MASS DETERMINATION OF SILICON SPHERES USED FOR THE AVOGADRO PROJECT

Michael Borys, Michael Gläser, Michael Mecke

Physikalisch-Technische Bundesanstalt (PTB), Germany

ABSTRACT

Spheres made of a silicon single crystal with a mass of about 1 kg are used as density standards and in the context of a project for the determination of the Avogadro constant. The status of the mass determination of such silicon spheres at the PTB is presented. Special facilities and procedures used for the mass determination in air are described. Results for a single sphere and the mass difference between two spheres are given with a discussion of the measurement uncertainty and mass stability.

1. INTRODUCTION

The Avogardo constant N_A represents an equal number of elementary entities, e. g. atoms or molecules, in one mole of a substance, e. g. in 12 g of the carbon isotope ^{12}C or 28 g of the silicon isotope ^{28}Si. Microscopic and macroscopic quantities are linked by the Avogadro constant. Thus the unified atomic mass unit is defined by [1]

$$1\,\mathrm{u} = \frac{10^{-3}\,\mathrm{kg}}{N_A} \qquad (1)$$

and e. g. for a silicon single crystal, the Avogadro constant can be derived from

$$N_A = \frac{\text{mole volume}}{\text{atomic volume}} = \frac{M\,V}{m}\,\frac{n}{V_0}\,, \qquad (2)$$

where M is the molar mass of silicon, V the volume and m the mass of a silicon body, V_0 the volume and n the number of atoms of the unit cell.

Based on Eq. (2), a value $N_A = 6{,}0221353 \cdot 10^{23}\ \mathrm{mol}^{-1}$ was recently derived from measurements of the lattice parameter, volume, mass and molar mass of a silicon single crystal with a relative standard uncertainty ($k = 1$) of $3{,}4 \cdot 10^{-7}$ [2]. This result was derived from a single silicon crystal sphere named AVO#1. The AVO#1 sphere is one of three spheres, which were fabricated at CSIRO (National Metrology Laboratory, Australia) from the silicon crystal WASO 04. Details of the measured crystal properties and parameters of the sphere AVO#1 are given in [2].

Between June 2000 and September 2004 several measurements for the determination of the mass of the sphere AVO#1 and the mass difference between the spheres AVO#1 and AVO#2 in air were performed at the PTB. The procedures, experimental set-up and the results are described and discussed in the following.

2. EXPERIMENTAL SET-UP AND PROCEDURES

The 1 kg mass comparator used for the mass determination of 1 kg silicon spheres is based on the hydrostatic principle, i. e. instead of the usual counterweight the weight force is compensated by hydrostatic buoyancy in water (Fig. 1). This mass comparator has been developed at the PTB and was operational in 1983. Several improvements were carried out until the end of 1997. The hydrostatic comparator is operated in a pressure-resistant chamber and has an exchange mechanism with six positions. Over a cardan joint the balance pan hangs on a rod. The rod is connected with the floating system. An electromagnetic force compensation system ensures constant submergence depth during mass comparisons. With this comparator a pooled standard deviation of about 2 µg can be achieved. A detailed description of this comparator is given in [3].

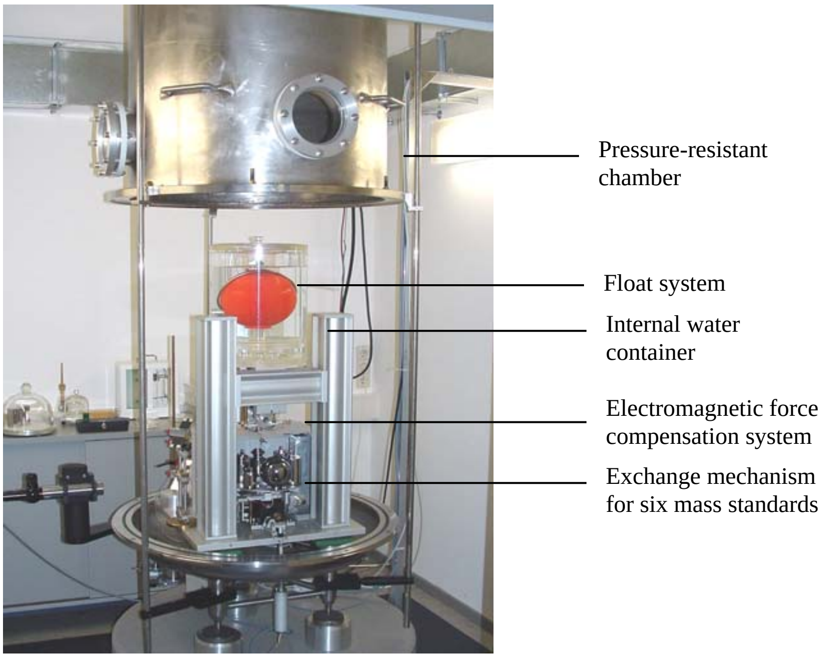

Fig. 1: PTB’s liquid balance based on the hydrostatic weighing principle

The hydrostatic mass comparator is located in an air-conditioned room with a temperature stabilisation better 0,05 K within 12 h. Over the same period the temperature changes inside the pressure-resistant chamber are smaller than 0,01 K.

According to the recommendations given for the handling of silicon spheres by the CSIRO-NML a resting of the highly polished silicon surface on any hard surface, especially metal surface, has to be avoided. Therefore a special support ring with three conducting Teflon pins and a mass of about 10 g was constructed and used for the weighing process (Fig. 2). The uncertainty contribution of this support ring is included in the uncertainty of the auxiliary weights in the uncertainty budget (Tables 2 and 3).

For the measurements described in the following the spheres were cleaned with pure ethanol. The period between cleaning and weighing varied between 40 days and about 12 hours. It is known that after cleaning it takes several days for the surface of a stainless steel weight to be covered again with a water layer in equilibrium with the ambient humidity [6]. An increase of the mass by water adsorption, however, could not be observed. It is assumed that the sorption process was either already completed at the time of the weighing or significantly smaller than the measurement uncertainty (Table 1).

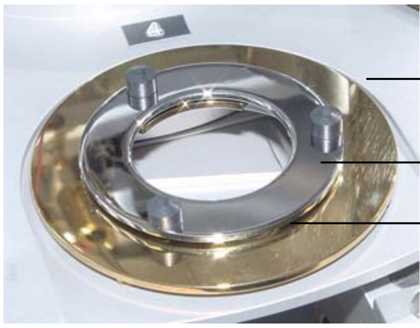

Fig. 2: Support ring for silicon spheres with conducting Teflon pins

The main source of uncertainty for the mass determination of a silicon sphere in air is the uncertainty of the buoyancy correction. Between a platinum-iridium prototype and a silicon sphere of about 1 kg a volume difference of about 380 cm^3 has to be considered. If the air density is determined according to the air density equation, internationally recommended by the Comité International des Poids et Mesures (CIPM), the relative standard uncertainty of the air density $u(\rho)/\rho$ is in the order of magnitude of $1\cdot10^{-4}$ [4, 5] which leads to an uncertainty contribution of about 50 µg. This contribution can be significantly reduced if two buoyancy artefacts with a similar mass and surface, but different volumes, are used for a gravimetric determination of the air density [7, 9]. With these buoyancy artefacts the relative standard uncertainty for the air density determination can be reduced to less than $5\cdot10^{-5}$, which leads to a standard uncertainty of the buoyancy correction of less than 25 µg.

3. RESULTS AND DISCUSSION

3.1 Mass determination of silicon sphere AVO#1

The mass of the sphere AVO#1 was determined between June 2000 and March 2001 and in a second period between October 2003 and September 2004. Figure 3 shows the sphere AVO#1 together with the platinum-iridium prototype No. 70 and buoyancy artefacts on the six-position load mechanism of the hydrostatic mass comparator. The history of the mass determination of the sphere AVO#1 is given in Table 1.

The traceability was realised by the prototypes No. 55 and No. 70 and the 1 kg stainless steel standards No. 6 and No. F. In the period between 2000 and 2004 all prototypes were calibrated annually, in January, against the German national prototype No. 52, which was calibrated at the Bureau International des Poids et Mesures (BIPM) in 1996. Since that time it had been corrected for a long-term drift known from previous calibrations at the BIPM and by comparison in June 2002 with the prototype No. 70, which was calibrated at the BIPM in April 2002, and in July 2003 with the prototype No. 55, which was calibrated at the BIPM in April 2003. The 1 kg stainless steel standard No. 6 was calibrated in October 2000 against the prototype No. 70, which was calibrated against the prototype No. 52 in January 2000 and the 1 kg stainless steel standard No. F was calibrated in March 2001 against the 1 kg stainless steel primary standard No. G, which was calibrated against the prototype No. 52 in January 2001.

For each set of measurements given in Table 1 the measurement uncertainty was estimated. For example in Tables 2 and 3, the uncertainty budget for the last measurement in September 2004 is given for both, the mass determination of the sphere AVO#1 with air density determination for buoyancy correction according to the CIPM formula 1981/91 and with buoyancy artefacts. Figure 4 shows a summary of the results. The systematic difference between the values for the air density determination according to the CIPM formula and with buoyancy artefacts is remarkable. A systematic difference between the two methods is already known from previous measurements [5, 9]. In a summary of air density measurements performed by different laboratories with buoyancy artefacts, Picard et al. reported recently on a mean relative air density difference of approximately $6{,}4\cdot10^{-5}$ between the gravimetric method and the CIPM formula 1981/91 [10]. These results were confirmed by a redetermination of the argon content of air by Park et al. [11]. Together with the most recent CODATA recommendation for the molar gas constant [12], these new values for the air composition would increase the air density of the CIPM formula by[1] $\Delta\rho/\rho = 7{,}6\cdot10^{-5}$, i. e. the curve for the CIPM formula in Fig. 4 would be shifted up to 35 µg depending on the volume difference between the silicon sphere and the reference weight.

Fig. 3: Silicon sphere AVO#1 together with platinum-iridium prototype No. 70 and buoyancy artefacts on the six position load mechanism of the hydrostatic mass comparator

Table 1: History of mass determination of silicon sphere AVO#1 at the PTB (Index CIPM: Air density determination according to the CIPM formula 1981/91, Index BA: Gravimetric air density determination with buoyancy artefacts)

Beginning	End	m_{CIPM} / g	U_{CIPM} / g (k = 2)	m_{BA} /g	U_{BA} / g (k = 2)	t / °C	h / %	p / hPa	Ref.
22.06.2000	11.07.2000	1000,914779	$8{,}5\cdot10^{-05}$	1000,914876	$4{,}3\cdot10^{-05}$	21,24–21,35	45–60	1013,8–1016,2	Pt 55
26.09.2000	30.09.2000	1000,914790	$8{,}5\cdot10^{-05}$	1000,914868	$4{,}3\cdot10^{-05}$	20,26–20,29	51–59	1010,7–1012,9	Pt 55
10.01.2001	17.01.2001	1000,914832	$8{,}6\cdot10^{-05}$	1000,914861	$3{,}8\cdot10^{-05}$	19,96–20,11	48–62	1002,9–1007,7	St 6
19.01.2001	27.01.2001	1000,914815	$8{,}6\cdot10^{-05}$	1000,914842	$3{,}8\cdot10^{-05}$	19,97–19,99	48–62	1006,5–1007,6	St 6
27.03.2001	30.03.2001	1000,914837	$8{,}6\cdot10^{-05}$	1000,914872	$4{,}3\cdot10^{-05}$	19,51–19,61	49–57	1009,9–1010,5	St F
07.10.2003	17.10.2003	1000,914808	$8{,}5\cdot10^{-05}$	1000,914915	$5{,}0\cdot10^{-05}$	19,88–19,93	52–56	1006,3–1007,1	Pt 55
27.04.2004	07.05.2004	1000,914834	$8{,}5\cdot10^{-05}$	1000,914874	$4{,}8\cdot10^{-05}$	19,96–19,99	41–46	1006,5–1008,2	Pt 70
02.09.2004	11.09.2004	1000,914869	$8{,}5\cdot10^{-05}$	1000,914968	$4{,}8\cdot10^{-05}$	19,84–20,02	44–52	1006,7–1008,6	Pt 70
14.09.2004	25.09.2004	1000,914826	$8{,}5\cdot10^{-05}$	1000,914933	$4{,}8\cdot10^{-05}$	19,95–20,00	43–53	1007,3–1007,9	Pt 70

[1] This value is valid only, if for the CIPM formula the more exact value of the molar mass of dry air is obtained by an additional measurement of the concentration of carbon dioxide. If the concentration of carbon dioxide is not considered, a shift of about $\Delta\rho/\rho = 6{,}5\cdot10^{-5}$ would be obtained.

Table 2: Uncertainty budget for the mass determination of the sphere AVO#1 with air density determination for buoyancy correction according to the CIPM formula 1981/91 [4, 8] (values for September 2004)

Parameter X_i	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Uncertainty contribution $u_i(m)$ / g
CIPM formula	$7{,}7 \cdot 10^{-05}$ kg / m^3	$3{,}8 \cdot 10^{-04}$ m^3	$3{,}0 \cdot 10^{-05}$
Pressure	3 Pa	$4{,}5 \cdot 10^{-06}$ g / Pa	$1{,}4 \cdot 10^{-05}$
Temperature	$1{,}0 \cdot 10^{-02}$ K	$1{,}7 \cdot 10^{-03}$ g / K	$1{,}7 \cdot 10^{-05}$
Humidity	$5{,}0 \cdot 10^{-03}$	$4{,}1 \cdot 10^{-03}$ g	$2{,}1 \cdot 10^{-05}$
Mole fraction CO_2	$1{,}0 \cdot 10^{-05}$	$1{,}8 \cdot 10^{-01}$ g	$1{,}8 \cdot 10^{-06}$
Mass of reference/auxiliary weights	$8{,}3 \cdot 10^{-06}$ g	1,0	$8{,}3 \cdot 10^{-06}$
Volume of AVO#1	$3{,}6 \cdot 10^{-05}$ cm^3	$1{,}2 \cdot 10^{-03}$ g / cm^3	$4{,}3 \cdot 10^{-08}$
Volume of reference/auxiliary weights[2]	$1{,}1 \cdot 10^{-03}$ cm^3	$1{,}2 \cdot 10^{-03}$ g / cm^3	$1{,}3 \cdot 10^{-06}$
Weighing difference	$5{,}8 \cdot 10^{-07}$ g	1,0	$5{,}8 \cdot 10^{-07}$
$u(m)$			$4{,}3 \cdot 10^{-05}$

Table 3: Uncertainty budget for the mass determination of the sphere AVO#1 with air density determination for buoyancy correction based on buoyancy artefacts (values for September 2004)

Parameter X_i	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Uncertainty contribution $u_i(m)$ / g
BA mass difference in vacuum	$2{,}4 \cdot 10^{-06}$ g	4,7	$1{,}1 \cdot 10^{-05}$
BA weighing difference in air	$4{,}1 \cdot 10^{-06}$ g	4,7	$1{,}9 \cdot 10^{-05}$
BA sorption correction	$2{,}4 \cdot 10^{-07}$ g	4,7	$1{,}1 \cdot 10^{-06}$
BA volume difference	$5{,}6 \cdot 10^{-04}$ cm^3	$5{,}8 \cdot 10^{-03}$ g / cm^3	$3{,}2 \cdot 10^{-06}$
Mass of reference/auxiliary weights	$8{,}3 \cdot 10^{-06}$ g	1,0	$8{,}3 \cdot 10^{-06}$
Volume of AVO#1	$3{,}6 \cdot 10^{-05}$ cm^3	$1{,}2 \cdot 10^{-03}$ g / cm3	$4{,}3 \cdot 10^{-08}$
Volume of reference/auxiliary weights[2]	$1{,}1 \cdot 10^{-03}$ cm^3	$1{,}2 \cdot 10^{-03}$ g / cm^3	$1{,}3 \cdot 10^{-06}$
Weighing difference	$5{,}8 \cdot 10^{-07}$ g	1,0	$5{,}8 \cdot 10^{-07}$
$u(m)$			$2{,}4 \cdot 10^{-05}$

In the period between June 2000 and March 2001 the PTB buoyancy artefacts No. A3 were used for the gravimetric determination of the air density. From several previous measurements, the mass difference of these artefacts in vacuum has been proven to be stable, i. e. within a drift of less than 2 µg per year. In October 2003 it was not possible to use these artefacts because they were used in the context of a EUROMET project at other laboratories [13]. Therefore the PTB buoyancy artefacts No. A5 were used for the succeeding measurements. As also seen in Fig. 4, the air density determined by these artefacts seems to be higher than the air density determined by the A3 artefacts. The mean difference between the curve for the CIPM formula and the curve for the A3 artefacts is 58 µg, and 88 µg for the curve for the A5 artefacts. Even though both values are within the given uncertainties a systematic influence seems to be obvious, which was the reason for several comparison measurements performed between the A5 and the A3 artefacts in the year 2004. As a result a systematic difference of about $7{,}9 \cdot 10^{-5}$ was confirmed. This value corresponds to a difference between 29 µg and 36 µg in Fig. 4. The reason for this systematic shift of the A5 artefacts is still unclear and the subject of current investigations.

[2] Since the uncertainty of the volume of the reference and auxiliary weights is already part of the uncertainty of the mass of these weights, this contribution has to be considered in the calculation of the combined uncertainty with a negative sign (cf. [3], p. 271).

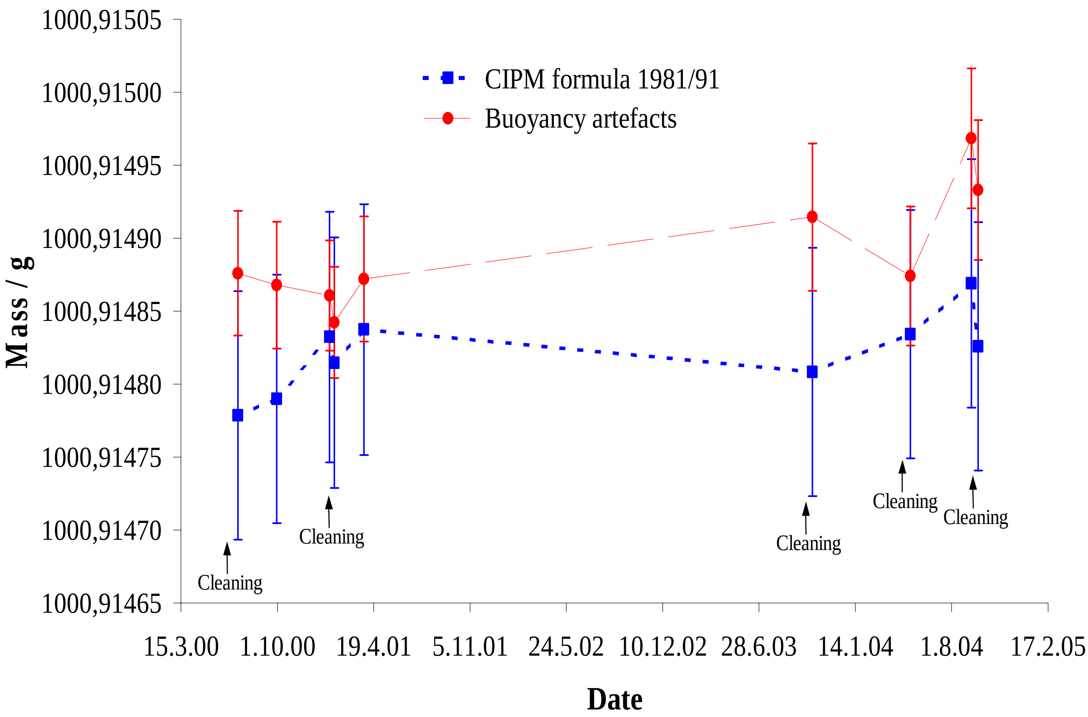

Fig. 4: Mass of silicon sphere AVO#1 determined with air density determination for buoyancy correction according to the CIPM formula 1981/91 and with buoyancy artefacts (uncertainty bars indicate expanded uncertainties U (k = 2))

In January 2001 and September 2004 the mass of the sphere AVO#1 was measured immediately before and after the cleaning procedure. In both cases, a considerable mass reduction between 20 µg and 40 µg could be observed. This corresponds to a mass reduction per surface area between 0,07 µg/cm^2 and 0,15 µg/cm^2.

3.2 Measurement of mass differences between the spheres AVO#1 and AVO#2

The mass difference between the spheres AVO#1 and AVO#2 was determined in October 2003 and April/May 2004. Table 4 gives a summary of these measurements and Table 5 an example of the uncertainty budget. Since for the measurement of the mass difference between two spheres no buoyancy correction is necessary, the uncertainties are significantly smaller than for the mass determination of one sphere. The difference of 14 µg between the two values is, however, out of the sum of the two expanded uncertainties (10,8 µg). It is assumed that the different history of the spheres in the half year between the measurements and a not perfect cleaning process are two reasons for this result.

Table 4: Results for the determination of the mass difference between the silicon spheres AVO#1 and AVO#2

Beginning	End	$\Delta m_{1\text{-}2}$ / g	$U_{\Delta m}$ / g (k = 2)	T / °C	h / %	p / hPa
07.10.2003	17.10.2003	-0,013478	$5{,}0 \cdot 10^{-6}$	19,88 - 19,93	52 - 56	1006,3 - 1007,1
27.04.2004	07.05.2004	-0,013492	$5{,}8 \cdot 10^{-6}$	19,96 - 19,99	41 - 46	1006,5 - 1008,2

Table 5: Uncertainty budget for the determination of the mass difference between the spheres AVO#1 and AVO#2 (values for April/May 2004)

Parameter X_i	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Uncertainty contribution $u_i(m)$ / g
Mass of auxiliary weights	$3{,}2\cdot10^{-06}$ g	1,0	$3{,}2\cdot10^{-06}$
Volume of auxiliary weights[2]	$1{,}2\cdot10^{-03}$ cm^3	$1{,}2\cdot10^{-03}$ g/cm3	$1{,}4\cdot10^{-06}$
Volume of AVO#1 and AVO#2	$9{,}8\cdot10^{-05}$ cm^3	$1{,}2\cdot10^{-03}$ g/cm3	$1{,}2\cdot10^{-07}$
Weighing difference	$7{,}3\cdot10^{-07}$ g	1,0	$7{,}3\cdot10^{-07}$
$u(m)$			$2{,}9\cdot10^{-06}$

3. SUMMARY AND CONCLUSIONS

The mass of the silicon sphere AVO#1 was determined in several measurements within the period June 2000 and September 2004 with an expanded uncertainty between 38 µg (buoyancy artefacts) and 86 µg (CIPM formula). The main source for the uncertainty is the buoyancy correction. When a pair of buoyancy artefacts was used in air and in vacuum, the uncertainty of the air density could be determined with a considerably smaller uncertainty than by use of the CIPM formula 1981/91 for the air density. Also, a systematic difference between the buoyancy correction based on a determination of the air density by the CIPM formula 1981/91 and a gravimetric determination with buoyancy artefacts was observed. One reason for this difference is probably the deviation between the air composition used for the CIPM formula 1981/91 and the recently measured values. In addition, a possible unexpected drift of the buoyancy artefacts A5 has to be considered. Within the given uncertainties no systematic drift of the mass of the sphere AVO#1 could be observed.

The mass difference between two silicon spheres can be determined with a significantly smaller uncertainty than the mass of a single sphere. Between the spheres AVO#1 and AVO#2 a mass difference was measured in October 2003 and April/May 2004 with an expanded uncertainty of 5 µg and 6 µg, respectively.

Although a relative standard uncertainty of about $2\cdot10^{-8}$ could be obtained for the mass determination of a single sphere, for an investigation of the mass drift of silicon spheres a further reduction of the measurement uncertainty and a unified handling and cleaning procedure is considered to be indispensable. A reduction of the measurement uncertainty by 50% seems to be realistic within the next two or three years.

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Addresses of the Authors:

Michael Borys, Michael Gläser, Michael Mecke, Physikalisch-Technische Bundesanstalt (PTB), Bundesallee 100, 38116 Braunschweig, Germany, E-mail: Michael.Borys@PTB.de , Internet: http://www.ptb.de/en/org/1/11/111