Density of moist air

The comparison of two mass standards in air generally requires a correction for air buoyancy which is the product of the air density and the volume difference between the two masses. The density of air at sea level is approximately \(1.2 \text{ kg} \cdot \text{m}^{-3}\). For the comparison of a stainless steel 1 kg mass standard against a 1 kg Pt/Ir prototype this correction is about 95 mg. However the precision of the comparison can be less than 0.001 mg (1 µg). Generally, the volumes of the masses at a reference temperature are known by hydrostatic weighing to a relative uncertainty of a few parts in \(10^6\). The relative combined standard uncertainty of air density is at best equal to \(7.5 \times 10^{-5}\) which implies an uncertainty of about 7 µg for the comparison between two mass standards. Thus the evaluation of the air density is a limitation on mass comparisons.

Two absolute methods and one relative (optical) were compared at the BIPM in order to improve the knowledge of the density of moist air:

- **CIPM 81/91 air density determination (absolute determination)**

  The most widely used method for determining air density is the application of the CIPM-81/91 formula recommended by the Comité International des Poids et Mesures in 1981 and modified slightly in 1991:

  \[
  \rho_a = \frac{pM_a}{ZRT} \left[ 1 - x_v \left(\frac{M_v}{M_a}\right) \right]
  \]

  where \(p\) is the pressure, \(T\) the thermodynamic temperature, \(x_v\) the mole fraction of water vapour, \(M_a\) the molar mass of dry air, \(M_v\) molar mass of water (18.015 \(\times 10^{-3}\) \text{ kg} \cdot \text{mol}^{-1}), \(Z\) the compressibility factor and \(R\) the molar gas constant (8.314510 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}). In practice, the mole fraction of water vapour \(x_v\) in moist air is not measured directly but is determined from the relative humidity \(h\) or from the temperature \(t_d\) of the dew point. The quantity \(M_a\) depends weakly on the mole fraction of carbon dioxide.

  The uncertainty on the air density determination when using the CIPM formula comes mainly from the formula itself and from the type B uncertainty of dew-point measurements. The relative combined standard uncertainty obtained is \(7.5 \times 10^{-5}\), which is difficult to reduce.
- **Air buoyancy artefacts method (absolute determination)**

The method is based on the weighing of two artefacts having the same nominal mass and the same surface area but with very different volumes. Two weighings are necessary to determine the air density \( \rho_a \), one in air and one in vacuum:

\[
\rho_a = \frac{\Delta m_{\text{vacuum}} - \Delta m_{\text{air}}}{\Delta V}
\]

where \( \Delta m_{\text{vacuum}} \) and \( \Delta m_{\text{air}} \) represent respectively the apparent mass difference between the two masses in vacuum and in air and \( \Delta V \) is their volume difference. Surface adsorption and water desorption of water vapour are negligible because the adsorption coefficient of water vapour and surface area difference between two artefacts are very small.

Two 1 kg stainless-steel artefacts were polished and the masses were adjusted at the BIPM. Designated Cc (hollow cylinder) and Cp (solid cylinder), these masses have the same nominal surface area (194 cm\(^2\)) but the volumes are quite different (\( V_{\text{Cc}} = 207 \text{ cm}^3 \) and \( V_{\text{Cp}} = 124 \text{ cm}^3 \)). The relative combined standard uncertainty of air density obtained at the BIPM for the air buoyancy artefacts is \( 7 \times 10^{-6} \).

- **Refractometry method (relative determination)**

Changes in air density can be determined with high precision using an optical method based on the strong correlation between air density and air index of refraction. Specifically, the relation between \( \rho_a \), the density of air, and \( n \), the refractive index of air is:
where the ratio \( R' \) is called the specific refraction or the refractional invariant. A heterodyne refractometer, similar to one in use at the BNM/INM-CNAM, was developed at the BIPM. The air index of refraction is determined in real time by an optical beat-frequency measurement.

We have compared experimentally the three methods for air density determinations inside the air-tight enclosure of our FB2 balance, which is equipped with accurate instruments for air parameter measurements. The heart of the refractometer, a double Fabry-Perot interferometer, is placed inside the balance. The following figure shows the evolution of air density by means of three methods during a series of weighings. The variation of the air density was determined with a satisfactory coherence among the three methods, within \( 4 \times 10^{-6} \) kg\cdot m\(^{-3} \). This indicates that, in the short term, the responses of each method to small changes are essentially equivalent. Nevertheless, for the long term, a discrepancy varying from \( 5 \times 10^{-5} \) kg\cdot m\(^{-3} \) to \( 3 \times 10^{-4} \) kg\cdot m\(^{-3} \) was observed between the two absolute determinations [1, 2]. To clarify this discrepancy, a comparison between 1 kg stainless steel mass against 1 kg Pt-Ir mass standard has been made in air, in vacuum and in dry nitrogen. A good agreement of 1 µg between vacuum and dry nitrogen measurements was obtained.
We believe that this work demonstrates the validity of the air buoyancy artefacts method. The use of air buoyancy artefacts could improve significantly the air density determination. Nevertheless, this method requires measurements in vacuum to monitor the evolution of the mass artefacts as a function of time. The optical method could be used, in combination with one of the absolute methods, to follow with very high sensitivity the small changes in air density inside a balance case during a weighing.
