METRICA
METRology Institutional CAtalog

ISTITUTO NAZIONALE DI RICERCA METROLOGICA
Repository Istituzionale

Measurement of the (30)Si Mole Fraction in the New Avogadro Silicon Material by Neutron Activation and High-Resolution γ-Spectrometry

This is the author's accepted version of the contribution published as:

Original
Measurement of the (30)Si Mole Fraction in the New Avogadro Silicon Material by Neutron Activation and High-Resolution γ-Spectrometry / Di Luzio, Marco; Stopic, Attila; D'Agostino, Giancarlo; Bennett, John W; Mana, Giovanni; Oddone, Massimo; Pramann, Axel. - In: ANALYTICAL CHEMISTRY. - ISSN 0003-2700. - 89:12(2017), pp. 6726-6730-6730. [10.1021/acs.analchem.7b00963]

Availability:
This version is available at: 11696/55329 since: 2020-05-21T11:27:23Z

Publisher:
American Chemical Society

Published
DOI:10.1021/acs.analchem.7b00963

Terms of use:
Visibile a tutti

This article is made available under terms and conditions as specified in the corresponding bibliographic description in the repository

Publisher copyright
American Chemical Society (ACS)
Copyright © American Chemical Society (after peer review and after technical editing by the publisher)

(Article begins on next page)

29 July 2022

Measurement of the ^{30}Si mole fraction in the new Avogadro silicon material by neutron activation and high-resolution gamma-spectrometry.

Marco Di Luzio[†,‡], Attila Stopic[§], Giancarlo D'Agostino[*,†], John W. Bennett[§], Giovanni Mana[†], Massimo Oddone[‡], Axel Pramann[¶]

[†] Istituto Nazionale di Ricerca Metrologica (INRIM), Strada delle Cacce 91, 10135 Torino, Italy

[‡] Department of Chemistry, University of Pavia, via Taramelli 12, 27100 Pavia, Italy

[§] Australian Nuclear Science and Technology Organisation (ANSTO), New Illawarra Road, Lucas Heights, New South Wales 2234, Australia

[¶] Physikalisch-Technische Bundesanstalt (PTB), Bundesallee 100, 38116, Braunschweig, Germany

ABSTRACT: The use of new silicon single crystals highly enriched in ^{28}Si recently produced for the upcoming redetermination of the Avogadro constant requires knowledge of their molar masses. The isotopic composition data are collected independently in different laboratories but all using the virtual element technique with multi-collector inductively coupled plasma mass spectrometers. In this framework, the comparison of the results with an independent measurement of the amount of at least one of the depleted isotopes is useful to limit hidden systematic errors. To this aim, the ^{30}Si mole fraction of a sample of the new material was measured using a relative measurement protocol based on instrumental neutron activation analysis. The protocol is similar to that previously applied with the AVO28 silicon material used for the last determination of the Avogadro constant value with the exception that unknown and standard samples are not co-irradiated. The $x(^{30}\mathrm{Si}) = 5.701 \times 10^{-7}$ mol mol^{-1} estimate is close to the expected one and is given with a standard uncertainty of 8.8×10^{-9} mol mol^{-1}. This value, if adopted, gives a contribution to the relative standard uncertainty of the Avogadro constant of 6.3×10^{-10}.

The redefinition of units of measurement in terms of fundamental constants represents the main task in the revision of the International System of Units (SI), scheduled for 2018 during the 26$^{\mathrm{th}}$ General Conference on Weights and Measures. The Avogadro constant, N_{A}, is of paramount importance both for the unit of mass and amount of substance.[1] For what concerns the kilogram, the new definition will be based on the Planck constant, h, obtained as well from N_{A} through the well-known value of the molar Planck constant, $N_{\mathrm{A}}h$.

The most precise N_{A} value was achieved with the x-rays crystal density (XRCD) method using a ^{28}Si-enriched silicon material, called AVO28, and reached the 2.0×10^{-8} relative uncertainty required to accept the value for redefinition.[2]

A collaboration involving the Stock Company "Production Association Electrochemical Plant" (SC "PA ECP"), the G. G. Devyatykh Institute of Chemistry of High-Purity Substances of the Russian Academy of Sciences (IChHPS RAS), the Leibniz-Institut für Kristallzüchtung (IKZ), the ISOTOPE company and the Physikalisch-Technische Bundesanstalt (PTB) started to manufacture a new generation of silicon materials even further enriched in ^{28}Si. The outcomes were three silicon batches with a ^{28}Si mole fraction $x(^{28}\mathrm{Si}) \cong 0.999\,98$ mol mol^{-1}, compared to the $x(^{28}\mathrm{Si}) \cong 0.999\,96$ mol mol^{-1} of the AVO28 crystals. Mass spectrometric methods were applied to investigate the isotopic composition and molar mass. Specifically, the expected $x(^{29}\mathrm{Si})$ and $x(^{30}\mathrm{Si})$ values are 5×10^{-6} mol mol^{-1} and 7×10^{-7} mol mol^{-1}.[3]

It was demonstrated that the application of Instrumental Neutron Activation Analysis (INAA) can add useful information to the isotopic composition of highly-enriched ^{28}Si material.[4] A measurement protocol based on the INAA comparator method was applied to determine the $x(^{30}\mathrm{Si})$ of the AVO28; the resulting value, $1.043(19) \times 10^{-6}$ mol mol^{-1}, was obtained by irradiating a 5 g mass sample at the central channel, CC, of the Triga Mark II reactor of the University of Pavia.[5] Here and hereafter the standard uncertainty ($k = 1$) in parenthesis applies to the last respective digits. The thermal neutron flux, $\Phi_{\mathrm{th}} = 6.1 \times 10^{12}$ cm^{-2} s^{-1}, and the thermal to epithermal neutron flux ratio, $f = 15.6$, at the Triga Mark II reactor CC were recently re-determined.[6]

An independent check of the molar mass of the new ^{28}Si-enriched material via the $x(^{30}\mathrm{Si})$ measurement by INAA is valuable to limit hidden systematic errors. Thus, in view of the expected lower amount of ^{30}Si with respect to the AVO28, we modified the protocol to take advantage of the higher neutron flux of the 20MW OPAL reactor of the Australian Nuclear Science and Technology Organisation (ANSTO). In addition, a larger mass sample, 13.5 g, was used for the analysis.

The measurement model together with the details of the experiment and the result obtained at the ANSTO facility are given in this paper.

Determination of the ^{30}Si Mole Fraction. The measurement protocol and the derivation of the measurement equation, in the case of co-irradiation of the unknown and standard samples, have been described elsewhere.[4] The experiment was based on the simultaneous irradiation of the ^{28}Si-enriched unknown sample and a natural Si standard sample of known isotopic composition, followed by counting the 1266.1 keV γ-photons emitted by the ^{31}Si radioisotope produced from the ^{30}Si isotope via neutron capture reaction. Preliminary experimental results anticipated that the contribution to the uncertainty due to the knowledge of the natural isotopic composition of the standard was negligible.

In the case of separated irradiations of the samples and different irradiation times, the following measurement equation applies:

$$x(^{30}\mathrm{Si}_{28\mathrm{Si}}) = \kappa_{\mathrm{ti}}\kappa_{\mathrm{td}}\kappa_{\mathrm{R}}\kappa_{\varepsilon}\kappa_{\mathrm{ss}}\kappa_{\mathrm{sa}}\kappa_{\mathrm{g}}\frac{C_{28\mathrm{Si}}(t_{\mathrm{d}\,28\mathrm{Si}})}{C_{\mathrm{natSi}}(t_{\mathrm{d}\,\mathrm{natSi}})}x(^{30}\mathrm{Si}_{\mathrm{natSi}})\frac{m_{\mathrm{natSi}}}{m_{28\mathrm{Si}}}\frac{M_{28\mathrm{Si}}}{M_{\mathrm{natSi}}}, \quad (1)$$

where the subscripts 28Si and natSi refer to the ^{28}Si-enriched sample and natural Si standard, respectively, m is the silicon mass, M is the molar mass, and $C(t_{\mathrm{d}})$ is the 1266.1 keV full-energy γ-peak count rate at a time t_{d} after the end of the irradiation. The correction factors, $\kappa_{\mathrm{ti}} = (1 - e^{-\lambda t_{i\,\mathrm{natSi}}})/(1 - e^{-\lambda t_{i\,28\mathrm{Si}}})$, $\kappa_{\mathrm{td}} = e^{-\lambda(t_{\mathrm{d}\,\mathrm{natSi}} - t_{\mathrm{d}\,28\mathrm{Si}})}$, $\kappa_{\mathrm{R}} = R_{\mathrm{natSi}}/R_{28\mathrm{Si}}$, $\kappa_{\varepsilon} = \varepsilon_{\mathrm{natSi}}/\varepsilon_{28\mathrm{Si}}$, $\kappa_{\mathrm{ss}} = k_{\mathrm{ss\,natSi}}/k_{\mathrm{ss\,28Si}}$, $\kappa_{\mathrm{sa}} = k_{\mathrm{sa\,natSi}}/k_{\mathrm{sa\,28Si}}$, and $\kappa_{\mathrm{g}} = k_{\mathrm{g\,natSi}}/k_{\mathrm{g\,28Si}}$ concern differences of irradiation time, decay time, reaction rate, detection efficiency, self-shielding, self-absorption and geometry of the samples. A detailed description of the measurement parameters can be found elsewhere,[5] with the exception of the κ_{R} factor hereafter discussed.

Neutron flux. The reaction rate per target nucleus, R, depends on the neutron energy spectrum during the irradiation. According to the Høgdahl convention, $R = \Phi_{\mathrm{th}}\,\sigma_0\,(1 + Q_0(\alpha)/f)$, where σ_0 is the (target) thermal neutron cross section and $Q_0(\alpha)$ is the (target) resonance integral, $I_0(\alpha)$ (for a $1/E^{1+\alpha}$ spectrum), to the σ_0 ratio.[7,8]

A flux monitor having a $Q_{0\,\mathrm{m}}(\alpha)$ value is co-irradiated with the sample to obtain the κ_{R} factor according to:

$$\kappa_{\mathrm{R}} = \kappa_{\mathrm{R\,m}}\frac{(1+Q_{0\,\mathrm{m}}(\alpha)/f_{28\mathrm{Si}})}{(1+Q_{0\,\mathrm{m}}(\alpha)/f_{\mathrm{natSi}})}\frac{(1+Q_0(\alpha)/f_{\mathrm{natSi}})}{(1+Q_0(\alpha)/f_{28\mathrm{Si}})}, \quad (2)$$

where $\kappa_{\mathrm{R\,m}} = K_{\mathrm{m}}^{-1}\frac{C_{\mathrm{m\text{-}natSi}}(t_{\mathrm{d\,m\text{-}natSi}})}{C_{\mathrm{m\text{-}28Si}}(t_{\mathrm{d\,m\text{-}28Si}})}\frac{m_{\mathrm{m\text{-}28Si}}}{m_{\mathrm{m\text{-}natSi}}}$, and $K_{\mathrm{m}} = \kappa_{\mathrm{ti\,m}}\kappa_{\mathrm{td\,m}}\kappa_{\varepsilon\,\mathrm{m}}\kappa_{\mathrm{ss\,m}}\kappa_{\mathrm{sa\,m}}\kappa_{\mathrm{g\,m}}$. The subscripts m-28Si and m-natSi refer to the monitor co-irradiated with the ^{28}Si-enriched sample and natural Si standard, respectively.

In eq 2, $f_{28\mathrm{Si}} = f$ and $f_{\mathrm{natSi}} = f + \Delta f$, where f is the nominal thermal to epithermal neutron flux ratio and Δf is a possible difference between the ratios during the irradiation of 28Si and natSi samples. Variations affecting the α value are neglected for the calculation of $Q_0(\alpha)$ and $Q_{0\,\mathrm{m}}(\alpha)$.

EXPERIMENTAL SECTION

Materials. A sample of the new ^{28}Si-enriched material was cut from one of the produced batches and coded Si28-23Pr11 part Q.4.1, while the standard sample was cut from a natural silicon material and coded Si-V1382 part 8.1. Hereafter, the ^{28}Si-enriched sample and the standard sample are called 28Si and natSi, respectively. The isotopic composition of the Si-V1382 was measured by PTB using multicollector-ICP-mass spectrometry.[5] After cutting, the diameter, ϕ, and length, l, of the samples were $\phi_{28\mathrm{Si}}$ = 20.07 mm, ϕ_{natSi} = 20.05 mm and $l_{28\mathrm{Si}}$ = l_{natSi} = 19.06 mm. A picture of the 28Si sample is shown in Figure 1.

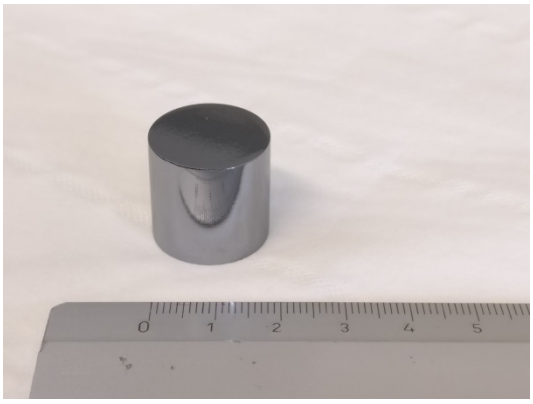


Figure 1. The 28Si sample.

Two samples, about 70 mm length, of a high purity Co-Al wire (IRMM-527RB, 0.1% Co mass fraction, purity, 0.5 mm diameter) were cut to monitor the neutron flux during the irradiation.

Preparation of the samples. Both samples were deeply etched according to the procedure adopted with the AVO28 material to eliminate the surface contamination due to machining.[5] The final masses, $m_{28\mathrm{Si}}$ = 13.5073(1) g and m_{natSi} = 13.5496(1) g, were measured using a digital analytical balance calibrated with SI-traceable weights. Care was applied to avoid cross-contamination of ^{30}Si between samples during the preparation. To this aim, 28Si was handled and measured before natSi. The weighed masses of the Co-Al monitors used for 28Si and natSi, hereafter called m-28Si and m-natSi, were 0.03395(1) g and 0.04104(1) g, respectively. Each sample was wrapped in an ultra-pure Al foil and surrounded by a single helix of the Co-Al wire. A second Al foil was finally used to tightly envelop the sample and fix the monitor in its position. Afterwards, the sample (and monitor) was closed in a container used for the neutron irradiation.

Neutron Irradiation and Gamma Spectrometry. The neutron irradiation was performed in the LE7-1C channel (Φ_{th} = 1.0 × 10^{14} cm^{-2} s^{-1}, f = 44.3) of the 20 MW OPAL reactor. This channel is equipped with a pneumatic transfer system to load and release the samples with a good reproducibility of irradiation position. The resolution for measurement of the irradiation time is 60 s.

To balance the amount of ^{31}Si radioisotope produced in 28Si and natSi, the neutron activation was performed separately with different exposure times. The set point of the neutron flux was fixed to the same value for both the irradiations. The irradiation of 28Si lasted 10800(17) s while the irradiation of natSi lasted 3600(17) s, the uncertainty being due to the 60 s resolution. The online measurement of the neutron flux fluctuation during each irradiation showed no significant departures from the mean value.

After irradiation, the Al foils fixing the monitor and surrounding the sample were removed. Each monitor wire was bent in a ring shape, 1 cm diameter, to obtain a compact source geometry and was located in a polyethylene vial for counting.

Several γ-spectrometric sequences were recorded with a HPGe detector ORTEC GMX50-P4 (70 mm crystal diameter, 65% relative efficiency, 1.87 fwhm resolution at 1332 keV) connected to a digital signal processor ORTEC DSPEC-Pro and a

HPGe detector ORTEC GEM GEM25-P4 (57 mm crystal diameter, 25% relative efficiency, 1.66 fwhm resolution at 1332 keV) also connected to a digital signal processor ORTEC DSPEC-Pro. The data acquisition was performed with the ORTEC software (MAESTRO V7).

The 1266.1 keV ^{31}Si γ-spectrometry sequence of 28Si started at $t_{d\ 28Si}$ = 286.9 min after the end of the irradiation. It consisted of 3 consecutive counts performed with a fixed counting window lasting 7200 s; the dead to counting time ratio, t_{dead}/t_c, was 17%, 14% and 12%, respectively. The sequence of natSi started at $t_{d\ natSi}$ = 2284.0 min after the end of the irradiation. It consisted of seven consecutive counts performed with a fixed counting window lasting 4000 s; the t_{dead}/t_c value for the first three counts was 18%, 14% and 11%, and thereafter below 10%.

Both cylindrical samples were directly placed on a paper sheet in contact with the end-cap of the ORTEC GMX50-P4 detector (axis of the sample parallel to the axis of the Ge crystal). A template previously printed on the paper was used to assure the best horizontal reproducibility of the position.

The counting of the monitors concerned the 1332.5 keV γ-emission of the ^{60}Co produced by ^{59}Co via the neutron capture reaction. The γ-spectrometry sequence of m-28Si started at $t_{d\ m\text{-}28Si}$ = 1412.5 min after the end of the irradiation. It consisted of three consecutive counts performed with a fixed counting window lasting 65 min, 72 min and 150 min, respectively. The sequence of m-natSi started at $t_{d\ m\text{-}natSi}$ = 2879.5 min after the end of the irradiation. It consisted of three consecutive counts performed with a fixed counting window lasting 140 min, 278 min and 265 min, respectively. The acquisition was performed in Zero Dead-Time Mode.

Both the monitor vials were fitted to the central slit of a plastic support located at 22 cm from the end-cap of the ORTEC GEM25-P4 detector (axis of the ring wire parallel to the axis of the Ge crystal) in order to have negligible effects due to differences of detection efficiency and geometry.

RESULTS AND DISCUSSION

Gamma Peak Fitting and Count Rate. The 1266.1 keV ^{31}Si and 1332.5 keV ^{60}Co γ-peak net counts were extracted from the γ-spectra using the Gaussian function implemented in the regular peaks and moderate count rate algorithm of the software HyperLab.[9]

The full-energy γ-peak count rate, $C_i(t_d)$, extrapolated at t_d from ith count of the γ-sequence was computed according to the equation reported elsewhere.[5] The ^{31}Si and ^{60}Co decay constants were calculated using $t_{1/2}(^{31}\text{Si})$ = 157.23(16) min and $t_{1/2}(^{60}\text{Co})$ = 462.067(34) × 10^2 h.[10] The $t_{1/2}(^{31}\text{Si})$ value is the weighted average of a recent estimate, 157.16(20) min,[11] and the presently adopted value 157.36(26) min.[12]

The resulting count rates of silicon samples and monitors are plotted in Figure 2a and b, and Figure 3a and b, respectively; the error bars show the 95% confidence interval due to counting statistics.

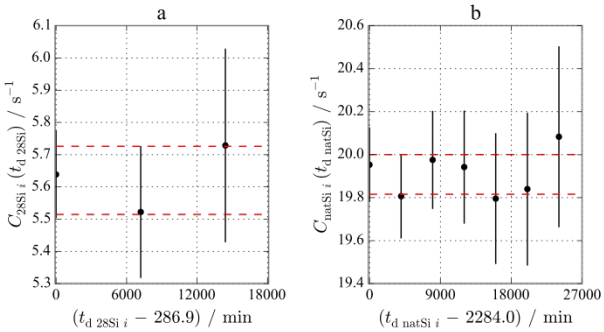


Figure 2. (a) ^{31}Si count rates of the 28Si sample extrapolated at $t_{d\ 28Si}$ = 286.9 min. (b) ^{31}Si count rates of the natSi sample extrapolated at $t_{d\ natSi}$ = 2284.0 min. The error bars indicate a 95% confidence interval. The horizontal lines show the 95% confidence interval associated with the weighted mean of the count rate values.

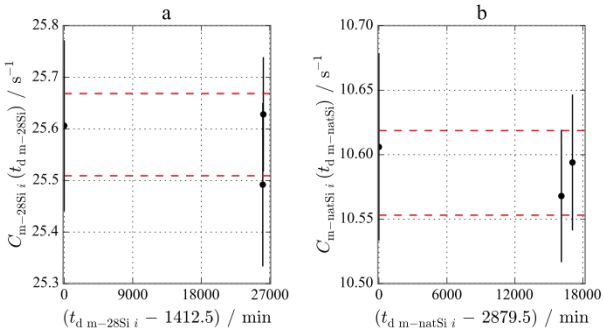


Figure 3. (a) ^{60}Co count rates of the monitor of the 28Si sample extrapolated at $t_{d\ m\text{-}28Si}$ = 1412.5 min. (b) ^{60}Co count rates of the monitor of the natSi sample extrapolated at $t_{d\ m\text{-}natSi}$ = 2879.5 min. The error bars indicate a 95% confidence interval. The horizontal lines show the 95% confidence interval associated with the weighted mean of the count rate values.

The mean values obtained by weighting the single values with the uncertainty due to counting statistics are $C_{28Si}(t_{d\ 28Si})$ = 5.617(53) s^{-1}, $C_{natSi}(t_{d\ natSi})$ = 19.900(46) s^{-1}, $C_{m\text{-}28Si}(t_{d\ m\text{-}28Si})$ = 25.589(40) s^{-1}, and $C_{m\text{-}natSi}(t_{d\ m\text{-}natSi})$ = 10.586(16) s^{-1}; the 95% confidence interval associated with the weighted mean are showed by the horizontal lines in Figure 2a and b, and Figure 3a and b.

The chi-squared statistics, χ^2, and the degrees of freedom, dof, of the ^{31}Si count rates of the 28Si and natSi samples are 1.51 (2 dof) and 3.15 (6 dof) whereas the ones of the ^{60}Co monitor count-rates are 2.05 (2 dof) and 0.89 (2 dof), respectively. Since the χ^2 upper-tail values at 5% significance level for 2 dof and 6 dof are 5.99 and 12.59, respectively, the data-consistency hypothesis is accepted.

Correction Factors. The neutron irradiation times of 28Si and natSi were $t_{i\ 28Si}$ = 10800(17) s and $t_{i\ natSi}$ = 3600(17) s, respectively. Accordingly, the κ_{ti} correction factor in eq 1 is 0.4243(18); the main contributor to the uncertainty is the $t_{i\ natSi}$ value.

The difference in time between the starts of the two γ-counting sequences of the samples is $t_{d\ natSi} - t_{d\ 28Si}$ = 1997 min with negligible uncertainty, i.e. about 13 times $t_{1/2}(^{31}\text{Si})$. The resulting κ_{td} is 0.0001502(13); the main contributor to the uncertainty is the $t_{1/2}(^{31}\text{Si})$ value.

After etching, the difference in mass between the silicon samples was 40 mg, i.e. about 10 µm thickness of material. Taking into account the dimensions before etching, the difference between the diameters and the lengths of the samples are assumed to be lower than 0.05 mm. Thus, $\kappa_{sa} = \kappa_g = 1 \pm 1.5 \times 10^{-4}$. Here and hereafter, the value following the ± symbol defines the half-width of a rectangular distribution of possible values assigned to the estimated parameter.

The effect of neutron self-shielding was evaluated according to the model discussed by Martinho et al.,[13] and applying the equation as previously described.[5] The corresponding κ_{ss} is 0.9944 $\pm 2 \times 10^{-4}$.

Taking into account the high reproducibility of the vertical position with respect to the detector end-cap, the main contribution to the detection efficiency is the length of the samples. Accordingly, $\kappa_\varepsilon = 1.000(3)$.

The reaction rate correction factor, κ_R, was computed using eq 2. According to the experimental conditions $\kappa_{ti\ m} = 0.333(3)$; the main contributor to the uncertainty is the $t_{i\ natSi}$ value. In addition, $\kappa_{td\ m} = 0.9996$ and $\kappa_{\varepsilon\ m} = \kappa_{ss\ m} = \kappa_{sa\ m} = \kappa_{g\ m} = 1$ with negligible uncertainty. The adopted Q_0 values for ^{30}Si and ^{59}Co are 1.11(7) and 1.99(6), respectively.[14] Thus, $\kappa_R = 1.0281(58)$, under the conservative assumption of ± 20% relative variation of f; the main contributor to the uncertainty is the $\kappa_{ti\ m}$ value.

Isotopic Composition of the Silicon Samples. The measured molar mass and ^{30}Si mole fraction of the natural silicon material used to cut the natSi are $M_{natSi} = 28.08570(21)$ g mol^{-1}, $x(^{30}Si_{natSi}) = 0.031031(48)$ mol mol^{-1}. Since the expected $x(^{29}Si)$ and $x(^{30}Si)$ values are 5×10^{-6} mol mol^{-1} and 0.7×10^{-6} mol mol^{-1}, $M_{28Si} = M(^{28}Si) + 6.4 \times 10^{-6}$ g mol^{-1}; consequently, $M_{28Si} = (27.976933 \pm 6.4 \times 10^{-6})$ g mol^{-1}.[3]

The ^{30}Si Mole Fraction. According to eq 1, the ^{30}Si mole fraction of the silicon sample cut from the Si28-23Pr11 batch is $5.701(88) \times 10^{-7}$ mol mol^{-1}. Table 1 reports the uncertainty budget computed according to the Guide to the Expression of Uncertainty in Measurement.[15]

Table 1. Uncertainty budget of the ^{30}Si mole fraction of the ^{28}Si-enriched material obtained by INAA. The input quantities, x_i, are discussed in the text. The index column reports the relative contributions of $u_c(x_i)$ to the combined standard uncertainty.

quantity	unit	Value	std uncertainty	Index
X_i	$[X_i]$	x_i	$u(x_i)$	%
κ_{ti}	1	0.4243	0.0018	8.0
κ_{td}	1	0.0001502	0.0000013	33.5
κ_R	1	1.0281	0.0058	13.5
κ_ε	1	1.000	0.003	4.1
κ_{ss}	1	0.9944	0.0001	0.0
κ_{sa}	1	1.0000	0.0001	0.0
κ_g	1	1.0000	0.0001	0.0
C_{28Si}	s^{-1}	5.617	0.053	37.6
C_{natSi}	s^{-1}	19.900	0.046	2.3
$x(^{30}Si_{natSi})$	mol mol^{-1}	0.031031	0.000048	1.0
m_{natSi}	g	13.5496	0.0001	0.0
m_{28Si}	g	13.5073	0.0001	0.0
M_{28Si}	g mol^{-1}	27.976933	0.000004	0.0
M_{natSi}	g mol^{-1}	28.08570	0.00021	0.0
Y	$[Y]$	y	$u(y)$	%
$x(^{30}Si_{28Si})$	mol mol^{-1}	0.0000005701	0.0000000088	100.0

It is worth mentioning that, due to the high ^{28}Si enrichment of the 28Si sample, the effect of the dependence of M_{28Si} on $x(^{29}Si_{28Si})$ and $x(^{30}Si_{28Si})$ is negligible. Thus, since the INAA comparator method has been demonstrated to be a primary ratio method,[16] the estimated $x(^{30}Si_{28Si})$ value via eq 1 is traceable to the SI (or SI-derived) units via the $x(^{30}Si_{natSi})$ value.

The protocol applied in this study was not validated for the specific use using reference samples. However, neutron activation analysis is based on sound technical principles and the evidence of suitability for providing useful analytical data is available by positive participation in comparisons and pilot studies organized by the Consultative Committee for Amount of Substance – Metrology in Chemistry and Biology (CCQM) of the International Bureau of Weights and Measures (BIPM).

CONCLUSIONS

A protocol based on neutron activation analysis and previously used to measure a ^{28}Si-enriched sample having a ^{30}Si amount at the level of 1×10^{-6} mol mol^{-1} was adapted and applied to a sample of new generation silicon materials having a significant lower amount of ^{30}Si that was produced for the upcoming redetermination of the Avogadro constant.

The uncertainty budget showed that the main contributors to the combined uncertainty were the count rate of the ^{30}Si-depleted sample and the correction factors concerning the decay and reaction rates.

The quantified $x(^{30}Si)$ value is close to the expected one,[3] and reached a 8.8×10^{-9} mol mol^{-1} standard uncertainty, which corresponds to a contribution to the relative standard uncertainty of the Avogadro constant of 6.3×10^{-10}.

Accordingly, as this datum is virtually unaffected by the potential natural silicon contamination that might bias the results obtained with mass spectrometric methods, it adds valuable and independent information to the knowledge of the molar mass of the new Avogadro silicon materials.

AUTHOR INFORMATION

Corresponding Author

* g.dagostino@inrim.it

Notes

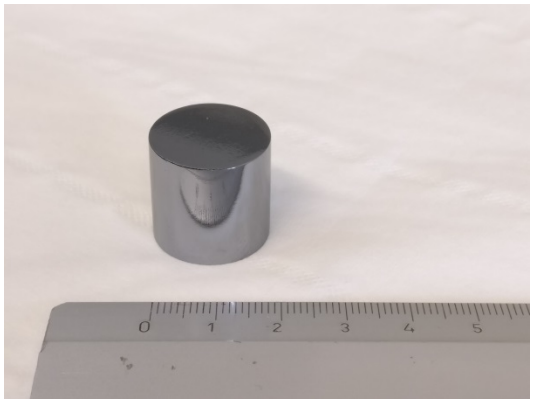
The authors declare no competing financial interest.

ACKNOWLEDGMENT

This work was funded by the Italian Ministry of Education, University, and Research (awarded Project P6-2013, implementation of the new SI). The authors would like to thank the PTB workshop for cutting the ^{28}Si-enriched sample.

REFERENCES

(1) CCM, Report of the 15th Meeting to the International Committee for Weights and Measures; February **2015**.

(2) Azuma, Y.; Barat, P.; Bettin, H.; Borys, M.; Busch, I.; Cibik, L.; D'Agostino, G.; Fujii, K.; Fujimoto, H.; Hioki, A.; Krumrey, K.; Kuetgens, U.; Kuramoto, N.; Mana, G.; Massa, E.; Meess, R.; Mizushima, S.; Narukawa, T.; Nicolaus, A.; Pramann, A.; Rabb, S. A.; Rienitz, O.; Sasso, C.;

Stock, M.; Vocke Jr, R. D.; Waseda, A.; Wundrack, S.; Zakel S. *Metrologia* **2015**, *52*, 360–375.
(3) Pramann, A.; Rienitz, O. *Analytical Chemistry* **2016**, *88*(11), 5963−5970.
(4) D'Agostino, G.; Mana, G.; Oddone, M.; Prata, M.; Bergamaschi, L.; Giordani, L. *Metrologia* **2014**,51, 354-360.
(5) D'Agostino, G.; Di Luzio, M.; Mana, G.; Oddone, M.; Pramann, A.; Prata, M. *Analytical Chemistry* **2015**, 87, 5716-5722.
(6) Di Luzio, M.; Oddone, M.; Prata, M.; Alloni, D.; D'Agostino, G. *Journal of Radioanalytical and Nuclear Chemistry* **2017**, DOI: 10.1007/s10967-017-5191-4.
(7) Høgdahl, O. T. *Proceedings, Symposium Radiochemical Methods of Analysis* **1965**, 23–40.
(8) De Corte, F. *Habilitation thesis* **1987**, University of Gent, Belgium.
(9) HyperLab 2009, *HyperLabs Software*, Budapest, Hungary.
(10) Tulli, J. K. *Nuclear Data Sheets* **2003**, 100, 347-481.
(11) D'Agostino, et al., 2017, *Metrologia*, at press: https://doi.org/10.1088/1681-7575/aa6edf
(12) Ouellet, C.; Singh, B. *Nuclear Data Sheets* **2013**, 114, 209-396.
(13) Martinho, E.; Salgado, J.; Goncalves, I. F. *Journal of Radioanalytical and Nuclear Chemistry* **2004**, 261(3), 637-643.
(14) k_0-Nuclear data subcommittee of k_0-International Scientific Committee **2016**, http://www.kayzero.com/k0naa/k0naaorg/Nuclear_Data_SC/Entries/2016/1/11_New_k0-data_Library_2015.html.
(15) JGCM 100:2008, Evaluation of measurement data - Guide to the expression of uncertainty in measurement, BIPM: France, 2008; http://www.bipm.org/utils/common/documents/jcgm/JCGM_100_2008_E.pdf.
(16) Greenberg, R. R.; Bode, P.; De Nadai Fernandes, E. A. *Spectrochimica Acta Part B* **2011**, 66(3), 193−241.