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Mass determination of 1 kg silicon spheres for Avogadro project

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Abstract

Our work concerns the mass determination of 1 kg silicon spheres in the framework of the international Avogadro project with a view to an improved definition of the kilogram. It has been shown that the original method developed by the BIPM will attain reach the uncertainty target requested by the Avogadro group. New investigations have been initiated at the BIPM using a well adapted mass comparator and more appropriate sorption transfer masses. Preliminary measurements carried out on several 1 kg silicon spheres having a natural-oxide surface are presented.

Key words: Mass comparison, Avogadro, balance, water vapour sorption

1. Introduction

To contribute to a redefinition of the kilogram, the Avogadro project uses the x-ray crystal density method, making use of an almost perfect 1 kg silicon single crystal sphere [1].This project is a world-wide collaboration among many laboratories, and is coordinated by the Working Group on the Avogadro constant of the CCM (Consultative Committee for Mass and Related Quantities). The BIPM is the coordinator of the mass determination of silicon spheres. To achieve the relative uncertainty target for the value of the Avogadro constant, 2 × 10-8, requires a mass determination to an accuracy of 4 µg for a 1 kg silicon sphere. It seems difficult to achieve this level of accuracy by classical comparisons in air. A novel method has been developed and validated at the BIPM to reach the target [2]. In order to confirm and extend the previous results and to better evaluate the physical and chemical water sorption on silicon sphere surfaces, a broad work plan has been initiated at the BIPM this year. Measurements were carried out using a new Sartorius CCL 1007 mass comparator, well adapted to weigh 1 kg silicon spheres, and improved sorption artefacts in Pt/Ir having larger surface area difference. We present here the preliminary results obtained on several silicon spheres.

2. Mass determination of 1 kg silicon spheres

The Avogadro constant N_A forms the link between macroscopic and atomic mass scales and is based on the number of entities per mole of any substance. In order to circumvent the difficulty of directly counting a large number with a small uncertainty, the Avogadro project uses the x-ray crystal density (XRCD) molar mass method making use of an almost perfect silicon single crystal [1]. In practice, the crystal is a 1 kg sphere and the N_A is determined by the following equation:

$$N_\mathrm{A} = \frac{M_\mathrm{Si}}{m} \cdot \frac{V}{(\alpha^3/8)} \qquad (1)$$

where M_{Si} represents the mean molar mass of the silicon, α the lattice spacing parameter of the nearly perfect silicon crystal, *V* the volume of the crystal and *m* its mass. The Avogadro constant evaluation requires the mass of the core of the silicon sphere, excluding other substances covering its surface:

$$m_\mathrm{sphere} = m_\mathrm{meas} - m_\mathrm{oxide} - m_\mathrm{ads} \qquad (2)$$

Where m_{meas} represents the total mass of the sphere determined by mass comparison with respect to a 1kg Pt/Ir mass standard, m_{oxide} the mass of silicon oxide on the surface of the sphere and m_{ads} the mass of hydrocarbon contamination and water vapour adsorbed on the surface of the sphere. The mass of silicon oxide is deduced from its thickness evaluated using XPS measurements carried out in other laboratories involved in the Avogadro project. The contamination can be easily removed by using a well defined washing protocol proposed by the NMIA. The effectiveness of this method has already been demonstrated. The mass of adsorbed water vapour contains two components: the reversible physical sorption, which is removed by placing the sphere in vacuum, and the irreversible chemical sorption, which can only be removed by baking under vacuum or in a neutral dry gas.

The classical way to determine the mass of the silicon sphere is by mass comparison in air against a 1 kg Pt/Ir mass standard by taking into account both air buoyancy and reversible water sorption corrections. The air buoyancy correction is the product of the density of the ambient air and the volume difference between the two masses. It is as large as 460 mg for comparison between a silicon sphere and a Pt/Ir mass standard and its knowledge is limited by the uncertainty on air density determination [3]. Air density can be determined by means of two methods: the commonly used CIPM formula requiring a number of input parameters and a gravimetric method based on two buoyancy artefacts having the same nominal mass and surface area but very large volume difference. Reversible water vapour adsorption on the silicon surface is evaluated by gravimetric measurements using two sorption artefacts having the same nominal mass, the same volume, but very large surface-area difference. The ellipsometric method can also be employed, and we have used this method as well [4]. Large discrepancies among silicon samples were observed in the results obtained by several laboratories [5, 6]. It is thus difficult to achieve an uncertainty less than 10 µg on the mass determination by classical mass comparison in air due to uncertainties of both air buoyancy and reversible water sorption corrections.

In order to circumvent the main uncertainties in the classical mass comparison method, a novel method has been proposed and developed at the BIPM [2] to reach the uncertainty target of 4 µg required by the Avogadro group. The silicon sphere is weighed under vacuum and a set of two 1 kg sorption artefacts weighed under vacuum and in air is employed as transfer masses. The pair consists of a classical cylindrical mass standard and a special artefact. Such a set of artefacts should have the same volume and nominal mass but a large surface area difference. Mass comparison of the classical cylinder against a 1 kg Pt/Ir mass standard in air and against the silicon sphere under vacuum directly links the silicon mass under vacuum to a national prototype in air for example). The change in mass (desorption) of the transfer standard (classical cylinder) from air to vacuum is obtained by applying reversible water vapour sorption correction on its surface. The correction is directly deduced from the mass change from air to vacuum between the transfer standard and the special sorption artefact. Uncertainty due to this correction is reduced compared to the classical method of comparisons in air because the sorption correction is applied on a 1 kg Pt/Ir mass which has a surface area much smaller than a 1 kg silicon sphere. Moreover, air buoyancy corrections applied during all the chain of comparisons are practically negligible and consequently their uncertainties no longer limit the accuracy of mass determination.

3. Equipment and procedure

A new Sartorius CCL 1007 comparator was used for mass comparisons in air and under vacuum. This 1 kg mass comparator is designed to accommodate Pt/Ir as well as silicon spheres and to compare up to eight 1 kg masses. The balance is equipped with instruments to measure the required parameters for air density determination using the CIPM formula (a dew-point gauge, a pressure gauge, a CO_2 gas analyser, a 25 Ω platinum resistance thermometer and associated resistance bridge) and several thermocouples to measure air temperature gradients inside the balance case. A vacuum lower than 0.01 Pa can be achieved inside the balance case using a 100 % oil-free pumping system.

Air density inside the balance case was also determined using two stainless steel buoyancy artefact. One is a hollow cylinder (207 cm^3) and the other has a tube shape (124 cm^3). The two artefacts have the same nominal surface area (194 cm^2). They occupied two of the eight positions of the mass comparator. Two other positions were dedicated to the pair of sorption artefacts in Pt/Ir used as transfer masses. One is a classical prototype (cylindrical form with height and diameter equal to 39 mm). The special artefact is made in form of a stack of eight discs separated from one another by three bent Pt/Ir rods. The difference in surface area between two artefacts is large, 186 cm^2, thus providing good sensitivity to water sorption effects.

In total, four silicon spheres have been investigated. Two silicon spheres (with natural oxide layer) obtained from the Okamoto Co., Japan, named S1 and S2, were employed. The first one is always maintained in air and used as a reference whilst the second is weighed in air as well as under vacuum. A third silicon sphere named NMIJ-CZ, kindly lent by the NMIJ/AIST, was weighed in air and under vacuum to investigate water sorption effects; first on natural oxide and afterwards on a well controlled thermal oxide layer of 5 nm (thermal oxide deposit kindly performed by the Institute for Microelectronics Stuttgart, Germany). Weighings using the new balance were also carried out on a forth silicon sphere, AVO#3, used in the previous international mass comparison and which had been weighed at the BIPM using the FB2 balance, in order to confirm the previous results.

For all silicon spheres, measurements were first carried out in air followed by successive measurements in vacuum and air. Two sets of measurements were also made in an atmosphere of dry nitrogen. From time to time, the transfer standard (classical cylinder of the set of sorption artefacts) was compared in air against our 1 kg working standard, No.77.

4. Results

For mass determinations in air and dry nitrogen, the buoyancy corrections due to the volume difference between the artefacts were calculated from gas densities determined by buoyancy artefacts method. We note that the ambient air inside the weighing room, recently renovated, is slightly contaminated by volatile organic chemicals (VOCs) so that densities deduced from the CIPM formula were not used. Investigations are ongoing to find the origin of contamination. The volumes of the masses were known with a relative combined standard uncertainty less than 2 x 10^{-7} and 1 x 10^{-5} for all silicon spheres and Pt/Ir artefacts, respectively. The correction for the reversible adsorption of water vapour on the surface of silicon spheres (275 cm2) was made using the results obtained in a previous study [4]. The deduced mass of adsorbed water vapour on the surface of silicon sphere is about 8.2 µg, corresponding to an adsorption coefficient of 30 ng/cm^2.

For measurements under vacuum, the change in mass of the transfer standard (classical cylinder) between air and vacuum was corrected to deduce the mass of silicon spheres under vacuum.

4.1. Pt/Ir 1 kg sorption artefacts (transfer masses)

In total, nine sets of weighings under vacuum and ten in air were realized during a period of four months. Each set of measurements contains more than five series of weighings, and in general takes ten hours. The difference in masse between the two artefacts weighed in air and under vacuum (or in dry nitrogen) is used to deduce the physical sorption coefficient between vacuum (or dry nitrogen) and air of approximately 50 % relative humidity.

We obtained the same sorption coefficient of 40(10) ng/cm^2 with a good reproducibility for both air-vacuum and air-dry nitrogen determinations. Thus the two sorption artefacts are well behaved and are well adapted for physical water sorption evaluation. We note that the value of 40 ng/cm^2 is consistent with the results obtained in the previous study taken at the BIPM [4].

4.2. Mass determination of 1 kg silicon spheres

The masses of silicon spheres $m_{Si\text{-}a}$ determined by classical mass comparison in air are compared to those obtained $m_{Si\text{-}v}$ using the new BIPM method under vacuum. Preliminary results show the following differences in mass of silicon spheres weighed in air and under vacuum:

NMIJ-CZ	$m_{Si\text{-}a} - m_{Si\text{-}v} < 1$ µg
S2	$m_{Si\text{-}a} - m_{Si\text{-}v} = 19$ µg
AVO#3	$m_{Si\text{-}a} - m_{Si\text{-}v} = 19$ µg.

The combined standard uncertainty of the mass determination of each of the three silicon spheres in air and under vacuum was around 24 µg and 9 µg, respectively. The uncertainty in air came mainly from an unexpected position effect of the balance, which influences the air density determination using artefacts as well as the mass comparisons themselves. Another important source of uncertainty was the instability of weighings in air, probably due to the thermal gradient and air convection inside the mass comparator.

5. Discussions and conclusions

We recall that the difference in mass between air and vacuum determination should be null if the real water vapour adsorption coefficient corresponds to that we applied (30 ng.cm^{-2}). It is the case for the NMIJ-CZ sphere which confirms the expected adsorption amount of water vapour on silicon samples. For S2 and AVO#3 spheres, the difference observed was 19 µg which can be explained by larger sorption effects on their surfaces than those evaluated in our previous study. The difference of 19 µg corresponds to a desorption coefficient of 100 ng.cm^{-2}, which is more than three times larger than the value anticipated. Nevertheless, we point out that the differences among NMIJ-CZ, S2 and AVO#3 are within the large uncertainty of the mass determination in air and under vacuum.

Efforts are ongoing to get a better knowledge on the position effect of mass comparator and reduce the undesirable thermal gradient inside the balance enclosure. We have recently received the NMIJ-CZ sphere after a well-controlled thermal oxide was deposited. Measurements are being repeated to investigate water sorption effect on the new oxide layer.

A study of irreversible chemical water vapour sorption effects which were not taken into account up to now is planned. This work requires backing the silicon spheres under vacuum or dry neutral gas at about 500 °C in order to remove the water vapour adsorbed with a stronger molecular bonding. To carry out his task, we are developing a system to transfer masses from the oven in inert gas to the mass comparator under vacuum.

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