International Standard **ISO** 6142

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Gas analysis — Preparation of calibration gas mixtures — Weighing 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 :

Australia	Germany, F.R.	South Africa, Rep. of
Belgium	Italy	Spain
Bulgaria	Netherlands	United Kingdom
Czechoslovakia	Philippines	USSR
France	Poland	

No member body expressed disapproval of the document.

Gas analysis — Preparation of calibration gas mixtures — Weighing methods

1 Scope and field of application

This International Standard specifies weighing methods for the preparation of calibration gas mixtures for which the accuracy of the concentration of each component is better than 1 %, whatever the values of the selected concentrations.

It is applicable only to gaseous components which do not react between themselves or with the cylinder walls, and to condensable components which are totally vaporized under the test conditions.

2 Principles of the methods

2.1 General principles

A chamber is weighed before and after the introduction of a certain quantity of a gaseous component of known quality.

The weight of the gaseous component introduced is defined by the difference in the weights read during the two weighings.

The introduction of different components produces a gaseous mixture.

The weight concentration of each component of the mixture is defined as being the ratio of the weight of this component to the sum of the component weights. The weight ratio thus obtained is equivalent to a mass ratio.

In order to avoid having to weigh very small masses of gases, a lower concentration limit is fixed for the concentration of each of the components in the final mixture or, alternatively, the minor component may be weighed in a separate smaller cylinder on a low capacity balance and transferred without loss into a cylinder in which the major component is weighed on a higher capacity balance. In cases where the value of the desired concentration is less than this limiting value, a known quantity of the preceding mixture is diluted with a known mass of a given gas.

This dilution operation may have to be repeated twice to reach molar concentrations at the level of 10^{-6} with acceptable errors which depend upon the characteristics of the balances and the procedure used.

Under these conditions, the concentrations are evaluated as follows.

2.1.1 Method by single dilution

This is applicable to concentrated mixtures having concentrations in the range $10^{-3} \leqslant x_i \leqslant 1$ (molar). The concentration x_i in the mixture (mixture a) is given by the formula

$$x_i = \frac{n_i}{n_i + \Sigma n_j} = \frac{n_i}{n}$$

where $i, j \in [1, p]$ and $j \neq i$

where

i, j are indices of the components considered, of molar concentrations x_i, x_j ;

p is the total number of components in the mixture;

n_i is the number of moles of component i, of molar mass M_i, corresponding to the mass m_i introduced so that

$$n_i = \frac{m_i}{M_i}$$

n_j is the number of moles of component j, of molar mass M_j, corresponding to the mass m_j introduced so that

$$n_j = \frac{m_j}{M_j}$$

In the following text and the error calculations, the following quantities are also considered :

$$m = m_i + \Sigma m_j$$

$$n = n_i + \Sigma n_j$$

2.1.2 Method by double dilution

This is applicable to mixtures having concentrations in the range $10^{-4} \leqslant x_{2i} \leqslant 10^{-3}$ (molar). A mass μ_1 of a concentrated

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mixture (obtained in 2.1.1, called mixture a) is diluted with a mass μ_{d1} of a gas of molar mass M_d; generally, the complementary gas used in 2.1.1 is also used for this purpose. The concentration x_{2i} of the dilute mixture (mixture b) is given by the formula

$$x_{2i} = \frac{\dfrac{\mu_1}{m} \times n_i}{\dfrac{\mu_1}{m} \times n + \dfrac{\mu_{d1}}{M_d}} = \frac{N_{2i}}{N_{2t} + N_{d1}} = \frac{N_{2i}}{N_{S2}}$$

where

$N_{2i} = \dfrac{\mu_1}{m} \times n_i$ is the number of moles of component i introduced in the mass μ_1 of mixture a;

$N_{d1} = \dfrac{\mu_{d1}}{M_d}$ is the number of moles of the diluting gas introduced in the mass μ_{d1};

$N_{2t} = \dfrac{\mu_1}{m} \times n$ is the number of moles of components i, j introduced in the mass μ_1 of mixture a;

$N_{S2} = N_{2t} + N_{d1}$ is the total number of moles of the mixture b thus obtained.

The following quantity is also considered :

$$m_{S2} = \mu_1 + \mu_{d1}$$

i.e. the total mass of the mixture b thus obtained.

2.1.3 Method by triple dilution

This method is applicable to mixtures of low concentrations in the range $10^{-6} < x_{3i} < 10^{-4}$ (molar). A mass μ_2 of mixture b is diluted with a mass μ_{d2} of a gas of molar mass M_d, the same as that used in 2.1.2. The concentration x_{3i} of the diluted mixture (mixture c) is given by the formula

$$x_{3i} = \frac{\dfrac{\mu_2}{m_{S2}} \times N_{2i}}{\dfrac{\mu_i}{m_{S2}} \times N_{S2} + \dfrac{\mu_{d2}}{M_d}} = \frac{N_{3i}}{N_{3t} + N_{d2}} = \frac{N_{3i}}{N_{S3}}$$

where

$N_{3i} = \dfrac{\mu_2}{m_{S2}} \times N_{2i}$ is the number of moles of component i introduced in the mass μ_2 of the mixture b;

$N_{d2} = \dfrac{\mu_{d2}}{M_d}$ is the number of moles of the diluting gas introduced in the mass μ_{d2};

$N_{3t} = \dfrac{\mu_2}{m_{S2}} \times N_{S2}$ is the number of moles of components i, j, d, introduced in the mass μ_2 of the mixture b;

$N_{S3} = N_{3t} + N_{d2}$ is the total number of moles of the mixture c thus obtained.

The following quantity is also considered :

$$m_{S3} = \mu_2 + \mu_{d2}$$

i.e. the total mass of the mixture c thus obtained.

The method thus defined can be carried out in three ways :

— weighing of the chamber carried out at atmospheric pressure under normal operating conditions;

— weighing carried out at atmospheric pressure using a reference cylinder;

— weighing carried out under low pressure in order that necessary corrections due to buoyancy are negligible.

2.1.4 General precautions

The results thus obtained by one of the formulae can be valid only if all precautions with respect to the handling of pure gases are strictly fulfilled, that is, in relation to :

— the nature and state of the transfer line;

— the nature and state of the devices connected to this line (valve, cut-off elements, etc.);

— the nature and state of packaging materials (in particular non-significant adsorption of the mixture components).

In addition, the gases used must be the subject of strict quality control. In particular, one has to determine the concentration of all components that can exist in the final mixture or that can cause interferences at the level of analytical utilization of the mixture.

The gas mixture thus prepared shall only be used when homogeneity has been attained.

Cylinders shall comply with the requirements of all corresponding International Standards and shall not be in contradiction with national regulations.

2.2 Sources of error

2.2.1 Precautions for gas handling

The equipment used for gas handling may be an important source of errors if its cleanliness and tightness are not periodically verified (replacement, in particular, of the vacuum pump filter and of the tightness seals of the connecting fittings). Before the introduction of each component into the cylinder, the various pipelines shall be evacuated to vacuum or purged by a compression-decompression cycle. From the introduction of the second component, the pressure of the gas introduced shall always be much higher than the pressure in the cylinder in order to avoid any loss of the gas previously weighed. In order to avoid back-diffusion, the cylinder shall also be isolated over the period during which thermal equilibrium is being achieved.

2.2.2 Errors specific to weighing in ambient atmospheres

The total absolute error in the concentration of each of the components depends on the equipment and the operating conditions used.

Errors which are introduced by the balance into gas quantities are due to :

— absolute errors due to the weights having been changed between two successive weighings;

— the variation in buoyancy due to variation in the volume of the weights used during two weighings of the same gas.

Errors introduced by the operating conditions used are mainly due to the large volume of the cylinder on which the buoyancy operates.

Parameters that may affect the error are the following :

— ambient temperature;

— atmospheric pressure;

— relative humidity of the air;

— increase in volume sustained by the cylinder during its filling.

The parameters listed above can be determined accurately.

A correction formula permits detecting the value of buoyancy and thus correcting the apparent mass of the gas cylinder and obtaining the real mass of the cylinder for each weighing.

The absolute uncertainty of the value of the real mass is thus a function of the accuracy to which the values of the parameters are known.

The relative error in the concentration of each of the components is thus a function of the quantity of each of these components. It thus depends on the concentration desired. This error, according to each case, is less than 5×10^{-3} if the molar concentration is greater than 10^{-3}, and less than 10^{-2} if the molar concentration is less than or equal to 10^{-3}.

2.2.3 Errors specific to weighing under vacuum

Weighing under vacuum enables the influence of buoyancy to be neglected. Under these conditions, the absolute error in the value of the concentration of each component no longer depends on the weights employed and correction calculations are therefore unnecessary.

As before (see 2.2.2), the relative error is a function of the amount of each component introduced into the cylinder. It thus depends on the concentration desired. According to each case, this error is less than 1×10^{-3} if the molar concentration is greater than 10^{-3}, and less than 5×10^{-3} if the molar concentration is less than or equal to 10^{-3}.

3 Weighing in ambient atmospheres

3.1 Simple weighing

3.1.1 Procedure

The balance used shall have sufficient sensitivity and measuring dynamics to ensure the required relative accuracy.

The chambers used may be metal cylinders, suitably evacuated and heated before use.

The pressure in the cylinders at the end of this preliminary treatment shall be less than 1 Pa.

For weighing, the following operations are performed :

— set the balance to zero;

— place the empty cylinder on the balance and weigh it;

— introduce the first component into the cylinder;

— check the zero of the balance;

— weigh the cylinder containing the first component;

— introduce the second component;

— continue as before.

All operations shall be performed in a clean and stable atmosphere (constant pressure and temperature). During weighing, the cylinder shall have the same temperature as the environment.

3.1.2 Practical example

The weights used in the balance are approximately of class E_2 (OIML Recommendation No. 20). The balance used operates under a constant load equal to 8 kg and has a sensitivity of 1 mg.

A number of weights covers the range 8 kg to 10 g; an optical device with a vernier scale permits reading of variations of mass between 10 g and 1 mg.

3.2 Weighing against a reference cylinder

3.2.1 Procedure

Components are introduced one at a time and, after thermal equilibrium of the cylinder and components with the environment is attained, the cylinder is weighed. It is considered that thermal equilibrium is attained when the cylinder weight remains constant.

The cylinder weight and the additional weight of each added component are measured by comparison with a similar cylinder on which no operation is performed other than weighing. This procedure automatically corrects for variations of buoyancy due to barometric pressure.

3.2.2 Practical example

The analytical balance used has a capacity of 240 g and a resolution of 0,1 mg.

The cylinders are made of aluminium alloy and have a mass of approximately 200 g.

4 Weighing under vacuum

4.1 Procedure

The balance is placed in a reduced pressure chamber (less than or equal to 1 Pa).

Weighing under reduced pressure is the only modification to the procedure described in 3.1.

With this type of device, the cylinder is preferably introduced into the chamber through a lock chamber and the filling and weighing operations are carried out in the same manner as previously.

Weighing under reduced pressure permits the carrying out of operations on a cylinder which is not in thermal equilibrium with the environment. It is thus possible to weigh a cylinder as soon as filling is terminated.

4.2 Results obtained

The method thus defined can give rise to three means of realization.

4.2.1 Case of mixtures obtained by single dilution

— Concentration expression :

$$x_i = \frac{\dfrac{m_i}{M_i}}{\dfrac{m_i}{M_i} + \sum \dfrac{m_j}{M_j}}$$

— Expression of relative uncertainty in the molar concentration of component i :

$$\frac{\Delta x_i}{x_i} < \frac{\Delta m_i}{m_i}(1 - x_i) + \sum \frac{\Delta m_j}{m_j} \times x_j + $$
$$+ \frac{\Delta M_i}{M_i}(1 - x_i) + \sum \frac{\Delta M_j}{M_j} \times x_j$$

where

m_i is the mass of component i introduced, i.e.

$(P + \varepsilon)_2 - (P + \varepsilon)_1$;

P_1 and P_2 are the two weight assemblies having a common part a and an individual part b_1 for P_1 and b_2 for P_2;

ε_1 and ε_2 are the values read on the vernier scale, respectively, during the two weighings determining the quantity of gas introduced.

It is possible to write :

$$\frac{\Delta m_i}{m_i} < \frac{\Delta b_2 + \Delta b_1 + 2\Delta\varepsilon}{(P_2 + \varepsilon_2) - (P_1 + \varepsilon_1)}$$

and

$$\frac{\Delta m_i}{m_i} < \frac{\Delta b_2 + \Delta b_1 + 2\Delta\varepsilon}{m_i}$$

where

$$\Delta\varepsilon = \Delta\varepsilon_p + \Delta\varepsilon_o$$

$\Delta\varepsilon_p$ is the absolute error of the reading on the vernier scale during the weighing operation;

$\Delta\varepsilon_o$ is the absolute error of the reading on the vernier scale during setting to zero prior to each weighing;

M_i is the molar mass of component i assumed to be known to the nearest 10^{-5}.

4.2.2 Case of mixtures obtained by double dilution

— Concentration expression :

$$x_{2i} = \frac{\dfrac{\mu_1}{m} \times n_i}{\dfrac{\mu_1}{m} \times n + \dfrac{\mu_{d1}}{M_d}}$$

In most cases, the diluting gas is the same as that used as the major component in mixture a. This is the case considered here.

— Expression of relative uncertainty of the molar concentration of component i :

$$\frac{\Delta x_{2i}}{x_{2i}} < \frac{\Delta\mu_1}{\mu_1}\left(1 - \frac{n}{N_{S2}} \times \frac{\mu_1}{m}\right)$$
$$+ \frac{\Delta\mu_{d1}}{\mu_{d1}} \times \frac{N_{d1}}{N_{S2}}$$
$$+ \frac{\Delta m_i}{m_i}\left[1 - \frac{m_i}{m} - \left(x_i - \frac{m_i}{m}\right)\frac{n}{N_{S2}} \times \frac{\mu_1}{m}\right]$$
$$+ \sum \frac{\Delta m_j}{m_j}\left[\frac{m_j}{m} + \left(x_j - \frac{m_j}{m}\right)\frac{n}{N_{S2}} \times \frac{\mu_1}{m}\right]$$
$$+ \frac{\Delta M_i}{M_i}\left(1 - x_i \times \frac{n}{N_{S2}} \times \frac{\mu_1}{m}\right)$$
$$+ \sum \frac{\Delta M_j}{M_j} \times x_j \times \frac{n}{N_{S2}} \times \frac{\mu_1}{m}$$
$$+ \frac{\Delta M_d}{M_d} \times \frac{N_{d1}}{N_{S2}}$$

It is noted, in the differential expression $\dfrac{\mathrm{d}x_{2i}}{x_{2i}}$, that the same sign for factors of $\dfrac{\mathrm{d}M_j}{M_j}$ and $\dfrac{\mathrm{d}M_d}{M_d}$ keep the validity of the previous terms when one of the components j is identical to the diluent d.

4.2.3 Case of mixtures obtained by triple dilution

— Concentration expression :

$$x_{3i} = \frac{\dfrac{\mu_2}{m_{S2}} \times N_{2i}}{\dfrac{\mu_2}{m_{S2}} \times N_{S2} + \dfrac{\mu_{d2}}{M_d}}$$

— Expression of relative uncertainty of the molar concentration of component i :

$$\frac{\Delta x_{3i}}{x_{3i}} < \frac{\Delta \mu_2}{\mu_2}\left(1 - \frac{N_{S2}}{N_{S3}} \times \frac{\mu_2}{m_{S2}}\right)$$

$$+ \frac{\Delta \mu_1}{\mu_1}\left[1 - \frac{\mu_1}{m_{S2}}\left(1 - \frac{N_{S2}}{N_{S3}} \times \frac{\mu_2}{m_{S2}} + \frac{n}{N_{S3}} \times \frac{\mu_2}{m}\right)\right]$$

$$+ \frac{\Delta \mu_{d2}}{\mu_{d2}} \times \frac{N_{d2}}{N_{S3}}$$

$$+ \frac{\Delta \mu_{d1}}{\mu_{d1}}\left[\frac{\mu_{d1}}{m_{S2}}\left(1 - \frac{N_{S2}}{N_{S3}} \times \frac{\mu_2}{m_{S2}}\right) + \frac{N_{d1}}{N_{S3}} \times \frac{\mu_2}{m_{S2}}\right]$$

$$+ \frac{\Delta m_i}{m_i}\left[1 - \frac{m_i}{m} - \left(x_i - \frac{m_i}{m}\right)\frac{n}{N_{S3}} \times \frac{\mu_2}{m_{S2}} \times \frac{\mu_1}{m}\right]$$

$$+ \sum \frac{\Delta m_j}{m_j}\left[\frac{m_j}{m} + \left(x_j - \frac{m_j}{m}\right)\frac{n}{N_{S3}} \times \frac{\mu_2}{m_{S2}} \times \frac{\mu_1}{m}\right]$$

$$+ \frac{\Delta M_i}{M_i}\left(1 - x_i \times \frac{n}{N_{S3}} \times \frac{\mu_1}{m} \times \frac{\mu_2}{m_{S2}}\right)$$

$$+ \sum \frac{\Delta M_j}{M_j} \times x_j \times \frac{n}{N_{S3}} \times \frac{\mu_1}{m} \times \frac{\mu_2}{m_{S2}}$$

$$+ \frac{\Delta M_d}{M_d}\left(\frac{N_{d2}}{N_{S3}} + \frac{N_{d1}}{N_{S3}} \times \frac{\mu_2}{m_{S2}}\right)$$

It is noted, in the differential expression $\dfrac{\mathrm{d}x_{3i}}{x_{3i}}$, that the same sign for factors of $\dfrac{\mathrm{d}M_j}{M_j}$ and $\dfrac{\mathrm{d}M_d}{M_d}$ keep the validity of the previous terms when one of the components j is identical to the diluent d.

4.2.4 Numerical examples of mixture preparation

Numerical calculations enable a better grasp of the size of the terms used.

NOTE — The relative errors on molar masses of 10^{-6} to 10^{-5} are, for the time being, negligible in relation to the measurement techniques currently available.

4.2.4.1 Simple dilution

Consider a binary mixture (argon in nitrogen) prepared by the weighing method under vacuum :

— mass of the empty cylinder : 5 931 000 mg

— mass of the cylinder containing argon : 5 952 154 mg

— mass of the cylinder containing nitrogen and argon : 6 617 949 mg

from which

the mass of argon introduced, $m_1 = 21\ 154$ mg

the mass of nitrogen introduced, $m_2 = 665\ 795$ mg

and

$$m_1 + m_2 = 686\ 949\ \text{mg}$$

From :

$$M_A = 39{,}948 \text{ g/mol, and}$$

$$M_{N_2} = 28{,}013\ 4 \text{ g/mol}$$

the following quantities are calculated :

$$n_1 = 0{,}529\ 538$$

$$n_2 = 23{,}767\ 019$$

$$n = n_1 + n_2 = 24{,}296\ 557$$

$$x_1 = 2{,}179\ 5 \times 10^{-2} \text{ in argon}$$

$$x_2 = 1 - x_1 = 0{,}978\ 205 \text{ in nitrogen}$$

and

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

from

$$\Delta m_1 = 6 \text{ mg}$$

$$\Delta m_2 = 69 \text{ mg}$$

$$\frac{\Delta m_1}{m_1} = 2{,}84 \times 10^{-4}$$

$$\frac{\Delta m_2}{m_2} = 1{,}04 \times 10^{-4}$$

$$\frac{\Delta x_1}{x_1} < (2{,}84 \times 10^{-4} + 1{,}04 \times 10^{-4}) \times 0{,}98$$

$$\frac{\Delta x_1}{x_1} < 3{,}802\ 4 \times 10^{-4}$$

i.e

$$\frac{\Delta x_1}{x_1} < 4 \times 10^{-4}$$

or

$$\Delta x_1 < 9 \times 10^{-6}$$

and

$$x_1 = 2,179\,5 \times 10^{-2} \pm 9 \times 10^{-6}$$

$$2,178\,6 \times 10^{-2} < x_1 < 2,178\,04 \times 10^{-2}$$

4.2.4.2 Double dilution

Consider this mixture as a primary mixture and dilute it in nitrogen :

— mass of the empty cylinder : 5 881 938 mg

— mass of the cylinder containing the primary mixture : 5 888 061 mg

— mass of the cylinder containing nitrogen + mass of the primary mixture : 6 897 619 mg

where

the mass of the primary mixture introduced, $\mu_1 = 6\,123$ mg

the mass of nitrogen introduced, $\mu_{d1} = 1\,009\,558$ mg

The molar concentration of argon in the new mixture is therefore :

$$x_{2.1} = \frac{\dfrac{\mu_1}{m} \times n_1}{\dfrac{\mu_1}{m} \times n + \dfrac{\mu_{d1}}{M_d}} = \frac{N_{2i}}{N_{2t} + N_{d1}} = \frac{N_{2i}}{N_{S2}}$$

$$x_{2.1} = \frac{\dfrac{6\,123}{686\,949} \times 0,529\,538}{\dfrac{6\,123}{686\,949} \times 24,296\,557 + \dfrac{1\,009,558}{28,013\,4}}$$

$$x_{2.1} = \frac{4,719\,944 \times 10^{-3}}{0,216\,563 + 36,038\,396}$$

$$x_{2.1} = \frac{4,719\,944 \times 10^{-3}}{36,254\,959} = 0,130\,188 \times 10^{-3}$$

$$x_{2.1} = 1,301\,88 \times 10^{-4}$$

The weighing errors evaluated are :

$$\Delta \mu_1 = 4 \text{ mg, i.e. } \frac{\Delta \mu_1}{\mu_1} = \frac{4}{6\,123} = 6,54 \times 10^{-4}$$

$$\Delta \mu_{d1} = 65 \text{ mg}$$

i.e

$$\frac{\Delta \mu_{d1}}{\mu_{d1}} = \frac{65}{1\,009\,558} = 6,44 \times 10^{-5}$$

For evaluation of the error $\dfrac{\Delta x_{2.1}}{x_{2.1}}$, the following quantities are evaluated

$$N_{S2} = 36,255$$

$$N_{d1} = 36,038$$

$$\frac{m_1}{m} = \frac{21\,154}{686\,949} = 0,030\,8 = 3,08 \times 10^{-2}$$

$$\frac{m_2}{m} = \frac{665\,795}{686\,949} = 0,969\,2$$

$$\frac{n}{N_{S2}} \times \frac{\mu_1}{m} = \frac{24,30}{36,25} \times \frac{6\,123}{686\,949} = 6 \times 10^{-3}$$

$$\frac{N_{d1}}{N_{S2}} = \frac{36,038}{36,255} = 0,994$$

$$x_1 - \frac{m_1}{m} = (2,18 - 3,08) \times 10^{-2} = -9 \times 10^{-3}$$

$$x_2 - \frac{m_2}{m} = 0,978\,2 - 0,969\,2 = 9 \times 10^{-3}$$

From 4.2.2, the error for $x_{2.1}$ is evaluated according to the formula :

$$\frac{\Delta x_{2.1}}{x_{2.1}} \leqslant \frac{\Delta \mu_1}{\mu_1} \left(1 - \frac{n}{N_{S2}} \times \frac{\mu_1}{m} \right) + \dots$$

i.e.

$$6,54 \times 10^{-4} (1 - 6 \times 10^{-3}) = 6,5 \times 10^{-4} + \dots$$

$$+ \frac{\Delta \mu_{d1}}{\mu_{d1}} \times \frac{N_{d1}}{N_{S2}}$$

i.e.

$$6,44 \times 10^{-5} \times 0,994 = 0,65 \times 10^{-4} + \dots$$

$$+ \frac{\Delta m_1}{m_1} \left[1 - \frac{m_1}{m} - \left(x_1 - \frac{m_1}{m} \right) \frac{n}{N_{S2}} \times \frac{\mu_1}{m} \right] + \dots$$

i.e.

$$2,84 \times 10^{-4} (1 - 3 \times 10^{-2} + 9 \times 10^{-3} \times 6 \times 10^{-3})$$

$$= 2,75 \times 10^{-4} +$$

$$+ \frac{\Delta m_2}{m_2} \left[\frac{m_2}{m} + \left(x_2 - \frac{m_2}{m} \right) \frac{n}{N_{S2}} \times \frac{\mu_1}{m} \right]$$

i.e.

$$1{,}04 \times 10^{-4} \, (0{,}97 + 9 \times 10^{-3} \times 6 \times 10^{-3})$$

$$= 1{,}01 \times 10^{-4}$$

Thus the sum of the various components is :

$$\frac{\Delta x_{2.1}}{x_{2.1}} < 10{,}91 \times 10^{-4}$$

or

$$\frac{\Delta x_{2.1}}{x_{2.1}} < 1{,}1 \times 10^{-3}$$

which leads to the absolute error

$$\Delta x_{2.1} < 1{,}3 \times 10^{-4} \times 1{,}1 \times 10^{-3} = 1{,}42 \times 10^{-7}$$

and

$$1{,}300 \, 4 \times 10^{-4} < x_{2.1} < 1{,}303 \, 3 \times 10^{-4}$$

or

$$1{,}300 \times 10^{-4} < x_{2.1} < 1{,}304 \times 10^{-4}$$

4.2.5 Remarks on the expression and importance of error calculations

4.2.5.1 Consider the use of these methods to obtain low concentration components by means of several successive dilutions with a diluent d identical to one of the components j_d predominant during the first dilution. Let x_i be a low concentration, x_{jd} and x_d be close to 1, and large dilutions be characterized by

$$\frac{m_i}{m_{jd}} \ll 1, \qquad \frac{\mu_1}{\mu_{d1}} \ll 1, \qquad \frac{\mu_2}{\mu_{d2}} \ll 1$$

The expressions obtained are very close to :

$$\frac{\Delta x_i}{x_i} < \frac{\Delta m_i}{m_i} + \sum \frac{\Delta m_j}{m_j} + \sum \frac{\Delta \mu_k}{\mu_k}$$

$$+ \sum \frac{\Delta \mu_{dk}}{\mu_{dk}} + \frac{\Delta M_i}{M_i} + \sum \frac{\Delta M_j}{M_j}$$

$$j \in [1, p], \, j \neq i \text{ and } k \in [0, 1, 2]$$

with a slight increase of the relative error compared to those given by the formulae given in 4.2.1 to 4.2.3; the correcting terms to be applied to each of the errors on weighing or on molecular mass are of the type $1 - \varepsilon$, where ε is smaller as the successive dilutions are larger.

4.2.5.2 When these same mixtures are very dilute, it is necessary to take account of the residual concentration x_{ri} of the component i in the diluting gas.

In fact the true concentration x_i is :

$$x_i = x_{ri} \, (1 - x_{ni}) + x_{ni}$$

$$= x_{ri} + x_{ni}$$

where x_{ni} is the result of the diluting operations and the term $x_{ri} \times x_{ni}$ is negligible if the diluent used is very pure.

The relative uncertainty in the concentration of the component i changes to :

$$\frac{\Delta x_i}{x_i} < \frac{\Delta x_{ri}}{x_{ri}} \times \frac{x_{ri}}{x_i} + \frac{\Delta x_{ni}}{x_{ni}} \times \frac{x_{ni}}{x_i}$$

Consider, as an example, the molar concentration of argon in nitrogen after a second dilution :

$$x_{2i} = 9 \times 10^{-6}$$

$$\frac{\Delta x_{2i}}{x_{2i}} = 0{,}23 \times 10^{-2}$$

$$x_{ri} = 0{,}5 \times 10^{-6} \pm 0{,}1 \times 10^{-6}$$

which gives

$$x_i = 9{,}5 \times 10^{-6}$$

The present methods of analysis, in the case of argon, very seldom have a detection threshold (assimilated to the relative error on x_r) better than $0{,}1 \times 10^{-6}$.

$$\frac{\Delta x_i}{x_i} < 20 \times 10^{-2} \times \frac{0{,}5}{9{,}5} + 0{,}23 \times 10^{-2} \times \frac{9}{9{,}5}$$

$$< (1{,}05 + 0{,}22) \times 10^{-2}$$

$$< 1{,}27 \times 10^{-2}$$

with a major contribution of

$$\frac{\Delta x_{ri}}{x_{ri}} = 20 \times 10^{-2}$$

COMMENT — It would thus appear that the utilization of the weighing method under vacuum is not a limit to the accuracy of the mixtures thus prepared. It is very obvious that the purity of the gases used, the skill used in the preparation of the cylinder and in the manipulations are the real limits to this process of preparing calibration gas mixtures.