

International Standard



7395

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION • МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ • ORGANISATION INTERNATIONALE DE NORMALISATION

Gas analysis — Preparation of calibration gas mixtures — Mass dynamic method

Analyse des gaz — Préparation des mélanges de gaz pour étalonnage — Méthode dynamique massique

First edition — 1984-10-01

ITEH STANDARD PREVIEW
(standards.iteh.ai)

ISO 7395:1984

<https://standards.iteh.ai/catalog/standards/sist/e2047e73-4cc4-49ee-8a6c-94608fd04a39/iso-7395-1984>

UDC 543.27 : 53.089.68

Ref. No. ISO 7395-1984 (E)

Descriptors : gas analysis, calibration, gas mixtures, preparation.

Price based on 5 pages

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 7395 was prepared by Technical Committee ISO/TC 158, *Analysis of gases*.

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Gas analysis — Preparation of calibration gas mixtures — Mass dynamic method

1 Scope and field of application

This International Standard specifies a method for the continuous production of calibration gas mixtures. It may be used if static methods are inapplicable because one (or several) constituents may either be absorbed on to or react with the material of the cylinder intended to contain them, or react with other constituents under normal conditions; in these cases the mixture shall be used as fast as it is produced.

For molar concentrations above 0,01, the accuracy of the concentration is better than 2 % (relative).

The method can provide calibration mixtures at flow rates up to 4 m³/h at pressures between atmospheric and 2 bar*.

$$x_i = \frac{\frac{m_i}{M_i}}{\sum_{j=1}^n \frac{m_j}{M_j}}$$

where

x_i is the concentration of component i , expressed as a mole fraction;

m_i is the mass of component i consumed during the preparation of the mixture;

M_i is the molar mass of component i ;

n is the number of components;

j is equal to 1, 2, ..., i , ..., n .

2 Reference

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

3 Principle

Prew weighed cylinders, containing separately the individual constituents, are connected to a manifold into which each of the gaseous constituents is introduced by means of a device which ensures constant flow. The maintenance of constant flow during the whole period of production of the gas mixture is essential. At the end of this period, the cylinders are reweighed.

The composition of the mixture is calculated from the differences in mass of the cylinders.

If it is necessary to have available very dilute mixtures, the minor constituents shall be provided from cylinders in which these constituents are already mixed with complementary gas, provided that the reservations in clause 1 are observed.

The composition of the mixture cannot be predicted exactly but is calculated after the test. It is only possible to provide one mixture at a time and the cylinders shall be weighed between each preparation.

The concentration of a component i is given by the formula

4 Apparatus — Description

The cylinders are connected to the manifold as shown in figure 1. The analyser may be either the analyser to be calibrated or a unit for the control of the constancy of the gas mixture being produced for calibrating other analysers. It shall have been recently checked, particularly as regards the response time, absence of drift and repeatability, and calibrated at least approximately just before use.

The size of each cylinder is chosen so that weighing before and after test permits an accurate measurement of the amount of gas used. The cylinder containing the complementary gas is placed at the far end of the analytical chain to purge the manifold and transfer line.

Each cylinder is fitted with a two-stage pressure regulator and shut-off valve. The constant flow device may be connected either directly (in those cases where it can be weighed with the cylinder), or via a tee-piece, as shown in figure 1. Shut-off valves V2, V3, V4 and V5 isolate the regulator, tee-piece and constant flow device. The constant flow device may be a sonic orifice, an electronic mass flow controller or a high quality needle valve. It need not be calibrated accurately, as the composition of the mixture is determined subsequently from the changes in mass.

* 1 bar = 10⁵ Pa

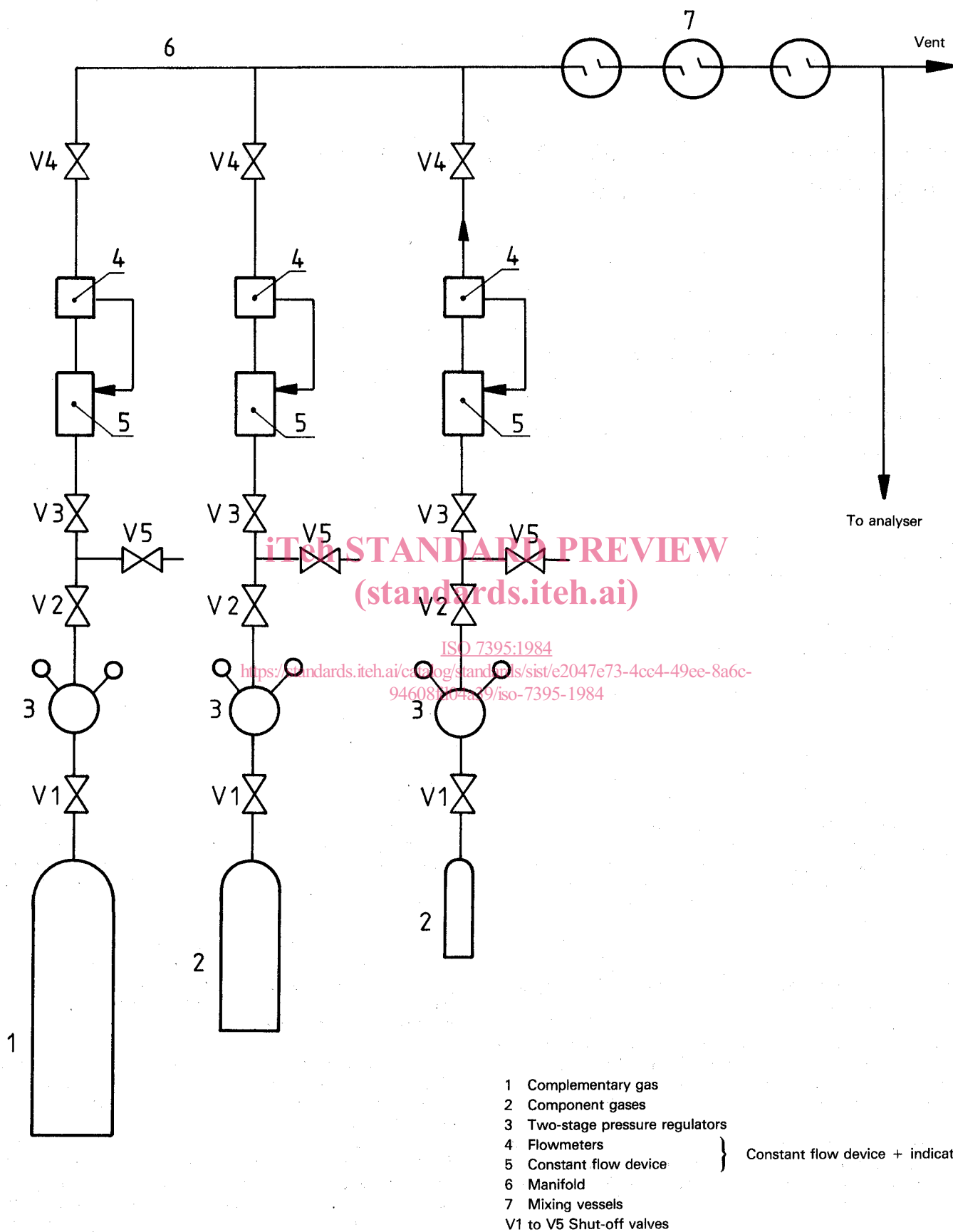


Figure 1 — Schematic arrangement of mixing system

The mixing vessels [see figure 1 (7)] shall each be of sufficient volume to allow complete mixing at the flow rates used. A stable reading of the analyser indicates that mixing is satisfactory.

When a gas mixture contains a constituent at a concentration which is close to saturation, any drop in temperature which may cause condensation shall be avoided.

NOTE — If any of the components of the mixture are very reactive, the elements of the flow control system or the mixing vessels must be constructed of suitably resistant materials, for example PTFE.

5 Procedure

It may be convenient to perform a preliminary trial so as to obtain an approximate adjustment of the constant flow devices. After this, the cylinders are shut off, disconnected and weighed. The cylinders are then reconnected so that the test can be started.

The apparatus is selected to ensure constancy of flow during the test period, but some flow variation is inevitable at the beginning and end of the period. The following procedure, which assumes for the weighing procedure that the cylinders are disconnected from the constant flow devices, is intended to minimize the resulting errors.

During the preliminary trial, the pressures and flows of each component are adjusted to the desired values. When steady flows have been established, each gas is shut off at valve V4, followed in turn by closing valves V3, V2 and V1. The contents of the tee-piece are vented through valve V5, then each cylinder is disconnected at the outlet of valve V2. Each cylinder, with its regulator and valve V2 still connected, is weighed using one of the procedures described in ISO 6142.

Each cylinder is reconnected to its tee-piece, which is then evacuated via valve V5 to remove air. The tee-piece is then pressurized by opening valves in the order V1, V2 and V3. The test period starts with the opening of valve V4. The valves, V4, of all the cylinders should preferably be opened simultaneously so that each component flow starts at the same time. If the valves are not opened simultaneously (it may, for example, be advisable to purge the manifold with the complementary gas), the exact time at which each is opened shall be noted.

The test period shall be long enough for the mass of gas taken from each cylinder to be measured accurately and for the effects of flow variation on start-up to be minimized. During the test period, the analyser readings shall be taken regularly. The readings to be used for calibration are those observed after the initial stabilization of the analyser response.

At the end of the test period, the cylinders are isolated, again following the sequence of closing valves in the order V4 (which defines the end of the test), V3, V2 and V1. The gas in each tee-piece is vented via V5, and each cylinder with its regulator and valve V2 is weighed as before. As for start-up, the valves, V4, of all the cylinders should preferably be closed simultaneously. The time at which each valve V4 is closed shall be noted if they are shut off at different times, or if the gas flows were started at different times.

If the constant flow device is of a size and mass such that it can be weighed with the cylinder and regulator, the procedure can be simplified. Flow is started and stopped at valve V4 on the outlet of the constant flow device as before, and the cylinder, regulator and constant flow device are weighed after disconnection at the outlet of valve V4.

If the gases were allowed to flow for different periods, the mass of each gas is corrected to the mass used during the time when all gases were flowing.

$$m'_i = \frac{m_i \cdot t_{\min}}{t_i}$$

where

m'_i is the corrected mass of component i ;

m_i is the total mass of component i used;

t_i is the time during which component i flowed;

t_{\min} is the time during which all components were flowing.

The molar concentrations are calculated from the corrected masses according to the formula in clause 3.

6 Sources of error

It is considered that the purity of the constituents and the complementary gas is such that it does not introduce any significant error.

The total mass of each component which has been used can be measured with a high degree of accuracy. The accuracy of the mixture produced at any moment is principally affected by the constancy of the flows of each component. These can be estimated either from knowledge of the stability of the constant flow devices or from observation of the readings of a continuous analyser which is being fed from the mixing system. In this latter case, the characteristics of the analyser, particularly its response time, drift and discrimination, have an overriding influence on the evaluation of the stability of the system.

Flow variations on start-up and the small amount of gas which is vented from the tee-piece are further sources of error. The sequence of closing valves means that the constant flow device becomes pressurized throughout to the pressure set on the cylinder regulator. This is bound to cause a flow surge when the valve is reopened for the test. The size of the resulting error cannot be greater than the amount of gas required to pressurize the constant flow device relative to the total amount of gas let through, and so may be estimated from knowledge of the internal geometry of the device. In the same way, the gas lost from the tee-piece can be estimated from its dimensions.

Alternatively, any contribution from these variations may be measured by observing whether a linear relationship exists between the change in the observed mass of the assembly and the time during which the gas is let through, subject to the limitation on the minimum mass of gas used as previously described.

The sequence of the procedure may be summarized as follows.

- Initial weighing of the assembly: cylinder + pressure regulator + V2, giving M .
- At time t_r , connection of V2 to the tee-piece and pressurization: filling of the tee-piece by the mass m_t .

 Δm_r is the mass variation in the constant flow device between pressure p_r of the pressure regulator (V4 closed) and the service pressure p_f , generally close to atmospheric pressure.
- At time t_o , opening of V4: the flow rate starts from zero, reaches a maximum and then stabilizes at the operation flow rate with or without oscillation.
- Production of the mixture: during which $\Delta m/\Delta t$ is constant within the regulation errors.

- At time t_f , closing of V4 followed by V3, V2 and V1: the tee-piece and the volume of the constant flow device are filled to pressure p_r , $\Delta m_r \gg m_t$ and m_t are delivered from the cylinder after t_f , the end of the calibration procedure.
- At time t_d , disconnection between V2 and the tee-piece, and weighing of cylinder which gives $M - \Delta M$.

These operations are illustrated in figures 2 and 3 which respectively represent the variations of

- the flow rate Q ;
- the total mass of the cylinder + the pressure regulator + V2

throughout the operation.

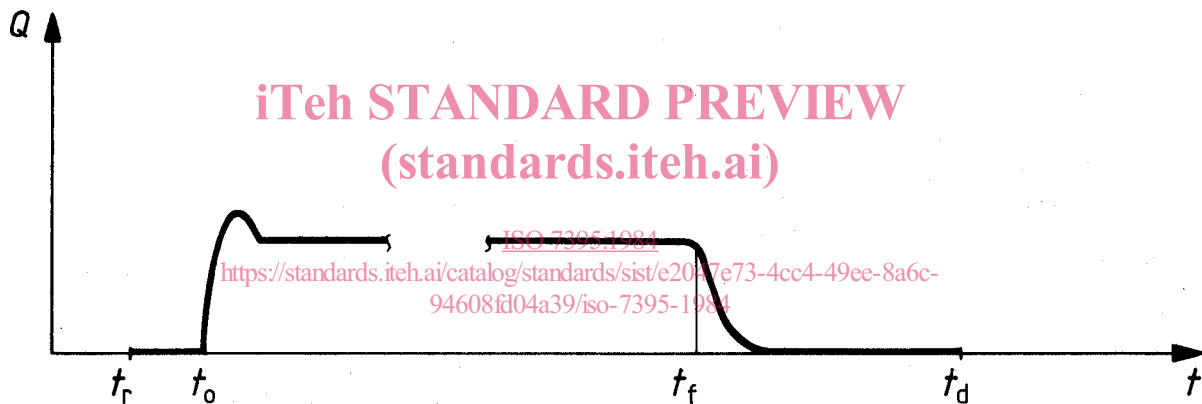


Figure 2 — Flow variation with time

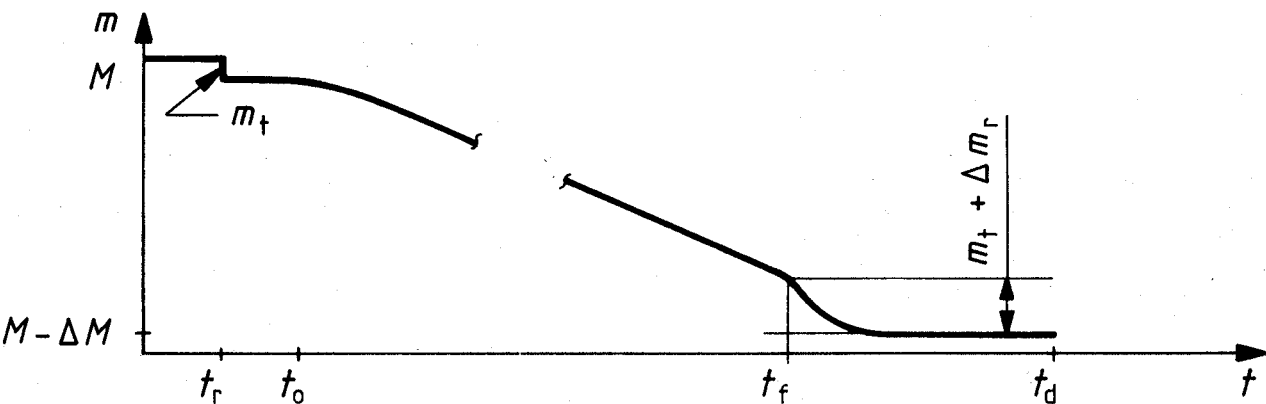


Figure 3 — Mass variation of the assembly considered with time

Finally, Δm being the mass loss during the time of theoretical operation between t_0 and t_f ,

$$\Delta M = \Delta m + 2m_t + f(\Delta m_t)$$

where $f(\Delta m_t)$ is the effect of Δm_t , which has a tendency to cancel out since the constant flow device is filled under the same conditions at t_0 and immediately after t_f , the maximum possible extent of this effect is given by adopting as the error on m , $\pm \Delta m_t$,

$$\Delta m = \Delta M - 2m_t \pm \Delta m_t$$

$$\frac{\Delta m}{m} < \frac{\Delta M}{M} + \frac{2\Delta m_t}{M} + \frac{\Delta m_t}{M}$$

The error on Δm_t (assessed from the geometry of the tee-piece) can be taken as 10 % of m_t assessed.

7 Numerical example

7.1 Weighing errors

Weighing errors are assessed as follows. A mixture of approximately 5 % carbon monoxide in nitrogen is required. Nitrogen is supplied from a cylinder of mass 70 kg, which is weighed on a balance with a 100 kg range, to the nearest 0,1 g — hence the nitrogen is weighed to the nearest 0,2 g. Carbon monoxide is supplied from a cylinder of mass 2,5 kg, which is weighed on a balance with a 10 kg range, to the nearest 0,01 g — hence the carbon monoxide is weighed to the nearest 0,02 g.

The nitrogen cylinder is connected via a tee-piece of 5 ml dead volume at 2 bar absolute pressure, which volume is equivalent to 0,012 g of nitrogen, and a constant flow device of 50 ml dead volume which will be pressurized from 1 to 2 bar absolute, which volume is equivalent to 0,058 g of nitrogen. The corresponding figures for carbon monoxide are 1 ml and 20 ml, or approximately 0,002 g and 0,023 g respectively.

With the direct results from the weighing, i.e. for CO : $m_1 = 16,83$ g and for N₂ : $m_2 = 331,2$ g, the intermediate calculations on m_1 , m_2 , Δm_1 and Δm_2 are made giving $m_2 = 331,2 - 0,024$; in view of the accuracy on the weighing, the error due to the dead volume is in this case negligible and therefore $m_2 = 331,2$ g is taken.

$$\frac{\Delta m_2}{m_2} < \frac{0,2 + 2(0,012 \times 0,1) + 0,058}{331,2} \approx \frac{0,26}{331,2}$$

$$\approx 0,8 \times 10^{-3}$$

for $0,6 \times 10^{-3}$ error on the weighing alone.

$$m_1 = 16,83 - 0,004$$

It is therefore possible in this case to make the same assumption as for m_2 and therefore $m_1 = 16,83$ g is taken.

$$\frac{\Delta m_1}{m_1} < \frac{0,02 + 2(0,002 \times 0,1) + 0,023}{16,83} \approx \frac{0,043}{16,83}$$

$$\approx 2,6 \times 10^{-3}$$

for $\approx 1,2 \times 10^{-3}$ error on the weighing alone.

It may be noted that the effect of the error on m_t is practically negligible.

Therefore the concentration of carbon monoxide is

$$x_1 = \frac{\frac{16,83}{28}}{\frac{331,2}{28} + \frac{16,83}{28}} = 0,048\ 36$$

$$\frac{\Delta x_1}{x_1} < \frac{\Delta m_1}{m_1} (1 - x_1) + \frac{\Delta m_2}{m_2} (1 - x_1)$$

$$\frac{\Delta x_1}{x_1} < (2,6 \times 10^{-3} + 0,8 \times 10^{-3}) 0,95 < 3,3 \times 10^{-3}$$

whence

$$x_1 = 0,048\ 36 \pm 0,000\ 16$$

7.2 Additional errors due to flow controller

Constant flow is ensured by the use of an electronic flow controller on each gas, with a relative stability of 5×10^{-3} .

The instantaneous concentration, x_1 , of carbon monoxide has a relative error

$$\frac{\Delta x_1}{x_1} < (3,3 \times 10^{-3}) + 2(5 \times 10^{-3})$$

$$\frac{\Delta x_1}{x_1} < 1,3 \times 10^{-2}$$

whence

$$x_1 = 0,048\ 36 \pm 0,000\ 63$$

7.3 Additional errors due to analyser

Constancy of individual flows is not checked but constancy of composition is checked by an analyser. If the analyser signal is seen to be constant to 0,8 % (relative), the instantaneous concentration of carbon monoxide has a relative error

$$\frac{\Delta x_1}{x_1} < (3,3 \times 10^{-3}) + (8 \times 10^{-3})$$

$$\frac{\Delta x_1}{x_1} < 1,1 \times 10^{-2}$$

whence

$$x_1 = 0,048\ 36 \pm 0,000\ 53$$