Avogadro constant measurements using enriched 28Si monocrystals

Metrologia

SHORT COMMUNICATION • OPEN ACCESS

# Avogadro constant measurements using enriched $^{28}$Si monocrystals

To cite this article: K Fujii *et al* 2018 *Metrologia* **55** L1

OPEN ACCESS
IOP Publishing | Bureau International des Poids et Mesures Metrologia

Metrologia 55 (2018) L1–L4 https://doi.org/10.1088/1681-7575/aa9abd

Short Communication

# Avogadro constant measurements using enriched $^{28}$Si monocrystals

**K Fujii[1], E Massa[2], H Bettin[3], N Kuramoto[1] and G Mana[2]**

[1] NMIJ—National Metrology Institute of Japan, National Institute of Advanced Industrial Science and Technology, 1-1-1 Umezono, Tsukuba, Ibaraki 305-8563, Japan
[2] INRIM—Istituto Nazionale di Ricerca Metrologica, str. delle Cacce 91, 10135 Torino, Italy
[3] PTB—Physikalisch Technische Bundesanstalt, Bundesallee 100, 38116 Braunschweig, Germany

E-mail: g.mana@inrim.it

Received 19 September 2017, revised 9 November 2017
Accepted for publication 15 November 2017
Published 12 December 2017

**Abstract**
Since 2011, the International Avogadro Coordination has been measuring the Avogadro constant by counting the atoms in enriched $^{28}$Si monocrystals. This communication provides guidance on how the recently published results should be used to update the values of the Avogadro constant measured so far.

Keywords: Avogadro constant, silicon lattice parameter, silicon molar mass, kilogram redefinition

## 1. Introduction

Since 2011, the International Avogadro Coordination (IAC) has been determining the Avogadro constant, $N_A$, by counting the atoms in $^{28}$Si-enriched monocrystals. As a redefinition of the kilogram is being considered by the International Committee for Weights and Measures, and is expected to be adopted by the 26th General Conference on Weights and Measures to be held in 2018, a special least-squares adjustment of the fundamental physical constants was undertaken by the Committee on Data for Science and Technology (CODATA) to determine the numerical values of the Planck constant $h$, the elementary charge $e$, the Boltzmann constant $k$ and the Avogadro constant $N_A$ to be used for the unit definitions in a revised Système International (SI). Since refinements of the measurement apparatuses and procedures (as well as consistency checks and the quantification of systematic effects) have been made by the IAC, to provide the CODATA our best knowledge of the $N_A$ values acquired to date, we summarize the published values and show how they should be updated in light of the measurement results.



## 2. Published values of $N_A$

The first measured value, published in 2011 [1],

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

was obtained by using a crystal named AVO28. Since the surfaces of the two 1 kg spheres (AVO28-S5 and AVO28-S8) polished from this crystal were contaminated by a monolayer of Ni and Cu, the mass and thickness of the surface layers were only determined to within a large uncertainty. INRIM measured the AVO28 lattice parameter; PTB and NMIJ determined the sphere volumes by using independent optical interferometers to measure their diameters, although the NMIJ measurements of the surface-layer masses and thicknesses relied on the PTB determination of the carbonaceous contamination. PTB measured the molar mass by using a novel isotopic dilution mass spectrometry technique.

After the extraordinary calibration [2, 3] conducted at the International Bureau of Weights and Measures (BIPM), which was organized to provide an updated traceability to the International Prototype of the Kilogram (IPK), the mass

 

measurements conducted at the BIPM, NMIJ and PTB had to be corrected. Consequently, the value given in equation (1) was updated to [4]

$$N_A(\text{IAC-11}) = 6.022\,140\,99(18) \times 10^{23}\ \text{mol}^{-1}. \quad (2)$$

A second $N_A$ value,

$$N_A = 6.022\,140\,66(28) \times 10^{23}\ \text{mol}^{-1}, \quad (3)$$

was published in 2013 [5]. PTB removed the metallic contamination of the sphere AVO28-S8 surface (renamed AVO28-S8b) by Freckle etch and remeasured its volume, surface and mass; the values of the other quantities necessary to determine $N_A$ were the same as those used in 2011 [1]. Since this value is not corrected for the extraordinary calibration of primary mass standards, and its uncertainty is rather large (because of the deterioration of the sphere shape), we do not recommend using it.

The third $N_A$ value,

$$N_A(\text{IAC-15}) = 6.022\,140\,76(12) \times 10^{23}\ \text{mol}^{-1}, \quad (4)$$

was published in 2015 [4]. To reduce the measurement uncertainty, PTB repolished the two spheres (renamed AVO28-S5c and AVO28-S8c) to restore the sphere shape after the Freckle etch. INRIM redetermined the AVO28 lattice parameter using an improved optical interferometer. PTB and NMIJ independently measured the surface layers and volumes of the repolished spheres (although the measurements still used the PTB value of the carbonaceous surface contamination). The results of the extraordinary calibration [2, 3] of the mass standards, were taken into account. A summary of the uncertainty budgets and an estimate of the correlation of the 2011 and 2015 values are given in [6]; the determination of molar mass is discussed in section 4.

In 2017, NMIJ used the AVO28-S5c sphere to remeasure $N_A$, after the development of new apparatuses—a spectroscopic ellipsometer (operated both in vacuum and in air) [7], and an x-ray photoelectron spectroscopy system capable of accommodating 1 kg Si spheres [8]—to investigate the surfaces of the sphere independently from PTB. The measurement result,

$$N_A(\text{NMIJ-17}) = 6.022\ 140\,84(15) \times 10^{23}\ \text{mol}^{-1}, \quad (5)$$

given in [9, 10], was reported to the CCM pilot study on the comparison of future realizations of the kilogram [10, 11] and takes the results of the extraordinary calibration [2, 3] of the NMIJ mass standard into account. The molar mass and lattice parameter values published in 2015 [4] were used to obtain $N_A$ (NMIJ-17).

PTB acquired a new crystal (Si28–23Pr11) with a higher $^{28}$Si enrichment [12], polished two additional 1 kg spheres, Si28kg01a and Si28kg01b, and characterized their surfaces using a combined x-ray fluorescence and x-ray photoelectron spectroscopy apparatus [13]. The Si28kg01a surface was also consistently characterized by NMIJ by means of the same measurement systems described in [7, 8]. The AVO28 lattice parameter given in equation (11) was taken as a reference; the difference in lattice parameter between the AVO28 and Si28-23Pr11 crystals was estimated independently and consistently by correcting for the different contamination (PTB) and by using a self-referenced lattice comparator (NMIJ). The molar mass was independently and consistently measured by both PTB and NMIJ; the $^{30}$Si fraction and purity were confirmed by INRIM via nuclear activation [14, 15]. The measurement result,

$$N_A(\text{IAC-17}) = 6.022\,140\,526(70) \times 10^{23}\ \text{mol}^{-1}, \quad (6)$$

takes the extraordinary calibration [2, 3] of the mass standards into account and is published in [16].

## 3. Lattice parameter measurements

Two values were reported in 2011 [17] and 2015 [18] for the spacing of the {2 2 0} lattice planes of the AVO28 crystal at 20.000 °C and 0 Pa,

$$d_{220} = 192.014\,712\,67(67)\ \text{pm} \quad (7)$$

and

$$d_{220} = 192.014\,711\,98(34)\ \text{pm}. \quad (8)$$

They were used in the IAC-11 and IAC-15 determinations of $N_A$ given in equations (2) and (4), respectively. Subsequently, it was found that two corrections were necessary. One is for the diffraction of the laser beam; the other is for the surface stress.

A joint investigation of PTB and INRIM evidenced that a reevaluation of the effect of diffraction in the optical interferometer used to measure the $d_{220}$ values given in equations (7) and (8) was necessary. The relevant corrections were recalculated by using the same data files used in 2011 and 2015; the results are in [19].

In 2011 and 2015, the lattice strain induced by the surface tension [20] was not considered, but in 2015 a standard uncertainty of 0.6 nm m$^{-1}$ was included in the uncertainty budget. Since then, measurements at INRIM and NMIJ/KEK using a dual-thickness x-ray interferometer [21] to study lattice strain have revealed that an additional fractional correction equal to 1.25 (72) nm m$^{-1}$ [16] should be applied to the values given in equations (7) and (8).

### 3.1. Updated lattice spacing values

By taking the corrections for the laser beam diffraction and surface stress into account, the lattice spacing values given in equations (7) and (8) become

$$d_{220} = 192.014\,713\,37(73)\ \text{pm} \quad (9)$$

and

$$d_{220} = 192.014\,712\,53(35)\ \text{pm}. \quad (10)$$

The uncertainties of the values given in equations (9) and (10) are slightly different from those of (7) and (8) because the correction uncertainties were also re-evaluated. By taking the 15% correlation given in [6] into account, the weighted mean of the values given in equations (9) and (10) is [16]

$$d_{220} = 192.014\,712\,65(33)\ \text{pm}, \tag{11}$$

at 20.000 °C and 0 Pa. This estimate of the AVO28 lattice spacing takes all the information into account to date, and as previously noted was used for the IAC-17 determination of $N_A$ given in equation (6). However, the IAC-11, IAC-15 and NMIJ-17 values of $N_A$ given in equations (2), (4) and (5) should be updated based on the new consensus $d_{220}$ value for AVO28 given in equation (11).

## 4. Molar mass measurements

PTB completed the first molar mass measurements of the AVO28-S5 and AVO28-S8 spheres in 2011. The results,

$$M\,(\text{S5}) = 27.976\,970\,26(15)\ \text{g mol}^{-1} \tag{12}$$

and

$$M\,(\text{S8}) = 27.976\,970\,29(16)\ \text{g mol}^{-1}, \tag{13}$$

are given in [1] and were used to calculate the $N_A$ value given in equation (2).

Subsequently, these molar masses were independently and consistently re-measured by the National Institute of Standards and Technology (NIST), NMIJ and PTB [5] by using a water solution of tetramethylammonium hydroxide (TMAH) as a basic Si solvent in place of a solution of sodium hydroxide (NaOH). INRIM confirmed the $^{30}$Si fraction and purity by nuclear activation analysis [22, 23]. The result,

$$M\,(\text{S5c}) = M\,(\text{S8c}) = 27.976\,970\,09(15)\ \text{g mol}^{-1}, \tag{14}$$

was used to obtain the values of $N_A$ given in equations (4) and (5). Since the molar mass value for spheres S5c and S8c given in equation (14) is the most reliable one available, it can be used to update the IAC-11 value of $N_A$ given in equation (2).

## 5. Conclusions

### 5.1. Updated $N_A$ values

The basic equation for determining $N_A$ by the x-ray crystal density (XRCD) method is

$$N_A = \frac{1}{\sqrt{8}}\frac{M}{\rho d_{220}^3}, \tag{15}$$

where $M$ is the molar mass of the silicon of which the sphere is composed, $\rho$ is the density and $d_{220}$ is the $\{2\,2\,0\}$ lattice plane spacing. Thus, the fractional change of the Avogadro constant $\Delta N_A/N_A$ for a small fractional change in lattice spacing $\Delta d_{220}/d_{220}$ and in molar mass $\Delta M/M$ is

$$\frac{\Delta N_A}{N_A} = -3\frac{\Delta d_{220}}{d_{220}} + \frac{\Delta M}{M}. \tag{16}$$

For IAC-11, there is a correction for both the lattice spacing and molar mass. The value of $d_{220}$ used in the original determination of IAC-11 is 192.014 712 67 pm, which is to be compared with the consensus reference value in equation (11). This leads to a fractional correction of $N_A$ from the first term in equation (16) of $+0.3125 \times 10^{-9}$. The value of the molar mass used in the original determination of IAC-11 based on sphere S5 is 27.976 970 26 g mol$^{-1}$ and for sphere S8, 27.976 970 29 g mol$^{-1}$. Comparison of these values with that in equation (14) leads to a fractional correction to $N_A$ obtained from sphere S5 due to the second term of equation (16) of $-6.0764 \times 10^{-9}$ and for sphere S8, $-7.4187 \times 10^{-9}$. A simple average of these two values together with the lattice spacing correction then yields a total fractional correction of $-6.300 \times 10^{-9}$ for the IAC-11 value of $N_A$.

**Table 1.** List of correlation coefficients.

| | IAC-11 | IAC-15 | IAC-17 | NMIJ-17 |
|---|---|---|---|---|
| IAC-11 | 1.000 | 0.245 | 0.188 | 0.134 |
| IAC-15 | | 1.000 | 0.303 | 0.276 |
| IAC-17 | | | 1.000 | 0.205 |
| NMIJ-17 | | | | 1.000 |

The fractional correction that needs to be applied to the IAC-15 and NMIJ-17 values of $N_A$ only arises from the lattice spacing term in equation (16), because, as already noted, both are based on the molar mass value given in equation (14). Further, the correction is the same for each since each uses the value of $d_{220}$ in equation (8) to determine $N_A$. Comparison of the latter value with the consensus reference value in equation (11) yields a total fractional correction of $-10.468 \times 10^{-9}$ for the IAC-15 and NMIJ-17 values of $N_A$.

In summary, we have

$$\frac{\Delta N_A}{N_A}(\text{IAC-11}) = -6.30 \times 10^{-9}, \tag{17a}$$

$$\frac{\Delta N_A}{N_A}(\text{IAC-15}) = -10.47 \times 10^{-9}, \tag{17b}$$

$$\frac{\Delta N_A}{N_A}(\text{NMIJ-17}) = -10.47 \times 10^{-9}, \tag{17c}$$

which, when applied to equations (2), (4) and (5), yield

$$N_A(\text{IAC-11}) = 6.022\,140\,95(18) \times 10^{23}\ \text{mol}^{-1}, \tag{18a}$$

$$N_A(\text{IAC-15}) = 6.022\,140\,70(12) \times 10^{23}\ \text{mol}^{-1}, \tag{18b}$$

$$N_A(\text{NMIJ-17}) = 6.022\,140\,78(15) \times 10^{23}\ \text{mol}^{-1}, \tag{18c}$$

$$N_A(\text{IAC-17}) = 6.022\,140\,526(70) \times 10^{23}\ \text{mol}^{-1} \tag{18d}$$

where, for easy reference, the recent $N_A$ result IAC-17 from the new enriched crystal Si28-23Pr11 as given in equation (6) is included.

### 5.2. Correlations of the $N_A$ values

Table 1 shows the correlations between the four values of $N_A$ given in equations (18*a*)–(18*d*). The correlations of IAC-11 versus IAC-15, IAC-11 versus NMIJ-17, IAC-15 versus NMIJ-17 and IAC-17 versus NMIJ-17 are given in [6, 9].

They are reevaluated here to take the new values and uncertainties of the lattice parameter and molar mass into account using the same procedures given in [6, 9]. The correlations of IAC-11 versus IAC-17 and IAC-15 versus IAC-17 are given here as a new evaluation. The reevaluated four $N_A$ values and their correlation coefficients were used in the CODATA 2017 special adjustment [24, 25].

By taking the uncertainties and correlations into account, the weighted mean of the $N_A$ values (18*a*)–(18*d*) is

$$N_A = 6.022\,140\,588(65) \times 10^{23}\ \mathrm{mol}^{-1}, \tag{19}$$

with a relative standard uncertainty of $1.09 \times 10^{-8}$ and a Birge ratio of 1.6. When the relative uncertainty is multiplied by the Birge ratio, the uncertainty increases to $1.73 \times 10^{-8}$.

## Acknowledgment

This work was supported in part by the Grant-in-Aid for Scientific Research (B) (KAKENHI 16H09301) from the Japan Society for the Promotion of Science.

## ORCID iDs

K Fujii https://orcid.org/0000-0002-5578-0038
E Massa https://orcid.org/0000-0002-7764-3106
N Kuramoto https://orcid.org/0000-0002-4375-5214
G Mana https://orcid.org/0000-0002-4109-7254

## References

[1] Andreas B *et al* 2011 Counting the atoms in a $^{28}$Si crystal for a new kilogram definition *Metrologia* **48** S1–13
[2] Stock M *et al* 2015 Calibration campaign against the international prototype of the kilogram in anticipation of the redefinition of the kilogram part I: comparison of the international prototype with its official copies *Metrologia* **52** 310–6
[3] de Mirandés E *et al* 2016 Calibration campaign against the international prototype of the kilogram in anticipation of the redefinition of the kilogram, part II: evolution of the BIPM as-maintained mass unit from the 3rd periodic verification to 2014 *Metrologia* **53** 1204–14
[4] Azuma Y *et al* 2015 Improved measurement results for the Avogadro constant using a $^{28}$Si-enriched crystal *Metrologia* **52** 360–75
[5] Nicolaus A *et al* 2013 Current state of Avogadro $^{28}$Si sphere S8 *IEEE Trans. Instrum. Meas.* **62** 1499–505
[6] Mana G *et al* 2015 The correlation of the $N_A$ measurements by counting $^{28}$Si atoms *J. Phys. Chem. Ref. Data* **44** 031209
[7] Fujita K *et al* 2017 Surface layer analysis of a $^{28}$Si-enriched sphere both in vacuum and in air by ellipsometry *IEEE Trans. Instrum. Meas.* **66** 1283–8
[8] Zhang L *et al* 2017 Thickness measurement of oxide and carbonaceous layer on a $^{28}$Si sphere by XPS *IEEE Trans. Instrum. Meas.* **66** 1297–303
[9] Kuramoto N *et al* 2017 Determination of the Avogadro constant by the XRCD method using a $^{28}$Si-enriched sphere *Metrologia* **54** 716–29
[10] Stock M *et al* 2017 A comparison of future realizations of the kilogram *Metrologia* in preparation (https://doi.org/10.1088/1681-7575/aa9a7e)
[11] Stock M *et al* 2017 Maintaining and disseminating the kilogram following its redefinition *Metrologia* **54** S99–107
[12] Abrosimov N V *et al* 2017 A new generation of 99.999% enriched $^{28}$Si single crystals for the determination of Avogadro's constant *Metrologia* **54** 599–609
[13] Müller M, Beckhoff B, Beyer E, Darlatt E, Fliegauf R, Ulm G and Kolbe M 2017 Quantitative surface characterization of silicon spheres by combined XRF and XPS analysis for the determination of the Avogadro constant *Metrologia* **54** 653–61
[14] D'Agostino G, Di Luzio M, Mana G, Oddone M, Pramann A and Prata M 2015 $^{30}$Si mole fraction of a silicon material highly enriched in $^{28}$Si determined by instrumental neutron activation analysis *Anal. Chem.* **87** 5716–22
[15] D'Agostino G, Di Luzio M, Mana G, Oddone M, Bennett J W and Stopic A 2016 Purity of $^{28}$Si-enriched silicon material used for the determination of the Avogadro constant *Anal. Chem.* **88** 6881–8
[16] Bartl G *et al* 2017 A new $^{28}$Si single crystal: counting the atoms for the new kilogram definition *Metrologia* **54** 693–715
[17] Massa E, Mana G, Kuetgens U and Ferroglio L 2011 Measurement of the {2 2 0} lattice-plane spacing of a $^{28}$Si x-ray interferometer *Metrologia* **48** S37–43
[18] Massa G Mana E, Sasso C P and Palmisano C 2015 A more accurate measurement of the $^{28}$Si lattice parameter *J. Phys. Chem. Ref. Data* **44** 031208
[19] Mana G, Massa E, Sasso C P, Andreas B and Kuetgens U 2017 A new analysis for diffraction correction in optical interferometry *Metrologia* **54** 559–65
[20] Melis C, Giordano S, Colombo L and Mana G 2016 Density functional theory calculations of the stress of oxidised (1 1 0) silicon surfaces *Metrologia* **53** 1339–45
[21] Quagliotti D, Mana G, Massa E, Sasso C and Kuetgens U 2013 A finite element analysis of surface-stress effects on measurement of the Si lattice parameter *Metrologia* **50** 243–8
[22] Di Luzio M, Stopic A, D'Agostino G, Bennett J W, Mana G, Oddone M and Pramann A 2017 Measurement of the $^{30}$Si mole fraction in the new Avogadro silicon material by neutron activation and high-resolution gamma-spectrometry *Anal. Chem.* **89** 6726–30
[23] Di Luzio M, Stopic A, D'Agostino G, Bennett J W, Mana G and Oddone M 2017 Impurities in a $^{28}$Si-enriched single crystal produced for the realization of the redefined kilogram *Anal. Chem.* **89** 6314–7
[24] Mohr P J *et al* 2017 Data and analysis for the CODATA 2017 special fundamental constants adjustment for the revision of the SI *Metrologia* in preparation (https://doi.org/10.1088/1681-7575/aa99bc)
[25] Newell D B *et al* 2017 The CODATA 2017 values of *h*, *e*, *k*, and $N_A$ for the revision of the SI *Metrologia* in preparation (https://doi.org/10.1088/1681-7575/aa950a)