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Gas analysis — Preparation of calibration gas mixtures — Static volumetric methods

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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.

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It has been approved by the member bodies of the following countries :

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| | | |
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| Australia | France | Poland |
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No member body expressed disapproval of the document.

Gas analysis — Preparation of calibration gas mixtures — Static volumetric methods

1 Scope and field of application

This International Standard specifies static volumetric methods for the preparation of calibration gas mixtures at pressures close to atmospheric pressure.

The methods are applicable to gas mixtures having concentrations between 10^{-6} and 10^{-1} (V/V) for which the relative uncertainty is between 10^{-3} and 10^{-2} .

where

C_0 is the initial concentration of the component used ($C_0 \approx 1$);

D_1 is the dilution factor for the first operation.

The procedure described above is usually sufficient to give a relative uncertainty of less than 10^{-2} on concentrations of 10^{-3} to 10^{-1} (V/V).

2 Principles of the methods

2.1 General principles

Operations are carried out in three stages at a given temperature :

- Measurement : a container of known volume v is filled with the component to be analysed at a measured pressure p close to or, most often, equal to atmospheric pressure.
- Transfer : the volume v of the component is transferred into a receiver of known volume V in which at least a partial vacuum has been created beforehand.
- Dilution : the filling of this receiver is completed by means of the chosen complementary gas until the desired final pressure P is obtained; this is usually greater than atmospheric pressure to permit easy use of the mixture.

The volume concentration C_1 of the component, obtained after the first dilution, is practically equal at these pressure levels to the molar fraction concentration, and is given by the formula

$$C_1 = C_0 \frac{p_1 v_1}{P_1 V_1} = C_0 D_1 \quad \dots (1)$$

In fact, values p and P act as correction factors in this case in order to achieve the volume concentration. For this reason, only the non-dimensional ratio p/P is significant and it is therefore possible to measure p and P with a simple system such as a mercury gauge. When the molar concentration is given, the corrections for the compressibility factor Z should be taken into account, if necessary.

In the present state of knowledge regarding "compressibility" factors Z for gas mixtures, it is assumed that the variation of Z for a binary mixture is a linear function of the concentrations of the components. For gas mixtures for calibration with a minor polar component in a complementary gas not very different from ideal gases, the correction factor Z is therefore only significant on the level of measurement [i.e. $(p_1 v_1)/Z_1$]¹⁾. For gas mixtures in which the complementary gas shows considerable deviations in relation to ideal gases, the correction factors Z shall be calculated using the same hypothesis of linearity; it does not seem desirable to go into any further detail on other corrections in the light of the present final purpose for which calibration gas mixtures are intended.

In the case of mixtures of lower concentrations [10^{-6} to 10^{-4} (V/V)], it is necessary to carry out a succession of dilutions in order to obtain an acceptable accuracy : a primary mixture of concentration C_1 between 10^{-3} and 10^{-1} is prepared and then diluted using the same procedure (measurement, transfer, dilu-

1) In order to eliminate this source of error, for a component of low concentration and which is not ideal, the volume v_1 can, for example, be filled by a mixture obtained by a gravimetric method in which the component is at a sufficiently low concentration for the correction Z to be negligible.

tion). The desired final concentration C_2 for the second stage dilution is given by the formula :

$$C_2 = C_1 D_2$$

where

C_1 is the concentration of the component in the mixture after the first dilution;

D_2 is the dilution factor for the second dilution, calculated from the pressure and volume data as in formula (1), i.e.

$$D_2 = \frac{p_2 v_2}{P_2 V_2}$$

where

p_2, v_2 are the values for the pressure and volume of the mixture at concentration C_1 ;

P_2, V_2 are the corresponding values for the receiver containing the final gas concentration C_2 .

It follows, therefore, that

$$C_2 = C_1 \frac{p_2 v_2}{P_2 V_2} = C_0 \frac{p_1 v_1}{P_1 V_1} \times \frac{p_2 v_2}{P_2 V_2} \dots (2)$$

A third dilution may also be carried out which gives (with similar notations) :

$$C_3 = C_2 D_3 = C_2 \frac{p_3 v_3}{P_3 V_3} = C_0 \frac{p_1 v_1}{P_1 V_1} \times \frac{p_2 v_2}{P_2 V_2} \times \frac{p_3 v_3}{P_3 V_3}$$

2.2 Precautions to be taken, evaluation of uncertainties

2.2.1 In order to achieve valid results using the dilution procedure described in 2.1 :

a) use containers and transfer lines which are made of materials which do not give rise to absorption phenomena with the intended constituents, for example glass and PTFE;

b) carry out the operations so as to avoid increasing the temperature of the measuring vessel or the receiver at the time of filling by using gloves, for example, when handling.

2.2.2 As there are practical difficulties in evaluating uncertainty by statistical methods, the values recorded are those defined by the following error calculation derived from formula 2.

$$\frac{\Delta C_n}{C_n} = \frac{\Delta C_0}{C_0} + \sum_1^n \frac{\Delta p}{p} + \sum_1^n \frac{\Delta P}{P} + \sum_1^n \frac{\Delta v}{v} + \sum_1^n \frac{\Delta V}{V} \dots (3)$$

where n is the number of dilutions.

2.2.3 As in other methods, account has to be taken of the purity corrections of the constituent samples and of the complementary gas used :

a) **constituent sample** : it is usually considered as having a concentration $C > 1 - y$, where y is the maximum quantity of impurity in the component.

For the purpose of calculations, one may assume $C = 1 - \frac{y}{2}$ and for the level of error calculation, one can introduce $\pm \frac{y}{2}$.

b) **sample of complementary gas** : for mixtures of low component concentrations, it is often necessary to measure the residual component concentration $C_c \pm \Delta C_c$ in the complementary gas used, and to add this to the concentration calculated from the data from the dilution coefficients.

The effect on the error calculation is generally negligible at high concentrations.

At low concentrations, formula (3) becomes

$$\frac{\Delta C_2}{C_2} = \frac{\Delta C_0}{C_0} + \sum \frac{\Delta p}{p} + \sum \frac{\Delta V}{V} + \frac{\Delta C_c}{C_2} \dots (3')$$

$$= \frac{\Delta C_0 D}{C_0 D} + \frac{\Delta C_c}{C_2}$$

3 Examples of use

3.1 Method using glass vessels

3.1.1 Principle

Measurement of the component to be analysed is carried out in calibrated gas pipettes having capacities of approximately 10 to 400 cm³.

These pipettes are calibrated by weighing water or mercury : the volumes are determined with accuracies varying from 0,01 to 0,1 cm³ for pipettes of capacity 10 to 400 cm³.

Filling (see figure 1) of these calibrated gas pipettes, which are fitted with polytetrafluoroethylene (PTFE) vacuum stopcocks, is carried out by sweeping with the component to be analysed : a fairly long outlet tube prevents ambient air flowing backwards towards the pipette.

Transfer of the measured volume into the mixture receiver (see figure 2) takes place through glass tubes. When glass tubes are joined by rubber tubing, the contact area between the rubber and the gases should be minimal. Firstly, a vacuum is created in the receiver and the measured component is conveyed from the calibrated gas pipette towards the receiver by sweeping with the diluent gas.

Filling of the receiver with the diluent gas is completed slowly (see figure 2); the mercury gauge may be used since the component is never in contact with the mercury. Filling of the receiver is adjusted to twice atmospheric pressure for convenience in transferring the mixture for subsequent use.

3.1.2 Apparatus

3.1.2.1 Flask, made of thick borosilicate glass, of capacity approximately 3 dm^3 , containing three PTFE tubes ($V < 0,3 \text{ cm}^3$), fitted with two PTFE vacuum stopcocks of 3 mm bore.

3.1.2.2 U-tube mercury manometer, the height of the two limbs being approximately 1 m; the right limb has, at the top, two PTFE vacuum stopcocks of 2 mm bore.

3.1.2.3 Water valve.

3.1.2.4 Paraffin oil bubbler.

3.1.2.5 Gas meter.

3.1.2.6 Calibrated gas pipettes, of capacity approximately 10 to 400 cm^3 . The shape of these pipettes shall be such as to ensure complete transfer of the component with a reasonable volume of complementary gas : it is recommended that a cylindrical shape should be adopted with a length/diameter ratio between 3 and 5. In practice, the absence of the component after transfer is verified by analysis when the pipette is first used.

3.1.2.7 Vane pump, having a liquid nitrogen-cooled trap and a differential mercury manometer.

3.1.2.8 Cylinder of component gas.

The gas shall be of known purity.

NOTE — For the example given in 3.1.3 and 3.1.4, this gas is carbon monoxide (CO) having a guaranteed concentration $> 99,99 \%$.

3.1.2.9 Cylinder of complementary gas.

The purity and concentration of the component shall be known.

NOTE — For the example given in 3.1.3 and 3.1.4, this gas is nitrogen having a guaranteed concentration $> 99,998 \%$ and containing $0,5 \pm 0,1 \text{ ppm}$ of carbon monoxide.

3.1.2.10 Needle valve, for controlling the flow of the component gas during the measurement.

3.1.2.11 Two stage reducing valve, with stainless steel diaphragms and fitted with a needle valve at the outlet, for the transfer and dilution processes.

3.1.3 Procedure for preparation of a mixture of carbon monoxide in nitrogen

WARNING — Carbon monoxide is a very toxic gas [threshold limit value = 50 ppm (V/V)]. All necessary precautions should be taken to ensure that apparatus containing the gas is leak tight and that any outlet is vented to the outside atmosphere. All handling operations shall be carried out in a fume cupboard.

Risks of explosion could occur when shaking the evacuated flask in 3.1.3.2 and this should be carried out wearing gloves and protective glasses. If necessary, a safety container should be used.

3.1.3.1 Measurement of pure CO (see figure 1)

a) Filling of the gas pipette with CO

Open stopcocks 1 and 2 of the gas pipette, close stopcock 3 and flush the gas pipette with a volume of CO 20 times greater than its own volume (as read on the meter). Then decrease the flow of CO in order to produce one bubble at a time at the bubbler. Close stopcock 2, the needle valve and stopcock 1 in that order.

b) Correction of the CO in the gas pipette to atmospheric pressure

Open stopcock 3, then stopcock 2; the excess CO comes out through the valve, the central tube of which touches the surface of the water.

When there is no more gas coming from the valve, close stopcock 2 taking care not to touch the gas pipette with the hands. Note the ambient temperature and atmospheric pressure.

Disconnect the gas pipette and create a vacuum in the external tubing of the stopcocks in order to expel the CO.

NOTE — All the handling operations shall be carried out in a fume cupboard.

3.1.3.2 Preparation of the mixture (see figure 2)

The reducing valve and the valve of the nitrogen cylinder are initially closed, the needle valve being fully opened.

Connect the gas pipette containing the measured quantity of CO to the right limb of the U-tube manometer and to stopcock 4 on the flask, then connect the vane pump to stopcock 5.

Open stopcocks 4 and 5, and create a vacuum in the flask. When the vacuum has been attained (as read on the differential mercury manometer), close stopcock 5.

Connect the vane pump to stopcock 6 of the right limb of the manometer, open stopcock 1 slowly, open the nitrogen cylinder valve, and regulate the pressure using the reducing valve so that it is slightly greater than twice the desired pressure.

Slightly open stopcock 6; nitrogen from the cylinder passes into the right limb of the manometer, and is then sucked through the pump. Flush for 1 min then close stopcock 1 and open stopcock 6 completely.

When a vacuum has been created in the right limb of the U-tube manometer, close stopcock 6, partly open stopcock 1 and check the adjusted pressure. Open stopcock 3, then slowly open stopcock 2; the nitrogen flushes the gas pipette. So that the measured component is completely transferred from the calibrated gas pipette to the receiver, it is recommended that a volume of complementary gas at least 10 times greater than the volume of the gas pipette should be used for this operation.

Regulate the opening of stopcock 2 so that the pressure in the right limb of the manometer remains greater than atmospheric pressure.

When stopcock 2 is completely open, regulate the nitrogen flow with stopcock 1 which allows adjustment to the desired pressure in the flask.

When this pressure has been reached (as read on the manometer), close stopcocks 1 and 4 in that order.

Slightly open stopcock 6 to bring the nitrogen to atmospheric pressure in the gas pipette and the right limb of the manometer. When this pressure has been reached, close stopcocks 6, 2 and 3 in that order.

Disconnect the flask from the gas pipette, and shake it by rotating it in each direction. Homogenization of the mixture is achieved by the displacement of the PTFE tubes which were placed in the flask at the beginning.

The mixture is then ready for use.

From this mixture, which is at a pressure equal to twice atmospheric pressure, several calibrated gas pipettes can be taken in order to prepare mixtures of lower CO contents by dilution, proceeding as above.

3.1.4 Example of preparation of a range of carbon monoxide/nitrogen mixtures by successive dilution

An initial mixture in the range 1 000 to 10 000 ppm (V/V) of carbon monoxide is prepared according to the procedure in 3.1.3 and, from this, further calibrated gas pipettes are filled and diluted according to the procedures in 3.1.3.1 and 3.1.3.2 to produce a series of mixtures in the ranges

- 100 to 1 000 ppm (V/V)
- 10 to 100 ppm (V/V)
- 1 to 10 ppm (V/V)

3.1.4.1 To perform these operations, use a range of vessels which have been calibrated by weighing water or mercury at a controlled temperature : an example of the range used for usual laboratory requirements is given in table 1 with the accuracy of volume measurements and the characteristics of the balances used for these measurements.

3.1.4.2 The results of operations carried out to prepare the mixtures in the four concentration zones intended are represented schematically in table 2.

3.1.4.3 Details of the calculations of errors on the concentrations obtained are given in annex B.

The errors in the volume measurements are taken from table 1.

The errors in the pressure measurement are :

- ± 0,1 mmHg on atmospheric pressure p (Fortin barometer);
- ± 1 mmHg on pressure P read on a mercury manometer.

3.2 Method using a moving piston

3.2.1 Apparatus

3.2.1.1 The apparatus is shown diagrammatically in figure 3.

It consists of a glass cylinder approximately 60 cm long and of diameter 10 cm. The cylinder carries a free floating piston made of stainless steel with PTFE piston rings which ensure a close fit with the glass walls of the cylinder. The gas in the cylinder can circulate past these rings.

The glass cylinder is positioned within a frame which can be rotated through 360°. In this turning movement, the piston will fall under its own weight to the bottom of the cylinder. The rate of fall of the piston can be controlled by adjusting the angle of the glass cylinder.

Inlet and outlet connections are joined to either end of the cylinder and the stainless steel lines are fed through flexible ball joints at the centre of the apparatus.

The main control panel of the system contains a gas chromatography sampling valve with a calibration loop. The same line also includes a port with septum for injections using a syringe. A valve is fitted to this line to allow the sample conditions to be adjusted to atmospheric pressure during the operations.

By selection of the appropriate valves, a closed system can be created. Turning of the glass cylinder then moves the piston and propels the enclosed gas around the system. Because some gas also escapes past the piston rings this circulation proves a very efficient mixing system.

3.2.1.2 Additional apparatus is required as follows :

a) Cylinder of component gas.

The gas shall be of known purity.

NOTE — For the example given in 3.2.3 to 3.2.5, this gas is carbon monoxide (CO) having a guaranteed concentration > 99,95 %.

b) **Cylinder of complementary gas.**

The gas shall be of known purity and the concentration of the component shown be known.

NOTE — For the example given in 3.2.3 to 3.2.5, this gas is nitrogen having a guaranteed concentration > 99,998 %, containing not more than 0,1 ppm of carbon monoxide.

Both cylinders [a) and b)] shall be equipped with a reducing valve giving an outlet pressure of at least 20 kPa.

c) **Gas sampling syringe.**

3.2.2 Operating conditions

The following precautions shall be taken.

3.2.2.1 Insulated holders shall be fixed to the syringe barrels to prevent temperature effects during handling operations.

3.2.2.2 To eliminate operator error, metal spacers shall be used with each syringe. These spacers fitted between the barrel of the syringe and its plunger allow only the corresponding set volume to be injected.

3.2.2.3 All syringes, the sampling valve and loop shall be accurately calibrated. Calibration of the syringe can be carried out by filling it with water and injecting this water into a pre-weighed container. The mass of several injections can then be determined and the syringe volume accurately calculated. The container is then emptied and the water is weighed. A calculation involving density gives the total volume.

3.2.3 Procedure

3.2.3.1 Connect the nitrogen cylinder to the inlet marked "complementary gas", and adjust the nitrogen regulator to 15 kPa.

3.2.3.2 Connect the carbon monoxide cylinder to the inlet marked "pure gas", and adjust the carbon monoxide regulator to 15 kPa (see 3.1.3, Warning).

Purge the apparatus of any contaminating gas. Refer to figure 3 to follow the manipulations for purging apparatus and preparing the gas mixture.

3.2.3.3 Turn the valve to position 1. The complementary gas passes into the glass cylinder, past the piston and is evacuated to the atmosphere.

3.2.3.4 Rotate the glass cylinder through 180° several times. The piston is then able to rise and fall in the cylinder to assist purging.

3.2.3.5 Turn the valve to position 2.

3.2.3.6 Adjust the carbon monoxide flow to 5 or 10 l/min.

3.2.3.7 Insert the syringe into the septum marked "sample extract".

3.2.3.8 Purge the syringe by moving the plunger in and out.

3.2.3.9 Fill the syringe with carbon monoxide and remove it from the septum.

3.2.3.10 Adjust the syringe to the predetermined setting.

3.2.3.11 Insert the syringe into the septum marked "sample injection".

3.2.3.12 Inject the set quantity of carbon monoxide into the apparatus.

3.2.3.13 Turn the valve to position 3.

3.2.3.14 Mix the gases in the apparatus by rotating the cylinder for at least 10 min. The free floating piston then falls slowly to the bottom of the cylinder. Some of the gas circulates round the system and some gas escapes past the piston ring, resulting in efficient mixing.

3.2.3.15 To utilize the prepared gas mixture for calibration purposes, connect the apparatus directly to the inlet of the measuring instrument. Turn the valve to position 4. Gas flow into the analyser is controlled by adjustment of the angle of the cylinder and the rate of fall of the piston. Approximately 2/3 of the volume of the glass cylinder is used for calibration purposes; the remaining gas escapes past the piston and mixes with incoming air.

NOTE — During the above procedure, the complementary gas is introduced with the vent valve in the open position. All gas mixing therefore takes place at atmospheric pressure. This prevents any pressure build up in the syringe which might cause errors of measurement during injection and possible leaks at the injection port or past the syringe piston. Any loss of complementary gas from the system is prevented because of the position of the piston between the injection port and the vent valve.

3.2.4 Example of calculation for preparation of a 100 ppm (V/V) mixture of carbon monoxide in nitrogen

The content of the glass cylinder, in parts per million [ppm (V/V)], is given by the formula

$$\frac{v}{V} \times 10^6$$

where

v is the volume, in millilitres, of component gas injected;

V is the total volume, in millilitres, of the glass cylinder and associated pipework.

For the example considered :

$$v \text{ (injected volume of carbon monoxide)} = 400 \pm 4 \mu\text{l}$$

$$V = 4\,032 \pm 5 \text{ ml}$$

Concentration of carbon monoxide in the final gas mixture :

$$\frac{0,4}{4\,032} \times 10^6 = 99,2 \text{ ppm (V/V)}$$

3.2.5 Calculation of the relative error, as a percentage, on the preparation of 100 ppm (V/V) carbon monoxide in nitrogen

Relative error on the determination of the final volume :

$$4\,032 \pm 5 \text{ ml, i.e. } \frac{5 \times 100}{4\,032} = 0,12 \%$$

Relative error on the determination of injected carbon monoxide :

$$400 \pm 4 \mu\text{l, i.e. } \frac{4 \times 100}{400} = 1 \%$$

That is, a total $\frac{\Delta C}{C}$ of 1,12 %.

Table 1 – Example of the range of containers which can be used

| Volume of container (cm ³) | Accuracy of volume determination (cm ³) | Characteristics of the balance used for weighing |
|--|---|--|
| 10,27 10,31 10,31 10,34 25,99 26,02 60,50 94,60 | ± 0,01 | Maximum mass : 200 g Sensitivity : ± 0,1 mg |
| 124,60 185,08 243,7 252,8 254,4 257,4 269,8 322,7 333,3 383,6 | ± 0,1 | Maximum mass : 1 200 g Scale : 100 g Sensitivity : ± 10 mg |
| 3 015 3 024 3 038 3 044 3 055 3 060 3 092 3 095 | ± 0,5 | Maximum mass : 5 500 g Direct reading on scale : 3 000 g Sensitivity : ± 0,25 g (1/4 of a division) |

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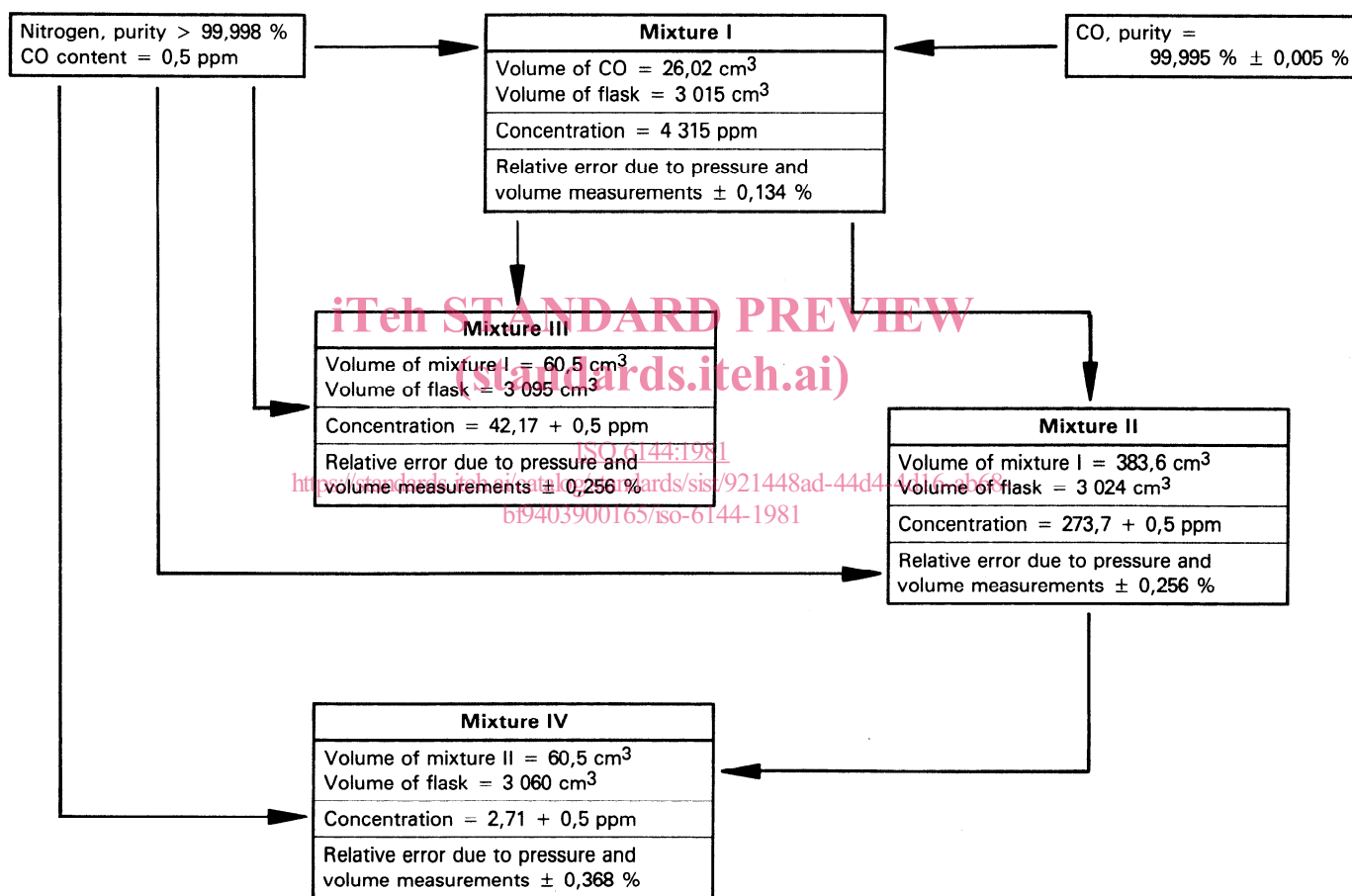
Table 2 — Example of schematic representation of preparation of calibration mixtures of carbon monoxide in nitrogen at 4 315 — 274,2 — 42,67 and 3,21 ppm (V/V) according to the procedure described in 3.1.3

Volumes of flasks used : 3 015 ± 0,5; 3 024 ± 0,5; 3 060 ± 0,5; 3 095 ± 0,5 cm³.

Volumes of gas pipettes used : 26,02 ± 0,01; 60,5 ± 0,01; 383,6 ± 0,1 cm³.

Atmospheric pressure = 760 ± 0,1 mmHg¹⁾.

Pressure in flask = 1 520 ± 1 mmHg¹⁾.



1) Measured on the same mercury gauge. It is not necessary to convert the readings to SI units.