The Avogadro constant: determining the number of atoms in a single-crystal $^{28}\text{Si}$ sphere

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The Avogadro constant, the number of entities in an amount of substance of one mole, links the atomic and the macroscopic properties of matter. Since the molar Planck constant—the product of the Planck constant and the Avogadro constant—is very well known via the measurement of the Rydberg constant, the Avogadro constant is also closely related to the Planck constant. In addition, its accurate determination is of paramount importance for a new definition of the kilogram in terms of a fundamental constant. Here, we describe a new and unique approach to determine the Avogadro constant from the number of atoms in 1 kg single-crystal spheres that are highly enriched with the $^{28}\text{Si}$ isotope. This approach has enabled us to apply isotope dilution mass spectroscopy to determine the molar mass of the silicon crystal with unprecedented accuracy. The value obtained, $N_A = 6.02214082(18) \times 10^{23} \text{mol}^{-1}$, is now the most accurate input datum for a new definition of the kilogram.

**Keywords:** fundamental constants; new kilogram definition; enriched silicon crystal

1. Introduction

Exploring the extent and precision to which our theoretical models and measurement techniques are valid across the different realms of physics is of utmost interest. Accurate measurements of the fundamental constants of physics are a way of carrying out such investigations and testing the limits of our knowledge and technologies. In these tests, the measurement of the Avogadro constant, $N_A$, holds a prominent position and appears both as an input and an output of an overall least-squares adjustment of the fundamental constants because it connects microphysics and macrophysics.

The Avogadro constant $N_A$ is the number of atoms or molecules in a mole of a pure substance, for instance, the number of atoms (unbound, at rest and in their ground state) in 12 g of the carbon isotope $^{12}\text{C}$. Therefore, $N_A$ expresses the mass of $^{12}\text{C}$ in kilograms according to $M(^{12}\text{C}) = N_A m(^{12}\text{C})$, where $M(^{12}\text{C}) = 12 \text{ g mol}^{-1}$ and $m(^{12}\text{C})$ are the molar mass and atomic mass of $^{12}\text{C}$, respectively. Many different measurements of the Avogadro constant, from that of

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Loschmidt to that of Perrin, supported the Maxwell and Boltzmann descriptions of matter in terms of atoms [1]. The Avogadro constant $N_A$ establishes detailed balances in chemical reactions. The Avogadro constant is a scale factor to convert atomic quantities and macroscopic quantities also as regards electromagnetism and thermodynamics, i.e. it connects the electron charge $e$ with a macroscopically measurable electrical charge via $F = N_A e$, where $F$ is the Faraday constant, and it also connects statistical mechanics with thermodynamics via $R = N_A k_B$, where $R$ and $k_B$ are the universal gas constant and the Boltzmann constant, respectively. The molar Planck constant, $N_A h$, is very well known via the measurement of the Rydberg constant, $R_\infty = \alpha^2 M(e^-) c/(2N_A h)$, where $\alpha$ is the fine-structure constant, $M(e^-)$ is the molar mass of the electron, $c$ is the speed of light and $h$ is the Planck constant. Therefore, an accurate measurement of $N_A$ also provides an accurate determination of the Planck constant, and vice versa.

As a forthcoming new definition of the kilogram will most probably be based on the Planck constant [2], a precise determination of the Avogadro constant is of paramount importance as well, since presently it is the only alternative way to obtain an independent value for the Planck constant via the molar Planck constant. Today, the kilogram is the only base unit still defined by a material prototype as stated by the 1st General Conference on Weights and Measures in 1889. The mass of the international prototype expressed in terms of the SI unit is invariable by definition, but since 1889 its absolute mass is suspected to have drifted by about 50 \( \mu \)g, or $5 \times 10^{-8}$ in relative terms.

While the uncertainty of the mass of the international prototype is zero by convention, any *mise en pratique* of a new definition will fix an uncertainty to the kilogram. In order to ensure continuity to mass metrology, it has been agreed that the relative uncertainty of any new realization must not exceed $2 \times 10^{-8}$. Presently two different experiments have the potential to achieve this challenging goal. One is the watt-balance experiment, which was first proposed in 1975 by Kibble [3]. It aims to measure the Planck constant by the virtual comparison of mechanical power with electrical power. The result is a measurement of the $m(K)c^2/h$ ratio, where $m(K)$ is the mass of the international prototype. The other experiment, whose basic principles are described by Becker [1], was outlined by Zosi [4] in 1983 and requires counting the atoms in 1 kg nearly perfect single-crystal silicon spheres by determining $N_A$. In this method, crystallization acts as a ‘low-noise amplifier’ making the lattice parameter accessible to macroscopic measurements, thus avoiding single atom counting. Silicon is used because it is one of the best-known materials and, owing to the needs of the semiconductor industry, it can be grown into high-purity, large and almost perfect single crystals.

Since 1998, a relative $1.2 \times 10^{-6}$ discrepancy has been observed when comparing the results of these two different experiments through the molar Planck constant [5]. Subsequently, it was conjectured that this discrepancy originated through the difficulty of accurately determining the isotopic composition of a natural silicon crystal, a key measurement for $N_A$ determination. To solve this problem, we started a research project to repeat the measurement by using a silicon crystal highly enriched with the $^{28}$Si isotope. In this way, the difficult absolute calibration of the mass spectrometer with the required small uncertainty could be overcome by applying isotope dilution mass spectrometry combined with multi-collector inductively coupled plasma mass spectrometry.
In his pioneering work on the Avogadro constant determination, Deslattes also foresaw in 1974 the need for enriched silicon to improve mass measurement uncertainties [6].

The project started in 2004 with the isotope enrichment being undertaken. Subsequently, a polycrystal was grown by chemical vapour deposition [7] and, in 2007, the 5 kg $^{28}$Si boule shown in figure 1 was grown. As an unexpected by-product, the availability of highly enriched and highly pure $^{28}$Si single crystals, as well as of highly enriched $^{29}$Si and $^{30}$Si crystals, brought about physical and technological investigations in the fields of quantum computing and semiconductor spectroscopy [8].

2. Principle of the measurement

Atoms were counted by exploiting their ordered arrangement in a crystal. Therefore, the crystal and the unit-cell volumes having been measured, the count requires their ratio to be calculated, the number of atoms per unit cell being
Table 1. Point-defect concentration in the AVO28-S5 and AVO28-S8 spheres and in the XINT crystal.

<table>
<thead>
<tr>
<th>defect</th>
<th>unit</th>
<th>AVO28-S5</th>
<th>AVO28-S8</th>
<th>XINT</th>
</tr>
</thead>
<tbody>
<tr>
<td>carbon</td>
<td>$10^{15}$ cm$^{-3}$</td>
<td>0.40(5)</td>
<td>1.93(19)</td>
<td>1.07(10)</td>
</tr>
<tr>
<td>oxygen</td>
<td>$10^{15}$ cm$^{-3}$</td>
<td>0.283(63)</td>
<td>0.415(91)</td>
<td>0.369(33)</td>
</tr>
<tr>
<td>boron</td>
<td>$10^{15}$ cm$^{-3}$</td>
<td>0.011(4)</td>
<td>0.031(18)</td>
<td>0.004(1)</td>
</tr>
<tr>
<td>vacancy</td>
<td>$10^{15}$ cm$^{-3}$</td>
<td>0.33(11)</td>
<td>0.33(11)</td>
<td>0.33(11)</td>
</tr>
</tbody>
</table>

known. Ideally, the crystal must be free of imperfections, monoisotopic (or the isotopic composition must be determined) and chemically pure. The count gives the Avogadro constant via

$$N_A = \frac{n V_{\text{mol}}}{a_0^3} = \frac{n M}{\rho_0 a_0^3},$$

where $n = 8$ is the number of atoms per unit cell, $V_{\text{mol}}$ and $a_0^3$ are the molar and unit-cell volumes, $M$ is the molar mass and $\rho_0$ is the density. We selected a spherical crystal shape to trace back the volume determination to diameter measurements and to make possible an accurate geometrical, chemical and physical characterization of the surface. Hence, two spheres, AVO28-S5 and AVO28-S8, were taken at 229 and 367 mm distances, respectively, from the seed crystal position and shaped as quasi-perfect spheres. Their masses and volumes were accurately measured to obtain their densities.

(a) Isotope enrichment, crystal growth and crystal purity

The isotope enrichment was carried out at the Central Design Bureau of Machine Building in Saint Petersburg, Russia, by centrifugation of SiF$_4$ gas. After conversion of the enriched gas into SiH$_4$, a polycrystal was grown by chemical vapour deposition at the Institute of Chemistry of High-Purity Substances of the Russian Academy of Sciences in Nizhny Novgorod, Russia. The 5 kg crystal was grown and purified by multiple float-zone crystallizations at the Leibniz-Institut für Kristallzüchtung in Berlin, Germany. The concentrations of the residual impurities (carbon, oxygen and boron) were determined at the Physikalisch-Technische Bundesanstalt (PTB), Braunschweig, Germany, by optical spectroscopy. The concentration of vacancy-related defects was deduced from positron lifetime spectroscopy at the Halle University, Germany. Results are shown in table 1.

(b) Lattice parameter

To measure the lattice parameter, the Istituto Nazionale di Ricerca Metrologica, Torino, Italy, upgraded a combined X-ray and optical interferometer to expand the measurement capabilities to many centimetres and to achieve a relative uncertainty approaching $10^{-9}$. To exploit this capability, PTB manufactured an X-ray interferometer crystal (XINT) with an unusually long 5 cm analyser crystal. The sample used for the XINT was taken from a point in the boule located between the two spheres, and the lattice parameter was...
measured at a distance of 306.5 mm from the seed crystal. To demonstrate the crystal homogeneity, the National Institute of Standards and Technology (NIST), Gaithersburg, MD, USA, measured the lattice parameter of crystal samples, taken above and below the two spheres, by means of a comparison with that of a natural Si crystal calibrated by X-ray interferometry. The National Metrology Institute of Japan (NMIJ) demonstrated the crystal perfection by 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), Tsukuba, Ibaraki, Japan. The mean spacing of the interferometer diffracting plane,

$$d_{220}^{(\text{XINT})} = 192.01471267(67) \text{ pm},$$  \hspace{1cm} (2.2)

was measured at 20°C and 0 Pa by combined X-ray and optical interferometry (figure 2).

(c) Surface

Silicon is covered with an oxide surface layer. For the determination of the oxide layer mass and thickness (table 2), synchrotron radiation-based X-ray reflectometry at specific sphere surface points was selected to calibrate a subsequent complete thickness mapping by spectroscopic ellipsometry [9]. To increase the contrast between the optical constants of the silicon and the oxide, and to increase the range of incidence angles, photon energies around the oxygen K absorption edge at 543 eV were used. However, additional measurements by X-ray photoelectron spectroscopy and X-ray fluorescence revealed unexpected surface contamination by copper and nickel. From near-edge X-ray absorption fine-structure measurements, these contaminants were found to be present as silicides, heavily affecting the optical constants of the surface layers. Therefore, the oxide thickness determination by X-ray reflectometry on the sphere was replaced by X-ray fluorescence measurements with an excitation energy of 680 eV,
Figure 3. Topographic maps of the SiO$_2$ thickness. (a) AVO28-S5, (b) AVO28-S8. The rainbow colour code ranges from 2.0 nm (blue) to 4.5 nm (yellow). (Online version in colour.)

Table 2. Mass and thickness of the total surface layer and mass correction due to the point defects of the AVO28-S5 and AVO28-S8 spheres.

<table>
<thead>
<tr>
<th></th>
<th>unit</th>
<th>AVO28-S5</th>
<th>AVO28-S8</th>
</tr>
</thead>
<tbody>
<tr>
<td>surface layer mass</td>
<td>µg</td>
<td>222.1(14.5)</td>
<td>213.6(14.4)</td>
</tr>
<tr>
<td>surface layer thickness</td>
<td>nm</td>
<td>2.88(33)</td>
<td>2.69(32)</td>
</tr>
<tr>
<td>mass correction</td>
<td>µg</td>
<td>8.1(2.4)</td>
<td>24.3(3.3)</td>
</tr>
</tbody>
</table>

where the oxygen K fluorescence intensity from the sphere surface was compared with that from flat samples for which the oxide layer thickness was determined by X-ray reflectometry.

The total surface layer was modelled, from top to bottom, as follows: a carbonaceous and an adsorbed water layer, a fictive layer of Cu and Ni silicides and an SiO$_2$ layer [10]. From this model, the SiO$_2$ thickness was re-evaluated from the ellipsometric data, showing excellent agreement with the X-ray reflectometry data. The mass deposition of the carbon, copper and nickel contaminants was obtained from X-ray fluorescence measurements. The stoichiometries of the oxide and the thickness of a possible SiO interface were investigated by X-ray photoelectron spectroscopy. These measurements also confirmed the amount of SiO to be below the detection limit of approximately 0.05 nm, which is in agreement with the literature [10]. Since the contribution of this intermediate layer, estimated on the basis of the present detection limit, is 10 times smaller than the contribution of any other layer, this has not been included in the model. Data for chemisorbed water on silicon were taken from the literature [11]. Figure 3 shows the mapping of the surface layer thickness, obtained by spectroscopic ellipsometry with a spatial resolution of 1 mm. In table 2, the mass and thickness of the two sphere surface layers are given.
Figure 4. Mass of the silicon spheres. The AVO28-S5 and AVO28-S8 spheres were weighed in vacuum by the BIPM, NMIJ and PTB. The absolute mass difference between the two spheres is $m_{S5} - m_{S8} = 23.042 \text{mg}$. The bars give the standard uncertainties.

(d) Mass

Mass comparisons of the two spheres with Pt–Ir kilogram standards were carried out in vacuum by the Bureau International des Poids et Mesures (BIPM), Sèvres, France, NMIJ and PTB. Owing to air–vacuum transfer, a sorption correction, which was measured by means of sorption artefacts, had to be considered for the Pt–Ir standards. The mass determinations are shown in figure 4; they are in excellent agreement and demonstrate a measurement accuracy of about 5 µg. Corrections for the surface layers and for the crystal point defects—the mass correction in table 2—have to be considered.

(e) Volume

The spheres were shaped and optically polished by the Australian Centre for Precision Optics, Lindfield, NSW, Australia, and their volumes were determined via diameter measurements. The NMIJ measured sets of diameters by means of a Saunders-type interferometer. PTB used a spherical Fizeau interferometer, which allowed about $10^5$ diameters to be measured and a complete topographical mapping to be achieved. Tunable diode lasers traced back to the frequency standards were applied for phase-shifting techniques. Each sphere is placed between the end-mirrors (plane, in one interferometer, and spherical, in the other) of a Fizeau cavity, and the distances between the mirrors and each sphere, as well as the cavity length, were measured. Since the sphere is almost perfect, its volume is the same as that of a mathematical sphere having the same mean diameter. Hence, a number of diameters were measured and averaged [12]. Figure 5 shows the deviations from a constant diameter in orthographic projections. For the volumes, the measured diameters were corrected for phase shifts in beam reflections at the sphere surface, as well for beam retardation through the surface layer.

(f) Molar mass

The amount-of-substance fractions of the Si isotopes were measured by the Institute for Reference Materials and Measurements (IRMM), Geel, Belgium, via gas mass spectrometry of the SiF$_4$ gas, and by PTB, via isotope dilution
combined with multi-collector inductively coupled plasma mass spectrometry. At IRMM, the spectrometer was calibrated by using synthetic mixtures of enriched Si isotopes. The natural Si contamination of the solutions used to convert the samples into SiF₄ was analysed at the University of Warsaw, Poland, by graphite-furnace atomic absorption spectroscopy. The isotope fractions were measured also at the Institute of Mineral Resources of the Chinese Academy of Science (via gas mass spectrometry, but using a different preparation of the SiF₄ gas based on fluorination by BrF₅) and at the Institute for Physics of Microstructures of the Russian Academy of Sciences (by means of a secondary ion mass spectrometer using a time-of-flight mass analyser).

The PTB measured only the amount-of-substance fractions of the $^{29}$Si and $^{30}$Si isotopes, both forming a virtual two-isotope element within the matrix of all the isotopes. To recover the unknown $^{28}$Si fraction, the crystal samples were blended with a spike, a crystal highly enriched with $^{30}$Si. In addition to the masses of the blended samples, the isotope ratio $x_{30}/x_{29}$, between the $^{30}$Si and $^{29}$Si fractions, was measured in the samples, spike and blends; but the ratio $x_{28}/x_{29}$, between the $^{28}$Si and $^{29}$Si fractions, needed to be measured only in the spike. The amount-of-substance fraction of the $^{28}$Si isotope was obtained indirectly. The spectrometer was calibrated online by using synthetic mixtures of natural Si and two crystals enriched with the $^{29}$Si and $^{30}$Si isotopes. Natural Si contamination, memory effects due to previous measurements and offsets were corrected online by sandwiching each measurement of a sample, spike, blend or
Table 4. Uncertainty budget of the Avogadro constant determination. The main contributions are due at present to the 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</td>
<td>7</td>
<td>5</td>
</tr>
<tr>
<td>lattice parameter</td>
<td>11</td>
<td>13</td>
</tr>
<tr>
<td>surface</td>
<td>14</td>
<td>22</td>
</tr>
<tr>
<td>sphere volume</td>
<td>23</td>
<td>57</td>
</tr>
<tr>
<td>sphere mass</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>point defects</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>total</td>
<td>30</td>
<td>100</td>
</tr>
</tbody>
</table>

mixture with blank—aqueous NaOH solutions—measurements. From samples cut in the vicinity of the spheres, an average molar mass was calculated and given in table 3.

3. Results and outlook

Fifty years ago, Egidi [13] thought about realizing an atomic mass standard. In 1965, Bonse & Hart [14] realized the first X-ray interferometer, thus paving the way to the accomplishment of this dream, and Deslattes [6] soon completed the first $N_A$ determination by counting the atoms in a natural silicon crystal. For the time being, we have concluded the project by carrying out a very accurate $N_A$ measurement by using a silicon crystal highly isotopically enriched.

The measured values of the quantities necessary to determine the Avogadro constant $N_A$ are summarized in table 3. The two values of the Avogadro constant $N_A$ based on the two spheres differ only by $37(35) \times 10^9 N_A$, thus confirming the crystal homogeneity. By averaging these values, the final value of the Avogadro constant is

$$N_A = 6.022\,140\,82(18) \times 10^{23} \text{ g mol}^{-1},$$

with a relative uncertainty of $3.0 \times 10^{-8}$. The majority of the material reported here can also be found in more detail in Andreas et al. [15].

The measurement uncertainty is 1.5 times higher than that targeted for a kilogram redefinition, but ‘close to the finish line of the marathon effort to tie the kilo to a constant of nature’ [16]. The measurement accuracy seems to be limited by the performance of all the working apparatus. In fact, we have not detected the effects of crystal imperfections with respect to the measurement uncertainties reached so far. One of the main contributions to the uncertainty budget (table 4) is due to the distortions of the optical wave fronts in the interferometric measurement of the sphere diameters. Another is because of the metallic contamination of the oxide layer, having an unknown influence on the layer optical constants. To achieve the desired uncertainty, we are planning to use improved optical interferometers, at present under test. Investigations are also under way to eliminate the contamination from the sphere surfaces, without jeopardizing the excellent roundness and nano-roughness of the spheres,
which are both essential to accurate volume measurements. Investigations are in progress to identify the source of natural Si contamination occurring in gas mass spectrometry; repetitions of the molar mass measurement will be carried out in additional laboratories.

For the first time, precise values of the Planck constant derived from different experiments can be compared. This comparison is a test of the consistency of atomic physics. A parallel experiment, having the purpose of measuring $N_A h$ by absolute nuclear spectroscopy, is aiming at extending this test to nuclear physics [17]. Figure 6 shows our result compared with those of the most accurate measurements so far carried out: the watt-balance experiments of the NIST (USA) [18], the National Physical Laboratory (NPL, UK [19], I. A. Robinson 2010, private communication) and the Bundesamt für Metrologie (METAS, Switzerland) [20]. The values of the Planck constant measured by these experiments were converted into the corresponding $N_A$ values by

$$N_A h = 3.9903126821(57) \times 10^{-10} \text{ J s mol}^{-1},$$

which has a relative uncertainty of $1.4 \times 10^{-9}$ [21].

By significantly reducing existing discrepancies, the present result leads to a set of numerical values for the fundamental physical constants with better consistency compared with previous sets. The result is also a significant step towards demonstrating a successful *mise en pratique* of a kilogram definition based on a fixed value of the Avogadro constant or of the Planck constant. The agreement between the different realizations is not yet as good as it is required to retire (for the time being) the Pt–Ir kilogram prototype, but, considering the capabilities already developed and the envisaged improvements, it seems to be realistic that the targeted uncertainty may be achieved in the foreseeable future [22].

We wish to thank A. K. Kaliteevski and his colleagues at the Central Design Bureau of Machine Building and the Institute of Chemistry of High-Purity Substances for their dedication and the punctual delivery of the enriched material, the directors of the participating metrology institutes for their advice and financial support, and our colleagues within the International Avogadro Cooperation (IAC) for their daily work. This research received funds from the European Community’s 7th Framework Programme ERA-NET Plus (grant 217257) and the International Science and Technology Center (grant 2630).

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