Volume determination of two spheres of the new $^{28}$Si crystal of PTB

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Abstract
In the scope of the redetermination of Avogadro’s constant $N_A$, a new isotopically enriched silicon crystal has been produced, from which two spheres were manufactured. After the crystal properties, the lattice parameter and molar mass, as well as the masses of the two spheres have been determined, the volume of the spheres was also measured. For this, the sphere interferometer of PTB was used. The methods of the interferometric measurements have been improved and the major contributions to the uncertainty have been investigated thoroughly. As a result, the total uncertainty could be reduced significantly, yielding a substantial impact on the determination of Avogadro’s constant. The mean diameter of each sphere was measured twice with a repeatability of $\pm 2 \times 10^{-10}$, and the relative uncertainty of the ‘apparent’ volume, which disregards the comparatively small influence of the optical effects of surface layers, was reduced to $7 \times 10^{-9}$. The final results of the volumes and comments on their uncertainties are given.

Keywords: Avogadro’s constant, sphere interferometer, kilogram, volume determination

(Some figures may appear in colour only in the online journal)
Firstly, the space between two opposing spherical reference faces, the etalon, is determined (see figure 1). Then the sphere is inserted and the resulting gaps between the reference surface and the corresponding area of the sphere are measured. If one light ray is assumed for each pixel \((x, y)\) of the camera array, the distance \(D\) of the empty etalon and the gaps \(d_1\) and \(d_2\), respectively, are measured at about 10'000 positions simultaneously. The diameters of the sphere in the current field of view are then obtained from the difference of the measurements: \(d(x, y) = D(x, y) - d_1(x, y) - d_2(x, y)\).

Despite the spherical arrangement, in all three measurement cases the interferences are almost interferences of equal thickness, and the values of \(D\), \(d_1\) or \(d_2\) have only a small spread. Due to the quality of the reference faces and the sphere, the deviations within the 60° field of view are below \(\lambda/10\)—showing a nearly completely dark interference.

With an orientation device, the sphere can be lifted out of the optical beams in order to measure the empty etalon. In this elevated position, it can be rotated around two axes. With about 30 different orientations, the sphere can be covered with measurement segments. Each point of the sphere is therefore measured numerous times and at different areas of the optics [3].

The interferences are evaluated using phase-shifting interferometry with wavelength tuning. For that, an iodine stabilized laser (BIPM recommendation for 633 nm [4]) works as a wavelength reference, whereas a tunable laser is used for the different measurements with changed wavelengths. Each wavelength of the extended cavity laser is controlled by means of a highly stabilized frequency tuner and a phase locked loop. This guarantees that the stability of the tunable laser works at the same 10⁻¹¹ uncertainty level as the iodine laser.

With phase-shifting interferometry the interferences are evaluated with high resolution—but only the fractional part inside one interference order. For the integer orders, which amount to about 300'000 for the sphere, a preliminary value of the diameter of the sphere is necessary. As the density of the probes of the crystal has been measured at the 10⁻⁸ level, only a rough mass determination of the sphere at the mg level is necessary to receive a sufficiently good value for the integer interference orders of the sphere.

The laser intensity at the entrance of the interferometer is influenced to a small extent by the thermal stability of the optical fibres. Therefore, the interferometer input was stabilized by means of a noise eater [5].

Each of the 28Si kg01-spheres was measured twice with different starting orientations and therefore with different mapping schemes. This was possible as every sphere was marked by a laser with different marks, two at (1 0 0) and one at (1 1 1) crystal lattice orientations (Miller indices). The temperature stabilization of the interferometer was adjusted in such a way that the measurements could be carried out over several days with only small deviations from 20 °C of maximally ±3 mK. The vacuum pressure was below 0.1 Pa, so that no correction of the refractive index was necessary. Autocollimation of the entrance beam, and of the exit beam was controlled carefully and the adjustment of both the sphere and empty etalon was accomplished to the best possible zero fringe, only limited by the topography of the sphere and the reference face. This scheme is a prerequisite to reach the lowest uncertainty due to optical imperfections [6]. Furthermore, an aperture correction has to be applied to consider the lateral size of the fibre output [7].

To ensure the smallest uncertainty of the temperature measurement of the spheres, the reference Pt-25 thermometer was investigated carefully. The two temperature fixed-points used—the melting point of gallium and the triple point of water—were prepared several times, and a repeatability of each fixed-point of 50 µK was achieved. An international comparison of several reference thermometers in a highly stabilized 20 °C-reference-point which overlap generously yielded standard deviations of better than 30 µK. For a self-heating-free measurement of the sphere, a system of thermocouples was used, detecting the small temperature differences between the sphere and a copper block containing the Pt-25 reference thermometer. Each pair of thermocouples was checked for zero offset (both sensors together on one isolated copper block) and for slope (the sensing arms of the thermocouples were divided onto two copper blocks, each one measured with a Pt-25 reference thermometer) [8, 9]. The main uncertainty contribution of the thermocouples was the noise of the amplifiers, which amounted to 0.3 mK, but was highly averaged through the slow temperature course with time.

### Table 1. ‘Apparent’ diameters of the 28Si spheres 28Si kg01a and 28Si kg01b.

| Sphere     | 28Si kg01a         | 28Si kg01b         |
|------------|--------------------|--------------------|
| Set of measurements A | 93.72372386     | 93.72065632     |
| Set of measurements B | 93.72372378     | 93.72065638     |
| Average   | 93.72372382(22)   | 93.72065635(22)   |

### 3. Results

#### 3.1. Evaluation of the volume

Following the diameter evaluation described, the correct average diameter or better of the volume of each sphere has to be determined. In the present case, two sets of measurements per sphere have been carried out, each of which consists of 31 single measurements and covers the surface of the
The topography of the spheres is then repeatedly represented by approximately 330,000 diameter values, in which influences on each value, as for example the aperture correction [7] or the temperature deviation from 20 °C, are considered by a respective correction. These single diameters are distributed all over the surface and cover the topographies thoroughly, but the densities of the measuring positions are locally different. This is considered in the evaluation by means of a fit of real spherical harmonics, in which the uncertainties of the single values are included as weighting factors. Then the volume of the sphere is the integral over its radius representation $V = \frac{1}{3} \int_0^\pi \int_0^{2\pi} [R(\theta, \phi)]^3 \sin \theta d\phi d\theta$.

The first fit parameter yields the average radius at 20 °C and 0 Pa which gives—multiplied by 2—the mean diameter. This is called the ‘apparent’ diameter because it is not corrected for the phase shift due to surface layers. To take the influence of the surface layers into account, ellipsometric, XRF and XPS measurements, in combination with a layer model, have to be applied. This is done in [10], and its influence on the optical path length is studied in [2]. As these corrections depend on specific measurements which are based on extrinsic apparatuses in the following, only the ‘apparent’ diameters of the two spheres will be dealt with. The corrections due to the phase change on reflection are typically on the order of some hundredths of nm and do not alter the final value substantially. Therefore, these corrections are the focus of [10].

### 3.2. Uncertainty assessment

Although a ‘real’ radius topography of each sphere can be calculated [11], here only diameter topographies are considered. Because the form deviations are small compared to the average diameter, the latter is sufficient for the evaluation of the volume. The fits are calculated with a number of 1225 spherical harmonic functions, which correspond to the functions up to the 48th order when only the even orders are used. The selection of the maximum order is based on a threshold in the asymptotic behavior of the figure of merit of the fit. The average diameters (to be understood as the diameter of a mathematical round sphere of volume $V$) of the measured spheres are listed in table 1 and the corresponding diameter topographies are shown in figure 2.

The noted contribution relating to the data evaluation sums up the outcome of the light intensity measurement, the frequency control, the effect of parasitic interferences—as the major contributions—and includes the statistical share resulting from the fit. The stated number is the maximum value occurring in the fitted topography.

It was possible to reduce the uncertainty of the temperature measurement to 0.6 mK due to the results of the examination which is described above in section 2 and will be discussed in more detail in a separate paper.

The formerly dominating contribution regarding the influence of wavefront aberrations on the measured lengths has been investigated in detail via optical simulations [6]. The wavefront effect is divided into two parts: one covers unavoidable misalignments of the optical system, and the other handles the retrace errors due to the form deviations of the spheres. As the former term is typical for the optical design of the interferometer and can therefore be determined principally, the latter has to be calculated individually for

### Table 2. Uncertainty budget for the volume measurements of the $^{28}$Si spheres 28SiKg01a and 28SiKg01b.

| Uncertainty of the interferometric data (including intensities, frequencies, parasitic interferences) | $1.1 \times 10^{-9}$ | $3.2 \times 10^{-9}$ |
| Temperature (alignment) | $1.5 \times 10^{-9}$ | $4.6 \times 10^{-9}$ |
| Wavefront aberrations (retrace error) | $0.2 \times 10^{-9}$ | $0.6 \times 10^{-9}$ |
| **Total** | **2.3** | **7.0** |

Figure 2. Diameter topographies of the $^{28}$Si spheres 28SiKg01a (left) and 28SiKg01b (right) plotted in Mollweide map projections. The differences between the minimum and the maximum values of the diameters amount to 58 nm and 84 nm, respectively.
each sphere. For this, the results of the measurement of the specific sphere, more precisely its representation in the form of spherical harmonics, were used as an input for an optical simulation. The simulation program applies the physical laws of propagation, refraction and reflection for every ray in the field of view and calculates the complete beam paths, interferometry and projection onto the camera sensor. Following the measurement with subapertures and subsequent reconstruction, one obtains a completely calculated topography of the whole sphere. This fully simulated sphere can—in the case of deviations—be used for a correction, or—in this case—to check the goodness of the actual measurement. The data of both spheres have been evaluated in this way. The results in the form of difference topographies between the measurement result and the simulated sphere are shown in figure 3.

These differences amount to maximally 0.07 nm and 0.13 nm for the peak values, but are zero for the mean diameters. Therefore, no corrections for the final volumes have been applied. The uncertainties for the wavefront aberrations due to the specific form of the sphere amount to 0.01 nm.

The total standard uncertainty is underpinned by the fact that the reproducibility of the diameter measurements is on the order of 0.1 nm, as has been observed for more than ten years. This involves the short-term comparison of measured diameters (i.e. over a few weeks or months) as well as a long-term comparison, as was reported in [12]. The latter case includes several fundamental realignments of the whole setup and also the replacement of key components of the optical system. An example of a short-term repetition is given by the measurement sets A and B in table 1.

4. Summary

The volumes of two spheres of a new $^{28}$Si crystal have been measured interferometrically as a contribution to the redetermination of Avogadro’s constant $N_A$. The interferometer used spherical wavefronts which allowed high-resolution diameter topographies to be measured. Compared to former approaches in the past, the measurement uncertainty could be reduced significantly. For the volume, a relative standard uncertainty of $7 \times 10^{-9}$ could be achieved. The stated uncertainties are underpinned by the long-term reproducibility of the diameter measurements. In the overview article [10] in which all individual quantities are put together for the evaluation of $N_A$, the influence of the surface layers on the volume determination is also addressed. The largest uncertainty contribution is given by the temperature measurement. Its direct influence on the dimensional quantities can be reduced by at least one order of magnitude in Avogadro’s constant by means of a joint consideration, where the quotient of the macroscopic volume (i.e. of the sphere) and of the microscopic volume (i.e. of the crystal’s unit cell) appears.

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