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Abstract

New results are reported from an ongoing international research effort to accurately determine the Avogadro constant by counting the atoms in an isotopically enriched silicon crystal. The surfaces of two $^{28}$Si-enriched spheres were decontaminated and reworked in order to produce an outer surface without metal contamination and improved sphericity. New measurements were then made on these two reconditioned spheres using improved methods and apparatuses. When combined with other recently refined parameter measurements, the Avogadro constant derived from these new results has a value of $N_A = 6.022\,140\,76(12) \times 10^{23} \, \text{mol}^{-1}$. The x-ray crystal density method has thus achieved the target relative standard uncertainty of $2.0 \times 10^{-8}$ necessary for the realization of the definition of the new kilogram.

Keywords: Avogadro constant, kilogram, Planck constant, enriched silicon, molar mass, lattice parameter, interferometry

(Some figures may appear in colour only in the online journal)

1. Introduction

In 2011, the International Avogadro Coordination (IAC) published a comprehensive survey of the different measurements contributing to the determination of the Avogadro constant $N_A$ by counting the atoms in a $^{28}$Si-enriched single crystal [1, 2]. This approach, called the x-ray-crystal-density (XRCD) method, is one of the candidate methods for the realization of the new kilogram definition that is based on fixing the value of the Planck constant $h$. Additionally, an accurate $N_A$ constant is important because its value will be used to define the mole.

One of the principal issues with the 2011 determination of $N_A$ [1] was the fact that the Si spheres used for the volume and mass determinations were covered by a thin layer of metallic contaminant, composed of Ni, Cu and Zn atoms. This contamination probably occurred during the polishing procedure due to a contamination of the slurry. The layer was localized in metal silicide islands ‘floating’ on the silicon core matrix [3]. As the optical constants of this layer were unknown, it was later removed by a Freckle™ etch with a selectively high etching rate for silicides [4]. After etching, the sphere AVO28-S8b (‘b’ for the status after etching) was...
remeasured at PTB and \( N_A \) was redetermined. The consist-
ency of the new result with the formerly obtained \( N_A \) value was excep-
tional [5]. Because the etching had degraded the shape of the
spheres, they were then reworked at PTB, using a new
procedure to improve their sphericity [6]. In June 2013, the
surface of the repolished sphere AVO28-S5c (‘c’ designating
the sphere after repoling) was checked by x-ray fluores-
cence (XRF) spectrometry, revealing negligible amounts of
foreign metals. Moreover, no subsurface damage to the crystal
could be detected by high-resolution x-ray diffractometry [7]
when compared with strain free etched reference crystal sur-
faces. The roughness of the surface was below 0.2 nm, near
the detection limit of the measurement. The topography of
the sphere was measured interferometrically, establishing that
the shape of the sphere was defined only by the orientation
of the crystallographic axes. Maximum peak-to-valley
\((p-v)\) of the shape of the sphere was defined only by the orientation
the sphere was measured interferometrically, establishing that
the detection limit of the measurement. The topography of
the sphere was measured interferometrically, establishing that
the shape of the sphere was defined only by the orientation
of the crystallographic axes. Maximum peak-to-valley
\((p-v)\) deviations of the diameter were below 70 nm (see section 2.5).
The second sphere, AVO28-S8, was then repolished using a
slightly different polishing process in order to achieve a better
roundness which produced a \( p-v \) value below 40 nm for the
sphere diameters.
A new measurement campaign was then initiated using
these repolished spheres and these new results are presented
in this paper together with the refinements to the measure-
ment methods and instrumentation that have occurred since
the 2011 review. All of these improvements were necessary
to reach a total relative standard uncertainty of \( 20 \times 10^{-9} \)
for \( N_A \), an essential goal for the realization of the new kilogram
definition.

2. Determination of the crystal quantities

The measurement of the Avogadro constant \( N_A \), using a sil-
icon crystal, is based upon the following equation,

\[
N_A = nM/(\rho a^3),
\]

where \( n \) is the number of atoms (8) per unit cell of a silicon
crystal and \( \rho \), \( M \) and \( a \) are its density, molar mass and lat-
tice parameter, respectively. Details on counting the atoms in
a silicon crystal are given in [1, 2]. A \( ^{28}\text{Si} \)-enriched silicon
single crystal was grown primarily to reduce the uncertainty
of measuring the molar mass \( M \). Two 1 kg spheres were manu-
factured from the crystal, and the density \( \rho \) of each sphere
was determined from its mass and volume measurements. The
sphere surfaces were covered with oxide layers having a total
thickness around 2 nm. In order to determine the density of the
crystal at the highest levels of accuracy, the surface of each
sphere needed to be chemically and physically characterized
at an atomic scale so that the density of the crystal could be
determined from the mass and volume data, excluding these
oxide layers. In this paper, these two parameters are design-
nated as ‘core mass’ and ‘core volume’, respectively.

In a real crystal, the lattice spacing and density are affected
by impurity atoms and vacancies. For example, interstitial
oxygen expands the lattice spacing and increases the unit cell
mass, and substitutional carbon shrinks the lattice spacing and
decreases the unit cell mass. When the effect of these point
defects on the density \( \rho \) of the crystal is considered, the sim-
plest way to implement measurement equation (1) is to cal-
culate the mass of an equivalent sphere, having the same core
volume and lattice parameter \( a \) measured by combined x-ray/
optical interferometry, but having Si atoms at all regular sites.
The concentrations of carbon, oxygen, boron and vacancy-related defects have already been reported [1]. The
concentration of nitrogen was additionally measured at PTB.
INRIM also developed a method based on instrumental neu-
tron activation analysis (INAA) to evaluate the concentra-
tions of various impurity elements. These results are given
in section 2.1.

The amount-of-substance fractions of the Si isotopes in the
crystal were measured independently by PTB, NMIJ and
NIST using isotope dilution and a multicollector inductively
coupled plasma mass spectrometer (MC ICP-MS). Instead
of using NaOH as solvent and diluent, tetramethylammo-
nium hydroxide (TMAH) was used by these three institutes
to reduce the baseline level of the ion current measurements
during the mass spectrometry. These results are given in
section 2.2.

To measure the lattice parameter, INRIM upgraded a com-
bined x-ray/optical interferometer to further reduce the uncer-
tainty. To demonstrate crystal homogeneity, NMIJ evaluated
the crystal perfection using strain topography, carried out by
means of a self-referenced x-ray diffractometer at the Photon
Factory of the High Energy Accelerator Research Organization
(KEK, Japan). Detailed results are given in section 2.3.

Sections 2.4–2.6 describe the measurement of the densities
of the two \( ^{28}\text{Si} \)-enriched spheres. PTB and NMIJ charac-
terized the composition, mass and thickness of the sphere sur-
face layers by XRF, x-ray reflectometry (XRR), and optical
spectral ellipsometry (SE). These results are given in sec-
tion 2.4. The sphere volumes were determined via diameter
measurements. NMIJ measured about a thousand diameters
for each sphere using an improved optical interferometer with a flat etalon. PTB used a spherical Fizeau interferometer
which allowed about 10^6 diameters to be measured, resulting
a complete topographical mapping of the spheres. Details are
given in section 2.5. Mass comparisons of the two spheres
with Pt–Ir kilogram standards were carried out both in air
and under vacuum by the BIPM, NMIJ and PTB. In order to
provide a better traceability to the international prototype of
the kilogram (IPK), the BIPM revised the mass values for the
BIPM calibrations following the Extraordinary Calibration
Campaign against the IPK conducted in 2014 [8]. NMIJ and
PTB also used the revised mass values of their Pt–Ir kilogram
standards that were reported by the BIPM in December 2014.
Details are given in section 2.6.

The final \( N_A \) values obtained from these measurements
are given in section 3 together with their uncertainty budget.
In section 4, the XRCD final result for \( N_A \) is compared with
those from the watt balance experiments.

2.1. Point defects

The infrared (IR) absorption measurements of dissolved
carbon, oxygen and boron within the silicon crystal have
already been reported in [1]. The gradients in the impurity concentrations are caused by the float zone technique used to purify and grow the single crystal. Additionally, the nitrogen present in the AVO28 crystal was determined by infrared measurements using the method developed by Itoh et al [9]. The average content of nitrogen in the spheres amounts to 0.17(10) in parentheses apply to the last respective digits. The use of aqueous TMAH solutions as sample diluent has been a factor of ten lower than the concentration necessary to create sufficient ions scattering in the detector region for the 30Si signal. This effect is amplified when the NaOH concentration of the matrix solution is increased [22].

Careful analysis of the published data using NaOH as solvent and matrix diluent suggests that this effect, together with possible memory carry-over, were contributing factors that gave rise to the discrepancy between the 2011 molar mass measurements reported by PTB [12, 13] and the 2012 results published by NRC [14] (see table 1). When measuring the AVO28 samples, PTB reported using a mass fraction of 1 mg g\(^{-1}\) NaOH as sample diluent while NRC reported using 24 mg g\(^{-1}\) NaOH. The extremely high levels of NaOH in the NRC samples magnified the 30Si signal of the blank, causing the very low 30Si signals of the AVO28 material (which were typically \(\leq 1 \text{ mV}\)) to be seriously over-corrected. The net effect of this bias was to produce the artificially high \((29\text{Si})/(30\text{Si})\) ratios reported in [14]. A more detailed analysis of the causes of the biasing of the NRC samples \((29\text{Si})/(30\text{Si})\) ratios is underway [20].

The NRC had also postulated that the PTB samples (and by implication, the NMJ and NIST samples) had undergone direct contamination by natural silicon [14]. This possibility was ruled out when the absolute mass fraction of silicon in the NaOH material used for the PTB analyses was found to be a factor of ten lower than the concentration necessary to explain the PTB-NRC molar mass differences. Given that these points of contention involve the use of NaOH as solvent and diluent and have not yet been fully resolved, this study has excluded all molar mass data reported using this particular solvent. Instead, the abundant molar mass data acquired using TMAH as solvent and diluent are used to deduce the molar mass results presented in this paper (table 2).

The use of aqueous TMAH solutions, as proposed and carried out for the first time at NIST [17], has many advantages. The extreme enrichment of the 28Si isotope in the AVO28 boule and another purity check is planned in the TRIGA Mark II reactor at the University of Pavia (with a neutron flux of \(20 \times 10^{12} \text{ cm}^{-2} \text{s}^{-1}\)) in parentheses apply to the last respective digits. This analysis is expected to include sixty-four elements and should also reach a detection limit of less than 1 ng g\(^{-1}\) for more than forty elements.

<table>
<thead>
<tr>
<th>NMI</th>
<th>Diluent</th>
<th>(M_0/\text{g/mol})</th>
<th>((28\text{Si})/(\text{mol/mol}))</th>
<th>((29\text{Si})/(\text{mol/mol}))</th>
<th>((30\text{Si})/(\text{mol/mol}))</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTB 2011</td>
<td>NaOH</td>
<td>27.97697027 (23)</td>
<td>0.99995750 (17)</td>
<td>0.00004121 (15)</td>
<td>0.00000129 (4)</td>
<td>[12, 13]</td>
</tr>
<tr>
<td>NRC 2012</td>
<td>NaOH</td>
<td>27.97696839 (24)</td>
<td>0.99995879 (19)</td>
<td>0.00004054 (14)</td>
<td>0.00000067 (6)</td>
<td>[14]</td>
</tr>
<tr>
<td>PTB 2014</td>
<td>TMAH</td>
<td>27.97697022 (17)</td>
<td>0.99995726 (17)</td>
<td>0.00004162 (17)</td>
<td>0.00000112 (6)</td>
<td>[15]</td>
</tr>
<tr>
<td>NMJ 2014</td>
<td>TMAH</td>
<td>27.97697009 (14)</td>
<td>0.99995763 (3)</td>
<td>0.00004120 (7)</td>
<td>0.00000118 (3)</td>
<td>[16]</td>
</tr>
<tr>
<td>NIST 2014</td>
<td>TMAH</td>
<td>27.976996880 (41)</td>
<td>0.99995701 (41)</td>
<td>0.000041223 (41)</td>
<td>0.0000011076 (88)</td>
<td>[17]</td>
</tr>
<tr>
<td>PTB 2015</td>
<td>TMAH</td>
<td>27.97697013 (12)</td>
<td>0.99995750 (12)</td>
<td>0.00004138 (12)</td>
<td>0.000001121 (14)</td>
<td>[18, this paper]</td>
</tr>
</tbody>
</table>

Table 1. A summary of the molar mass and amount-of-substance fraction determinations of the AVO28 crystal material. The uncertainties (\(k = 1\)) in parentheses apply to the last respective digits. Note that measurements prior to 2013 were carried out using solutions of aqueous NaOH while all subsequent measurements used aqueous TMAH.

2.2. Molar Mass

Following the 2011 report on the status of molar mass measurements for the Avogadro constant [12, 13], a number of additional investigations have been published, providing new molar mass data on additional crystals from the AVO28 boule [14–17]. In addition, a detailed molar mass and amount-of-substance fraction homogeneity study undertaken by the PTB produced data on an additional 14 crystals. The details of this homogeneity study will be published elsewhere [18]; however, the average molar mass result for the 14 new crystals is reported in table 1 while the individual molar masses are reported in table 2. Table 1 also lists all the average molar mass and amount-of-substance fraction results on the AVO28 crystal material published by national metrology institutes (NMIs) to date.

Subsequent to the original development and application of the virtual-element isotope dilution-mass spectrometric (VE-IDMS) approach to determine an accurate molar mass of the highly 28Si-enriched AVO28 boule [19], several studies [20, 21] have examined the analytical problems of Si isotope amount ratio measurements when aqueous sodium hydroxide (NaOH) is used as the diluent or solvent to prepare silicon solutions for inductively coupled plasma mass spectrometry (ICP-MS). The studies all noted that aqueous NaOH could create subtle but significant biases to Si isotope amount ratio measurements. For example, the presence of aqueous NaOH as sample diluent causes ion scattering in the detector region of an MC ICP-MS. This charged background elevates the 30Si baseline in particular [22]. Normally, this is not a problem when the Si isotope sample signals are more than a few hundred mV. However, when the sample signals for 30Si+ and 28Si+ are very low (\(\leq 1 \text{ mV}\)), such elevated baseline signals could lead to an overcorrection of measured sample signals. This is especially problematic for the 30Si+ sample signal in the AVO28 crystals and could lead to a significant biasing of the \((29\text{Si})/(30\text{Si})\) ratio. This effect is amplified when the NaOH concentration of the matrix solution is increased [22].

The use of aqueous TMAH solutions, as proposed and carried out for the first time at NIST [17], has many advantages. The extreme enrichment of the 28Si isotope in the AVO28...
The AVO28 crystals had been cut from the single crystal ingot (figure 1 in [12]) and analyzed for their isotopic composition across the AVO28 boule. The experimental design for this study called for 5 adjacent radial samples (each with a mass of approximately 300mg) to be taken from three distinct longitudinal positions (parts 4, 7, and 9) of the original crystal ingot (figure 1 in [12]) and analyzed for their molar mass. A detailed description of this study will be published elsewhere [18]. However, given that this homogeneity study incorporated most of the state-of-the-art improvements in the measurement of Si isotope-amount-ratios developed since 2011, the average and individual molar masses as well as the Si isotope amount fractions derived from these data are presented in tables 1 and 2. The (VE) IDMS approach [19] was used for measuring the molar mass, with the main experimental details given in [13, 15]. All measurements have been made on a commercial MC ICP-MS (Neptune™, Thermo Fisher Scientific). The calibration and sample runs were separated as originally suggested by colleagues from NRC, saving time and material without any significant loss in accuracy. TMAH was used as the solvent and matrix diluent. The marked increase of the Si+ ion signals resulting from the use of TMAH enabled all the Si isotope data to be measured with Faraday detectors (1011 Ω resistors). To date, five crystals from part 4, five crystals from part 7 and four crystals from part 9 of the Avogadro boule have been measured (table 2). Because the crystals from parts 4 and 7 bracket part 5 (the source location of sphere AVO28-S5), and parts 7 and 9 bracket part 8 (the source location of sphere AVO28-S8), the new PTB data listed in tables 1 and 2 are fully representative of the spheres AVO28-S5 and AVO28-S8 [18]. When combined together with the data given in [15], these measurements represent the PTB contribution that is combined with the NMIJ and NIST data for the calculation of a new molar mass. A detailed description of this study will be published elsewhere [18]. However, given that this homogeneity study incorporated most of the state-of-the-art improvements in the measurement of Si isotope-amount-ratios developed since 2011, the average and individual molar masses as well as the Si isotope amount fractions derived from these data are presented in tables 1 and 2. The (VE) IDMS approach [19] was used for measuring the molar mass, with the main experimental details given in [13, 15]. All measurements have been made on a commercial MC ICP-MS (Neptune™, Thermo Fisher Scientific). The calibration and sample runs were separated as originally suggested by colleagues from NRC, saving time and material without any significant loss in accuracy. TMAH was used as the solvent and matrix diluent. The marked increase of the Si+ ion signals resulting from the use of TMAH enabled all the Si isotope data to be measured with Faraday detectors (1011 Ω resistors). To date, five crystals from part 4, five crystals from part 7 and four crystals from part 9 of the Avogadro boule have been measured (table 2). Because the crystals from parts 4 and 7 bracket part 5 (the source location of sphere AVO28-S5), and parts 7 and 9 bracket part 8 (the source location of sphere AVO28-S8), the new PTB data listed in tables 1 and 2 are fully representative of the spheres AVO28-S5 and AVO28-S8 [18]. When combined together with the data given in [15], these measurements represent the PTB contribution that is combined with the NMIJ and NIST data for the calculation of a new $N_A$. NMIJ also carried out molar mass measurements of AVO28 crystals using a commercial MC ICP-MS (Neptune™, Thermo Fisher Scientific) with TMAH as the solvent. To correct for the mass bias arising in the plasma and sample source areas, three different blends, as described by NRC [14] were employed. Four AVO28 samples, identified as 5B1.2.2.1, 5B1.2.2.2, 8B3.2.2.1 and 8B3.2.2.5 were analyzed. All of the AVO28 crystals had been cut from the single crystal produced by the IAC specifically to determine the Avogadro...
constant. The axial positions of the 5B1 series and the 8B3 series are respectively 275 mm and 414 mm from the outer surface of the boule; their radial distance from the center of the 28Si-enriched crystal ingot is approximately 40 mm. The average molar mass of the four AVO28 crystals was determined to be 27.976 970 09(14) g mol⁻¹, with a relative standard uncertainty of 5.2 × 10⁻⁹ (table 1).

NIST analyzed 4 different crystals of the AVO28 silicon, two proximal to AVO28-S5 (5B2.1.1.3, 5B1.1.1.1) and two taken near AVO28-S8 (8A4.1.1.3, 8B1.1.1.1) [17]. All silicon samples were dissolved and diluted using TMAH and also analyzed on a commercial MC ICP-MS (Neptune™, Thermo Fisher Scientific) in high resolution mode. To correct for measurement mass bias, two independent sets of calibration solutions were created. The AVO28 samples were always run as pairs, with one from part 5 and the other from part 8. These samples were always run together with the calibration solutions. This particular experimental design optimized the detection of any small but measurable heterogeneities in the silicon isotope amount ratios of the different samples. The calibration corrections followed the approach originally developed by PTB [19]. One sample set was measured using only one calibration solution, while the other was analyzed using both solutions. The average molar mass of the four AVO28 crystals measured by NIST was 27.976 969 880(41) g mol⁻¹, with a relative standard uncertainty of 1.5 × 10⁻⁹ [17] (table 1).

In summary, the basis for the average molar mass of the AVO28 boule, with its associated uncertainty, was derived from molar mass measurements using TMAH as solvent and diluent. The individual molar masses of five crystal samples from part 4 (PTB [18], this paper), one crystal from part 5 (PTB [15]), two crystals from part 5 (NMIJ [16]), two crystals from part 5 (NIST [17]), five crystals from part 7 (PTB [18, this paper]), one crystal from part 8 (PTB [15]), two crystals from part 8 (NMIJ [16]), two crystals from part 8 (NIST [17]) and four crystals from part 9 (PTB [18, this paper]) were used. These data allow a robust molar mass to be calculated for updating the Avogadro constant that is based on 24 different sample crystals spread longitudinally across the AVO28 boule and measured by three different NMIIs, each employing a different experimental approach (table 2).

The uncertainty weighted mean (UWM) of all 24 results was determined to be 27.976 970 030(38) g mol⁻¹ with an associated uncertainty expanded by the Birge ratio (σ_U = 1.70) calculated according to [26]. The arithmetic mean including all 24 results was 27.976 970 09(1) g mol⁻¹ with a standard deviation of the mean of 0.000 000 03 g mol⁻¹. The UWM would normally be the estimator of choice for combining these data, as they show a relatively large spread in their associated uncertainties. However, a data consistency check (chi-squared test) recommended in [27] was carried out, yielding a $X^2_{obs}$ ≈ 66 which is larger than the 95th percentile of $X^2_{0.05,23}$ ≈ 35, with 23 degrees of freedom. This data set is therefore not entirely internally consistent. This suggests that one or more of the contributions to the overall uncertainty have not been considered fully. Possible sources for the observed inconsistency may come from either the external reproducibility of the measurement due to tiny yet uncontrollable blank variations, the signal detection itself, the reproducibility of the sample preparation, a tiny but detectable variability in the Si isotopic composition, or an as-yet-unknown additional influence. In order to render these data internally consistent, an additional uncertainty contribution with an expectation value of zero was added to the overall uncertainty of the mean, by adapting the recommendations from [28]. The criterion for determining the value of this additional element of uncertainty, $u_{disp}$, is the normalized error [29]. Following [30], $u_{disp}$ was adjusted so that all normalized errors were equal to or less than 1.

Combining the 24 results from PTB, NMIJ, and NIST (table 2), the average molar mass for AVO28 is calculated to be 27.976 970 09(15) g mol⁻¹, with an associated relative standard uncertainty of 5.4 × 10⁻⁹. These data clearly suggest that, at the present level of measurement accuracy and precision, there are no longitudinal or axial molar mass gradients within the AVO28 boule. The individual molar masses of the spheres AVO28-S5 and AVO28-S8 were calculated from the PTB, NMIJ, and NIST results listed in table 2 and labelled ‘S5’ and ‘S8’, respectively. Table 3 summarizes the molar mass data for each separate sphere, as well as the combined data. The average individual molar mass data for the two spheres are indistinguishable, thus the average AVO28 boule value derived by combining all results is the number that is used in the calculation of the new $N_A$ reported in this study.

### Table 3. Summary of the measured molar masses of spheres AVO28-S5 and AVO28-S8 as well as the average of all molar masses combined. Uncertainties ($k = 1$) in parentheses apply to the last two digits. The final column lists the number of crystals ($n$) used to compute the respective averages. Note that the average molar masses for S5 and S8 each include the 5 molar mass measurements made on the 5 crystals from part 7, as noted in table 2. The average molar mass for the AVO28 boule is the arithmetic mean of all 24 molar mass measurements listed in table 2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_i$ (g/mol)</th>
<th>$u_{rel} \times 10^{-9}$</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average S5</td>
<td>27.976 970 09(09)</td>
<td>3.1</td>
<td>15</td>
</tr>
<tr>
<td>Average S8</td>
<td>27.976 970 06(15)</td>
<td>5.4</td>
<td>14</td>
</tr>
<tr>
<td>AVO28 boule</td>
<td>27.976 970 09(15)</td>
<td>5.4</td>
<td>24</td>
</tr>
</tbody>
</table>

2.3. Lattice parameter

INRIM’s combined x-ray/optical interferometer, used to determine the [2 20] lattice-plane spacing of the enriched silicon crystals, was upgraded and measurements repeated to either confirm the previous result [31] and its uncertainty or to identify possible errors.

First, a 532 nm frequency-doubled Nd:YAG laser was substituted for the 633 nm diode laser. The pressure in the vacuum chamber was also reduced to less than 0.04 Pa. This made any correction for the refractive index of the residual gas essentially inconsequential and ensured a calibration of the optical interferometer with negligible uncertainty.

Next, the delivery, collimation, phase-modulation, and pointing systems of the laser beam were rebuilt to conform
to the new wavelength. The beam divergence was reduced, thereby halving the correction for diffraction effects. To have real-time control of the beam pointing, a home-made telescope was placed at the interferometer output port; to ensure stability, it was clamped on the same base plate of the x-ray/ optical interferometer.

Then, a plate beam-splitter was substituted for the previously used cube beam-splitter. This ensured that the length difference of the transmitted and reflected light paths was insensitive to any beam translations and rotations. The fixed components of the interferometer—beam splitter, quarter-wave plates, and fixed mirror—were replaced and assembled anew.

In order to produce parallel interfering beams, the interferometer fixed-components were cemented onto a glass plate supported by three piezoelectric actuators. A new power supply, producing sub part-per-million noise and stability, was designed and built to eliminate instabilities between the x-ray and optical interferometers.

PTB also found that the surfaces of the x-ray interferometer crystals were contaminated with Cu, Fe, Zn, Pb, and Ca, caused by the wet etch used to remove any residual surface stress after crystal machining. These contaminants were removed by cleaning the crystals in aqueous solutions of HF and (NH₄)₂S₂O₈.

The final upgrade focussed on more accurate temperature measurements. The fixed point cells of INRIM and PTB were compared to establish their temperature difference and to link the INRIM and PTB extrapolations of the lattice parameter compared to establish their temperature difference and to link measurements. The fixed point cells of INRIM and PTB were identical to within the uncertainty of the fixed-point cell temperatures; this uncertainty, all the systematic effects were scrutinized and reevaluated.

PTB also found that the surfaces of the x-ray interferometer crystals were contaminated with Cu, Fe, Zn, Pb, and Ca, caused by the wet etch used to remove any residual surface stress after crystal machining. These contaminants were removed by cleaning the crystals in aqueous solutions of HF and (NH₄)₂S₂O₈.

The final upgrade focussed on more accurate temperature measurements. The fixed point cells of INRIM and PTB were compared to establish their temperature difference and to link the INRIM and PTB extrapolations of the lattice parameter and sphere volume to 20 °C. It was not yet possible to verify if the thermometer readings at 20 °C were identical to within the same uncertainty of the fixed-point cell temperatures; this non-uniqueness error was cautiously set to 0.1 mK [32].

To make a reassessment of the measured value and its uncertainty, all the systematic effects were scrutinized and reevaluated with a view to reducing the overall uncertainty and to confirm that the intended goals could be met. Seven surveys of the lattice spacing (with the interferometer crystals aligned as they were originally in the boule and in a reversed arrangement) were carried out from February to June 2014. These surveys were made over 0.95 mm crystal segments centered in 48 different positions. At each position, x-ray counts were recorded in eight different pixels of the interference pattern (11.2 mm high) and then processed using linear regression to obtain 48 values from the A VO28 crystal by means of a self-referenced lattice comparator at the Photon Factory of the High Energy Accelerator Research Organization (KEK, Japan) [34, 35]. The analyser crystal of the x-ray interferometer and a sample, identified by the 4.R1 code and cut from the seed end of the crystal, show a smooth and homogeneous distribution of lattice spacing values. The standard deviation of the observed variations is 4.9 × 10⁻⁹ for the 4.R1 crystal. This value is consistent with what is observed by x-ray interferometry, 1.5 × 10⁻⁹ d₂₂₀, with a strain smoothing over (2 × 4) mm² areas. By way of contrast, a tail-end sample, identified by the 9.R1 code, shows a 2D swirl-like pattern and a greater variability in its lattice spacing values. This observation is consistent with the segregation of impurities into the tail of a crystal purified by the float-zone process. Therefore, the tail sample can be expected to be more contaminated and to display significant variations in its lattice spacing [35].

The mean lattice parameter of each sphere,

\[ a(S) = \left(1 + \sum \beta_i \Delta N_i\right) a(XINT), \]  

was calculated by taking account of the different point-defect concentrations in the spheres and the interferometer. In equation (3), S is sphere AVO28-S5 or AVO28-S8, and XINT is the x-ray interferometer [67]. The subscript \( i \) refers to point defects, where \( \beta_i \) is the strain coefficient [12, 36] and \( \Delta N_i \) is the concentration difference of the point-defect \( i \) between the sphere and the interferometer. Unlike the previous determination, where only carbon, oxygen, and boron contamination were considered, the newly measured gradient of nitrogen concentration was also taken into account.

### 2.4. Surface

The surface layer of the Si sphere must be accurately characterized and measured to refine the correction values required for the mass and volume determinations of the spheres. The basic requirements and details of the methods used for surface characterisation are described in [3]. The next section will outline the characterisation techniques, highlighting any changes to the procedures described in [3].

To completely analyze the surface of a Si sphere, a rapid measurement method is required. An ideal technique for investigating a SiO₂ layer on a Si substrate is SE which combines fast measurements (a thickness measurement at a single point in less than 10 s) and high precision (repeatability around 10 pm). Using SE, the automatic measurement of a spherical surface with 2600 data points can be completed in 12 h. Unfortunately, SE has two shortcomings: its accuracy (approximately 1 nm) is insufficient for the present application and, as an inverse method, a model of the surface layers must be generated, which then becomes part of the data refinement process. To overcome these limitations, a calibration of the ellipsometric measurement process must be carried out. Surface characterisation thus becomes a two-step process. First, the ellipsometer is calibrated based on reference methods such as XRR at NMII and the combination of XRR and XRF analysis at PTB. The second step, the mapping of the surface using ellipsometry, can then proceed.
Subsequent to the last determination of N_A in March 2013, the 28Si spheres, AVO28-S5 and AVO28-S8, were repolished. The surface layer was therefore modified and, more importantly, simplified when compared to the measurements made in 2009 and 2010. The surficial metallic contaminants (Cu, Ni and Zn) were removed and were therefore no longer part of the surface layer model. For the new N_A determination, the surface layer model illustrated in figure 1 is now applicable.

The measurements for the surface layer characterisation were performed at NMIJ and PTB. NMIJ has recently installed a new spectral ellipsometer, which enables the automatic measurement of an entire sphere surface, accumulating a large number of data points. PTB used the identical equipment as for the 2010 Avogadro constant determination, which is also capable of automatic surface coverage producing several thousand data points.

NMIJ and PTB used different approaches for the calibration of their spectral ellipsometers. The general methodology has already been described in detail in [3]. At the synchrotron radiation laboratory of PTB at BESSY II [37], direct measurements of the oxide layer (OL) and carbonaceous layer (CL) thicknesses were made using XRF. The calibration of the XRF thickness measurement was done using the ratio of the O-K peak to the Si-L peak of SiO_2 reference samples, whose thickness had been determined by XRR at different photon energies in the vicinity of the oxygen absorption edge at 529eV. Because these measurements were made in a vacuum, only the chemisorbed water layer (CWL) was present. For the OL thickness determination, it was assumed that all measured O atoms were in the SiO_2 layer. To correct for the CWL, the measured thicknesses were adjusted using the mass deposition of the chemisorbed water given in [38] to derive the OL thickness.

For the determination of the CL, the ratio of the C-K peak to the Si-L peak was used and compared to a reference carbon layer whose thickness was again determined by XRR. To derive a thickness for the CL, a mass density of 1.1 g cm$^{-3}$ was assumed, this being about half of the carbon bulk density. This thickness was required for the NMIJ ellipsometric measurements as input data for the surface layer model used in their data refinement. This thickness was also used in the volume determinations. Since the chemical structure of the CL is highly unpredictable and unclarified, a generous uncertainty was applied to this measurement.

In addition to XRF, XRR was performed directly on the spheres in the vicinity of the O-K edge as described in [3, 39]. The thicknesses determined for the involved layers were in good agreement with the values from XRF. However, as the total layer thickness was well below 2 nm, no oscillations with multiple periods could be observed and the thickness determination was therefore based on previously obtained optical constants, which lead to increased uncertainties.

For the calibration of the ellipsometric measurements at PTB, the OL thickness of a few well defined points on the sphere were determined using the XRR-based XRF measurements. These points could be located using three different markings (cross, 'T' and triangle) to an accuracy better than 0.5°. The calibration points were then used for the calibration of the PTB spectral ellipsometer during the mapping of the sphere surface (in effect, an 'in-vivo' calibration). By adjusting the alignment of the sphere, a calibration point could be included in each measurement of a great circle. This meant that a short term stability of the instrument of less than 30 min was required, which could be expressed as an uncertainty contribution of less than 20 pm. With this 'in-vivo' calibration, requirements for the simulation model for the refinement of the ellipsometric data were dramatically simplified because the influence of the CWL and CL are inherently included in the calibration constant C. Only the linearity of the ellipsometer and the homogeneity of the CWL and CL were required for the simulation model.

The calibration measurements of the spheres at the PTB synchrotron radiation laboratory were carried out in November 2013 and January 2014 (AVO28-S5c) and in January 2014 and July 2014 (AVO28-S8c), respectively. The ellipsometric mapping of sphere AVO28-S5c was done with 5184 data points, while sphere AVO28-S8c had 15 552 data points. The results of these measurements are listed in tables 4(a) and (b).

NMIJ used a different approach for the calibration of their ellipsometer. The oxide layer thickness on the two spheres was measured by a spectroscopic ellipsometer at NMIJ. The reliability of the spectroscopic ellipsometer was checked by using SiO_2 layers on Si wafers with thicknesses certified by XRR [3]. In the previous paper [3], the oxide layer thickness was measured at only 20 points on the surface of the spheres. To increase the number of measurement points for improving the reliability of the measurement, a new spectroscopic ellipsometer equipped with an automatic sphere rotation system was developed [40]. This new instrument was a spectral ellipsometer with a rotating polarizer. Its spectral bandwidth ranged from 250nm to 990nm. The Si sphere was placed on two rollers made of PEEK (Polyether ether ketone) and could be rotated by the automatic sphere rotation system around both its vertical and horizontal axes. The sphere rotation system was integrated into the spectroscopic ellipsometer, thereby enabling the automatic mapping of the oxide layer thickness.
over the entire surface of the sphere. The measurements were based on 2594 points, regularly distributed over the entire sphere surface. The sphere surface was subdivided into small cells of equal area and the measurement points were distributed uniformly to each cell.

The oxide layer thickness of AVO28-S8c was measured in June 2014 and that of AVO28-S5c was measured in July and September 2014. Although the 2594 points were distributed almost uniformly over the sphere surface, the uniformity was not perfect. To estimate the effect of this non-uniform distribution of the measurement points on the average value of the oxide layer thickness, the measurements at the 2594 points were repeated 3 times. Between each set of measurements, the sphere was rotated to distribute 7782 (=2594 × 3) points as uniformly as possible. Before each set of measurements, the spheres were washed using the same procedure used for the international comparisons of the mass and diameter of a Si sphere in the International Avogadro Coordination project [42]. The standard deviation of the mean OL thickness for 3 sets of the measurements was less than 0.1 nm, showing the uniformity of the distribution of the 2594 points and the reliability of the measurement system.

The ellipsometric data were analyzed at NMIJ based on the surface model with four layers to evaluate the SiO2 thickness. Since the ellipsometric measurement was performed in air, the model consists of a carbonaceous layer (CL), a physisorbed water layer (PWL), a chemisorbed water layer (CWL) and an oxide layer (OL). The thickness of PWL was estimated to be 0.39(9) nm and 0.43(9) nm for AVO28-S5c and AVO28-S8c, respectively. These results were obtained at NMIJ from the comparison weighings in nitrogen gas of about 1200 Pa and in water vapour of about 1200 Pa [42]. The density of the PWL was assumed to be 1.0 g cm⁻³.

To evaluate the OL thickness, the measured ellipsometric parameters were fitted by the aforementioned four-layer model, fixing all the sub-layer parameters, except the thickness of the OL. The evaluated OL thicknesses were 0.76 (27) nm and 0.64 (25) nm for AVO28-S5c and AVO28-S8c, respectively. The thickness of each layer is summarised in table 4(a). The dominant uncertainty source for the OL thickness determination may be that NMIJ used the CL thickness value of PTB and the surface cleaning status was not perfect. To estimate the effect of this non-uniform distribution of the measurement points on the average value of the OL thickness, the measurements at the 2594 points and the reliability of the measurement system.

### Table 4. (a) The thickness of the surface layer and its constituent sub-layer components, \(d_{\text{CL}}, d_{\text{CWL}}, d_{\text{PWL}}\) and \(d_{\text{OL}}\). (b) Mass of the surface layer and its constituent sub-layers. See figure 1 for the key to the subscript abbreviations.

<table>
<thead>
<tr>
<th>Sphere</th>
<th>Lab</th>
<th>(d_{\text{CL}}/\mu\text{g})</th>
<th>(m_{\text{CWL}}/\mu\text{g})</th>
<th>(d_{\text{PWL}}/\mu\text{g})</th>
<th>(m_{\text{OL}}/\mu\text{g})</th>
<th>Date of measurement (OL)</th>
<th>Date of measurement (CL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AVO28-S5c</td>
<td>PTB</td>
<td>16.6 (5.7)</td>
<td>7.7 (2.2)</td>
<td>10.8 (2.5)</td>
<td>46.1 (16.5)</td>
<td>Jan. 2014</td>
<td>0.60 (18)</td>
</tr>
<tr>
<td></td>
<td>NMIJ</td>
<td>16.6 (5.7)</td>
<td>7.7 (2.2)</td>
<td>10.8 (2.5)</td>
<td>53.4 (7.7)</td>
<td>July and Sep. 2014</td>
<td>0.60 (18)</td>
</tr>
<tr>
<td></td>
<td>average</td>
<td>16.6 (5.7)</td>
<td>7.7 (2.2)</td>
<td>10.8 (2.5)</td>
<td>50.3 (7.1)</td>
<td>77.7 (10.0)</td>
<td>0.60 (18)</td>
</tr>
<tr>
<td>AVO28-S8c</td>
<td>PTB</td>
<td>13.5 (5.2)</td>
<td>7.7 (2.2)</td>
<td>11.9 (2.7)</td>
<td>38.9 (15.3)</td>
<td>July 2014</td>
<td>0.49 (16)</td>
</tr>
<tr>
<td></td>
<td>NMIJ</td>
<td>13.5 (5.2)</td>
<td>7.7 (2.2)</td>
<td>11.9 (2.7)</td>
<td>64.3 (13.7)</td>
<td>June 2014</td>
<td>0.49 (16)</td>
</tr>
<tr>
<td></td>
<td>average</td>
<td>13.5 (5.2)</td>
<td>7.7 (2.2)</td>
<td>11.9 (2.7)</td>
<td>52.4 (11.7)</td>
<td>85.5 (14.8)</td>
<td>0.49 (16)</td>
</tr>
</tbody>
</table>

*The thickness of the CL measured by XRF at PTB was based on the assumption that the density of the CL was 1.1 g cm⁻³. The uncertainty of this thickness was estimated using the surface analysis results from the previous measurement [3].

*The thickness of the CWL was calculated from data reported by Mizushima [43].

*The mass of PWL was not included in this value.

2.5. Volume

Optical interferometers were utilised to determine the volume of the two spheres by measuring the diameters of the spheres and calculating their volumes. Although the elementary dimensional measurements were based on the same principle,
different types of interferometers with different optical setups were used. A precise measurement typically takes advantage of a differential approach. Thus, the measurement of a sphere proceeds in two steps: first is the measurement of the dimensions of a stable optical etalon, \( D \). The second step then involves the insertion of a sphere into the etalon and the measurement of the gaps between the sphere and the etalon, \( d_1 \) and \( d_2 \). The diameter of the sphere is calculated from the difference of these measurements \( d = D - d_1 - d_2 \). To fully characterise a sphere, the diameter is measured in many different directions.

NMIJ measured 1450 and 870 diameters of AVO28-S5c and AVO28-S8c, respectively, using an improved optical interferometer with a flat etalon [40]. The \( ^{28} \)Si sphere was placed between the two flat etalon plates, and \( d_1 \), \( d_2 \) and \( D \) were measured by phase shifting interferometry with optical frequency tuning. The main improvements from the previous work [44] are summarized below.

Firstly, the geometrical shapes of the optical components were optimized. The largest uncertainty source in the previous volume measurement at NMIJ was the analysis of the interference fringes [44]. An analysis using the ray-tracing method showed that a possible cause for the uncertainty in the analysis of the interference fringes is the multiple reflection of the beam between the tilted surface of the etalon and the sphere surface. An increased tilt of the etalon surface was therefore expected to reduce the effect of the multiple reflections. Based on this analysis, a new etalon with a larger wedge angle was installed [40].

Secondly, the uniformity of the diameter measurement directions was improved. One of the major uncertainty sources in the previous volume measurement was the experimental standard deviation of the mean volume. The diameter measurement directions were based on 70 directions and the non-uniform distribution of these 70 directions was estimated to increase the experimental standard deviation of the mean volume [44]. To decrease this uncertainty, a strategy to distribute the measurement directions as uniformly as possible was developed [40]. The new distribution consists of 145 directions. The sphere surface is subdivided into small cells of equal area and the measurement points are distributed uniformly to each cell.

Thirdly, the optical frequency standard was upgraded. An iodine-stabilized He-Ne (HeNe/I2) laser was used as the optical frequency standard in the NMIJ interferometer [44]. However, the HeNe/I2 laser was highly sensitive to acoustic noise. An optical frequency comb was therefore employed as the standard to obtain more precise and reliable volume measurements [40]. This light source system is much more robust than the HeNe/I2 laser and can be operated for a long period of time such as 10d. The relative uncertainty of the frequency of the laser is estimated to be approximately \( 1 \times 10^{-11} \) at 1s averaging time. This uncertainty is limited by the statistical frequency fluctuation of the offset laser and can be ignored for the volume measurement.

The measured diameter is the ‘apparent’ diameter, which is not corrected for the phase shift due to the surface layer. The mean apparent diameters at 20.000 °C and 0Pa are 93 710.81111(62)µm and 93 701.52629(68)µm for AVO28-S5c and AVO28-S8c, respectively. The relative standard uncertainties of the volume measurement are \( 2.0 \times 10^{-8} \) and \( 2.2 \times 10^{-8} \) for AVO28-S5c and AVO28-S8c, respectively.

Table 5 shows the uncertainty budget for the determination of the apparent volumes. In the previous work, the volumes of the two spheres were determined by NMIJ with relative standard uncertainties of \( 5.0 \times 10^{-8} \) and \( 4.4 \times 10^{-8} \) for AVO28-S5 and AVO28-S8, respectively [44]. Because of the improvements described above, the uncertainty contributions from the interferogram analysis and the random component were decreased, resulting in the significant reduction in the uncertainty of the volume measurement. The dominant uncertainty source at present is the correction of the diffraction effect on the diameter measurement [45]. The value of this correction was estimated to be 0.45(50)nm.

The PTB interferometer was based optically on a completely spherical geometry [46]. This means that the reference faces were spherical, so that the etalon forms opposing segments (caps) which surround the sphere. Furthermore, the illuminating light wave was converted by a set of objectives into a focused beam, so that these conical rays would hit the reference face and the sphere perpendicularly. Thus, the relationship \( d = D - d_1 - d_2 \) would be true for all points \( \theta, \phi \) within the field of view (covering 60°). This enabled the acquisition of high resolution topographies of the sphere. Each sphere was provided with three different marks (following the orientation of the crystallographic axes) so that a sphere could be initially oriented by one mark with the help of the interferometer camera. Subsequently it was oriented by means of the high-resolution encoder equipment of the sphere positioning motors. Each measurement, at all orientations of the sphere, could then be related to its absolute position on the sphere [47]. The volume of this ‘sphere’ (see figure 2) was calculated by considering the areal weighting of each measuring point [48]. To eliminate any possible stability problems of the etalon and to monitor the stability of the interferometer, PTB always alternated measurements between sphere and empty etalon.

The dimensional measurement is traced back to the laser wavelength of a 633 nm He–Ne laser recommended by BIPM. The stability of the stabilised He-Ne laser, the auxiliary unmodulated He-Ne laser and the extended-cavity-diode-laser (ECDL) for the wavelength-tuning was at the \( 10^{-12} \) level and therefore did not contribute to the volume uncertainty budget.

For the measurements used in this paper, the interferometer was improved by stabilizing the irradiance of the laser.

<table>
<thead>
<tr>
<th>Interferogram analysis</th>
<th>Avo28-S5c</th>
<th>Avo28-S8c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>10.3</td>
<td>10.3</td>
</tr>
<tr>
<td>Diffraction effect</td>
<td>4.8</td>
<td>4.8</td>
</tr>
<tr>
<td>Standard deviation of</td>
<td>16</td>
<td>16</td>
</tr>
<tr>
<td>the mean volume</td>
<td>3.3</td>
<td>9.6</td>
</tr>
<tr>
<td>Total</td>
<td>20</td>
<td>22</td>
</tr>
</tbody>
</table>

\[
(u(V)/V) /10^{-9} = \frac{1}{u(V)} \times 10^{-9}
\]
light. The light from the ECDL was split into two parts and guided to the two arms of the interferometer by multi-mode fibres. Two aspects of these measurements were taken into account: a mode scrambler provided a uniform intensity distribution within the field of view, and a monitor photo-diode combined with a ‘noise eater’ (i.e. a servo control with a fast liquid crystal light modulator) stabilised the intensity of the interferometer input [49].

Sphere AVO28-S5c was measured in August 2013. It was washed, following the suggestions of the IAC, with distilled water and deconex OP162, a pH neutral, salt-free cleaning concentrate for precision optical components. After extensive purging with distilled water, the sphere was rinsed with alcohol (p.A., pro analysi, analytically pure). The measurement followed a 50%-overlapping procedure: with a field of view of 60°, the sphere was rotated for the next measurement by only 30°. The sphere was measured from both sides, so that a complete set of diameters measured through arm 1 and a complete set measured through arm 2 of the interferometer were derived. For each single measurement, the temperature was corrected by a recently calibrated Pt25 resistance thermometer as well as with a set of thermocouples [50].

Sphere AVO28-S8c was measured in a like manner in September 2014. In this case, the data came from two sets of completely overlapping measurements, each taken in a different sequence and with different rotation steps. Nevertheless, the volume characterization was based on $7 \times 10^5$ diameter values.

Compared to the initial spherical state produced by the Australian polishing, the PTB polishing removed about 12 µm from the diameter of sphere AVO28-S5. The $p\nu$ value of the diameter was reduced from 98 nm to 69 nm, illustrating nicely the effects of anisotropy of the modulus of elasticity (E-modulus) of a silicon single crystal [51, 52]. For AVO28-S8, two previous measurement cycles, AVO28-S8a and AVO28-S8b, have already been reported [5, 12, 48]. The diameter of the sphere AVO28-S8 has now been reduced by 20 µm and its $p\nu$ value decreased from 90 nm to 38 nm.

The uncertainties follow the considerations and calculations presented in [48]. Due to the smaller deviations from roundness (decreased $p\nu$ values) for the repolished spheres, the influence of the wave front aberrations were also presumably reduced (table 6), but such distortions remain the principal uncertainty contribution for the present sphere interferometer at PTB. A new interferometer, with a set of objectives with considerably reduced wave front aberrations, is currently being tested. Results for this new instrument together with optical simulation calculations will be reported soon.

To take into account the optical behaviour of the surface layers, a layer model was created [48] and is illustrated in figure 1. The optical constants of the different surface layers are given in table 7.

Table 6. Uncertainty budgets for the apparent volume measurements of the $^{28}$Si spheres at PTB [48].

<table>
<thead>
<tr>
<th></th>
<th>AVO28-S5c</th>
<th>AVO28-S8c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interferometry</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Temperature</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Wavefront distortions</td>
<td>25</td>
<td>19</td>
</tr>
<tr>
<td>Parasitic interferences</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Volume</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Total</td>
<td>27</td>
<td>21</td>
</tr>
</tbody>
</table>

Table 7. The optical constants (refractive index $n$ and the absorption index $k$) of the surface layers (SiO$_2$, H$_2$O and C$_m$H$_n$) and the silicon core (Si). The Abbr column refers to the abbreviations of the model layers in figure 1.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Abbr</th>
<th>$n$</th>
<th>$k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>Si Core</td>
<td>3.881 (1)</td>
<td>0.019 (1)</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>OL</td>
<td>1.457 (10)</td>
<td>0</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>CWL, PWL</td>
<td>1.332 (10)</td>
<td>1.54 (1.00) $\times 10^{-8}$</td>
</tr>
<tr>
<td>C$_m$H$_n$</td>
<td>CL</td>
<td>1.45 (10)</td>
<td>0 (0.1)</td>
</tr>
</tbody>
</table>
a zero-crossing for thicknesses in the range of 1.5 nm to 2 nm. As regards the structure of the Si-SiO₂ interface, density-functional calculations of the lattice strain suggested that the effect of surface relaxation and reconstruction is an order of magnitude smaller than the present uncertainty of the volume measurement [68].

2.6. Mass

The masses of the spheres AVO28-S5c and AVO28-S8c were determined in air and under vacuum by the BIPM, NMII and PTB.

All measurements at the BIPM were carried out using their Sartorius CCL 1007 mass comparator. Before weighing, the two spheres were cleaned three times, using the cleaning procedure recommended by the National Metrology Institute of Australia, NMII [53]. A set of stainless steel air buoyancy artefacts, consisting of a tube (Cp) and a hollow cylinder (Cc), was used to determine the air density for the buoyancy correction. A set of Pt-Ir sorption artefacts, consisting of a cylinder (A₀) and a stack of 8 disks (A₁₈), was used to establish the link between masses in air and vacuum. The masses in air were measured three times, with weighings in vacuum occurring in-between. After each change of condition, a stabilization period of at least 3 d was observed before starting the next set of measurements under the new conditions.

The weighings of the two spheres were carried out directly after the first phase of the Extraordinary Calibrations against the following references:

Table 8. Diameter and volume of ²⁸Si spheres (t_rts,90 = 20°C, vacuum).

<table>
<thead>
<tr>
<th>Sphere</th>
<th>Lab.</th>
<th>Mean apparent diameter/nm</th>
<th>Date of measurement</th>
<th>Δφ/nm²</th>
<th>Mean diameter of Si core/nm</th>
<th>Volume V of Si core/cm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>AVO28-S5c</td>
<td>PTB</td>
<td>93710811.38 (83)</td>
<td>August 2013</td>
<td>0.000 (17)</td>
<td>93710811.38 (83)</td>
<td>430.891 291 (12)</td>
</tr>
<tr>
<td>AVO28-S5c</td>
<td>NMII</td>
<td>93710811.11 (62)</td>
<td>June–July 2014</td>
<td>-0.001 (25)</td>
<td>93710811.11 (62)</td>
<td>430.891 288 (9)</td>
</tr>
<tr>
<td>AVO28-S5c</td>
<td>weighted mean</td>
<td>93710811.21 (50)</td>
<td></td>
<td></td>
<td>93710811.21 (50)</td>
<td>430.891 289 (7)</td>
</tr>
<tr>
<td>AVO28-S8c</td>
<td>PTB</td>
<td>93701526.24 (66)</td>
<td>September 2014</td>
<td>0.010 (32)</td>
<td>93701526.26 (66)</td>
<td>430.763 222 (9)</td>
</tr>
<tr>
<td>AVO28-S8c</td>
<td>NMII</td>
<td>93701526.29 (68)</td>
<td>Nov.–Dec. 2014</td>
<td>-0.009 (28)</td>
<td>93701526.27 (68)</td>
<td>430.763 223 (9)</td>
</tr>
<tr>
<td>AVO28-S8c</td>
<td>weighted mean</td>
<td>93701526.26 (47)</td>
<td></td>
<td></td>
<td>93701526.26 (47)</td>
<td>430.763 223 (7)</td>
</tr>
</tbody>
</table>

Δφ = phase shift corrections.

Table 9. Masses of the ²⁸Si spheres as measured in air (without a correction for the reversible water layer).

<table>
<thead>
<tr>
<th>Sphere</th>
<th>Laboratory</th>
<th>Mass/kg</th>
<th>Mass unc./µg</th>
<th>Date of measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td>AVO28-S5c</td>
<td>PTB</td>
<td>0.999698447</td>
<td>12</td>
<td>Nov./Dec. 2013</td>
</tr>
<tr>
<td>AVO28-S5c</td>
<td>BIPM</td>
<td>0.999698423</td>
<td>13</td>
<td>Feb./March 2014</td>
</tr>
<tr>
<td>AVO28-S5c</td>
<td>NMII</td>
<td>0.999698437</td>
<td>16</td>
<td>May/June 2014</td>
</tr>
<tr>
<td>AVO28-S8c</td>
<td>BIPM</td>
<td>0.999401303</td>
<td>13</td>
<td>Feb./March 2014</td>
</tr>
<tr>
<td>AVO28-S8c</td>
<td>NMII</td>
<td>0.999401328</td>
<td>13</td>
<td>Apr./May 2014</td>
</tr>
<tr>
<td>AVO28-S8c</td>
<td>PTB</td>
<td>0.999401325</td>
<td>12</td>
<td>Oct./Nov. 2014</td>
</tr>
</tbody>
</table>

Table 10. Masses of the ²⁸Si spheres as measured in vacuum.

<table>
<thead>
<tr>
<th>Sphere</th>
<th>Laboratory</th>
<th>Mass/kg</th>
<th>Mass unc./µg</th>
<th>Date of measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td>AVO28-S5c</td>
<td>PTB</td>
<td>0.999698438 5</td>
<td>6.9</td>
<td>Nov./Dec. 2013</td>
</tr>
<tr>
<td>AVO28-S5c</td>
<td>BIPM</td>
<td>0.999698430 1</td>
<td>4.4</td>
<td>Feb./March 2014</td>
</tr>
<tr>
<td>AVO28-S5c</td>
<td>NMII</td>
<td>0.999698437 3</td>
<td>7.6</td>
<td>May/June 2014</td>
</tr>
<tr>
<td>AVO28-S5c</td>
<td>weighted mean</td>
<td>0.999698433 2</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>AVO28-S8c</td>
<td>BIPM</td>
<td>0.999401309 5</td>
<td>4.3</td>
<td>Feb./March 2014</td>
</tr>
<tr>
<td>AVO28-S8c</td>
<td>NMII</td>
<td>0.999401320 9</td>
<td>7.8</td>
<td>Apr./May 2014</td>
</tr>
<tr>
<td>AVO28-S8c</td>
<td>PTB</td>
<td>0.999401316 0</td>
<td>7.3</td>
<td>Oct./Nov. 2014</td>
</tr>
<tr>
<td>AVO28-S8c</td>
<td>weighted mean</td>
<td>0.999401312 8</td>
<td>3.5</td>
<td></td>
</tr>
</tbody>
</table>

Table 11. The traceability path between the reference masses used for the mass determination of the ²⁸Si spheres at PTB and the prototypes of the kilogram at the BIPM.

<table>
<thead>
<tr>
<th>Sphere</th>
<th>Date</th>
<th>Name</th>
<th>Last calibration by PTB</th>
<th>Name</th>
<th>Last calibration by PTB</th>
<th>Name</th>
<th>Last calibration by PTB</th>
</tr>
</thead>
<tbody>
<tr>
<td>AVO28-S5c</td>
<td>Nov./Dec. 2013</td>
<td>PtSk-Z</td>
<td>Nov. 2013 (against No. 70)</td>
<td>Name</td>
<td>Last calibration by PTB</td>
<td>Name</td>
<td>Last calibration by PTB</td>
</tr>
</tbody>
</table>
the IPK [69]. The spheres were compared in air with BIPM working standard No. 77, which had itself been weighed against working standards Nos. 91 and 650. The two latter working standards had already been compared directly with the IPK, in air. Tables 9 and 10 give the masses of both spheres, in air and in vacuum, with respect to the mass of the IPK. During the Extraordinary Calibrations, it was observed that the BIPM ‘as-maintained’ mass unit was 35 µg smaller than the mass of the IPK. The standard uncertainty of this mass difference is estimated as 3 µg. Therefore, the masses of AVO28-S5c and AVO28-S8c, expressed in the mass unit maintained formerly at the BIPM, are 35 µg larger than the values given in tables 9 and 10.

A study was undertaken at the BIPM to determine the mass of the CWL present on the surface of a natural silicon sphere. Two methods were used: baking the sphere under vacuum and immersing the sphere in doubly distilled water [54]. For both methods, the chemical adsorption coefficient was obtained by determing the mass difference under vacuum conditions (to reduce the uncertainty) prior to and after placing the sphere in air, in order to reintroduce the chemisorbed water to the surface of the sphere. The mean chemical adsorption coefficient thus obtained was 0.026±2 µg cm−2 with a standard uncertainty (k = 1) of 0.012±2 µg cm−2. The BIPM results confirmed those obtained by NMIJ/AIST (Japan) which had measured the adsorption isotherms on SiO2/Si(1 0 0) plane surfaces [43].

NMIJ conducted mass measurements using an early version of the Mettler-Toledo M_one mass comparator [55]. The measurements under vacuum showed a higher reproducibility than those in air, where air buoyancy and convection effects affected the weighing stability. The standard uncertainty of the mass difference measurement under vacuum was about 5 µg.

The silicon spheres were washed manually by rubbing their surfaces with nitride rubber gloves using a neutral detergent for optical components for about 10 min, followed by a rinse with 30 dm3 of pure water and 1 dm3 of ethanol. The surface area difference between the artefacts amounts to 28Si spheres’ distributed to the participants in April 2008 [53]. The protocol does not clearly specify the number of washings. Therefore, NMIJ investigated the washing effects on reproducibility by washing AVO28-S5c three times and by washing AVO28-S8c twice. The repeated washings, with subsequent mass measurements at NMIJ, showed a mass decrease between 3 µg and 8 µg after each washing. This phenomenon could be interpreted as a decrease of a carbonaceous layer (CL) on surfaces by the washing procedure. The result of the washing experiment suggests the number of washings specified in the protocol should not be less than three to achieve a stable mass value at the low microgram level. It should be also noted that the washing effect on the mass determination would be compensated, to a great extent, by the surface characterization described in section 2.4 if we specify the washing procedure rigorously. For now, NMIJ estimated the standard uncertainty of the reproducibility of the washing procedure specified in the aforementioned protocol to be 4 µg, assuming uniform distribution with a half width of 7 µg.

The traceability of NMIJ’s mass value to the IPK was achieved by using the mass value 1 kg + 0.360 mg for the Pt-Ir prototype No. 94 (BIPM Certificate No. 59, 2009) measured at the BIPM in August 2009 and also by applying a correction of −0.0301 mg, which corresponded to the value during this time period recommended by the BIPM in December 2014 [8]. In addition, the mass value 1 kg + 0.176 mg for the Pt–Ir prototype No. 6 (BIPM Certificate No. 8, 1993) at the third periodic verification of national prototypes of the kilogram was used to determine the long-term drift rate of NMIJ’s mass value. The results for the weighings are shown in tables 9 and 10. The NMIJ measurement results are the average obtained by two measurement cycles.

At PTB, the mass determinations of the 28Si spheres AVO28-S5c and AVO28-S8c were performed in air and under vacuum during the periods November/December 2013 and October/November 2014, respectively. The procedure agreed to in [53] for the Avogadro project was used for cleaning the spheres. After cleaning, the measurements were made on a Mettler-Toledo M_one mass comparator using the prototype of the kilogram No. 70 and the Pt-Ir mass standard PSk-Z as reference masses. Table 11 shows the traceability path between the reference masses used for the mass determination of the 28Si spheres and the prototypes of the kilogram at the BIPM. The last calibration of prototype No. 70 at the BIPM was performed in June 2013 (Certificate No. 70, BIPM 2013). The BIPM determined the mass of this prototype to be 1 kg − 0.207(7) mg. Mass comparisons with other prototypes of the kilogram were made at PTB before and after the prototype was hand-carried between PTB and BIPM. The results showed a mass loss of 5 µg. Because it is unknown whether this mass change occurred before or after the calibration of the prototype, this mass difference had to be considered in the uncertainty budget as an uncertainty contribution due to the instability of the mass of the prototype.

The Pt-Ir cylinder PtSk-Z is one of two Pt-Ir artefacts used as sorption artefacts for the determination of the sorption correction and as a link between the mass of the silicon spheres in vacuum and the prototype of the kilogram No. 70 in air [53]. The surface area difference between the artefacts amounts to 183 cm2. In order to apply a buoyancy correction in air with the lowest uncertainty, the air density was measured using buoyancy artefacts [53].

For the sphere AVO28-S5c, a mass of 0.999 698 483(13) kg and 0.999 698 4743(93) kg was determined in air (without correction of reversible sorption) and in vacuum, respectively. For sphere AVO28-S8c, a mass of 0.999 401 362(14) kg was determined in air (again without correction of reversible sorption) and 0.999 401 3534(94) kg in vacuum. For both spheres, the mass difference between the measurements in air and in vacuum amounted to about 8.5 µg. This value corresponds to a change in the sorption coefficient between vacuum and air of 30 ng cm−2, which is in good agreement with the values published in [56] and [57].

In December 2014, PTB was informed by the BIPM about revised mass values for BIPM calibrations following the Extraordinary Calibration Campaign against the IPK [8, 69]. Consequently, revised mass values and revised drift
corrections of the involved prototypes, No. 70 and No. 52, had to be considered. Regarding the calibration of prototype No. 70 in June 2013, a corrected mass value of $1 \text{ kg} - 0.242(3) \text{ mg}$ was assigned by the BIPM. The difference between the original and the corrected mass value amounts to $35 \mu\text{g}$. In due consideration of the traceability path given in table 11, the mass values determined for the $28\text{Si}$ spheres $A\ VO_{28}\ -S5c$ was assigned by the BIPM. The difference between the original and the corrected mass value amounts to $35 \mu\text{g}$. In due consideration of the traceability path given in table 11, the mass values determined for the $28\text{Si}$ spheres $A\ VO_{28}\ -S5c$ and $A\ VO_{28}\ -S8c$ at PTB were revised correspondingly (tables 9 and 10).

The weighted mean of the masses measured in vacuum was used for the determination of the Avogadro constant (table 10). The effect of the correlation arising from the common traceability of all masses to the IPK was taken into account for the weighted mean and its uncertainty, although its magnitude is nearly negligible.

To determine the mass of the silicon core, the mass of the surface layers was subtracted from the mass of the sphere. In addition, owing to point defects, there is a difference between the mass of a sphere having $\text{Si}$ atoms occupying all regular sites and the measured mass value.

$$m_{\text{deficit}} = V\Sigma(m_{28} - m_i)N_i$$  \hspace{1cm} (4)

In equation (4), $m_{28}$ and $m_i$ are the masses of a $28\text{Si}$ atom and of the point defect named $i$, respectively (a vacancy mass is zero.) Oxygen was associated with an interstitial lattice site, so that $m_O$ is the sum of the oxygen and $28\text{Si}$ masses. The same applies to nitrogen impurities. $V$ is the sphere volume and $N_i$ is the concentration of the point defect $i$ (see section 2.1).

The etching did not completely remove the metals from the $A\ VO_{28}\ -S5$ sphere. Approximately $5\%$ of the original metallic contaminant remained (corresponding to $4 \mu\text{g}$) and had probably diffused into the sphere during the thermal oxidation that was performed before repolishing. After repolishing the spheres, no metals could be detected by XRF at the sphere’s surface. Therefore, a mass correction of $-4(3)\mu\text{g}$ was added to the mass deficit. A mass deficit of $3.8(3.8)\mu\text{g}$ was then calculated for the $A\ VO_{28}\ -S5c$ sphere and a mass deficit of $22.7(3.5)\mu\text{g}$ for the $A\ VO_{28}\ -S8c$ sphere.

After the surface-layer mass ($m_{\text{SL}}$, table 4(b) in section 2.4) was subtracted and the mass deficit ($m_{\text{deficit}}$) was added, the Si core mass $m = m_{\text{sphere}} - m_{\text{SL}} + m_{\text{deficit}}$ could be calculated for both spheres (table 12).

3. Avogadro constant

Table 12 gives the results of the new and refined measurements of the molar mass, lattice parameter, volume, mass, and density of the cores of the enriched silicon spheres. To evaluate

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Unit</th>
<th>$A\ VO_{28}\ -S5c$</th>
<th>$A\ VO_{28}\ -S8c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M$</td>
<td>g mol$^{-1}$</td>
<td>27.976 97009 (15)</td>
<td>27.976 97009 (15)</td>
</tr>
<tr>
<td>$a$</td>
<td>pm</td>
<td>543.099 6219 (10)</td>
<td>543.099 6168 (11)</td>
</tr>
<tr>
<td>$V$</td>
<td>cm$^3$</td>
<td>430.891 2891 (69)</td>
<td>430.763 2225 (65)</td>
</tr>
<tr>
<td>$m$</td>
<td>g</td>
<td>999.698 359 (11)</td>
<td>999.401 250 (16)</td>
</tr>
<tr>
<td>$\rho = m/V$</td>
<td>kg m$^{-3}$</td>
<td>2320.070 943 (46)</td>
<td>2320.070 976 (51)</td>
</tr>
<tr>
<td>$N_A$</td>
<td>10$^{23}$ mol$^{-1}$</td>
<td>6.022 140 72 (13)</td>
<td>6.022 140 80 (14)</td>
</tr>
</tbody>
</table>

Table 13. The uncertainty budget for the new $N_A$ determination using $A\ VO_{28}\ -S5c$. The percent contributions to the total uncertainty are the relevant variance fractions ratioed to the total variance. The principal uncertainty contributions are, at present, due to surface characterization and the volume determination.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Relative uncertainty/10$^{-9}$</th>
<th>Contribution/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar mass ($M$)</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>Lattice parameter ($a$)</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>Surface characterization ($m_{\text{SL}}$)</td>
<td>10</td>
<td>23</td>
</tr>
<tr>
<td>Sphere volume ($V$)</td>
<td>16</td>
<td>59</td>
</tr>
<tr>
<td>Sphere mass ($m$)</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Point defects</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>Total</td>
<td>21</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 14. Value of the Avogadro constant based upon the repolished $28\text{Si}$-enriched silicon spheres.

<table>
<thead>
<tr>
<th>Sphere</th>
<th>$N_A/10^{23}$ mol$^{-1}$</th>
<th>$u_r/10^{-9}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A\ VO_{28}\ -S5c$</td>
<td>6.022 140 72 (13)</td>
<td>21</td>
</tr>
<tr>
<td>$A\ VO_{28}\ -S8c$</td>
<td>6.022 140 80 (14)</td>
<td>23</td>
</tr>
<tr>
<td>Mean value</td>
<td>6.022 140 76 (12)</td>
<td>20</td>
</tr>
</tbody>
</table>

and express the measurement uncertainties, the approach recommended by the Guide to the Expression of Uncertainty in Measurement [58] was applied using the GUMWorkbench software [59]; covariances were calculated and folded into the uncertainty analysis. The quantities dominating the total uncertainty of the revised Avogadro constant $N_A$ were the apparent diameter, $D_{\text{app}}$, of the spheres and the mass of the surface layer, $m_{\text{SL}}$ (see table 13).

The new $N_A$ determinations, based on a careful reanalysis of the two $A\ VO_{28}$ spheres, are summarized in table 14; they differ by only $13(20) \times 10^{-9} N_A$. Averaging these two values, the final value for the Avogadro constant becomes

$$N_A = 6.022 140 76(12) \times 10^{23} \text{ mol}^{-1},$$

with a relative standard uncertainty of $20 \times 10^{-9}$.

4. Conclusions

The value $N_A = 6.022 140 82(18) \times 10^{23} \text{ mol}^{-1}$ given in a previous paper [12] must also be updated due to the recalibration of the mass standards following the recent Extraordinary Calibration Campaign against the IPK. A provisional corrected value would be $N_A = 6.022 140 99(18) \times 10^{23} \text{ mol}^{-1}$.

Some considerations of the potential correlations between the different measurement components contributing to the new and previously reported $N_A$ values should be addressed. The molar mass measurements are uncorrelated; they were amply repeated in three different laboratories using different calibration and measurement approaches as well as TMAH instead of NaOH as matrix diluent. The measurements of the lattice parameters differed in significant respects: the optical interferometer was rebuilt to accommodate a different wavelength, the temperature measurements relied on new equipment and new calibrations, and the apparatus was completely disassembled and realigned. However, because the same
An interferometer crystal was used for both measurements, and
the lattice parameter values relied on measurements from a
single laboratory, the past and present results may be corre-
lated by up to 50%. Because the AVO28-S5 and AVO28-S8
spheres were fully repolished, the contributions of their sur-
face properties to the error budget are not correlated. The
same applies to the volume measurements; however, diffrac-
tion effects—which are extremely difficult to model or inves-
tigate—may be correlated between the old and new values.
Mass measurements were newly calibrated and traceable back
to the IPK. Therefore, their correlation with the past measure-
ments is considered to be negligible. Finally, the point defect
contributions to the error budget are basically from the same
source and are thus 100% correlated. Details will be published
in a separate paper [60].

The forthcoming definition of the kilogram [61] will be based
on fixing the value of the Planck constant. To compare this new
$N_A$ value with the most recent Planck constant results by the
watt balance (WB) experiments [62, 63], we can convert them to
an equivalent Avogadro constant value using the molar Planck
constant ($N_Ah = 3.9903127176(28) \times 10^{-10}$ Js mol$^{-1}$), which
has a relative standard uncertainty of only $0.7 \times 10^{-9}$ [64]. The
NRC WB value was updated for the recalibration of mass stand-
ards following the Extraordinary Calibration Campaign against
the IPK, $h(NRC) = 6.62607011(12) \times 10^{-34}$ Js [65]. The NIST
updated their former $h$ values and published a combined $h$ value
for the NIST-3 WB, $h(NIST-3) = 6.6260936(37) \times 10^{-34}$ Js
[66]. Note however that we have been unable to update the
CODATA 2010 $N_A$ value. These results are compared in
figure 3. The accuracy and uncertainty of the new determination
of $N_A$ (equation (5)) is within the targeted relative uncertainty
so as to make the kilogram redefinition possible [61]; therefore,
this new measurement result demonstrates a successful mise en
pratique of a definition based upon a fixed value of the Planck
constant.

Because clear-cut effects of crystal imperfections have
not yet been detected, the uncertainty of equation (5) still
appears to be limited by the performance of the measurement
instrumentation. Therefore, provided the source material is
chemically and physically well characterized with respect to
the mass fractions of the minor isotopes and impurities, the
value of the lattice parameter, and the crystallographic per-
fection, material realizations of the kilogram and its submul-
tiples in the form of crystal artefacts require only volume
measurements and surface characterizations. These same two
parameters would also be the only two quantities necessary to
monitor the secular stability of the artefacts.

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Certain commercial equipment, instruments, or materials
are identified in this paper in order to specify the experimental
procedure adequately. Such identification is not intended
to imply recommendation or endorsement by the National
Institute of Standards and Technology, nor is it intended to
imply that the materials or equipment identified are neces-
sarily the best available for the purpose.

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