

MOLAR MASS OF DRY AIR IN MASS METROLOGY

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ABSTRACT

Since 1980, the different national metrology institutes use the same procedure and formula for air density determination. The formula employed assumes some hypotheses on the composition of dry air and is expressed in terms of its molar mass and the four environmental parameters: air pressure, air temperature and concentrations of carbon dioxide and water vapour. In this formula (known as CIPM-1981/91) recommended by the Comité International des Poids et Mesures, the mole fraction of argon is fixed at 9.17×10^{-3} . This value is now questioned and new measurements involving different techniques, are of great interest.

This paper describes the experimental set-up used to evaluate the concentration of argon relative to that of nitrogen contained in air sampled from mass laboratory. The method uses a flexible capillary tube, maintained at constant temperature, for gas admission. With this system, air from different samples of atmospheric air is introduced into the vacuum chamber to be analysed. Preliminary measurements show that the value of p_{Ar}/p_{N_2} is closer to 1.196×10^{-2} , given in some publications, than the value of 1.174×10^{-2} , used in the current method for air density determination. In the future, comparison between argon and oxygen concentration will allow a more precise measurement with regard to the existing values.

1. INTRODUCTION

In metrology, an unknown mass is determined from a set of comparisons with a standard carried out in ambient air. Nevertheless, even if today, we are able to do such mass comparisons in vacuum, we must at a given time, for the transfer of the mass unit, to accomplish the weighing in air. Like that, for air buoyancy corrections, it is necessary to determine the density of air inside the balance enclosure during the weighting. The standard procedure for determining air density uses the so called CIPM-81/91 formula [1, 2]. For some years, alternative method have been reported by some groups [3, 4, 5, 6]. The systematic discrepancy observed between the values of air density determined by these two methods raise a controversy about the used composition of dry air for molar mass air calculation.

2. DENSITY OF MOIST AIR

2.1. CIPM- 81/91 formula : indirect method

The procedure, recommended by the Comité International des Poids et Mesures, is to calculate the air density by using an equation based on the non-ideal gas equation and for a composition of dry air derived from empirical observations [1]. This empirical formulation for the air density, assumes first, that the relative concentrations of nitrogen, argon and the sum of oxygen and carbon dioxide are constant and second, the concentration of water vapour in air displaces an equal concentration of dry air. With this method (indirect determination) one needs the mass molar of dry air and the measurement of the environmental parameters (temperature, pressure, molar fraction of carbon dioxide x_{CO_2} and water vapour x_{H_2O}). The value used for the mass molar M_a of dry air is calculated from the standard composition of air given in table 1. The other components, such He, Kr, Xe, H₂, CH₄, N₂O, and CO present at a level of trace make, for small fluctuations, an insignificant contribution to the change in the value of M_a .

Table I : Major constituent gases of dry air

Component	Nitrogen	Oxygen	Argon	Carbon dioxide	Neon
Content [% olume]	78,101	20,939	0,917	0,040	1,82x10 ⁻³

On these assumptions, the molar mass of air considered for the calculation of the density of air in the CIPM procedure is given by :

$$M_a = (28,9635 + 12,011(x_{CO_2} - 0,0004)) \times 10^{-3} \text{ kg.mol}^{-1}$$

In this case, the relative uncertainty on the air density is assigned by the limitation on the formula of ρ_a itself. The component of this uncertainty associated with the formula is of the order of 6×10^{-5} in comparison with the combined uncertainty which is about 8×10^{-5} . Improvements in this uncertainty, needs a direct determination of air density by others methods.

2.2 . Weighing method: direct determination

The method which seems to be attractive is based on the determination of air density from mass comparisons. This procedure uses the results of comparisons, made alternately in air and in vacuum, between artefacts of equal weight and surface area but with very different volumes [3]. In this case, it is necessary to have a mass difference, associated with air buoyancy, relatively large and an insignificant one for that induced by the adsorption and desorption processes.

The measured mass difference Δm_i between the two artefacts of volume V_{m_1} et V_{m_2} are:

$$\Delta m_{air} = \delta m_1 + \rho_a (V_{m_1} - V_{m_2}) \text{ for the measurement made in ambient air}$$

$$\Delta m_{vacuum} = \delta m_2 \text{ in vacuum.}$$

δm_1 and δm_2 are the difference between the apparent mass measured and ρ_a is the density of air inside the balance enclosure.

Here, the principal difficulty is to evaluate the loss in mass from the surface of the artefacts when the environment where they are put changes progressively from ambient air (at pressure of about 10^5 Pa) to vacuum (10^{-2} Pa). The change in mass can be expressed as :

$\Delta m_{vacuum} = \Delta m_{air} - \sigma \Delta S$, where ΔS is the difference between the surface areas of the artefacts and σ the desorption coefficient per unit surface. In this way, the air density is deduced from the relation:

$$\rho_a = (\delta m_2 - \delta m_1 + \sigma \Delta S) / (V_{m_1} - V_{m_2}).$$

With this method, the air density is determined with a relative uncertainty of about 7×10^{-6} . The principal component of this uncertainty is associated with the knowledge of the difference between the volumes of the artefacts.

The values obtained for air density with this direct method (using artefacts object) show a systematic discrepancy with respect to those resulting from the indirect method (CIPM formula) for an air characterised by a value of ρ_a in the range of $1,15 \text{ kg.m}^{-3}$. In their experiment, A.

Picard et al. [3] vary the value of air density from $1,15 \text{ kg.m}^{-3}$ to about $1,21 \text{ kg.m}^{-3}$ by changing the total pressure or the relative humidity of air inside the balance enclosure. For the long term, they observe a discrepancy of the order of $1,1 \times 10^{-4} \text{ kg.m}^{-3}$, between results obtained by the two methods. So, as the dispersion of the different results is relatively large, the results obtained by a group at the National Metrology Institute of Japan [4] and those of another one at the Physikalisch Technische Bundesanstalt [5] have the same tendency and are in an acceptable mutual agreement.

Table II : Discrepancies observed between the values of air density obtained with the two methods

Reference	[3]	[4]	[5]
$[\rho_a(\text{artefact}) - \rho_a(\text{CIPM})] \times 10^{-4} \text{ kg.m}^{-3}$	1,1	2,0	0,5

This observation is for the moment partially explained as the consequence of the value of the molar fraction of argon in dry air considered in the air density determination from CIPM- 81/91 formula. However, the behaviour of the artefacts depending on their environment (moist air, dry nitrogen or vacuum) worth further studies.

3. MOLAR MASS OF DRY AIR

In the literature, we can find some other values for the molar fraction of argon in atmospheric dry air [7, 8, 9]. These values are slightly greater than that given in table 1. The most frequently used one, at least by NIST, is 0,934 in % of volume. The molar mass of moist air for the determination of air density is then:

$$M_a = (28,9644 + 12,011(x_{CO_2} - 0,0004)) \times 10^{-3} \text{ kg m}^{-3}$$

The variation in air density, induced by the difference between the two values of molar fraction of argon x_{Ar} , calculated by using the indirect method is:

$$\rho_a(x_{Ar} = 0,934) - \rho_a(x_{Ar} = 0,917) = +0,8 \times 10^{-4} \text{ kg.m}^{-3}$$

This discrepancy is significant because the uncertainties on the determination of air density ρ_a are respectively of the order of 7×10^{-6} (direct method) and 8×10^{-5} (indirect method). In reality, the discrepancy observed is reduced by an appreciable factor if the second value for x_{Ar} is considered in the determination of ρ_a from the CIPM- 81/91 indirect method.

Then, the question about what value of molar fraction of argon in dry air must be considered to calculate the value for air density is a preoccupation in mass metrology. In order to have an idea about this, we have undertaken a study, using a mass spectrometry technique, to estimate the relative fraction of argon in air in comparison with nitrogen.

4. EXPERIMENT

4-1. Experimental apparatus

The essential component of the set-up is represented by an analysis chamber made from a non- magnetic stainless steel and equipped with a quadrupole mass spectrometer. The total pressure in the chamber (in the vicinity of the ionisation source) is measured with a capacitive gauge. The pumping group associate a diaphragm pump to a turbo molecular one. The residual

vacuum, after some days of pumping and baking the chamber around 200 °C, is about $1,0 \times 10^{-5}$ Pa. The working mass spectrometer parameters such as electron energy (ionisation source) and ion detection (electron multiplier voltage) are chosen and fixed so as to minimize fragmentation and multiple ionisation processes of the different species analysed (N_2 , O_2 , CO_2 , H_2O , Ar,). Actually, ionic currents (output signal) lie between 1×10^{-13} A (noise level) and 6×10^{-8} A (saturation).

This instrument was tested from mass discriminating effect during gas transfer from sample to the spectrometer housing, by using a gravimetrically prepared gas mixture of nitrogen and carbon dioxide. It allows us, at least in the case of N_2 and CO_2 to introduce reliably in the form of a constant flow a gas mixture from a sample at a pressure of about 10^5 Pa into the ionisation chamber maintained at a pressure of about 10^{-5} Pa [10]. We plan to observe the behaviour of the inlet system in the case of a gas mixture of nitrogen, oxygen and argon. Figure 1 shows a schematic diagram of the experimental set-up.

The inlet system employs a molecular flow gas (air) leak consisting of a flexible silica tubing (1,80 m long, 0,15 mm in inner diameter and 0,085 mm thick), a needle sapphire valve and differential pumping. During measurement, both the capillary and the valve are heated and their temperature is regulated around 100 °C.

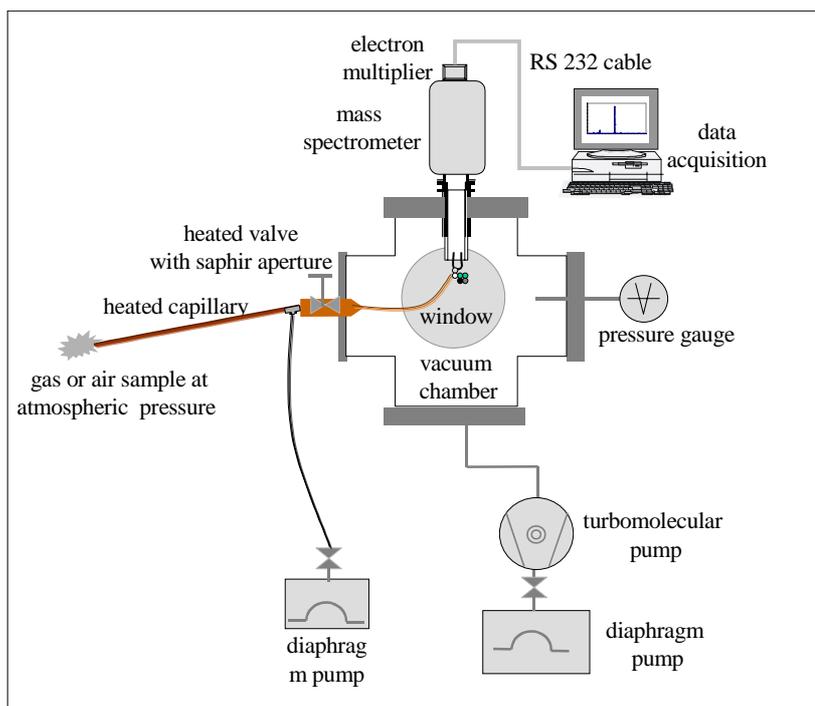


Figure 1 : Schematic view of the experimental set-up

4-2. Experimental method

The mass spectrometer apparatus has been tested and calibrated in order to know its response to a given pressure of a component (transfer, ionisation and detection) with a pure gas (N_2 , CO_2 and Ar). These gases are introduced separately in the ionisation source at different pressures $1,2 \times 10^{-5}$ and $8,0 \times 10^{-5}$ Pa. For a given flow corresponding to a pressure p in the chamber, mass spectra are taken every minute. The mean value for each ionic intensity peak is calculated. The

characteristic mass spectrum of residual vacuum is recording before and after each set of measurement. The mean mass spectrum is then subtracted from successive recordings.

The response curves $I_x^+(M) = f[P_P(M)]$ giving the ionic current associated with a mass x in terms of the partial pressure of the atomic or molecular species M yielding an ionic signal I_x^+ , are first obtained by a mean square root method applied to a set of experimental values. Figure 2 gives a picture of the mass spectrum, in arbitrary units, observed for each of the given species. For room air analysis, the partial pressure of nitrogen and argon are deduced from ionic currents intensity and the response curves obtained for nitrogen, carbon dioxide and argon.

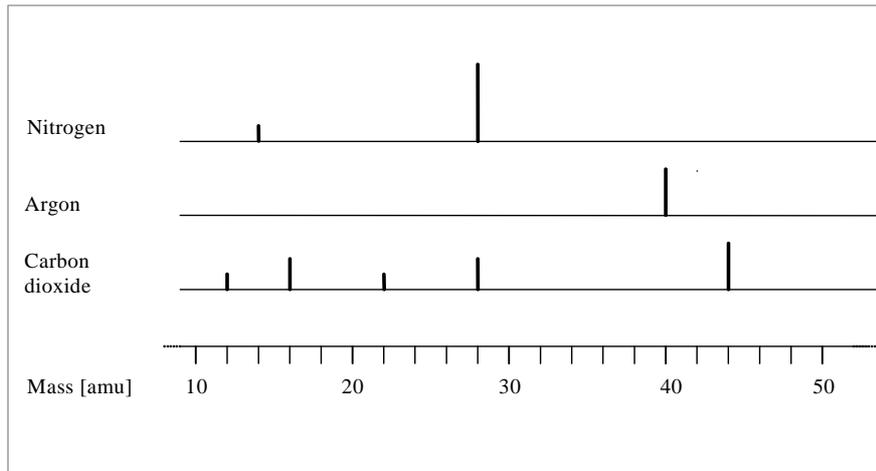


Figure 2 : Mass spectra observed with pure gas.

These partial pressures are expressed in terms of the intensities of ionic current observed for the masses 28, 40 and 44 amu:

$$P_P(Ar) = k I_{40}^+ \quad \text{and} \quad P_P(N_2) = k' (I_{28}^+ - r I_{44}^+)$$

k and k' are well defined from the calibration curves, of the mass spectrometer apparatus, obtained with pure gas.

$$I_{40}^+ = f(P_P(Ar)) \quad \text{and} \quad I_{28}^+ = f(P_P(N_2))$$

$r = I_{28}^+ / I_{44}^+ = 0,128 (0,002)$ represents the contribution of the carbon dioxide fragmentation by ionisation to the peak at mass-to-charge ratio 28.

5. RESULTS

5.1. Room air analysis

During admission of atmospheric air in the ionisation source, a manometer reads the change of the total gas pressure and mass spectrums are regularly recorded.. Figure 3 gives an example of typical mass spectrometric scan over mass positions between 1 and 50 amu, observed for air sampled from the manipulation room. The spectrum part between 50 and 100 amu, is not given because it was really flat. For all measurements, the total pressure inside the enclosure goes from about $9,8 \times 10^{-6}$ Pa (vacuum) to $5,0 \times 10^{-5}$ Pa (working air pressure).

The individual intensity associated to a given specie is obtained from mass spectrums stored about each minute when the valve between the vessel and the ionisation source is opened. The mean ions spectrum observed with residual gas (valve closed) respectively before and at the end of a set of measurement, is subtracted at every time.

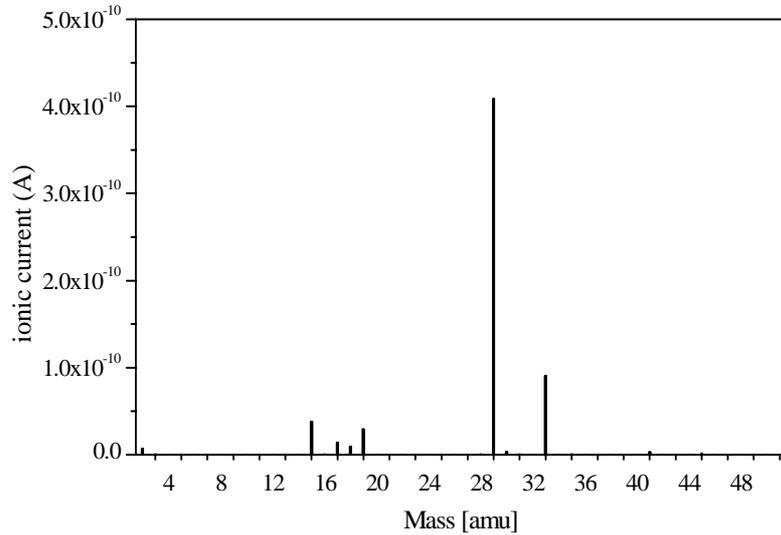


Figure 3a : Mass spectra for $P_{\text{air}} = 5,0 \times 10^{-5}$ Pa (experimental lab.)

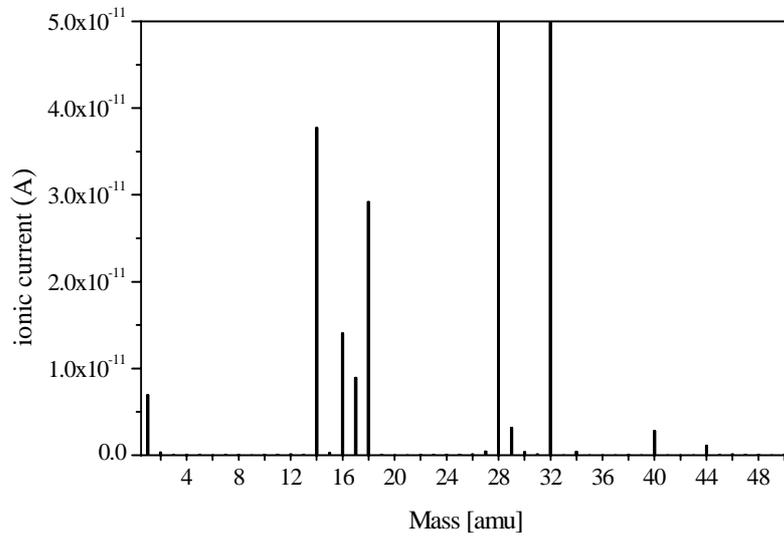


Figure 3b : Expanded view of figure 3a, showing the peak at $m=40$ a.m.u.

An other mass spectra, obtained with air sampled from the reading room of our institute are given in figure 4a and 4b.

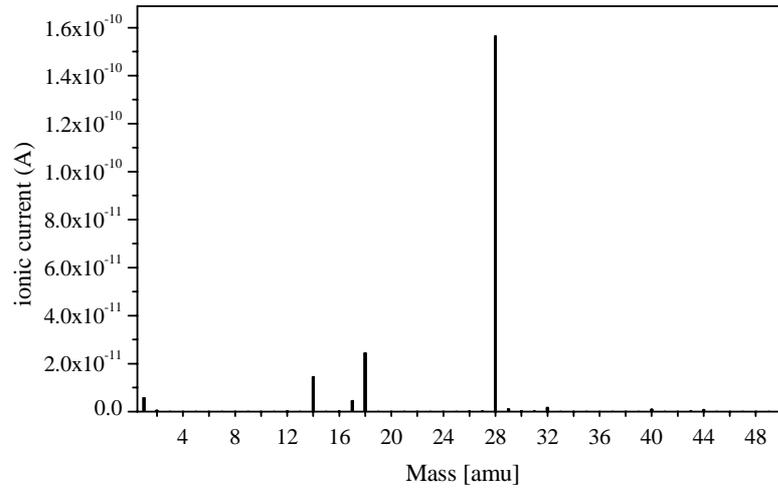


Figure 4a : Mass spectrum obtained with air at a pressure in the analysis chamber of $2,0 \times 10^{-5}$ Pa (sampled from the reading room)

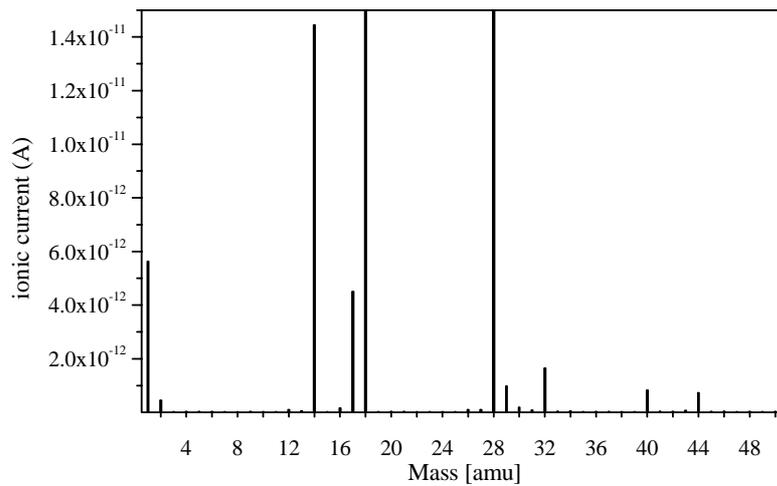


Figure 4b : Expanded view of the figure 3, showing the signal associated with argon

To determine the partial pressure of a given specie, we consider the ionic current intensity which is associated by calculating the mean value from the individual peak of about 20 spectrum. This method assumes that the intensity of a residual signal doesn't change if the different component, in the air sample introduced into the ionisation source, haven't a contribution to the considered peak.

5.2- Partial pressure of argon relative to nitrogen: $P_{P_{Ar}}/P_{P_{N_2}}$

The partial pressure of argon and nitrogen are deduced from the mean values of ionic current associated to these species and the calibration curves $I_x^+(M) = f[P_P(M)]$ of the instrument. Note that the ionic current I_{40}^+ at the mass-to-charge ratio 40 results completely from the

ionisation of argon $^{40}(Ar^+)$. Then the partial pressure of this specie is just a function of the signal intensity I_{40}^+ . In the case of nitrogen, the partial pressure is expressed as a function of the ionic currents I_{28}^+ and I_{44}^+ at the mass-to-ratios 28 and 44 because I_{28}^+ results from $^{28}(N_2)^+$ and fragmentation of $(CO_2)^+$. In each experimental measurement, the partial pressure are between $1,0 \times 10^{-7}$ and $1,5 \times 10^{-7}$ Pa for argon and around 1×10^{-5} Pa for nitrogen. The total pressure in the chamber is kept constant for each set of measurement and fixed to a value in the range $1,0 \times 10^{-5}$ Pa to 5×10^{-5} Pa. The results expressed in terms of partial pressure ratios, for two air sample, are represented by figure 5. The values of the ratio Pp_{Ar}/Pp_{N_2} , which are often mentioned in the literature are also indicated. The uncertainties on each value is expressed in term of one standard deviation and corresponds to the short term dispersion of about 20 measurement.

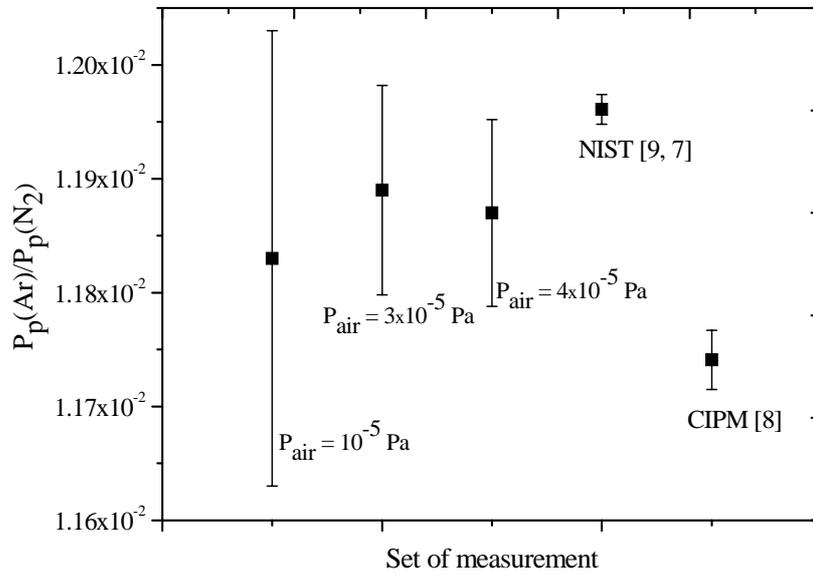


Figure 5 : Ratios of partial pressure of argon to that nitrogen contained in moist air.

We can note that the preliminary results are on the one hand, self-consistent between them and on the other hand, in agreement with the available values. The measurement of the fraction of argon in air relative to oxygen are in progress. To reduce the uncertainty on our measurement, we plan to improve the pressure measurement in order to work with smaller total pressure.

6. CONCLUSIONS

Using mass spectrometry technique with an adapted inlet gas system, we have measured the relative concentration of argon to that of nitrogen contained in different sample of moist air. In addition, despite the large uncertainty associated to the obtained ratios Pp_{Ar}/Pp_{N_2} , the mean value is more compatible with $1,196 \times 10^{-2}$ corresponding to a mole fraction of argon of about $9,34 \times 10^{-3}$. We hope that these results will be useful for further studies in the field of mass metrology relating to the molar mass of dry air.

Finally, new measurement involving different technique are of great interest in the progress towards a response to the raised question about the recommended CIPM's value of the mole fraction of argon present in dry air.

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