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Determination of the Atomic Weight of ^{28}Si-Enriched Silicon for a Revised Estimate of the Avogadro Constant

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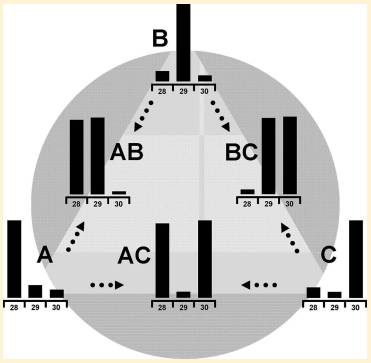
Supporting Information

ABSTRACT: The much anticipated overhaul of the International System of Units (SI) will result in new definitions of base units in terms of fundamental constants. However, redefinition of the kilogram in terms of the Planck constant (h) cannot proceed without consistency between the Avogadro and Planck constants, which are both related through the Rydberg constant. In this work, an independent assessment of the atomic weight of silicon in a highly enriched ^{28}Si crystal supplied by the International Avogadro Coordination (IAC) was performed. This recent analytical approach, based on dissolution with NaOH and its isotopic characterization by multicollector inductively coupled plasma mass spectrometry, is critically evaluated. The resultant atomic weight $A_r(\mathrm{Si}) = 27.976\,968\,39(24)_{k=1}$ differs significantly from the most recent value of $A_r(\mathrm{Si}) = 27.976\,970\,27(23)_{k=1}$. Using the results generated herein for $A_r(\mathrm{Si})$ along with other IAC measurement results for mass, volume, and the lattice spacing, the estimate of the Avogadro constant becomes $N_A = 6.022\,140\,40(19) \times 10^{23}\ \mathrm{mol}^{-1}$.



The International Avogadro Coordination (IAC), often simply called the "Avogadro project", is a collaboration that began in the early 1990s among National Metrology Institutes to determine the Avogadro constant using the X-ray crystal density method as first suggested in 1913.[1,2] The measurements, for a number of technical reasons, use highly polished one-kilogram spheres of silicon.[3,4] An overall relative target uncertainty of less than 2 in 10^8 is desired for the Avogadro constant to ensure a smooth transition between the definitions.[5] The project is part of an ongoing effort to redefine the kilogram in terms of a fixed value of an invariant quantity (a fundamental constant), thus abrogating the International Prototype Kilogram.[6,7] In addition, the "Avogadro project" complements determinations of the Planck constant using watt balances due to the fact that Avogadro and Planck constants are related via the Rydberg constant.[8]

To achieve the aforementioned uncertainty for the Avogadro constant, the atomic weight of natural silicon has to be established, and in doing so, isotope amount ratios $n(^{28}\mathrm{Si})/n(^{29}\mathrm{Si})$ and $n(^{30}\mathrm{Si})/n(^{29}\mathrm{Si})$ would need to be determined with parts-per-million uncertainty. However, the same relative uncertainty in the atomic weight can be attained with only a percent-level uncertainty required of both isotope amount ratios if the silicon material under study is initially enriched to contain 99.995% ^{28}Si.[9] Hence, the extreme constraints placed on isotope amount ratio determinations in natural silicon are obviated (against a commensurate initial investment in the cost of the material) when an isotopically enriched test material is used for such measurements.[10]

Atomic weight determinations of the enriched silicon have earlier been performed by the Institute for Reference Materials and Measurements (IRMM; Geel, Belgium)[11] and most recently by the Physikalisch-Technische Bundesanstalt (PTB; Braunschweig, Germany).[12,13] In both cases, the claimed relative uncertainty in the result was 1 in 10^8, but the two results disagreed by 4 parts in 10^7. To address this lack of agreement, an independent evaluation of the atomic weight is therefore necessary.

Determination of the Atomic Weight. The atomic weight (relative atomic mass) of an element with z stable isotopes is traditionally obtained from a full set of $(z - 1)$ isotope amount ratios.[14] For example, any two nonredundant isotope ratios can be used to obtain the atomic weight of silicon, $A_r(\mathrm{Si},\mathbf{X})$:

$$\bar{m}(\mathrm{Si},\mathbf{X}) = A_r(\mathrm{Si},\mathbf{X})m_u = \frac{m_{28}R^{\mathbf{X}}_{28/29} + m_{29} + m_{30}R^{\mathbf{X}}_{30/29}}{R^{\mathbf{X}}_{28/29} + 1 + R^{\mathbf{X}}_{30/29}} \quad (1)$$

where m_{28}, m_{29}, and m_{30} are the silicon nuclide masses, m_u is the atomic mass constant, and $R^{\mathbf{X}}_{i/j}$ is the isotope amount ratio of $n(^i\mathrm{Si})/n(^j\mathrm{Si})$ in the test sample of the ^{28}Si-enriched material ($\mathbf{X}$). Alternatively, a set of $(z - 1)$ isotope mass fractions (w) can be used to define the atomic weight of silicon:

$$\bar{m}(\mathrm{Si},\mathbf{X}) = A_r(\mathrm{Si},\mathbf{X})m_u = \frac{w^{\mathbf{X}}_{28} + w^{\mathbf{X}}_{29} + w^{\mathbf{X}}_{30}}{(w^{\mathbf{X}}_{28}/m_{28}) + (w^{\mathbf{X}}_{29}/m_{29}) + (w^{\mathbf{X}}_{30}/m_{30})} \quad (2)$$

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Such a change in variables has no advantage per se. However, a hybrid of the isotope amount ratio and isotope mass fraction approaches introduces flexibility into the measurement design. In particular, it obviates the need for the difficult measurement of the ^{28}Si amount content, based on the concept illustrated in Figure 1. On the contrary, to perform a direct measurement of

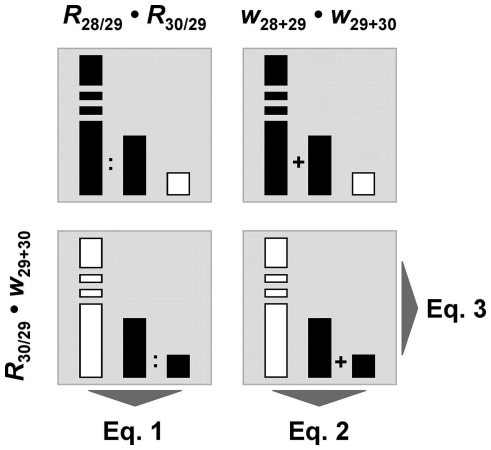

Figure 1. Conceptual variable grid for determination of the atomic weight. The black isotopes are subject to measurement, which can be done either by taking their amount ratio (ratio, ":") or their mass fraction (sum, "+"). The traditional (direct) approach to determine the atomic weight utilizes two ratio measurements, which leads to eq 1. The isotope mass fraction approach to determine the atomic weight leads to eq 2, whereas the hybrid route employed in this work corresponds to eq 3.

all three isotopes in the ^{28}Si-enriched material with the smallest acceptable signal for the ^{30}Si isotope being 1 mV, one would encounter a 1500 V signal for the ^{28}Si!

Two nonredundant variables need to be determined for silicon. These can be either the isotope amount ratios (eq 1), isotope mass fractions (eq 2), or combinations thereof (eq 3, below). The choice of eq 3 offers the advantage of bypassing the need for monitoring ^{28}Si in the material of interest (**X**). Using this hybrid isotope amount ratio and the isotope mass fraction approach, as championed by PTB,[10,15] the atomic weight of silicon can be obtained using eq 3.

$$\begin{aligned}\bar{m}(\mathrm{Si},\mathbf{X}) &= A_r(\mathrm{Si},\mathbf{X})m_u \\ &= \{m_{28}(m_{29}+m_{30}R^{\mathbf{X}}_{30/29})\} \\ &\quad /\{w^{\mathbf{X}}_{29+30}m_{28}(1+R^{\mathbf{X}}_{30/29}) \\ &\quad +(1-w^{\mathbf{X}}_{29+30})(m_{29}+m_{30}R^{\mathbf{X}}_{30/29})\}\end{aligned} \quad (3)$$

The mass fraction of ^{29}Si and ^{30}Si in the material **X**, $w^{\mathbf{X}}_{29+30}$, can be obtained from measurements characterizing a gravimetrically prepared mixture of materials **X** and **C** (^{30}Si enriched silicon), based on the method of isotope dilution:[16]

$$w^{\mathbf{X}}_{29+30} = w_{\mathbf{C}^*}\frac{m_{\mathbf{C}}}{m_{\mathbf{X}(\mathbf{CX})}}\frac{A_r(\mathbf{X}^*)}{A_r(\mathbf{C}^*)}\frac{(R^{\mathbf{C}}_{30/29}-R^{\mathbf{CX}}_{30/29})}{(R^{\mathbf{CX}}_{30/29}-R^{\mathbf{X}}_{30/29})} \times \frac{1+R^{\mathbf{X}}_{30/29}}{1+R^{\mathbf{C}}_{30/29}} \quad (4)$$

where $w_{\mathbf{C}^*}$ is the summed mass fractions of isotopes ^{29}Si and ^{30}Si in **C**,

$$w_{\mathbf{C}^*} = w_{\mathbf{C}}\frac{m_{29}+m_{30}R^{\mathbf{C}}_{30/29}}{m_{28}R^{\mathbf{C}}_{28/29}+m_{29}+m_{30}R^{\mathbf{C}}_{30/29}} \quad (5)$$

$m_{\mathbf{C}}$ is the mass of solution **C** used in the **CX** blend ($m_{\mathbf{C}(\mathbf{CX})} = w_{\mathbf{C}}m_{\mathbf{C}}$), $w_{\mathbf{C}}$ is the mass fraction of **C** in that solution, and $m_{\mathbf{C}(\mathbf{CX})}$ and $m_{\mathbf{X}(\mathbf{CX})}$ are the masses of pure material **C** and **X** in the **CX** blend, respectively. In addition, $A_r(\mathbf{X}^*)m_u = (m_{29}+m_{30}R^{\mathbf{X}}_{30/29})/(1+R^{\mathbf{X}}_{30/29})$ and $A_r(\mathbf{C}^*)m_u = (m_{29}+m_{30}R^{\mathbf{C}}_{30/29})/(1+R^{\mathbf{C}}_{30/29})$. Combining all the above equations yields the model equation for the atomic weight of silicon in the test material X used in this work:

$$\begin{aligned}\bar{m}(\mathrm{Si},\mathbf{X}) = A_r(\mathrm{Si},\mathbf{X})m_u = (m_{28}) \\ \Big/\left\{1+\frac{m_{\mathbf{C}(\mathbf{CX})}}{m_{\mathbf{X}(\mathbf{CX})}}\right. \\ \times\left(\frac{m_{28}(1+R^{\mathbf{X}}_{30/29})-m_{29}-m_{30}R^{\mathbf{X}}_{30/29}}{m_{28}R^{\mathbf{C}}_{28/29}+m_{29}+m_{30}R^{\mathbf{C}}_{30/29}}\right) \\ \left.\times\left(\frac{R^{\mathbf{C}}_{30/29}-R^{\mathbf{CX}}_{30/29}}{R^{\mathbf{CX}}_{30/29}-R^{\mathbf{X}}_{30/29}}\right)\right\}\end{aligned} \quad (6)$$

Uncertainty Requirements. The model equation for the determination of atomic weight (eq 6) contains nine variables. Six of these arise from the experimental measurements and three (nuclide masses) are available from the 2003 Atomic Mass Evaluation Report.[17] Typical values for these variables used to determine the atomic weight are summarized in Table S1 in the Supporting Information. A Monte Carlo routine was used to demonstrate that measurements of $m_{\mathbf{C}(\mathbf{CX})}$, $m_{\mathbf{X}(\mathbf{CX})}$, $R^{\mathbf{X}}_{30/29}$, and $R^{\mathbf{CX}}_{30/29}$ with associated standard uncertainties as high as 1% yield the atomic weight with a relative uncertainty, u_r, of 2×10^{-8}. In addition, the uncertainty in the isotope amount ratios $R^{\mathbf{C}}_{28/29}$ and $R^{\mathbf{C}}_{30/29}$ can be as high as 20% without a detrimental effect on A_r(Si) at the level of $u_r = 2 \times 10^{-8}$. In practice, both mass measurements, $m_{\mathbf{C}(\mathbf{CX})}$ and $m_{\mathbf{X}(\mathbf{CX})}$, can be readily delivered at a 1×10^{-4} level of relative uncertainty by gravimetry; hence, only two variables contribute significantly to the uncertainty of the atomic weight of the ^{28}Si-enriched silicon, i.e., $R^{\mathbf{X}}_{30/29}$ and $R^{\mathbf{CX}}_{30/29}$. Both of these must be determined to within a few percent. Since isotope amount ratios of silicon derived from multicollector-inductively coupled plasma mass spectrometry (MC-ICPMS) measurements can deviate from their absolute values by up to 5%[12,13,18] as a consequence of the differential transmission efficiency of the various nuclides, calibration must be performed to correct for this "mass bias" effect.

Characterization of Isotope Amount Ratios in Calibrators. Material of known isotopic composition must be available to correct for mass bias; the ratio of the known and observed isotope amount ratios yield the needed correction factor. When pure isotopes of an element are available, a calibrator with a known isotope amount ratio can be synthesized by gravimetrically blending the pure isotopes. In practice, however, isotopically enriched materials contain unknown amounts of other isotopes, and the above approach is no longer trivial. In the case of silicon, with three stable isotopes, if the isotopic composition of three isotopically enriched materials is determined

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along with at least two blends of any of the two materials, mass bias correction factors ($K_{i/j}$) can be derived, without the need to know a priori the isotopic composition of the enriched materials.[19] The principle of the isotope mixture deconvolution (iMD) model,[13,18,19] as employed in this work, is illustrated in Figure 2. Mathematical solutions for the mass bias correction factors are given in the Supporting Information.

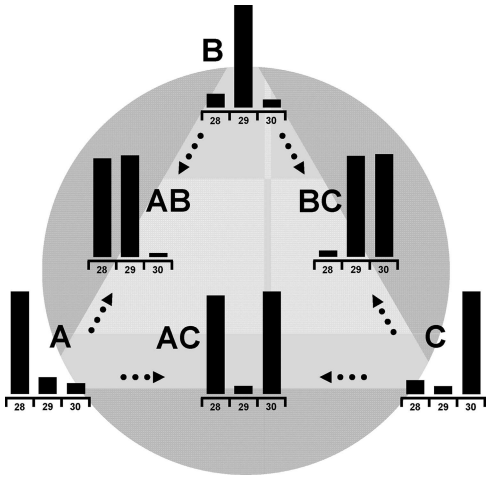

Figure 2. Isotopic mixture deconvolution (iMD) strategy for isotope amount ratio determination. Absolute isotopic composition of materials **A**, **B**, and **C** can be estimated from the uncalibrated measurements of materials **A**, **B**, **C**, and at least two gravimetrically prepared pairwise mixtures of these three materials. For example, measuring the isotopic composition of **A**, **B**, **C**, **AB**, and **AC** provides sufficient information to calibrate all measurement results which, in turn, leads to the absolute isotopic composition of materials **A**, **B**, and **C**.

EXPERIMENTAL SECTION

Instrumentation and Reagents. A Neptune MC-ICPMS (Thermo Fisher Scientific; Bremen, Germany) equipped with nine Faraday cups and a combination of cyclonic and Scott-type quartz spray chambers with a self-aspirating PFA nebulizer MCN50 (Elemental Scientific; Omaha, NE) was used for all measurements. The plug-in quartz torch with sapphire injector was fitted with a platinum guard electrode. The high mass resolution mode employed was described by the manufacturer.[20] The gain on each Faraday cup was monitored daily to ensure normalization of its efficiency. In addition, the "Virtual Amplifier" design was employed for all measurements in order to eliminate any bias caused by uncertainties in the gain calibration of the amplifiers.[21] Typical optimized operating conditions and further details regarding the source and purity of all chemicals are given in the Supporting Information.

Sample Description. All silicon samples were cut from single crystals produced by the IAC and supplied by PTB. The production of the silicon-28 (designated herein as material **A**), silicon-29 (**B**), and silicon-30 (**C**) enriched single crystals is described in detail elsewhere.[22,23] In addition, natural isotopic composition single crystal (WASO-04) was also used in this work.[3,24] Further details are given in the Supporting Information.

Sample Preparation. To avoid possible contamination from natural sources of silicon, all PFA bottles and PFA tubes were initially cleaned with 10% HNO_3 for 24 h and rinsed with high purity deionized water. Bottles and tubes were then filled with 0.1% HF for 2 h, rinsed with water, and then filled with 0.001% NaOH for 24 h. All bottles and tubes were again rinsed with water and dried in a fume hood prior to use. Sample preparation was conducted in a Class-100 clean room following the protocol of Pramann et al.[13,18] Prior to weighing, all silicon crystals were cleaned in an ultrasonic bath sequentially using acetone, ethanol, and water for 20 min, respectively. Silicon crystals were then etched for 20 min with 10 mL of a solution containing 0.380 g/g HF, 0.070 g/g H_2O_2, 0.086 g/g HNO_3, and 0.464 g/g H_2O. The cleaning and etching was done for each material in individual PFA bottles that were placed in the ultrasonic bath. Following a rinsing with water, the samples were air-dried in the clean fume hood prior to weighing and dissolution. All weighings were corrected for air buoyancy. Further details are given in the Supporting Information.

Preparation of Solutions for Determination of Atomic Weight. Four pieces of 0.2984, 0.4120, 0.4201, and 0.4541 g of ^{28}Si (**X**) were accurately weighed and placed in precleaned 100 mL PFA bottles. After adding 7.06, 9.75, 9.93, and 10.7 g of aqueous NaOH solution of w(NaOH) = 0.25 g/g to each bottle, they were loosely capped and placed within a plastic bag secured in an ultrasonic bath. Four procedural blanks were prepared using identical amounts of the same NaOH solution. Samples were subjected to sonication for four regularly spaced periods of 90 min daily until complete dissolution was achieved (4−7 weeks). Samples were diluted with appropriate amounts of water (52−76 g), resulting in a ^{28}Si mass fraction of approximately 5000 μg/g. Similarly, four blanks were diluted with identical amounts of water used for ^{28}Si-enriched samples in order to match total NaOH content and ensure accurate blank corrections.

For the **CX** blend, 36.5 g of 5000 μg/g solution **X** were accurately weighed into a precleaned 60 mL PFA tube. An amount of 5.425 g of the 1.4908 μg/g solution **C** (in w_{NaOH} = 0.1 mg/g) were then added to the tube, resulting in a ratio near 1:1 for $^{30}Si/^{29}Si$. Finally, 3.6 g of w_{NaOH} = 0.1 mg/g were added, resulting in a Si mass fraction of approximately 4000 μg/g and a w_{NaOH} = 0.024 g/g.

Four sets of samples (**X** and **CX**) were prepared with matched levels of Si and NaOH, i.e., w_{Si} = 4000 μg/g and w_{NaOH} = 0.024 g/g. Sample process blanks were diluted to match the matrix of w_{NaOH} = 0.024 g/g.

Isotope Amount Ratio Measurements. Two data acquisition sequences were designed for determination of Si isotope amount ratios. The measurement of all three Si isotope intensities in the test solutions was undertaken in the sequence **b-AB-AC-BC-A-B-C-AB-b** (sequence 1). A 3 min rinse with a solution containing w_{NaOH} = 0.1 mg/g effectively eliminated any carry-over from a previous solution. Short measurement times were used in an effort to minimize the effects of any instrument drift and ensure identical mass bias for each solution. Each sequence required only 46 min. Intensities (detector signals) of Si isotopes arising from a blank solution containing w_{NaOH} = 0.1 mg/g were subtracted from those of all samples. A static run was employed to collect all three silicon isotope ion beams, as shown in Table S4 in the Supporting Information. Data were collected between May and August of 2011.

In order to establish the atomic weight of silicon in material **X**, the isotope amount ratio $^{30}Si/^{29}Si$ in material **X** and blend **CX** was determined (sequence 2). Only ^{29}Si and ^{30}Si isotopes were monitored. Faraday cup L3 was moved off-axis during the measurements to avoid any potential damage due to the high ^{28}Si ion current. In addition, material **A** was monitored to account for mass bias correction. Samples were measured in the

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order b-**X**-**CX**-**A**-b, where b denotes the blank. Ion intensities of both Si isotopes obtained from the corresponding blank solutions, each containing w_{NaOH} = 0.024 g/g, were subtracted from the intensities of **X**, **CX**, and **A** test samples.

RESULTS AND DISCUSSION

The overall measurement strategy and procedure developed earlier by PTB[12,13,18] was essentially followed, with a few notable exceptions. These alterations, introduced after careful evaluation of the described protocols, are addressed in separate sections below as they warrant due consideration.

Instrumental Parameters. In the most recent measurement of A_r(Si, **X**), the mass bias calibration was performed using medium-mass resolution in order to maximize instrument response, whereas measurements on the sample were obtained in high-mass resolution in order to eliminate spectral interferences.[12,13] In our experiments, the high-mass resolution mode was exclusively employed to simplify the experimental design.

All measurements were performed using a standard quartz torch with a sapphire injector (central torch channel) as opposed to use of a complete sapphire torch, as recommended earlier.[12,13,18] Our measurements showed no elevated release of silicon from the standard torch, i.e., an identical instrumental background at ^{29}Si or ^{30}Si was observed when measuring a solution of w_{NaOH} = 0.024 g/g with either torch, i.e., 0.102(30) or 0.147(25) mV, suggesting the standard quartz torch with a sapphire injector setup is adequate for the isotope amount ratio measurements in material **X**.

Duration of the Measurement Sequence. Measurements on solutions containing high dissolved solids content (w_{Si} = 4 mg/g and w_{NaOH} = 0.024 g/g) are well beyond the recommended operational envelope of an ICPMS and will inevitably result in instrument drift, in part, due to the deposition of salt on the optical elements of the instrument. The overall measurement sequence of the most recent atomic weight determination lasted approximately 12 h.[12,13] Such a long sequence was employed because each cycle of atomic weight determination (**X**-**CX**; ∼1 h, repeated four times) was followed by a full battery of measurements (**A**-**B**-**C**-**AB**-**BC**; ∼2 h, repeated four times) to establish the mass bias correction factors. These two sequences were decoupled and shortened in this study, and their respective duration was reduced approximately 3-fold, resulting in diminished instrumental drift. In addition, a mass bias calibration was obtained from measurements performed within 10 mins of acquiring the intensities from the analyte solutions (**X** and **CX**) as compared to an earlier approach which spaced the calibration and sample measurement sequences several hours apart.[12,13]

Calibration Protocol. The current calibration approach employs measurement of a sequence of solutions **A**-**B**-**C**-**AB**-**BC**-**AC**, which gives access to three redundant sets of calibration factors, all based on an optimal 1:1 isotope ratio in the blends, i.e., $R^{AB}_{28/29}$, $R^{BC}_{30/29}$, and $R^{AC}_{28/30}$. This redundancy in calibration protocol allows for enhanced confidence in the resultant mass bias calibration factors. In contrast, the earlier studies employed measuring solutions of **A**, **B**, **C**, **AB**, and **BC** with only two pairwise mixtures, yielding a single set of two calibration factors.[12,13] Moreover, optimal 1:1 ratios for $R^{AB}_{28/29}$ and $R^{BC}_{30/29}$ compositions were not utilized to generate the calibration equations. Rather, $R^{AB}_{30/29}$ comprising approximately a 1:10 ratio and $R^{BC}_{30/29}$ comprising approximately a 1:1 ratio were employed.[12,13]

In this work, mass bias correction factors $K_{28/29}$ and $K_{30/29}$ were obtained from the isotope amount ratio determinations of three materials (**A**, **B**, **C**) and three blends (**AB**, **BC**, and **AC**) as illustrated in eqs S1−S6 for **A**-**B**-**C**-**AB**-**BC**. Typical results are given in the Supporting Information, wherein it is evident that all three sets of calibration factors agree within 5×10^{-4}, demonstrating consistency in the measurement process and providing triple redundancy in the estimates of $K_{28/29}$ and $K_{30/29}$. Utilizing these data, the mass bias corrected isotopic composition of materials **A** and **C** could be established:

$$R^{\mathbf{A}}_{30/29} = 0.6630(26)_{k=1}, \quad R^{\mathbf{C}}_{30/29} = 260(11)_{k=1}$$
$$\text{and} \quad R^{\mathbf{C}}_{28/29} = 1.074(69)_{k=1}$$

These values were used as input data for the determination of the atomic weight of silicon in material **X** (eq 6). The value of $n(^{30}\text{Si})/n(^{29}\text{Si})$ obtained for natural silicon (**A**) is in agreement with the most recent measurements, which report $R^{\mathbf{A}}_{30/29}$ = 0.6634(15).[12,13] In addition, our results agree with the earlier measurements of natural silicon[24] which were recently corrected for an inconsistency in mass bias correction factors, as disclosed by Valkiers et al.,[25] to yield $R^{\mathbf{A}}_{30/29} = 0.661\,53(4)_{k=1}$. Isotopic composition of material **C** differs significantly from the estimates provided by PTB for the same material ($R^{\mathbf{C}}_{30/29}$ = $219(5)_{k=1}$ and $R^{\mathbf{C}}_{28/29} = 1.021(115)_{k=1}$).[12,13]

Blank Corrections. Silicon impurities in the water and NaOH reagent must be accounted for by careful matching of the total content of NaOH present in all samples and blanks (and not the OH^- ion remaining in the solution after the reaction of NaOH with silicon[12,13]). Any mismatch between the amount of NaOH in the procedural blank and samples will preclude an accurate blank correction arising from natural silicon in the NaOH.

To mitigate blank-related issues, high-purity reagents were used and additional experiments were conducted to determine the Si content in the NaOH used. Following the traditional isotope dilution approach for quantitation of trace impurities,[16] the NaOH sample was blended with material **C**. Isotope amount ratio determinations were performed at high mass resolution in a fashion similar to that described above. A 0.5 μg/g solution of material **A** was used for mass bias correction. Raw signal intensities were used directly to obtain $r_{28/30}$, and the following equation was used to calculate the mass fraction of silicon in NaOH:

$$w_{Si} = \frac{m_C}{m_{NaOH}} \frac{x^{\mathbf{C}}_{28} - x^{\mathbf{C}}_{30} R_{28/30}}{x^{\mathbf{A}}_{30} R_{28/30} - x^{\mathbf{A}}_{28}} \frac{A_r(\text{Si}, \mathbf{A})}{A_r(\text{Si}, \mathbf{C})} \tag{7}$$

Here m_C is the mass of material **C** added to the sodium hydroxide of mass m_{NaOH}. $R_{28/30}$ is the mass bias corrected isotope amount ratio in the resulting blend of NaOH and **C**; A_r(Si,**A**) and A_r(Si,**C**) are the atomic weights of natural silicon and ^{30}Si standard, respectively. The following mass fraction of silicon was obtained: $w_{Si} = 0.62(3)_{k=1}$ μg/g (n = 3). This includes contributions from the NaOH itself, water, and instrumental background. The absence of NaOH in the test solution yielded $w_{Si} = 0.40(4)_{k=1}$ μg/g (n = 3). Therefore, the difference of $0.22(5)_{k=1}$ μg/g was considered to be the mass fraction of silicon in the NaOH reagent (monohydrate). Such an amount, even if left unaccounted for, which it was not, would only have a marginal effect on the estimate of the atomic weight.

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Signal Suppression. Measurements undertaken on solutions containing high NaOH and silicon content inevitably result in signal suppression. Therefore, it is important to evaluate their impact in order to attain proper blank correction for measurements of materials **X** and **CX**. We found that signal intensities for ^{29}Si and ^{30}Si in the w_{NaOH} = 0.024 g/g matrix from a 0.5 μg/g Si standard solution were a fraction of $0.57(2)_{n=3}$ of the signals obtained in the low w_{NaOH} = 0.001 g/g matrix of a 0.5 μg/g Si standard solution. In addition, similar signal intensities for ^{29}Si and ^{30}Si were obtained in two 0.5 μg/g Si standard solutions with different amounts of OH^- ions, one in a matrix of w_{NaOH} = 0.024 g/g (containing w_{Na} = 0.014 g/g and w_{OH} = 0.010 g/g) and the other in a matrix of w_{NaOH} = 0.024 which was acidified to yield w_{OH} = 0.001 g/g. This suggests that suppression of the silicon signal is caused mainly by the sodium content. Hence, an aqueous solution with w_{NaOH} = 0.024 g/g can be used for accurate blank subtraction for samples.

The extent of suppression due to high silicon content, w_{Si} = 4 mg/g, was estimated by determining the ratio of the net ^{30}Si signal intensity obtained from a solution of **CX** (w_X = 4 mg/g and w_C = 0.2 μg/g) subtracted from the signal measured in solution **X** to that for a solution of **C** (w_C = 0.2 μg/g) in w_{NaOH} = 0.024 g/g. The $^{29}Si^+$ and $^{30}Si^+$ signals were suppressed by 10(2)% in the presence of high Si and NaOH matrix (w_{Si} = 4 mg/g and w_{NaOH} = 0.024 g/g). Such suppression has a negligible effect on the estimate of atomic weight. Consequently, the blank correction using a w_{NaOH} = 0.024 g/g solution alone is adequate to generate unbiased $n(^{30}Si)/n(^{29}Si)$ amount ratios in materials **X** and **CX**.

Estimate of the Atomic Weight of Silicon. Experimental isotope amount ratios were calibrated using the previously determined $n(^{30}Si)/n(^{29}Si)$ ratio in material **A** ($K_{30/29} = R^{A}_{30/29}/r^{A}_{30/29}$). Corrected ratios $R^{X}_{30/29}$ and $R^{CX}_{30/29}$ were obtained from the measured ratios after multiplication by $K_{30/29}$. The atomic weight of silicon was calculated using eq 6; results are presented in Figure 3 and also in Table 1.

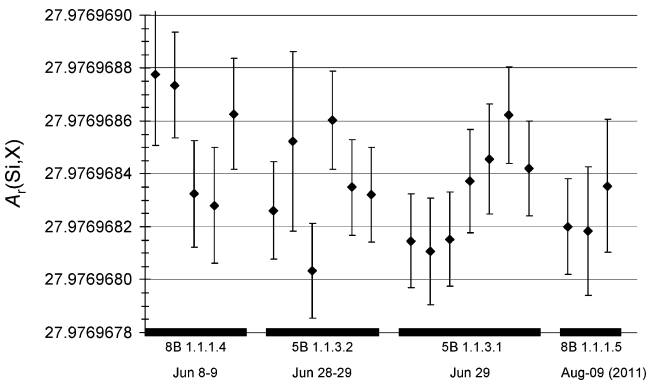

Figure 3. Atomic weight obtained for four samples of crystal Si28-10-Pr11 (**X**). Measurement dates are identified below the sample code. Uncertainty bars reflect combined measurement uncertainty (k = 1).

Table 1. Comparative Results of the Atomic Weight, A_r(Si,X)

AVO28-S5	AVO28-S8	ref
27.976 970 26(22)	27.976 970 29(23)	4
27.976 968 34(21)	27.976 968 44(27)	this work

The results for atomic weight in the four samples of ^{28}Si materials (Figure 3) differ from the most recent PTB estimate[4] by 7 parts in 10^8, whereas the uncertainty in both measurement results is 10-fold lower than this discrepancy. The atomic weight of silicon derived from material sampled from areas surrounding both spheres, AVO28-S5 and AVO28-S8, is identical to within the uncertainty of measurement, as reported earlier.[4]

Evaluation of Uncertainty. Estimates of the uncertainty for the mass bias correction factors, isotope amount ratios, as well as the atomic weight of ^{28}Si were done in accordance with the "Guide to the expression of uncertainty in measurement".[26] A typical uncertainty budget for the atomic weight result is given in the Supporting Information. It shows that measurement of $r^{X}_{30/29}$ is the single biggest contributor toward the uncertainty of A_r(Si,**X**).

Traceability. Traceability of our result to the SI kilogram was achieved due to the nature of the isotope mixture deconvolution approach described herein. An important aspect of this work with regard to the traceability of the presented results is the desire for full disclosure of all raw measurement data. The lack of such information in previous studies delayed the understanding of the errors inherent in the 2001−2003 atomic weight results derived from the silicon crystals of natural isotopic composition.[25] Further details are given in the Supporting Information.

Analysis of the Results. The results presented here differ significantly from their most recent estimate.[12,13] The reason for this is likely due to the changes introduced into the measurement procedure. The rationale for these modifications has been presented above, whereas in this section the potential impact of these changes is evaluated.

Silicon Impurities in Sodium Hydroxide. Contamination control during sample preparation (dissolution) of the ^{28}Si-enriched silicon is crucial due to the extremely small amounts of ^{29}Si and ^{30}Si present in this material. Trace amounts of natural silicon in the reagents used can therefore significantly bias the estimate of $n(^{30}Si)/n(^{29}Si)$ in material **X** if these sources are not properly identified and accounted for. Sodium hydroxide is the only reagent used to dissolve the silicon crystals. The commercial high-purity NaOH used by both PTB (Merck, 99.99+%) and NRC (Fluka, 99.9995+%) lists the natural silicon impurities to be $<5 \times 10^{-6}$ g/g (as SiO_2). To dissolve 400 mg of silicon (**X**), 3.6 g of NaOH (in the form of monohydrate) is used.[12,13] Such levels of impurity, if indeed present, would alter the ratio $R_{29/30}$:

$$R_{29/30} = \frac{m_{\mathbf{X}} x^{\mathbf{X}}_{29}/A_r(\mathrm{Si},\mathbf{X}) + w_{Si} m_{NaOH} x^{\mathbf{A}}_{29}/A_r(\mathrm{Si},\mathbf{A})}{m_{\mathbf{X}} x^{\mathbf{X}}_{30}/A_r(\mathrm{Si},\mathbf{X}) + w_{Si} m_{NaOH} x^{\mathbf{A}}_{30}/A_r(\mathrm{Si},\mathbf{A})} \approx \frac{R^{\mathbf{X}}_{29/30} + 0.4 w_{Si}/10^{-6}}{1 + 0.3 w_{Si}/10^{-6}} \quad (8)$$

The NaOH reagent used in this study only contains $0.22(5)_{k=1}$ μg/g of natural silicon, which is a negligible amount to have an effect on $R^{X}_{29/30}$, even if left unaccounted for. However, if less pure NaOH is used with, for example, w_{Si} = 2 μg/g, it could reduce the $R_{30/29}$ in material **X** by almost a factor of 2. Such correction alone can shift the estimate of the atomic weight by 6 parts in 10^8 (which is the difference between the NRC and PTB atomic weight estimates).

Previous Measurements by IRMM and PTB. For the ^{28}Si-enriched material, the ratio $n(^{29}Si)/n(^{30}Si)$ is of importance. In natural silicon, this ratio $n(^{29}Si)/n(^{30}Si) \approx 1.5$. During enrichment of ^{28}Si, ^{29}Si inevitably undergoes concurrent enrichment with respect to ^{30}Si. In the process, $n(^{29}Si)/n(^{30}Si)$ is significantly

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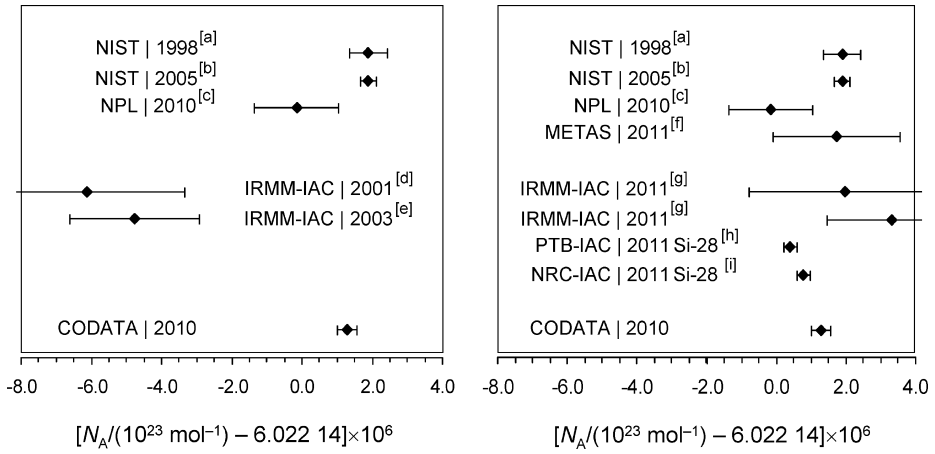

Figure 4. Estimates of the Avogadro constant: situation before and after 2011. Literature values of the Planck constant (h) are converted to the corresponding values of the Avogadro constant (N_A) via the molar Planck constant ($N_A h$).[8] References for all data ([a], [b] ... [i]) are given in the Supporting Information. The "X" in labels "X-IAC" refers to the source of the atomic weight estimates that are used to calculate the Avogadro constant.

increased. Consequently, any "contamination" of the enriched ^{28}Si material with natural silicon will only serve to decrease $n(^{29}\mathrm{Si})/n(^{30}\mathrm{Si})$. The first measurements on the enriched silicon by IRMM yielded $n(^{29}\mathrm{Si})/n(^{30}\mathrm{Si}) \approx 8$.[4,11] In 2011, PTB reported $n(^{29}\mathrm{Si})/n(^{30}\mathrm{Si}) \approx 30$[12,13] and concluded that the solutions used to convert the crystal samples into the SiF_4 gas utilized by IRMM for their measurement protocol were contaminated with natural Si.[4] In this study, $n(^{29}\mathrm{Si})/n(^{30}\mathrm{Si}) \approx 60$ was achieved.

General Remarks. The atomic weight arising from this study, when incorporated with all other relevant measurements of the IAC[4], yields an Avogadro constant that is different from the most recent IAC estimate by 6 parts in 10^8. It is noteworthy that measurements made using silicon of natural isotopic composition reached the tipping point in 2001−2003 when the estimates of N_A from the Avogadro route and watt balance disagreed by 1 part in 10^6 (Figure 4). This discrepancy was explained in 2011 to be a consequence of a faulty mass bias correction procedure.[25] Now, for the first time, IAC estimates of the Avogadro constant from both natural and enriched silicon crystals agree with each other.

The overall complexity and cost of this project could be significantly reduced by increasing the number of input assumptions. In particular, the value for the $n(^{30}\mathrm{Si})/n(^{29}\mathrm{Si})$ in natural silicon material does not need to be determined ab initio using the complicated iMD approach. Rather, values provided from earlier work on natural silicon can be used.[12,25]

CONCLUSIONS

Following the recent pioneering measurements by the PTB, NRC has performed an independent assessment of the atomic weight of the IAC highly enriched ^{28}Si crystal material. Approximately 2-fold smaller abundance of ^{30}Si is obtained than previously reported. The resulting atomic weight $A_r(\mathrm{Si}) = 27.976\,968\,39(24)_{k=1}$ differs significantly from the most recent value of $A_r(\mathrm{Si}) = 27.976\,970\,27(23)_{k=1}$[12] which was utilized in the recent IAC report[4] to give $N_A = 6.022\,140\,78(18) \times 10^{23}$ mol^{-1}. On the basis of results generated herein for the atomic weight of silicon, the revised IAC estimate of the Avogadro constant is $N_A = 6.022\,140\,40(19) \times 10^{23}$ mol^{-1}. It is noteworthy that in 2011, for the first time, the estimates of the Avogadro constant derived from both natural and enriched silicon crystals agreed with each other and also agree with all recent watt balance results within a few parts in 10^7.[2,7]

ASSOCIATED CONTENT

Supporting Information

Additional information as noted in text. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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