International Standard 6145/3

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Gas analysis — Preparation of calibration gas mixtures — Dynamic volumetric methods — Part 3 : Periodic injections into a flowing gas stream

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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 6145/3 was prepared by Technical Committee ISO/TC 158, *Analysis of gases.*

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INTERNATIONAL STANDARD **ISO 6145/3-1986 (E)**

Gas analysis — Preparation of calibration gas mixtures — Dynamic volumetric methods — Part 3 : Periodic injections into a flowing gas stream

1 Scope and field of application

This International Standard constitutes part 3 of ISO 6145, which deals with the various dynamic volumetric techniques used for the preparation of calibration gas mixtures.

It describes the periodic injection techniques which enable a concentration range of each component of between 10^{-6} and 10^{-2} with 1 % variability to be obtained. The concentration is expressed as a volume ratio (V/V).

2 Reference

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 Operating principle

Complementary gas B flows continuously through the system. At regular time intervals, a volume V of gas B is replaced by an equivalent volume of gas A.

A gas B (complementary gas) flows at a flow rate q in a tube T. A means is provided at a point P for periodically withdrawing a small sample of volume V of gas B and injecting an identical volume of gas A (the component for calibration) in place of gas B (figure 1), such that the flow rate is unchanged. The volume V_A of gas A together with gas B goes to a mixing chamber of volume V_0 where the mixture is made homogeneous.

3.2 Area of validity

Volume V_0 shall be large compared with the volume delivered by the component B during the time t between two successive injections. In practice, the following relationship shall be fulfilled :

$$3q_B \cdot t < V_0$$

Gases A and B shall be at the same pressure and temperature.

3.3 Principle of calculation

At a rate of n injections per minute of volume V, the mean flow volume ratio of gas A is $q_A = n \cdot V$, and the rate can be expressed as

$$C = \frac{\text{flow rate of gas A}}{\text{full flow rate}} = \frac{q_A}{q} = \frac{n \cdot V}{q}$$

4 Practical example

Figure 2 shows a practical example of a plug cock arrangement. Figures 3 and 4 show the schematic representation of the operation of a plug cock.

The cock is arranged so that the four plug holes are always communicating two by two (a and c, or b and d) forming a single passage of volume V. A synchronous motor drives the plug within its housing, and the motor is fed by a pulse generator. Each pulse causes the plug to perform a half turn in x seconds, at a constant rotational speed, and it rests between pulses.

In position 1, the plug is at rest while gas B is bypassed into the mixing chamber through check valves and the component for calibration (gas A) is drawn through the bubbler. After a given period of time (adjustable), the cock is turned by one-half of a revolution. The time is a function of the desired volume ratio and sets the value of n (number of pulses per unit time).

During movement of the cock to position 2, gas B passes through s, while gas A fills volume V expelling gas B, the pressure being limited by the action of the bubbler.

As the plug moves to position 3, volume V (now filled with gas A) is entrained by gas B into the mixing chamber. At the same time, gas A is drawn over the bubbler.

When the pulse terminates, the plug rests at position 4, equivalent to position 1.

5 Operating conditions of the example

The injection system (see figure 2) is supplied with gas A and is supplied with gas B by circuit 1 of pump P.

Delivery flow rates of gases A and B shall be high enough to permit complete sweeping during passage between positions 2 and 3.

Delivery volume V is about 0,04 cm^3, and the plug goes through a half turn in 5 s.

Feed circuit 2 for gas B supplies gas at a variable flow rate (100 to 1 000 cm^3/min) and serves to dilute the gas from M$_1$ at point M$_2$ (160 cm^3). The sum of gas delivery flow rates from 1 and 2 shall be very stable, supplied by a piston metering pump P driven by a synchronous motor. The gas mixture is ready for utilization after M$_2$.

It may also be feasible to employ the mixture from M$_2$ and dilute it in gas B in a second stage, using a second arrangement identical to the first. In this case, volume ratios of less than 50 ppm (V/V) can be obtained with an accuracy of 4 % relative.

6 Estimation of volume ratio

If q is the delivery flow rate of gas from mixing chamber M$_1$, and q' is the complementary gas delivery flow rate in circuit 2 at the entrance to mixing chamber M$_2$, then the following relationships hold:

At the exit of M$_1$: $C = \dfrac{n \cdot V}{q}$

At the exit of M$_2$: $C = \dfrac{n \cdot V}{q + q'}$

These formulae are useful for obtaining an approximation from the data on V, n and $q + q'$, but the accuracy of flow rate $n \cdot V$ is difficult to reach by conventional methods.

7 Calibration of the system and sources of error

7.1 General

The pressures and temperatures of gases A and B are the same at the level of the revolving cock, defining the delivered quantity of gas A for every cycle of the cock.

The pressure and temperature in the metering pump define the delivery flow rate of gas B.

If the difference in pressures in circuit 1 and circuit 2 is neglected, the difference in temperature between the cock and the metering pump (around 10 K, when the temperature equilibrium is reached) leads to a significant effect (about 3 %). These temperatures may be measured by thermocouples or mercury thermometers, one fixed on the rotating cock and one immersed in the pump oil.

A satisfactory approach is to define a "geometrical dilution factor", F_{DG}:

$$F_{\text{DG}} = \frac{q + q'}{n \cdot V}$$

which is only valid for an operation with the same temperature in the cock and in the pump.

The actual operation leads, after equilibrium of the system, to:

a) T_{r}, temperature of the cock, slightly higher than the ambient temperature;

b) T_{p}, temperature of the oil of the metering piston pump, 35 to 40 °C with ambient temperature around 20 °C.

NOTE — T_{r} and T_{p} are expressed in degrees Celsius for numerical examples but the units are converted into kelvins for calculations.

When in use, the actual dilution factor F_{D} is

$$F_{\text{D}} = F_{\text{DG}} \left(\frac{T_{\text{r}}}{T_{\text{p}}} \right)$$

The calibration of the system is obtained by the measurement of F_{DG} during an actual operation on a pure gas A, leading to T_{r} and T_{p}. The measurement of C_{AM} is performed at the outlet of the system by an analytical comparison method

$$F_{\text{DG}} = F_{\text{D}} \left(\frac{T_{\text{p}}}{T_{\text{r}}} \right) = \left(\frac{1}{C_{\text{AM}}} \right) \left(\frac{T_{\text{p}}}{T_{\text{r}}} \right)$$

7.2 Calibration error

The calibration error, ΔCal, is expressed as relative uncertainty:

$$\Delta \text{Cal} = \frac{\Delta F_{\text{DG}}}{F_{\text{DG}}} < \frac{\Delta C_{\text{AM}}}{C_{\text{AM}}} + \frac{\Delta T_{\text{p}}}{T_{\text{p}}} + \frac{\Delta T_{\text{r}}}{T_{\text{r}}}$$

where $\Delta C_{\text{AM}}/C_{\text{AM}}$ comes from the comparison method, using for example:

a) a calibration gas mixture of known concentration $C_{\text{AE}} \pm \Delta C_{\text{AE}}$[1]

b) an analytical method of comparison leading to

$$\frac{C_{\text{AM}}}{C_{\text{AE}}} = \bar{K}_1 \pm \Delta \bar{K}_1$$

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[1] If the complementary gas is the same for this calibration mixture as for gas B of the system, the purity of this gas does not act significantly as a correction factor on $F_{\text{D}} = 1/C_{\text{A}}$.

7.3 Precision error

When the system is calibrated for this set of conditions (n, V and $q + q'$), the precision error, Δf, comes only from the error of measurement of the two temperatures T_r and T_p, at the time of mixture generation:

$$\Delta f < \frac{\Delta T_p}{T_p} + \frac{\Delta T_r}{T_r}$$

The effects of temperature dependent volume variations in the pump and in the plug are negligible.

8 Numerical example: Binary mixture of methane in nitrogen

8.1 Estimation of F_{DG}, temperature conditions

With

$n = 4$

$V = 0{,}051\ 4$ cm³ of methane

$q + q' = 1\ 061$ cm³ of nitrogen per minute

$F_{DG} \approx 5\ 160$ (taken from manufacturer's instructions)

At equilibrium of the system,

$$T_r = 25 \pm 0{,}1\ °\mathrm{C} = 298{,}2 \pm 0{,}1\ \mathrm{K}$$

$$T_p = 36{,}6 \pm 0{,}1\ °\mathrm{C} = 309{,}8 \pm 0{,}1\ \mathrm{K}$$

8.2 Preparation of a mixture, by a static volumetric method, around 200 ppm of methane in nitrogen

$$C_{AE} = 196{,}4 \times 10^{-6}$$

$$\frac{\Delta C_{AE}}{C_{AE}} < 2{,}88 \times 10^{-3}$$

8.3 Gas chromatographic (FID) comparison of C_{AE} and C_{AM}

$$\frac{C_{AM}}{C_{AE}} = 1{,}000\ 7 \pm 1{,}13 \times 10^{-3}$$

from which

$$C_{AM} = 196{,}5 \times 10^{-6}$$

$$\frac{\Delta C_{AM}}{C_{AM}} < 4{,}01 \times 10^{-3}$$

8.4 Calibration results and error

$$F_{DG} = \frac{1}{196{,}5 \times 10^{-6}} \times \frac{309{,}8}{298{,}2}$$

$$= 5\ 286{,}9$$

$$\frac{\Delta F_{DG}}{F_{DG}} < 4{,}01 \times 10^{-3} + 0{,}32 \times 10^{-3} + 0{,}35 \times 10^{-3}$$

$$< 4{,}68 \times 10^{-3}$$

$$\Delta\mathrm{Cal} < 4{,}7 \times 10^{-3}$$

$$F_{DG} = 5\ 287 \pm 25$$

In this example of a set of conditions (n, V and $q + q'$), a periodical check has to be made on the results, which may be affected by mechanical wear.

Further calibrations checked over a period of one year give consistent results (5 293, 5 299, 5 323 ± 26) with T_r variations from 22,7 to 25 °C and T_p variations from 35,8 to 38 °C.

8.5 Precision error

When using this set of conditions, measuring T_p and T_r, at the time of mixture production, with an error of ± 0,1 K around 288,16 to 313,16 K (15 to 40 °C), there is a precision error of:

$$\Delta f < 0{,}7 \times 10^{-3}$$

8.6 Overall error on day-to-day use

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

$$< (4{,}7 + 0{,}7) \times 10^{-3}$$

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

$$< 6 \times 10^{-3}$$

This result depends mainly on the calibration (calibration mixture and analytical method).

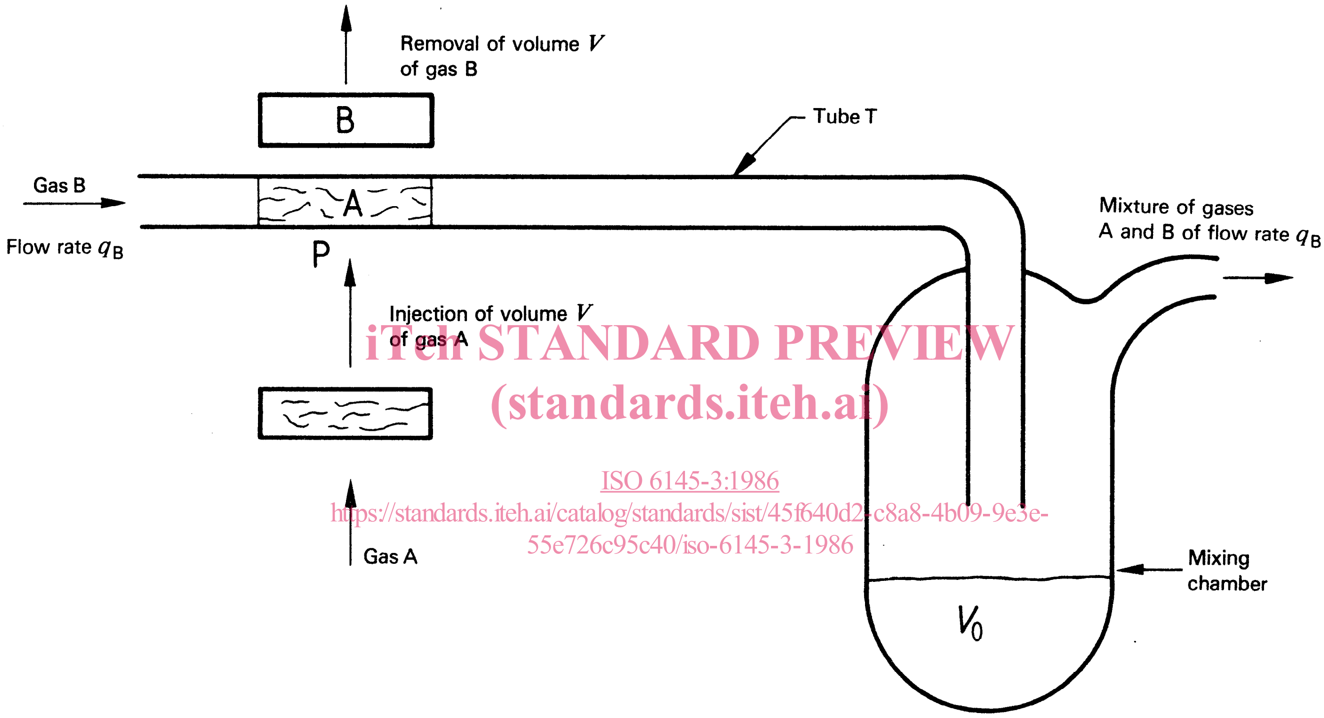
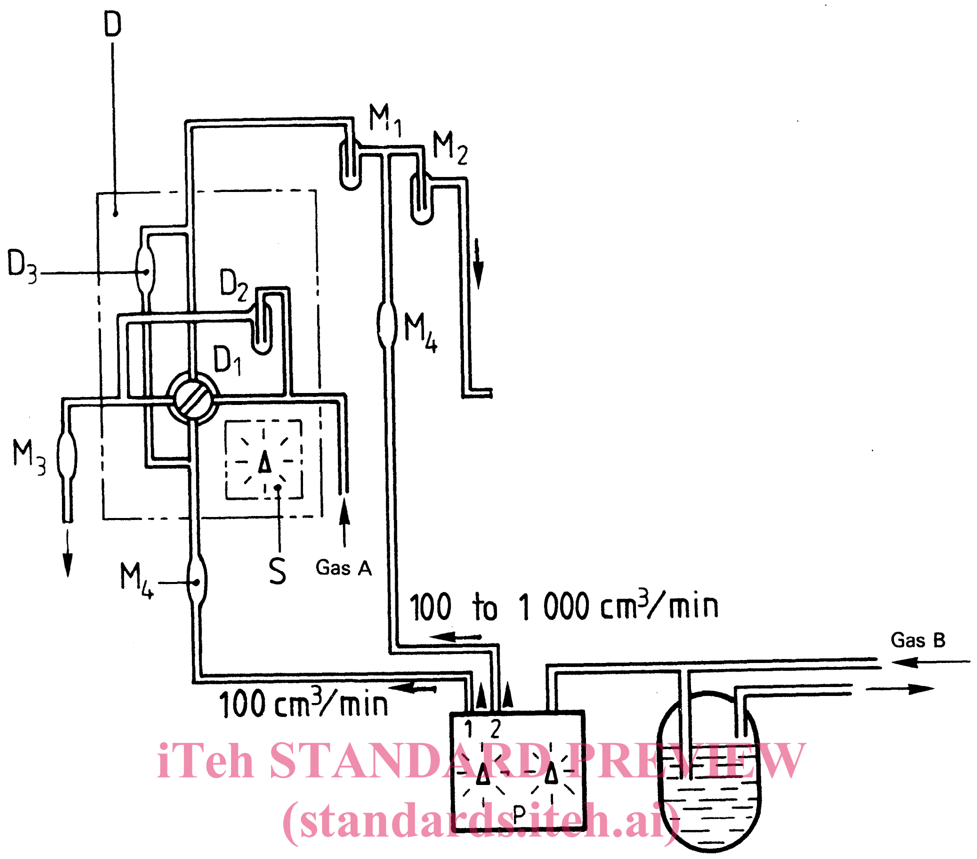


Figure 1 — Schematic representation of the method



D	Metering apparatus
D_1	Plug cock
D_2	Bubbler
D_3	Valve
M_1	Mixer of 300 cm^3
M_2	Mixer of 160 cm^3
M_3 and M_4	Filters
P	Metering pump
S	Pulse generator

Figure 2 — Schematic illustration of the apparatus for injection by plug cock

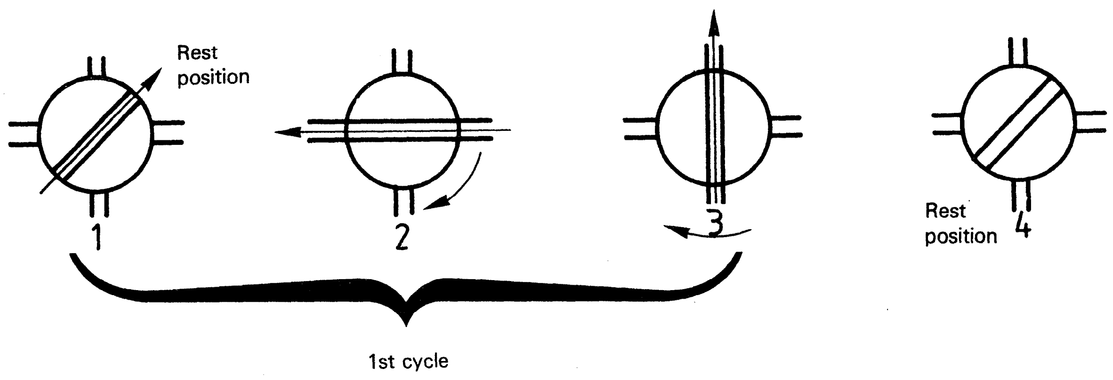
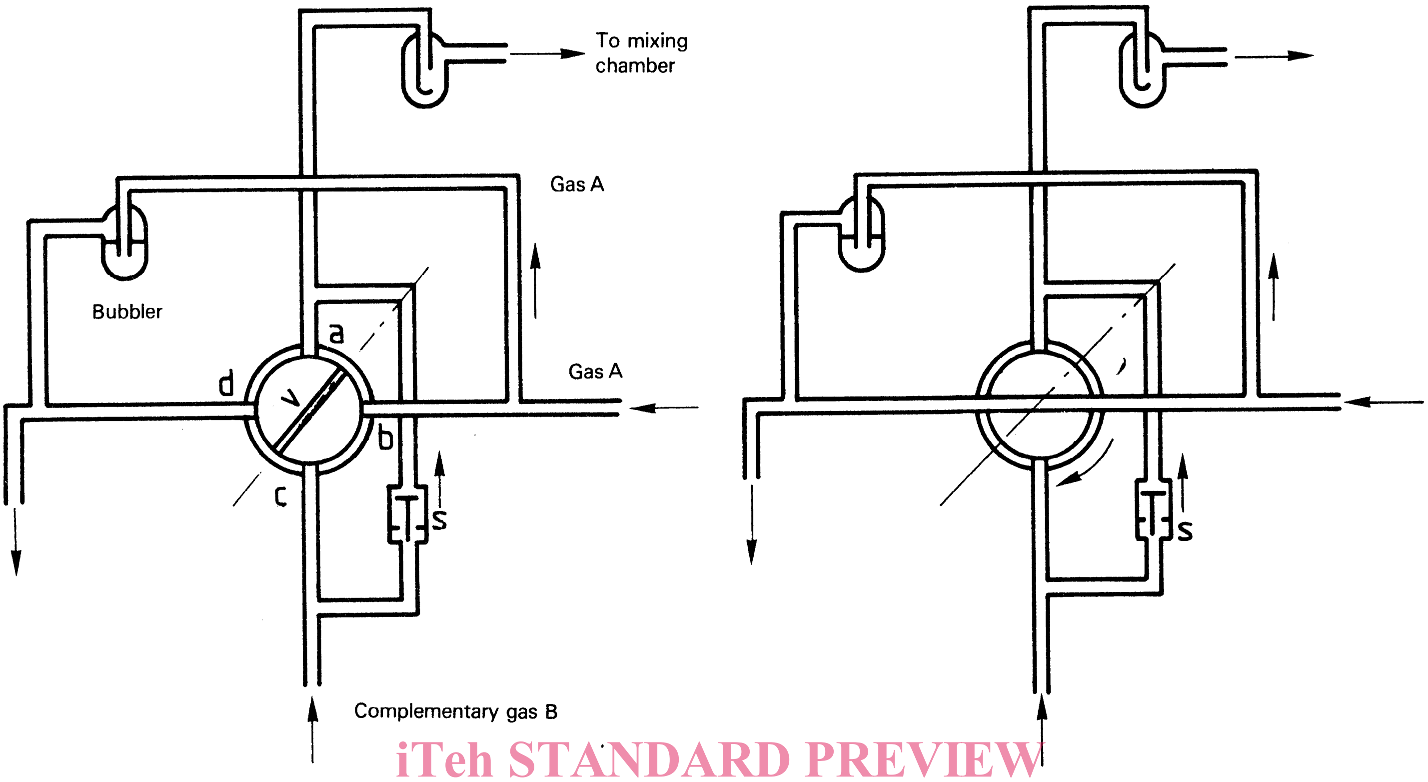
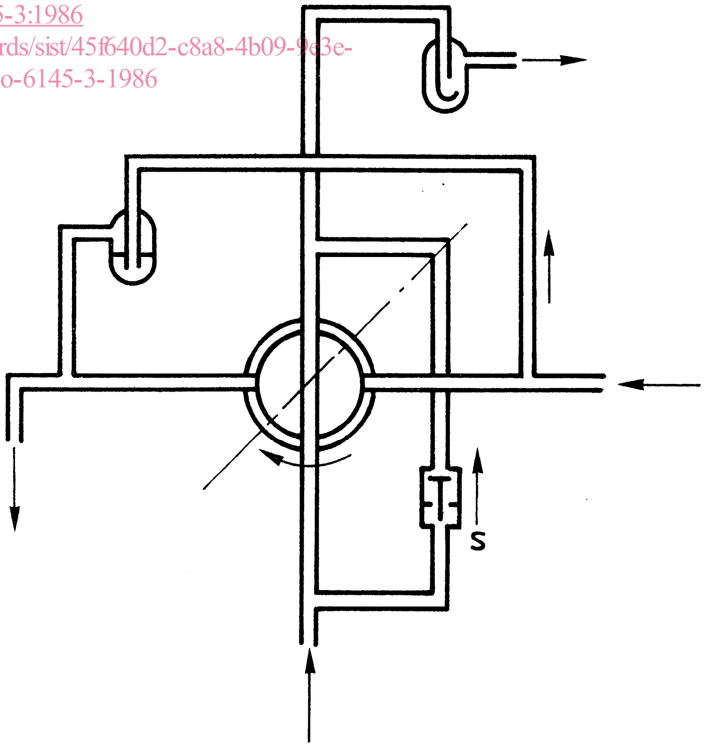


Figure 3 — Schematic representation of the functioning of the plug cock



Position 1 (rest)

Movement to position 2: traversed by gas A



Movement to position 3: dilution by complementary gas B

Figure 4 — Schematic representation of different positions of the plug