

CLEANING OF SILICON DENSITY STANDARDS

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Abstract – The cleaning of silicon density standards was investigated by mass comparison measurements. It was shown that even in clean laboratory air, the mass of silicon spheres increases considerably with time. On the other hand, after cleaning the sphere, mass stabilizes within only 8 hours and always yields the same mass within 10 µg. This is also true after using the spheres in liquids, e. g., for hydrostatic weighing. Additionally, an infrared absorption technique was used to identify hydrocarbons on silicon spheres and to estimate the layer thickness. A calibration of this method was possible with a mass determination of a paraffine layer deposited on a silicon sphere.

Keywords: Cleaning, silicon density standard, mass comparison, carbonaceous layer, infrared absorption.

1. INTRODUCTION

Nowadays, mainly silicon spheres are used as high-precision density standards. With spheres of about 1 kg, density uncertainties of less than 0.1 ppm have been reached [1]. Since the density standards are weighed in liquids like pentadecane during hydrostatic weighing, they have to be cleaned after the measurements. A simple check of the cleanness could be performed by mass determination, but the low density of silicon and the large volume of the spheres make it difficult to monitor the mass of the density standards by comparison to stainless steel weights. More accurate mass checks can be performed in comparison to a second silicon sphere of nearly the same mass and volume. For this purpose, a mass comparison apparatus was set up at the PTB WG “Density of Solids” [2, 3] that can compare the masses of 1 kg silicon spheres with an uncertainty below 10 µg. Similarly, the mass uptake of a silicon sphere during a long-term exposure to the laboratory air can be measured with mass comparisons. Such a mass increase can be caused by hydrocarbons from the air that adhere to the surface of the sphere. Since silicon is nearly transparent for infrared radiation, hydrocarbons on silicon spheres can also be measured by infrared absorption spectroscopy. The use of this method was developed in the PTB WG “Inorganic Analysis” in order to check the success of the cleaning procedures of silicon spheres. It was calibrated by mass measurements.

The mass increase due to atmospheric hydrocarbons is very important for mass standards made of silicon, in particular if the unit of mass, the kilogram, is re-defined by the Avogadro constant.

2. MASS COMPARISON APPARATUS

The mass comparisons are performed with a Mettler balance AT1006 having a maximum capacity of 1319 g and a resolution of 1 µg [2, 3], see Fig. 1. The electrical weighing range is 10 g. The balance is housed in a double-walled stainless steel bell, that is cooled with thermostatted water to a temperature of 20.0 °C. The base plate of the bell is also cooled by the same water. The closed bell is air-tight and, for the measurements, the air pressure is always adjusted to about 1013 hPa.



Fig. 1. Mass comparison apparatus used to check the cleaning of silicon density standards.

The temperature field in the sample area is measured with seven thermocouples in comparison to the temperature of a copper block, the temperature of which is determined with a standard platinum resistance thermometer. Near the samples, the temperature differences are below 10 mK and the temperature drift during the measurements is below 5 mK/h.

The measurements are performed fully automatically with a fixed timing of the weighing procedure. A complete ABBA cycle takes 60 min and the repeatability within a measurement series (i. e. the standard deviation of the mass differences of the ABBA cycles) is usually less than 1 μg . The spheres rest on special steel rings, thus allowing a perfect positioning of the samples. After closing the bell, a waiting time of 8 hours ensures the complete temperature equilibrium of samples and apparatus.

The apparatus is not only used for cleaning checks but also for the new method of hydrostatic density determination [1, 3]. In this method, the (apparent) weight of the sample is compared to the weight of the density standards not only in liquid but also in air. Thus, the density standards are also used for the mass determination of the sample instead of stainless steel mass standards. With this method the densities of the sample and standards can be compared with uncertainties of 0.05 ppm or less. Here, one precondition is again that the density standards are perfectly clean.

3. GRAVIMETRIC MEASUREMENTS

Monitoring the mass of silicon density standards over long periods of time is difficult, since mass comparisons to the usual mass standards of stainless steel have a large uncertainty due to the large volume difference. Additionally, all mass standards may also be drifting in mass. Therefore, the following procedures were used to investigate the cleanness of silicon density standards.

1) After a long exposure to the atmosphere, the silicon sphere is compared to another silicon sphere just before and right after the cleaning. The mass decrease is the amount of "dirt" that is washed off.

2) Mass comparisons to another silicon sphere before and after the use in a hydrostatic weighing or flotation apparatus prove the effectiveness of the cleaning procedure.

The following cleaning procedure was used: After the measurements in some liquids, the spheres are wiped off, then pre-cleaned with benzine and finally bathed in pure ethanol. Other similar cleaning procedures can be found in [4].

3.1. Mass uptake from the atmosphere

For the determination of the contamination of the sphere surface by the atmosphere, the sphere is first cleaned thoroughly and then exposed to the usual laboratory air for a long time. After the exposure, its mass is compared to the mass of another sphere before and after a new cleaning. Fig. 2 gives an example of when the spheres Si1PTB and Si2PTB were cleaned on 15 September 2006, then compared with each other on different occasions during 9 months, showing a constant mass difference of 1.550071 g with a standard deviation of 1.4 μg . Then, first the sphere Si2PTB

was cleaned which yielded a change of the mass difference of 16 μg due to the removal of the contamination. When also the sphere Si1PTB was cleaned, the mass difference was again 1.550071 g. Thus, both spheres showed a mass decrease of 16 μg through the cleaning and consequently an increase of 16 μg within 9 months.

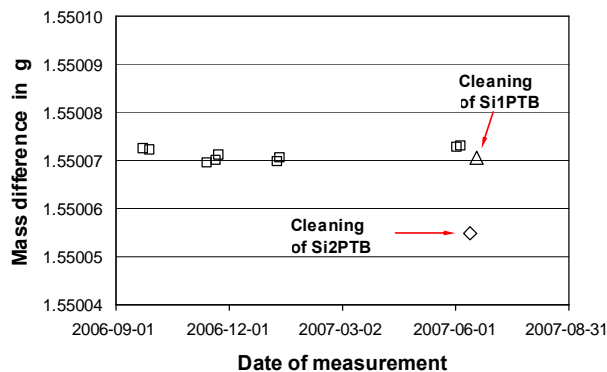


Fig. 2. Changes of the mass difference of the silicon spheres Si1PTB and Si2PTB by cleaning after a 9 month long exposure to air.

3.2. Reproducibility of mass after immersion in liquid

The spheres Si1PTB and Si2PTB are usually used for density comparisons by hydrostatic weighing and flotation methods. During the measurements, the spheres are immersed in different liquids: pentadecane for hydrostatic weighing and a mixture of dibromoethane and tribromopropane for flotation experiments [5]. After the density measurements, the spheres are cleaned. Mass comparisons with the silicon sphere Si7PTB that is used as a mass standard allows us to check whether the cleaning was successful. Figure 3 shows mass differences of Si7PTB to the sphere Si1PTB which were measured after such cleanings (indicated by the vertical lines). The values drift by 10(4) μg per year due to the mass uptake of Si7PTB. (This value agrees with the value of 12(6) μg per year determined from absolute mass calibrations of Si7PTB.) The measured values differ less than 10 μg from the drift line; the standard deviation is 6 μg .

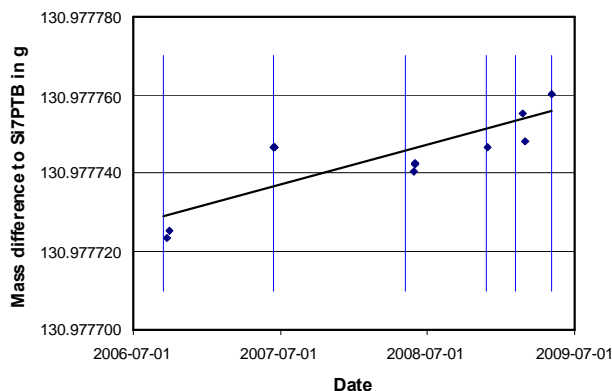


Fig. 3. Mass difference of the spheres Si7PTB and Si1PTB, measured shortly after cleaning Si1PTB. The dates of the cleanings are indicated by the vertical lines.

3.3. Mass stabilization time after cleaning

Figure 4 shows the mass difference of the spheres Si1PTB and Si2PTB measured just after cleaning Si2PTB. In the first 8 hours the values drift as usual since thermal equilibrium has not yet been reached. After the equilibrium is reached no drift can be detected. Thus, the mass of the silicon sphere Si2PTB is already stable after only 8 hours whereas stainless steel mass standards have to be stabilized for 7 to 10 days after cleaning [6].

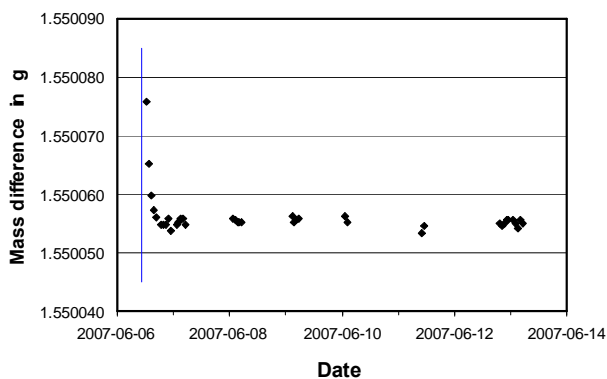


Fig. 4. Mass difference of the spheres Si1PTB and Si2PTB, measured shortly after cleaning Si2PTB. The time of the cleaning is indicated by the vertical line.

4. INFRARED ABSORPTION SPECTROSCOPY

Hydrocarbons absorb infrared radiation in the wavenumber range of 2800 cm^{-1} to 3000 cm^{-1} (corresponding to $3.6\text{ }\mu\text{m}$ and $3.3\text{ }\mu\text{m}$) due to vibrational transitions of the C-H stretching vibrations of paraffine. Since silicon is transparent in this wavelength region, hydrocarbons can be measured sensitively by infrared absorption spectrometry. For this purpose, a Fourier transform infrared spectrometer type Bruker IFS66 equipped with a CdHgTe-detector was used at PTB.

For the calibration of the method, paraffine vapour was homogeneously deposited on a silicon sphere (in a vacuum). Mass measurements were performed before the deposition, with the sphere contaminated with paraffine, and after the subsequent cleaning, resulting in a paraffine mass on the sphere of $88(5)\text{ }\mu\text{g}$. From the diameter of the sphere, 90.0 mm , and the density of paraffine, $0.88(2)\text{ g/cm}^3$, the thickness of the layer can be calculated to be $3.93(24)\text{ nm}$.

This result served for calibrating the IR measurements of the layer thickness. Since the noise in the spectrum is a factor of 40 smaller than the maximum peak in the spectrum, a detection limit of about 0.1 nm can formally be estimated. This sensitivity is appropriate to control cleaning procedures of the density standards. For the estimation of the homogeneity of the paraffine layer, measurements on 7 different locations on the sphere were performed and resulted in a relative standard deviation of 11 %.

Fig. 5 shows the absorption spectrum of the sphere in the frequency region of the C-H stretching vibrations. Three lines are distinguishable, due to the symmetric and the antisymmetric stretching vibrations of the CH_2 and CH_3 groups of the paraffine. The symmetric stretching vibrations

of the CH_3 groups are situated between the symmetric and antisymmetric stretching vibrations of the CH_2 groups and cannot be observed as a single peak.

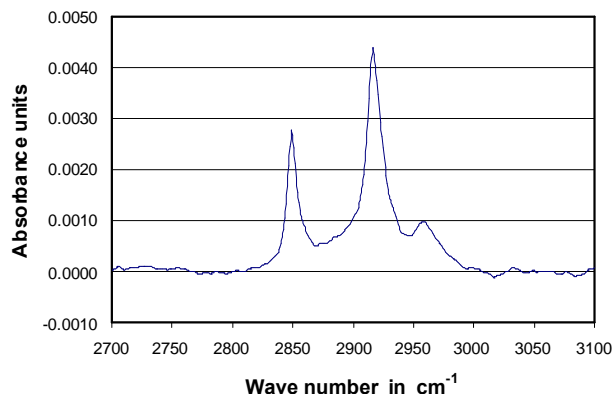


Fig. 5. Infrared absorption spectrum of a silicon sphere with a deposited 4 nm layer of paraffine. Peak assignments: $\nu_s(\text{CH}_2) = 2848\text{ cm}^{-1}$, $\nu_{as}(\text{CH}_2) = 2916\text{ cm}^{-1}$, $\nu_s(\text{CH}_3) \approx 2890\text{ cm}^{-1}$, $\nu_{as}(\text{CH}_3) = 2956\text{ cm}^{-1}$.

5. SUMMARY

The contamination and cleaning of silicon density standards were investigated by mass comparison measurements. It was shown that even in clean laboratory air, the mass of silicon spheres increases considerably with time. On the other hand, after cleaning the sphere, mass stabilizes within only 8 hours and always yields the same mass within $10\text{ }\mu\text{g}$. This shows that for mass and density measurements a cleaning just before the measurements is advisable.

Additionally, an infrared absorption technique was used to measure hydrocarbons on silicon spheres. A calibration of this method was possible with a mass determination of a paraffine layer deposited on a sphere. A detection limit of 0.1 nm was estimated. This corresponds to $2\text{ }\mu\text{g}$ on a sphere, 90 mm in diameter, if it is contaminated homogeneously on the whole surface.

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