillary.

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

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

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

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

3.2.1.6 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 %.

3.3 Procedure

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.

3.4 Calculations

3.4.1 Capillary flow rate

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

$$q_\mathrm{A} = \frac{\pi r^4 (p_1 - p_2)}{8 \eta L} \qquad (1)$$

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 this expression can be simplified:

$$q_\mathrm{A} = K_\mathrm{A} (p_1 - p_2) \qquad (2)$$

where K_A is an individual factor for gas A.

3.4.2 Volume fraction

The volume fraction of component A, φ_A is defined by the equation

$$\varphi_A = \frac{q_A}{q_A + q_B} \tag{3}$$

where

q_A is the volume flow rate of gas A;

q_B is the volume flow rate of gas B.

3.4.3 Uncertainty

Variations in pressure differential $\Delta p\ (= p_1 - p_2)$ will be affected by changes in atmospheric pressure acting on the outlet of the mixing manifold. In a binary system, both gases will be similarly affected and the combined error in the system will be compensated. There will be an error associated with the calibration measurement using the method defined in ISO 6145-1:1986, clause 3.

Referring to equation (2):

$$q_A = K_A \Delta p \tag{4}$$

where Δp is equal to $(p_1 - p_2)$.

The relative combined standard uncertainty u_c of q_A is:

$$\frac{u_c\,(q_A)}{q_A} = \sqrt{\left[\frac{u\,(K_A)}{K_A}\right]^2 + \left[\frac{u\,(\Delta p)}{\Delta p}\right]^2} \tag{5}$$

where

$u\,(K_A)$ is the standard uncertainty of K according to the calibration of the capillary;

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

For the example of a binary mixture the uncertainty of the composition can be expressed in the form of the relative uncertainty of the volume fraction of component A, as in equation (3):

$$\varphi_A = \frac{q_A}{q_A + q_B} \tag{6}$$

i.e.

$$\frac{U\,(\varphi_A)}{\varphi_A} = \frac{2q_B}{q_A + q_B}\sqrt{\left[\frac{u\,(q_A)}{q_A}\right]^2 + \left[\frac{u\,(q_B)}{q_B}\right]^2} \tag{7}$$

The reported expanded uncertainty of measurement $U\,(\varphi_A)$ is stated as the standard uncertainty of measurement multiplied by the coverage factor $k = 2$ calculated for a normal distribution to give a coverage probability of approximately 95 %.

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 Multiple capillary devices using gas dividers

4.1 Gas dividers

Commercially available units called gas dividers which contain combinations of similar capillaries can be used to further dilute calibration gas mixtures with complementary gas, thus generating further calibration standards.

The gas mixtures generated by these units are frequently used to assess the performance of analytical instrumentation. This instrumentation may be employed in cases where a requirement of traceability is mandatory. In such cases, it is necessary that these units be calibrated by a method traceable to national or international standards. An approved method is to select two generated gas mixtures at < 25 % and > 75 % of a given range and carry out a comparison check with these gas standards at similar volume fractions.

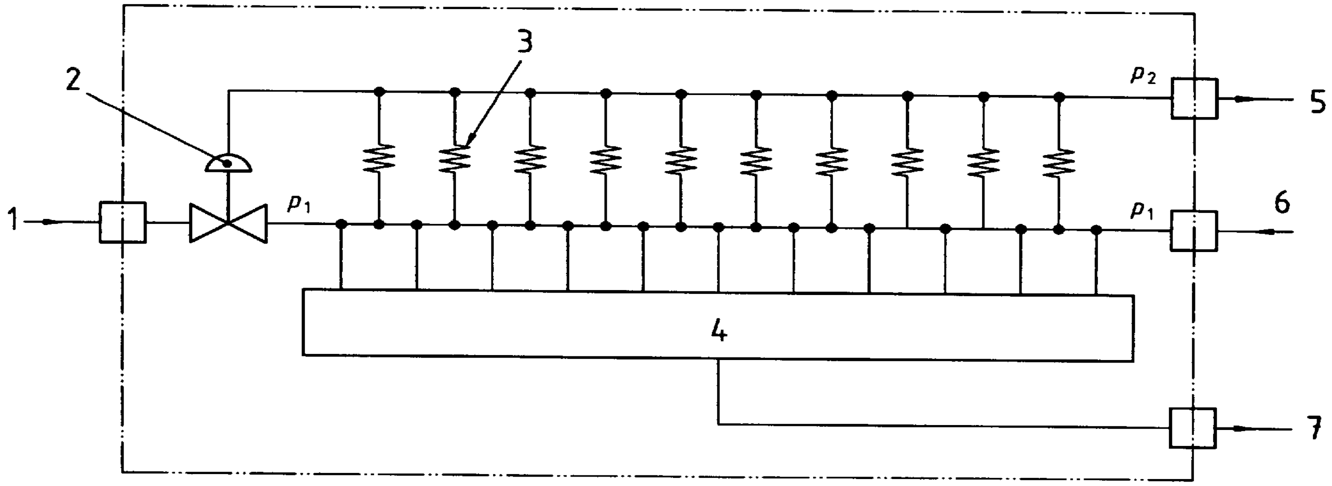
The agreement between the two results will confirm the accuracy of the gas divider and provide traceability to the other gas mixtures in that range. An example of this technique is given in annex A.

4.2 Principle

4.2.1 A gas divider contains a combination of capillary tubes of exactly the same lengths and diameters. Provided 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.

4.2.2 The flow rates of a component gas and a dilution gas are 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 component and dilution gas.

In the example illustrated in Figure 2, the gas divider has 10 capillaries.



Key

1 Dilution gas
2 Pressure regulator
3 Capillary
4 Division-switching valve
5 Generated gas
6 Component gas, volume fraction, φ_0
7 Exhaust gas

Figure 2 — Calibration gas generator using gas divider

By selecting the total number of capillaries through which the component and dilution gases flow, 11 stages of dilution, varying from 0 to 10, can be obtained.

Either the component gas or dilution gas always flows through the 10 capillaries. The volume fraction, φ_1, of the gas to be generated is calculated using the following equation.

$$\varphi_1 = \frac{n}{10} \times \varphi_0 \tag{8}$$

where

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

φ_0 is the volume fraction of the component gas.

As the flow characteristics of the 10 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.

4.3 Operating controls

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

4.4 Sources of errors in generating calibration gases

4.4.1 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 applies to both complementary and dilution gases and is compensated. Capillaries on separate blocks, whose temperatures vary, shall be thermostatically controlled.

4.4.2 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. Some 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.

4.4.3 Calibration of the gas divider

To achieve the stated accuracy of this technique, it is necessary to carry out a calibration of the gas divider. Two points on a range of volume fractions of gas mixtures, one at $< 25\ \%$ and the other at $> 75\ \%$ of the range, are compared in accordance with ISO 6143 using gas standards traceable to national or international bodies. The agreement obtained from this comparison determines the accuracy of the gas divider. An example of this comparison is given in annex A.

4.4.4 Pressure

Atmospheric pressure variations affect both gas flows equally and cancel out.

During operation, the gas pressures of the component and dilution gas shall be adjusted by external regulators. Care shall be taken to ensure that the required pressure differential does not substantially fall (to 70 %), otherwise the accuracy of the gas divider is affected.

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 of volume fractions from 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.

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

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

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, one at $<$ 25 % and the other at $>$ 75 % of the range measured in order to confirm individual points on the curve.

The results of the calibration process are given in Table A.2 below. 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 to 5) are shown in Table A.2.

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

Calibration gas %	Gas volume fraction %	Direct reading from the infrared analyser	Current curve value[b]	New generated curve value[c]	Relative point-by-point differences[d] of current curve %	Relative point-by-point differences[e] of new curve %	Relative point-by-point difference on FSR[f] of current curve %	Relative point-by-point difference on FSR[f] of 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 relative differences in columns 6 and 7 show a relative uncertainty of better than ±1,0 %.

[a] Measurement conditions:

System: traceable gas mixtures

Analyser: AIA-120

Date: 14 July 1994

Component: CO_2

Source: gas divider

Full scale range: 5,0 %

Status: not saved

Calibration gas: 45000/4/100794

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

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

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

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

[f] FSR: Full-scale range.

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

Spike gas	Gas volume fraction %	Direct reading from the infrared analyser	Current generated curve value [a]	New curve value [b]	Relative point-by-point differences [c] of current curve %	Relative point-by-point differences [d] of new curve %	Relative point-by-point difference on FSR [e] of current curve %	Relative point-by-point difference on FSR [e] of 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

In columns 4 and 5 are the values obtained on the spike gas mixtures based on the old calibration and that 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 relative difference in column 7.

NOTE The comparison shows that the new curve generated in Table A.1 and that generated using traceable spike gas mixtures agree within ± 0,5 %.

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

[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.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	40000/4/230393
2	25000/4/300493
3	CAL - 726
4	CAL - 892
5	10000/4/270892

The spike gas mixtures 3 and 4 have been provided by a standards institute. The other spike gases have been prepared traceably to known gas standards.

ICS 71.040.40
Price based on 10 pages