

INTRODUCTION

Determination of the atomic weight. Relevant to the determination of the Avogadro constant *via* the x-ray crystal density approach is the mean atomic mass of silicon in the material of silicon spheres. This quantity is known exclusively by its numerical value expressed in the atomic unit of mass, called the “atomic weight” or “relative atomic mass”.⁸ Hence, $A_r(\text{E})$ is the numerical value of the mean atomic mass, $\bar{m}(\text{E})$, expressed in m_{u} , where $m_{\text{u}} = m(^{12}\text{C})/12$.⁸

Uncertainty requirements. Typical values for all experimental variables used to determine the atomic weight are summarized in Table S1.

Table S1. Typical values for experimental variables used in the measurement model equation for determination of atomic weight

Quantity	Value	Note
$m_{\text{C}(\text{CX})}$	8 μg	Mass of material C mixed with X. Derives from the 5 g of a solution having mass fraction of C $w_{\text{C}} = 1.5 \mu\text{g/g}$. This solution was prepared by appropriate dissolution of 0.05 g sample of crystal C.
$m_{\text{X}(\text{CX})}$	0.2 g	Mass of the crystal sample X
$R_{28/29}^{\text{C}}$	1.1 mol/mol	Isotope amount ratio in material C
$R_{30/29}^{\text{C}}$	260 mol/mol	Isotope amount ratio in material C
$R_{30/29}^{\text{X}}$	0.02 mol/mol	Isotope amount ratio in material X
$R_{30/29}^{\text{CX}}$	1.0 mol/mol	Isotope amount ratio in blend CX

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Calibration. Based on a consideration of test solutions **A**, **B**, **C** and blends **AB** and **BC** and using only the two major isotopes from the two blends, *i.e.*, $R_{28/29}^{\text{AB}}$ and $R_{30/29}^{\text{BC}}$, mass bias correction factors can be defined:

$$K_{28/29} = \frac{m_{29} \cdot B}{m_{28} \cdot D} \text{ and } K_{30/29} = \frac{m_{29} \cdot A}{m_{30} \cdot D}, \quad (\text{Eq. S1})$$

where

$$\begin{aligned} A &= m_{\text{B(BC)}} m_{\text{B(AB)}} \cdot (r_A^{28/29} - r_C^{28/29}) \cdot (r_{\text{BC}}^{30/29} - r_B^{30/29}) \cdot (r_{\text{AB}}^{28/29} - r_B^{28/29}) \\ &\quad + m_{\text{B(BC)}} m_{\text{A(AB)}} \cdot (r_B^{28/29} - r_C^{28/29}) \cdot (r_{\text{BC}}^{30/29} - r_B^{30/29}) \cdot (r_{\text{AB}}^{28/29} - r_A^{28/29}) \\ &\quad + m_{\text{B(AB)}} m_{\text{C(BC)}} \cdot (r_A^{28/29} - r_B^{28/29}) \cdot (r_{\text{BC}}^{30/29} - r_C^{30/29}) \cdot (r_{\text{AB}}^{28/29} - r_B^{28/29}), \\ B &= m_{\text{B(BC)}} m_{\text{B(AB)}} \cdot (r_C^{30/29} - r_A^{30/29}) \cdot (r_{\text{BC}}^{30/29} - r_B^{30/29}) \cdot (r_{\text{AB}}^{28/29} - r_B^{28/29}) \\ &\quad + m_{\text{B(BC)}} m_{\text{A(AB)}} \cdot (r_C^{30/29} - r_B^{30/29}) \cdot (r_{\text{BC}}^{30/29} - r_B^{30/29}) \cdot (r_{\text{AB}}^{28/29} - r_A^{28/29}) \\ &\quad + m_{\text{B(AB)}} m_{\text{C(BC)}} \cdot (r_B^{30/29} - r_A^{30/29}) \cdot (r_{\text{BC}}^{30/29} - r_C^{30/29}) \cdot (r_{\text{AB}}^{28/29} - r_B^{28/29}), \\ D &= m_{\text{B(BC)}} m_{\text{B(AB)}} \cdot (r_B^{30/29} - r_{\text{BC}}^{30/29}) \cdot (r_{\text{AB}}^{28/29} - r_B^{28/29}) \cdot (r_C^{30/29} r_A^{28/29} - r_C^{28/29} r_A^{30/29}) \\ &\quad + m_{\text{B(BC)}} m_{\text{A(AB)}} \cdot (r_B^{30/29} - r_{\text{BC}}^{30/29}) \cdot (r_{\text{AB}}^{28/29} - r_A^{28/29}) \cdot (r_B^{28/29} r_C^{30/29} - r_B^{30/29} r_C^{28/29}) \\ &\quad + m_{\text{B(AB)}} m_{\text{C(BC)}} \cdot (r_C^{30/29} - r_{\text{BC}}^{30/29}) \cdot (r_{\text{AB}}^{28/29} - r_B^{28/29}) \cdot (r_B^{30/29} r_A^{28/29} - r_B^{28/29} r_A^{30/29}). \end{aligned} \quad (\text{Eq. S2})$$

Here, $m_{\text{A(AB)}}$, $m_{\text{B(BC)}}$, $m_{\text{C(AC)}}$, etc., are masses of the isotopically enriched materials **A**, **B** and **C** in the corresponding blends **AB**, **BC**, **AC**, etc. Similar equations can be obtained for the two other experimental designs, *i.e.*, **A-B-C-AB-AC** and **A-B-C-BC-AC**:

$$K_{30/28} = \frac{m_{28} \cdot H}{m_{30} \cdot G} \text{ and } K_{29/28} = \frac{m_{28} \cdot I}{m_{29} \cdot G}, \quad (\text{Eq. S3})$$

where

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$$\begin{aligned}
H &= m_{A(AC)} m_{A(AB)} \cdot (r_{AB}^{29/28} - r_A^{29/28}) \cdot (r_{AC}^{30/28} - r_A^{30/28}) \cdot (r_C^{29/28} - r_B^{29/28}) \\
&+ m_{A(AC)} m_{B(AB)} \cdot (r_{AC}^{30/28} - r_A^{30/28}) \cdot (r_B^{29/28} - r_{AB}^{29/28}) \cdot (r_A^{29/28} - r_C^{29/28}) \\
&+ m_{A(AB)} m_{C(AC)} \cdot (r_{AB}^{29/28} - r_A^{29/28}) \cdot (r_C^{30/28} - r_{AC}^{30/28}) \cdot (r_B^{29/28} - r_A^{29/28}), \\
I &= m_{A(AC)} m_{A(AB)} \cdot (r_{AB}^{29/28} - r_A^{29/28}) \cdot (r_{AC}^{30/28} - r_A^{30/28}) \cdot (r_B^{30/28} - r_C^{30/28}) \\
&+ m_{A(AC)} m_{B(AB)} \cdot (r_B^{29/28} - r_{AB}^{29/28}) \cdot (r_{AC}^{30/28} - r_A^{30/28}) \cdot (r_C^{30/28} - r_A^{30/28}) \\
&+ m_{A(AB)} m_{C(AC)} \cdot (r_{AB}^{29/28} - r_A^{29/28}) \cdot (r_C^{30/28} - r_{AC}^{30/28}) \cdot (r_A^{30/28} - r_B^{30/28}), \\
G &= m_{A(AC)} m_{A(AB)} \cdot (r_{AB}^{29/28} - r_A^{29/28}) \cdot (r_{AC}^{30/28} - r_A^{30/28}) \cdot (r_B^{29/28} r_C^{30/28} - r_C^{29/28} r_B^{30/28}) \\
&+ m_{A(AC)} m_{B(AB)} \cdot (r_{AC}^{30/28} - r_A^{30/28}) \cdot (r_B^{29/28} - r_{AB}^{29/28}) \cdot (r_C^{29/28} r_A^{30/28} - r_A^{29/28} r_C^{30/28}) \\
&+ m_{A(AB)} m_{C(AC)} \cdot (r_{AB}^{29/28} - r_A^{29/28}) \cdot (r_C^{30/28} - r_{AC}^{30/28}) \cdot (r_A^{29/28} r_B^{30/28} - r_B^{29/28} r_A^{30/28}).
\end{aligned} \tag{Eq. S4}$$

and

$$K_{28/30} = \frac{m_{30} \cdot M}{m_{28} \cdot L} \text{ and } K_{29/30} = \frac{m_{30} \cdot N}{m_{29} \cdot L}, \tag{Eq. S5}$$

where

$$\begin{aligned}
M &= m_{A(AC)} m_{C(BC)} \cdot (r_{AC}^{28/30} - r_A^{28/30}) \cdot (r_C^{29/30} - r_{BC}^{29/30}) \cdot (r_C^{29/30} - r_B^{29/30}) \\
&+ m_{C(AC)} m_{C(BC)} \cdot (r_C^{28/30} - r_{AC}^{28/30}) \cdot (r_C^{29/30} - r_{BC}^{29/30}) \cdot (r_B^{29/30} - r_A^{29/30}) \\
&+ m_{C(AC)} m_{B(BC)} \cdot (r_{BC}^{29/30} - r_B^{29/30}) \cdot (r_C^{28/30} - r_{AC}^{28/30}) \cdot (r_A^{29/30} - r_C^{29/30}), \\
N &= m_{A(AC)} m_{C(BC)} \cdot (r_C^{29/30} - r_{BC}^{29/30}) \cdot (r_{AC}^{28/30} - r_A^{28/30}) \cdot (r_B^{28/30} - r_C^{28/30}) \\
&+ m_{C(AC)} m_{C(BC)} \cdot (r_C^{28/30} - r_{AC}^{28/30}) \cdot (r_C^{29/30} - r_{BC}^{29/30}) \cdot (r_A^{28/30} - r_B^{28/30}) \\
&+ m_{C(AC)} m_{B(BC)} \cdot (r_{BC}^{29/30} - r_B^{29/30}) \cdot (r_C^{28/30} - r_{AC}^{28/30}) \cdot (r_C^{28/30} - r_A^{28/30}), \\
L &= m_{A(AC)} m_{C(BC)} \cdot (r_{AC}^{28/30} - r_A^{28/30}) \cdot (r_C^{29/30} - r_{BC}^{29/30}) \cdot (r_C^{28/30} r_B^{29/30} - r_B^{28/30} r_C^{29/30}) \\
&+ m_{C(AC)} m_{C(BC)} \cdot (r_C^{28/30} - r_{AC}^{28/30}) \cdot (r_C^{29/30} - r_{BC}^{29/30}) \cdot (r_B^{28/30} r_A^{29/30} - r_A^{28/30} r_B^{29/30}) \\
&+ m_{C(AC)} m_{B(BC)} \cdot (r_C^{28/30} - r_{AC}^{28/30}) \cdot (r_{BC}^{29/30} - r_B^{29/30}) \cdot (r_A^{28/30} r_C^{29/30} - r_C^{28/30} r_A^{29/30}).
\end{aligned} \tag{Eq. S6}$$

RESULTS AND DISCUSSION

Calibration. Typical mass-bias correction factors are shown in Table S2.

Table S2. Typical results for the mass-bias correction factors^a

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Blends	$K_{28/29}^b$	$K_{30/29}^b$	$K_{29/28}$	$K_{30/28}$	$K_{28/30}$	$K_{29/30}$
AB+BC	1.0613	0.9397				
AB+AC	1.0613	0.9400	0.9422	0.8857		
AC+BC	1.0610	0.9397			1.1291	1.0642
average	1.0612	0.9398				

^a Masses of materials A, B and C to form blends AB, BC and BC are given in Table 6.

^b The following expressions were used to convert the calibration factors: $K_{28/29} = 1/K_{29/28} = K_{28/30}/K_{29/30}$ and $K_{30/29} = K_{30/28}/K_{29/28} = 1/K_{29/30}$.

Evaluation of uncertainty. Estimations of 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 shown Table S3.

Table S3. Typical uncertainty budget for an individual atomic weight measurement result

Quantity, x_i	Unit, [x_i]	Typical value, { x_i }	Uncertainty, $u(x_i)$	Contribution to $u(A_r)$
m_{28}	Da	27.976 926 532 46	194×10^{-11}	0.0%
m_{29}	Da	28.976 494 700	22×10^{-9}	0.0%
m_{30}	Da	29.973 770 171	32×10^{-9}	0.0%
$m_{C(CX)}$	μg	8.0963	0.0039	0.4%
$m_{X(CX)}$	g	0.191 547	0.000 088	0.3%
$R_{28/29}^C$	mol/mol	1.084	0.096	0.2%
$R_{30/29}^C$	mol/mol	259	11	0.4%

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$\#R_{30/29}^A$	mol/mol	0.6630	0.0027	25.4%
$r_{30/29}^A$	V/V	0.706 85	0.000 49	0.7%
$r_{30/29}^X$	V/V	0.0172	0.0023	68.2%
$\#r_{30/29}^{CX}$	V/V	1.0388	0.0017	4.4%
$A_r(\text{Si})_i$	1	27.976 968 39	0.000 000 33	

$\#$: for mass bias correction of $K_{30/20} = R_{30/29}^A / r_{30/29}^A$

Traceability. All weighings were performed on a balance that was calibrated by the INMS Mass Metrology group and, as such, are traceable to the National kilogram etalon of Canada, K74. The chemical purity of all silicon materials used (**A**, **B**, **C**, and **X**) was assumed as $w_{\text{Si}} = 1 \text{ g/g}$, based on the work of Andreas *et al.*[4] Nuclide masses used in this work were obtained from the (most recent) 2003 Atomic Mass Evaluation report.[17] These results are traceable to the atomic unit of mass (dalton), $m_u = m(^{12}\text{C})/12$.

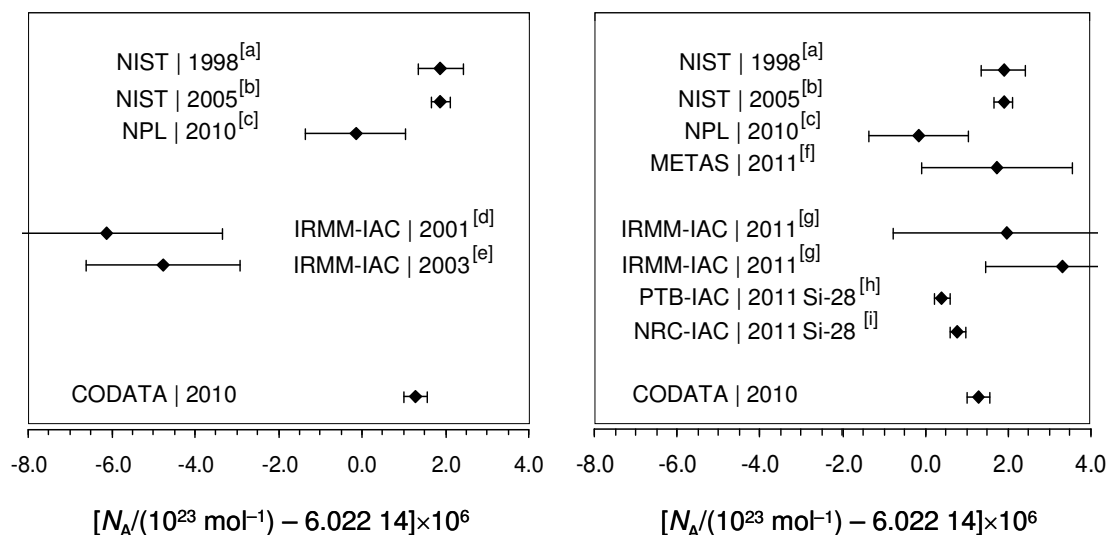
Recent estimates of the Avogadro constant.

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 ($N_{\text{A}}h$) whose relative uncertainty, given by the CODATA, is 30–60-fold lower than that of N_{A} or h .⁸

[a] Williams et al. (1998) *Phys. Rev. Lett.* 81, 2404-2407.

[b] R.L.Steiner et al. (2007) *IEEE Trans. Instrum. Meas.* 56(2), 592-596.

[c] I.A. Robinson (2012) *Metrologia* 49, 113-156.

[d] Ref. [24]

[e] DeBievre et al. (2001) *IEEE Trans. Instrum. Meas.* 50(2) 593-597.

[f] Eichenberger et al. (2011) *Metrologia* 48(3) 133-141.

[g] Ref. [25]

[h] Ref. [4]

[i] this work

EXPERIMENTAL SECTION

Instrumentation. Typical optimized operating conditions of MC-ICPMS are given in Table S4. A Branson 3510 ultrasonic system (Branson Ultrasonics Corp., Danbury, CT, USA) was used to aid dissolution of silicon crystal samples. Savillex 100 mL PFA bottles free from metal contact during their production, and 60 mL PFA tubes were purchased from Delta Scientific (Mississauga, ON, Canada) and used for sample preparation. A Mettler Toledo AG 245 dual scale balance (Mettler Toledo Canada, Mississauga, ON, Canada), calibrated with traceable weights, was used for all weighings. Crystal samples (40–400 mg) were weighed using the 0.01 mg readability mode and aqueous solutions (10–100 g) were weighed using the 0.1 mg readability mode.

Table S4. Optimized MC-ICPMS operating conditions

Instrument settings	
Reflected forward power	1290 W
Plasma gas flow rate	16.0 L Ar min ⁻¹
Auxiliary gas flow rate	1.00 L Ar min ⁻¹
Carrier gas flow rate	1.020 L Ar min ⁻¹
Orifice of the nickel sampler cone	1.1 mm
Orifice of the high-performance nickel skimmer cone	0.8 mm
Lens settings	Optimized for maximum analyte ion current
Data acquisition parameters	
Mass resolution, $R_{5, 95\%}$	~10 000
Signal integration time	4.09 s
Number of integrations, cycles, blocks	1, 8, 3 for three Si isotopes measurements; 1, 5, 4 for ^{30}Si and ^{29}Si measurements

Reagents and solutions. Fluka analytical grade nitric acid ($w(\text{HNO}_3) \geq 65\%$) was purchased from Sigma-Aldrich (Oakville, ON, Canada). Optima grade hydrogen peroxide ($w(\text{H}_2\text{O}_2) = 30\text{--}32\%$) was supplied by Fischer Scientific Canada (Ottawa ON, Canada). Environmental grade hydrofluoric acid ($w(\text{HF}) = 47\text{--}51\%$) was purchased from Anachemia Science (Montreal, QC, Canada). High-purity deionized water (18 M Ω cm resistivity) was obtained from a NanoPure mixed bed ion exchange system fed with reverse osmosis domestic feed water (Barnstead-Thermolyne; Iowa, USA). High purity sodium hydroxide monohydrate ($w(\text{NaOH} \times \text{H}_2\text{O}) = 0.999995\text{ g/g}$) was sourced from Fluka/Sigma-Aldrich Canada (Oakville, ON, Canada). HPLC grade acetone and ethanol were obtained from Fischer Scientific Canada (Ottawa ON, Canada). A 0.25 g/g NaOH solution, $w(\text{NaOH}) = 0.25\text{ g/g}$, was prepared by quantitative dissolution of sodium hydroxide monohydrate in water. An etching 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 water was used to clean the surfaces of silicon samples.

Sample description. Crystals of natural silicon (designated herein as material **A**), ^{29}Si -enriched silicon (material **B**) and ^{30}Si -enriched silicon (material **C**) were each available in 50-60 mg quantities. The IAC sample codes for crystals **A**, **B** and **C** are WASO 04, Si29-3-Pr10CzFz and Si30-3-Pr10CzFz, respectively. Two 50 mg samples of each crystal were used. These are identified as 41969/04/72-75 part Vn1 and 41969/04/72-75 part Vn2 (material **A**); part 1.5.1 and part 1.4.2 (material **B**); and part 2.5.1 and part 2.4.1 (material **C**). Four samples of the ^{28}Si -enriched silicon (material **X**) were available, each in 300-450 mg quantities. The IAC sample code for this crystal is Si28-10-Pr11 and the four samples are identified as parts 5B1.1.3.1, 5B1.1.3.2, 8B1.1.1.4, and 8B1.1.1.5. These crystals were cut from the vicinity of the boule from which both 1 kg spheres were fabricated.

The oxygen and carbon content in the ^{28}Si single crystal is estimated to be $< 1 \times 10^{15} \text{ cm}^{-3}$ [4], corresponding to mass fractions of these elements w_{C} , $w_{\text{O}} < 1 \times 10^{-8} \text{ g/g}$. The chemical purity of all crystals was therefore assumed ideal, i.e., $w_{\text{Si}} = 1 \text{ g/g}$ (exact).

Sample weighing. All weighings were corrected for air buoyancy with conventional masses (m_{c}) converted into masses (m) using the following equation:

$$m = m_{\text{c}} \frac{1 - \rho_{\text{air}} / \rho_{\text{ref}}}{1 - \rho_{\text{air}} / \rho}, \quad \text{Eq. S7}$$

where ρ_{air} , ρ_{ref} and ρ are the densities of air, reference and sample, respectively. The density of the steel reference used was $\rho_{\text{ref}} = 8000 \text{ kg m}^{-3}$. The density of ^{28}Si silicon crystal and of natural silicon was taken as $2320.070\,931(70) \text{ kg m}^{-3}$ [4] and $2329.037\,785(22) \text{ kg m}^{-3}$ [24], respectively. Densities of ^{29}Si (**B**) and ^{30}Si (**C**) were calculated based on the expressions $\rho_{\text{A}}/M_{\text{A}} \approx \rho_{\text{B}}/M_{\text{B}} \approx \rho_{\text{C}}/M_{\text{C}}$. The density of moist air (ρ_{air}) was calculated based on the CIPM-81/91 equation endorsed by the International Committee for Weights

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and Measures (CIPM)[S1]:

$$\rho_{\text{air}} = \frac{pM_{\text{air}}}{ZRT} \left[1 - x_{\text{H}_2\text{O}} \left(1 - \frac{M_{\text{H}_2\text{O}}}{M_{\text{air}}} \right) \right]. \quad \text{Eq. S8}$$

where p is the atmospheric pressure, T the temperature, $x_{\text{H}_2\text{O}}$ the amount fraction of water vapour in the air, M_{air} the molar mass of dry air, $M_{\text{H}_2\text{O}}$ the molar mass of water, R the molar gas constant and Z the compressibility factor of air. Typical values for quantities in Eq. S7 are shown in Table S5.

Table S5. Typical values used for air buoyancy correction.

Quantity	Value	$U, k=1$
ρ_{air}	1.177 kg/m ³	0.010
ρ_{ref}	8000 kg/m ³	10
ρ	2320.070 931 kg/m ³	0.000 070
m_{c}	0.453 96 g	0.000 022
m	0.454 12 g	0.000 022

Preparation of solutions for mass-bias calibration. In this study, the determination of mass bias correction factors is based on the use of three solutions: **A** (natural Si), **B** (^{29}Si) and **C** (^{30}Si) as well as three blends of **AB**, **BC** and **AC**. The dissolution procedure used is similar to that reported in previous studies employing NaOH.[13,18] Two sets of **A**, **B** and **C** stock solutions were prepared separately. Pre-cleaned silicon samples of 0.04914 g (**A**), 0.04741 g (**B**) and 0.04974 g (**C**) were accurately weighed and placed in individual pre-cleaned 100 mL PFA bottles. After adding 1.25 g, 1.50 g and 1.56 g of aqueous

NaOH solution of $w(\text{NaOH}) = 0.25 \text{ g/g}$ to these respective bottles, they were loosely capped (to avoid pressurization due to the subsequent evolution of hydrogen) and placed within a plastic bag tightly secured in the ultrasonic water bath. Samples were subjected to sonication for four regularly spaced periods of 90 min daily. This procedure lasted for 2–3 weeks until all pieces of silicon were fully dissolved and no visible particles could be detected in the solution. Sonication was reapplied for several more days to ensure total dissolution prior to dilution. Clear solutions were obtained. Samples of **B** and **C** were then diluted with appropriate amounts of water (83–86 g), resulting in the mass fraction of silicon $w(\text{Si}) = 550 \text{ }\mu\text{g/g}$. The natural Si sample (**A**) was first diluted with 9.5 g of water to provide $w(\text{Si}) = 5000 \text{ }\mu\text{g/g}$. This stock was then divided into two portions, one of which was (gravimetrically) diluted to 50 g with water to prepare the calibration stock solution having $w(\text{Si}) = 550 \text{ }\mu\text{g/g}$. Working standard solutions of $100 \text{ }\mu\text{g/g}$ of **A**, **B** and **C** were prepared by gravimetric dilution of their respective stocks of $w(\text{Si}) = 550 \text{ }\mu\text{g/g}$ using aqueous NaOH with $w(\text{NaOH}) = 0.1 \text{ mg/g}$.

Blends of **AB**, **BC** and **AC**, and test solutions of pure **A**, **B** and **C** were prepared gravimetrically from the $100 \text{ }\mu\text{g/g}$ Si **A**, **B** and **C** working standards. Care was taken to match analyte concentrations in the range $10\text{--}25 \text{ }\mu\text{g/g}$ total Si in $w(\text{NaOH}) = 0.1 \text{ mg/g}$. The typical masses of each **A**, **B** and **C** pure materials used for these calibration solutions are shown in Table S6.

Table S6. Masses of silicon derived from **A**, **B**, and **C** in the test solutions used for mass bias calibration (combined uncertainty, $k = 1$).

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Blend	m_A/mg	m_B/mg	m_C/mg
AB	0.504 68(24)	0.523 70(25)	0
BC	0	0.488 18(23)	0.616 20(29)
AC	0.527 10(25)	0	0.528 11(25)
A	0.990 22(46)	0	0
B	0	1.023 15(48)	0
C	0	0	1.061 00(50)

Preparation of solutions for determination of atomic weight. A 4000 $\mu\text{g/g}$ solution of **X** was prepared by diluting the remaining 50.1 g of 5000 $\mu\text{g/g}$ stock with 12.5 g of $w_{\text{NaOH}} = 0.1 \text{ mg/g}$ in the original bottle. Similarly, the process blank containing the same amount of $w_{\text{NaOH}} = 0.25 \text{ g/g}$ used initially was prepared by the addition of 21.5 g of $w_{\text{NaOH}} = 0.1 \text{ mg/g}$ to the 86.6 g process blank, resulting in a NaOH content matching that in solutions of **X** and **CX**. Mass-bias correction calibrator (**A**) of 4000 $\mu\text{g/g}$ Si was prepared by diluting the remaining 5 g of 5000 $\mu\text{g/g}$ natural Si with 1.25 g of $w_{\text{NaOH}} = 0.1 \text{ mg/g}$. A lower mass fraction of 1000 $\mu\text{g/g}$ Si (**A**) was prepared by diluting 1 g of 4000 $\mu\text{g/g}$ Si with 3 g of $w_{\text{NaOH}} = 0.024 \text{ g/g}$. Masses of pure materials of **C** and **X** in blends **CX** are shown in Table S7.

Table S7. Masses of silicon derived from **X**, **C** and **A** in the test solutions used for atomic weight determination (combined uncertainty, $k = 1$).

Blend	m_X/g	$m_C/\mu\text{g}$	$w_{\text{Si}}(\mu\text{g/g})$
CX-1	0.191 547(88)	8.0963(39)	~4000

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CX-2	0.217 585(92)	8.6564(44)	~4000
CX-3	0.217 788(86)	9.2629(47)	~4000
CX-4	0.192 840(72)	9.8634(50)	~4000
X			~4000
A			~1000-4000

Initially, the mass-bias calibrator (**A**) was also prepared to contain the same mass fraction of Si and NaOH. It was later determined that lowering the mass fraction of Si to $w_{\text{Si}} = 1000 \mu\text{g/g}$ had no effect on the resultant $N(^{30}\text{Si})/N(^{29}\text{Si})$ ratio. Thus, $1000 \mu\text{g/g}$ Si (**A**) prepared in $w_{\text{NaOH}} = 0.024 \text{ g/g}$ was used for mass-bias correction when the ^{29}Si signal from $4000 \mu\text{g/g}$ Si (**A**) exceeded 50 V.

For determination of the mass fraction of ^{29}Si and ^{30}Si isotopes in the ^{28}Si -enriched silicon, w_{29+30}^{X} , either $1.4908 \mu\text{g/g}$ or $1.6308 \mu\text{g/g}$ of the ^{30}Si -enriched material in $w_{\text{NaOH}} = 0.1 \text{ mg/g}$ was prepared by gravimetric dilution of two $100 \mu\text{g/g}$ ^{30}Si (**C**) working standard solutions.

Preparation of solutions for the determination of silicon impurity in sodium

hydroxide. To estimate the natural silicon content in the commercially available NaOH reagent, replicate 0.53 g samples of NaOH were weighed into pre-cleaned PFA tubes.

After adding 1.3 g of $1.6308 \mu\text{g/g}$ solution **C** to each tube, samples were diluted with 12 g of water. Three procedural blanks were prepared containing the same amount of water and material **C** but with no added NaOH.

Isotope amount ratio measurements. Samples were introduced into the plasma in a self-aspiration mode at a flow rate of $50\ \mu\text{L min}^{-1}$. A static run with the “Virtual amplifier” was used to simultaneously monitor intensities of the Si isotopes. The high mass resolution mode was used to resolve potential spectral interferences such as $^{12}\text{C}^{16}\text{O}^+$, $^{14}\text{N}_2^+$, $^{28}\text{Si}^1\text{H}^+$, $^{13}\text{C}^{16}\text{O}^+$, $^{12}\text{C}^{16}\text{O}^1\text{H}^+$, $^{14}\text{N}^{15}\text{N}^+$, $^{14}\text{N}_2^1\text{H}^+$, $^{14}\text{N}^{16}\text{O}^+$, $^{13}\text{C}^{16}\text{O}^1\text{H}^+$, and $^{14}\text{N}^{15}\text{N}^1\text{H}^+$. By measuring at the left shoulders of the peaks (typically at 28.951 Da for center cup of $^{29}\text{Si}^+$) instead of at the peak center, the signals for all three Si isotopes could be acquired free of any interference [20,21] see Figure S1. The raw data were imported into an *Excel* file for further calculation of mass-bias correction factors, corrected isotope amount ratios and atomic weight, as detailed in the accompanying electronic data file.

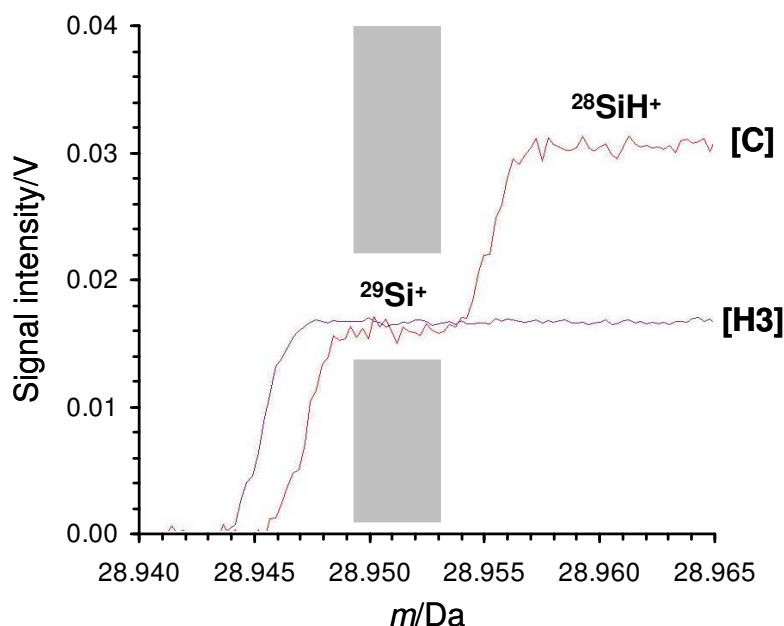


Figure S1. High resolution mass scan of a **CX** solution.

Table S8. MC-ICPMS detector configurations and typical ion intensities obtained for sample and blank solutions.^a

Faraday cup	L3	C	H3
Sequence 1: Calibration	^{28}Si	^{29}Si	^{30}Si
Cup position, mm	47.295	0	46.775
Signal intensity, V	36.97	1.97	1.39
Blank signal, mV	4.31	0.20	0.17
Mass fraction of silicon: $w_{\text{Si}} = 25 \mu\text{g/g}$; mass fraction of NaOH: $w_{\text{NaOH}} = 0.1 \text{ mg/g}$.			
	L3	C	H3
Sequence 2: Measurement	—	^{29}Si	^{30}Si
Cup position, mm	—	0	46.775
Signal intensity, V	—	0.0476	0.0011
Blank signal, mV	—	0.10	0.15
Mass fraction of silicon: $w_{\text{Si}} = 4000 \mu\text{g/g}$; mass fraction of NaOH: $w_{\text{NaOH}} = 0.024 \text{ g/g}$.			

^aAll measurements were performed in high mass resolution mode.

Calculation details and input variables. All model equations were independently reproduced from first principles and the results were calculated using *Excel*. The veracity of the analytical expressions was also confirmed using *Mathematica* v. 8.0.[S2] All partial derivatives were produced from first principles and uncertainty were calculated using Excel. Results were also confirmed using *Mathematica* v. 8.0.

Although the recent study showed $m(^{28}\text{Si})/m_{\text{u}}$ to be an important contributor to uncertainty (23.1%)[12,13], the 1993 Atomic mass value presented therein is outdated by almost two decades. The concerns raised in 1994 regarding the use of the above ‘gas-phase mass values for the determination of a condensed-phase constant’ are still

irrelevant at the parts in 10^8 level of uncertainty.[S3] The energy required to remove silicon atoms from the crystal and form a gas-phase ion is the sum of the enthalpies of atomization and ionization, *i.e.*, $(450 + 786) \text{ kJ mol}^{-1}$, which corresponds to a 10 nDa mass difference. The neglect of this energy, when comparing the atomic masses and the bulk mass of the Si crystal, yields a 4 parts in 10^{10} bias in the estimate of N_A and can be ignored.

SUPPLEMENTARY REFERENCES

S1. Davis, R.S. (1992) *Metrologia* 29: 67-70.

S2. Wolfram Mathematica v. 8.0.0.0 (Wolfram Research, Inc.)

S3. Dougherty, R.C.; Marshall, A.G.; Eyler, J.R.; Richardson, D.E.; Smalley, R.E. (1994)

J. Am. Soc. Mass Spectrom. 5: 120-123.