

Water Vapour Effects in Mass Measurement

N. Khélifa

Laboratoire National d'Essais, Institut National de Métrologie, Conservatoire National des Arts et Métiers 61,
rue du Landy, 93210, La Plaine Saint-Denis, France
Email: khelifa@cnam.fr

Water vapour density inside the mass comparator enclosure is a critical parameter whose fluctuations during mass weighing can lead to errors in the determination of an unknown mass. To monitor them, a method using DFB laser diode in the near infrared has been proposed and tested. Preliminary results of our observation of water vapour sorption and de-sorption processes from the walls and the mass standard are reported.

Keywords: mass metrology, air density, water vapour in air, sorption, de-sorption

1. INTRODUCTION

WATER VAPOUR contained in ambient air influences measurement in many fields of science. In mass metrology, it is necessary to evaluate correctly air moisture and its changes during mass comparisons. In practice, the air density [kgm⁻³] is deduced by using the so-called "CIPM-1981/91 formula" for the determination of air density [1], [2] with the measured parameters of ambient air.

$$\rho_{air} = \frac{p M_a}{Z R T} \left[1 - x_v \left(1 - \frac{M_v}{M_a} \right) \right] + \varepsilon_f \quad (1)$$

In this formula, M_a and M_v are the molar masses [kg mol⁻¹] of dry air and water respectively, Z the compressibility factor, R the ideal gas constant [J mol⁻¹K⁻¹], p the atmospheric pressure [Pa], T the thermodynamic temperature [K], x_v the molar fraction of water vapour and $\varepsilon_f = \pm 0.7 \times 10^{-4}$ kg m⁻³ the fitting error of the formula.

The combined relative standard uncertainty of air density, for normal atmospheric conditions, is at the level of 1×10^{-4} kgm⁻³, when uncertainties for p , T , M_a and x_v are included [2]. Recently, the determination of air density from the results of comparisons of special artefacts in ambient air and in vacuum has shown a significant difference compared with the value evaluated by the classical method (CIPM- 1981/91 formula). This discrepancy is of the order of the fitting error of the CIPM formula, *i.e.* 0.7×10^{-4} kg m⁻³ [3], [4]. This observation implies further studies are needed, particularly concerning the existing air density gradients inside the mass comparator chamber. In fact, adsorption and de-sorption processes of water vapour and hydrocarbon molecules by the mass standards and the walls of the chamber during the weighing procedure can induce fluctuations and inhomogeneities of air inside the enclosure. Then, when weights made from different

alloys are compared, the amounts of adsorbed air molecules onto the surface of weight are not the same.

2. AIR MOISTURE MEASUREMENT

In practice, the molar fraction x_v of water vapour is calculated from the measured value of the dew point temperature t_d or the relative humidity H_R by using the formula:

$$x_v = f(p, t_d) \frac{p_{sv}(t_d)}{p} = H_R f(p, t) \frac{p_{sv}(t)}{p}, \quad (2)$$

where $p_{sv}(t)$ is the water vapour pressure at saturation, $f(p, t)$ the enhancement factor and t the temperature in °C.

The contributions to global uncertainty on the molar fraction of water vapour, resulting from the saturation water vapour pressure and enhancement factor, are generally neglected [5]. However, uncertainties assigned to these parameters are temperature and pressure dependent, so one must be careful and require a close consideration of how the propagation of uncertainties in equation (2) is expressed [6].

In order to minimize air perturbations inside the chamber of the mass balance, the temperature of the dew point is generally measured only a long time before the start and at the end of a succession of weighing. During mass comparisons, which take several hours, a capacitive hygrometer is sometimes used to evaluate the drift in air humidity. Here we use an alternative method based on molecular absorption in the

near infrared, developed with the intention of following small changes in water vapour content. The associated near-infrared diode laser device has been described in previous reports [7],

[8]. Here, we use this sensor to confirm the indiscrete behaviour of the dew-point hygrometer and to observe water vapour adsorption and de-sorption from surfaces.

A schematic diagram and a general view of the experimental setup are represented in Figures 1 and 2. The apparatus consists of a vacuum housing equipped with some sensors and connected to a turbomolecular pump and oil-free backing pump. The working range of air pressure is between 1 Pa and one standard atmosphere (10^5 Pa). The pressure inside the enclosure (vacuum pump shut off) rises from 1 to 1800 Pa in about 2 hours

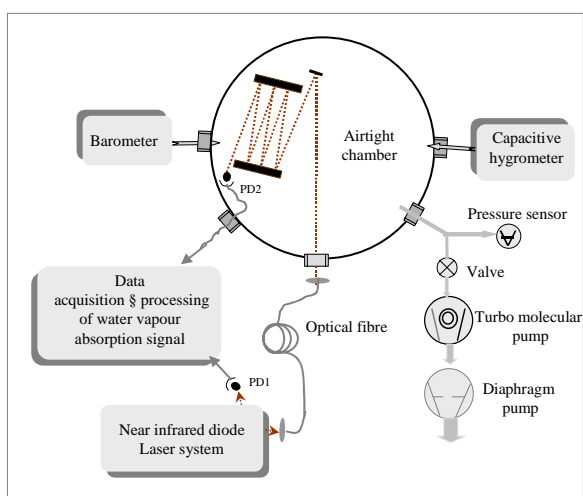


Fig. 1 Schematic diagram of experiment

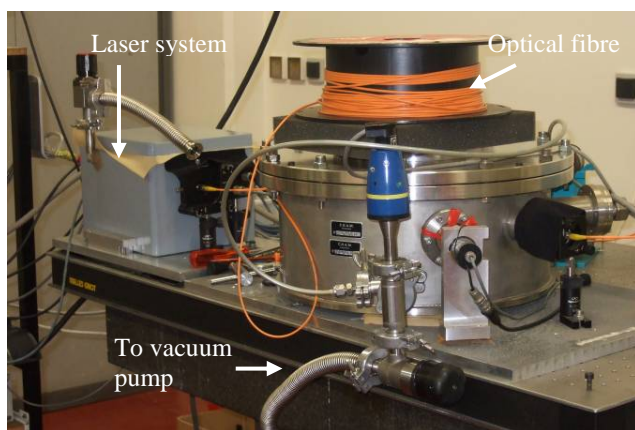


Fig. 2 General view of the set-up at LNE- INM for water vapour monitoring

In our analysis, the water vapour absorption was converted into partial pressure. For this operation, the absorption signal was normalised to the mean value of relative humidity measured with a calibrated capacitive hygrometer at the start of measurement.

As reported previously, this experiment demonstrates that the perturbation of air moisture, induced by the dew-point hygrometer operation, can be sensed in a real time. The signal to noise ratio allows detection, in a single sweep of the 1392.53 nm absorption line, down to 2 Pa in terms of partial pressure of water vapour for normal air conditions. Figure 3 shows the recording of the water vapor inside the enclosure, for different environmental conditions, observed over the course of time. The air environmental parameters are:

$p = 101532$ Pa, $t = 21.30$ °C and 52.8 % H_R for respectively, pressure, temperature and relative humidity of moist air.

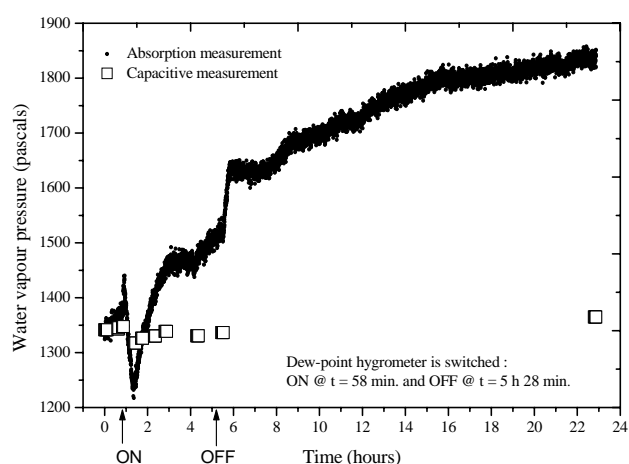


Fig. 3 Evolution of relative humidity within total air pressure inside the mass comparator housing

The results observed from a great number of repeated water vapour recordings show clearly the perturbations of the water vapour density in the chamber, when the dew-point hygrometer is switched ON or OFF. We can also notice from Figure 3 the advantage of the optical device compared to the capacitive one in terms of sensitivity and response time.

With this “home made” optical hygrometer, air moisture is monitored as air is progressively evacuated from the housing.

A. Evolution of water vapour and the air pressure inside the enclosure.

The changes of water vapour, when the total pressure of moist air inside the chamber is diminished progressively, from 1.03×10^5 to 0.8×10^5 Pa (tuning range of the barometer) by pumping, are given in Figure 4. As one can see, below the air pressure of about 0.82×10^5 Pa, the water vapour content is weakly affected. Finally, to take advantage of this apparatus, we tried to observe the water vapour de-sorption from the enclosure wall. To do that, the enclosure was evacuated from its air before it was isolated from the pumping system.

B. Water vapour pressure as a function of air pressure into the chamber

The evolution of water vapour pressure was then monitored as a function of the total air pressure in the enclosure. The result obtained, when the air pressure increased from about 600 Pa (poor vacuum) to 87150 Pa, is illustrated by Figure 5. We notice a significant decrease of water vapour content, induced by a combination of the sorption and de-sorption processes of the wall. The initial sorption and de-sorption processes within the vacuum are masked by the overall leak.

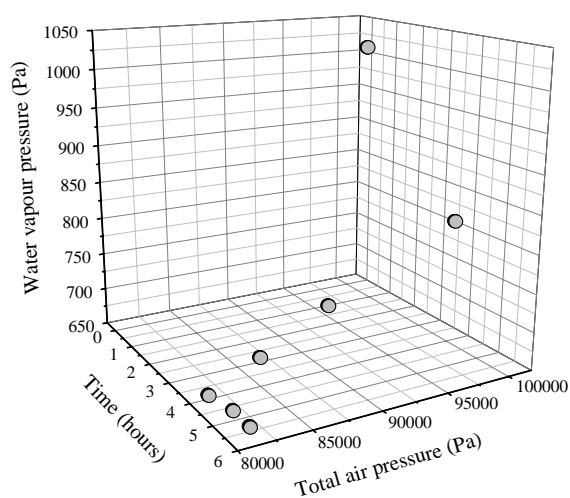


Fig. 4 Variation of water vapour pressure as a function of air pressure into the chamber

3. CONCLUSION

In mass vacuum comparisons, a supplementary correction must be made to allow for sorption processes. The amount of adsorbed mass per surface area depends on the mass standard (e.g. material allow, surface roughness). In fact, it is now acknowledged that a monolayer of adsorbed water vapour on the surface of a stainless steel kilogram standard corresponds to a mass variation of about 2 μg . In mass weighing, the effects of buoyancy in the air and the adsorption of air molecules onto the surface of weight need to be considered.

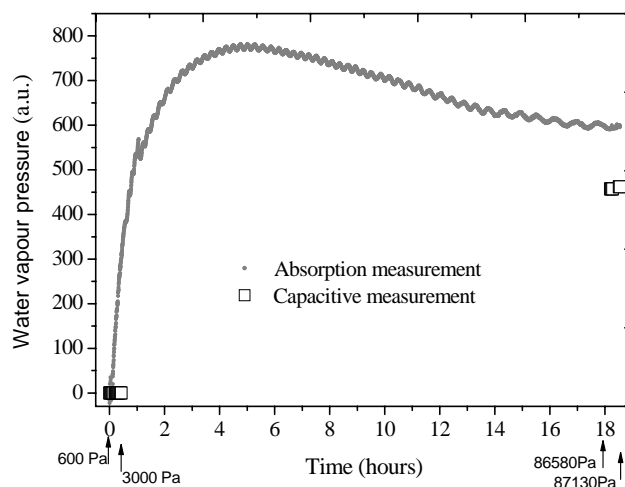


Fig. 5 Evolution of water vapour inside the enclosure initially under primary vacuum

REFERENCES

- [1] Giacomo, P. (1982). Equation for the determination of density of moist air (1981), *Metrologia*. 18, 33-40.
- [2] Davis, R.S. (1992). Equation for the determination of the density of moist air (1981/91), *Metrologia*. 29, 67-70.
- [3] Picard, A., Fang, H. (2004). Mass comparisons using air buoyancy artefacts. *Metrologia*. 41, 330-332.
- [4] Chung, J. W., Chang, K. H., Lee, W. G., Kim, K. P. (2002). Air density determination using 1 kg buoyancy mass comparisons. In Proceedings of IMEKO (273-277). Celle, Germany.
- [5] Hyland, R.W., Wexler, A. (1983). Formulations for the thermodynamic properties of the saturated phases of H_2O from 173,15 °K to 473,15 °K. *ASHRAE Trans.* 89, Part IIA, 500-535.
- [6] Lovell-Smith, J.W. (2006). On correlation in the water vapour pressure formulations. *Metrologia* 43, 556-560
- [7] Khélifa, N. (2005). Air Moisture Measurement: The Indiscreteness of the Dew-Point hygrometer. In Proceedings of the 19th International Metrology Symposium (83-86). Opatija, Croatia.
- [8] Khélifa, N., Guellati, S., Kerviel, P., Lecollinet, M. (2006). Capteur Optique pour le Contrôle de l'humidité de l'Air en Métrologie des Masses. *Physical Chemistry News* 28, 85-89.