

Article



Comparison of the Isotopic Composition of Silicon Crystals Highly Enriched in ²⁸Si

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Abstract: The isotopic composition and molar mass *M* of silicon in a new crystal (code: Si28-33Pr11) measured by isotope ratio mass spectrometry using a high-resolution multicollector-inductively coupled plasma mass spectrometer (MC-ICP-MS) is presented using the virtual-element isotope dilution mass spectrometry (VE-IDMS) method. For this new crystal, $M = 27.976\,950\,48$ (16) g/mol was determined with $u_{rel}(M) = 5.7 \times 10^{-9}$. The "X-ray-crystal-density (XRCD) method", one of the primary methods for realizing and disseminating the SI units kilogram and mole in the recently revised SI, is based on "counting" silicon atoms in silicon single crystal spheres. One of the key quantities is the isotopic composition—expressed by the molar mass *M*—of the three stable isotopes ²⁸Si, ²⁹Si, and ³⁰Si in the material highly enriched in ²⁸Si. *M* was determined with lowest possible uncertainty using latest improvements of the experimental techniques. All uncertainties were estimated according to the "Guide to the expression of uncertainty in measurement, GUM". The results of the new crystal are discussed and compared with the four previously available crystals, establishing a worldwide limited pool of primary reference spheres of highest metrological quality.

Keywords: silicon single crystals; molar mass; isotope ratios; mass spectrometry; SI revision; mole dissemination; kilogram dissemination

1. Introduction

The choice of silicon with the three stable natural isotopes ²⁸Si, ²⁹Si, and ³⁰Si as an element which is ideally suitable for the realization and dissemination of the SI base units kilogram and mole dates back to its first comprehensive use for the X-ray-crystal-density (XRCD) method in the 1970s, first applied by the National Bureau of Standards (now National Institute of Standards and Technology, NIST) [1,2]. During the 1980s up to the beginning of the 2000s, first silicon with a natural isotopic abundance has been used for the production of single crystals in a macroscopic manner ready to produce perfectly round spheres with a mass of approximately one kilogram each [3]. Silicon has a long tradition in semiconductor research and applications [4], the underlying knowledge and improved techniques for the growth of macroscopic single crystals marks Si an ideal candidate for the XRCD method [5]. Moreover, the mechanical robustness of the macroscopic spheres including the stability of oxide surface layers turns it into a material of choice [6]. The broader background of the research—focused on the isotopic composition and molar mass M of the silicon material—was the revision of the Si units defined by fixed fundamental physical constants in 2019 and the scientific methods used therein [7,8]. The kilogram, now defined via the numerical value of the Planck constant *h*, and the mole, defined via the numerical value of the Avogadro constant N_A , are best realized and disseminated by the Kibble balance (watt balance) and the XRCD method, respectively [5,9]. The exceptional advantage is that both units can be realized and disseminated by one of these two primary methods which are of comparative nature, yielding both smallest measurement uncertainties. From 2007, silicon highly enriched in ²⁸Si is

used in the XRCD method, because when taking silicon with natural isotopic composition, the relative uncertainty associated with the molar mass M, a key quantity in this procedure, reaches a lower limit in the 10^{-7} range, at least one order of magnitude too high for a respective small uncertainty of N_A and thus a precondition of the revision of the SI at that time. Using the enriched silicon crystal material, $u_{\rm rel}(M)$ is smaller than 10^{-8} applying the methods described later. The basic principle of the XRCD method is the "counting" of all silicon atoms of a macroscopic silicon sphere with lowest associated uncertainty yielding N_A using the relation

$$N_{\rm A} = \frac{8V}{a^3} \frac{M}{m} = \frac{N}{n} \tag{1}$$

here, $V = V_{\text{sphere}}$ is the volume of the macroscopic silicon sphere (\approx 430 mL), 8 is the number of atoms in the unit cell, *M* is the molar mass, *m* is the mass of the Si sphere (\approx 1 kg), *a* is the lattice parameter. This yields the total number *N* of silicon atoms and the amount of substance *n*. As stated, from 2018 N_A has a fixed numerical value $N_A = 6.022 \ 140 \ 76 \times 10^{23} \ \text{mol}^{-1}$ without an associated uncertainty by definition. This in turn shows, that a silicon sphere characterized by the XRCD method (second term in Equation (1)) can serve as a primary mass standard which is expressed by

$$m = \frac{8V}{a^3} \frac{2R_{\infty}h}{c\alpha^2} \frac{\sum_{i} \left[x(^i\mathrm{Si})A_\mathrm{r}(^i\mathrm{Si}) \right]}{A_\mathrm{r}(\mathrm{e})} + m_\mathrm{sur} - m_\mathrm{def}$$
(2)

with the Rydberg constant R_{∞} , the Planck constant h, the speed of light in vacuum c, the fine structure constant α , the relative atomic mass of the electron $A_r(e)$, the relative atomic masses $A_r(^iSi)$ of the silicon isotopes—given in respective updated tables [10], the mass of surface layers m_{sur} , and the mass of point defects m_{def} . In a similar way, the base quantity amount of substance n is realized and disseminated

$$n = \frac{8V}{a^3} \frac{2R_{\infty}h}{c\alpha^2} \frac{1}{A_{\rm r}({\rm e})M_{\rm u}} = \frac{8V}{a^3} \frac{1}{N_{\rm A}}$$
(3)

in the third term of Equation (3), the molar mass constant M_u must be considered with $M_u = 1.000\ 000\ 000\ 000\ (45)\ g\ mol^{-1}\ [11]$.

The application of the XRCD method for the realization and dissemination of the kilogram and the mole thus constitutes one of the two best (on a metrological scale) respective experiments. In case of the XRCD method this means that not only one single sphere but a pool of several rather similar spheres of highest quality should be available. Due to the extreme enrichment of $x(^{28}Si) > 0.999$ 9 mol/mol (with the amount-of-substance fraction *x*), the production of a respective crystal is both time consuming and extremely expensive which explains the very limited number of spheres available on that level [12]. In this article, we report on the isotopic composition $x(^{i}Si)$ and molar mass *M* of another new silicon single crystal highly enriched in ²⁸Si with the code Si28-33Pr11. From the new crystal ingot (Figure 1), two spheres were cut as schematically shown in Figure 2.

The molar mass *M* has been derived from four samples (\approx 500 mg each) bracketing the outer limits of the spheres in the regions N and V. All data were calculated using an uncertainty analysis with respect to the "Guide to Expression of Uncertainty in Measurement" (GUM) [13]. We compared the results of the present crystal with the other available crystals highly enriched in ²⁸Si: Si28-10Pr11 ("AVO28-crystal" (2007)), Si28-23Pr11 (2015), Si28-24Pr11 (2016), and Si28-31Pr11 (2018). From each crystal two spheres are available.



Figure 1. Single crystalline float-zone crystal ingot Si28-33Pr11 (length: 560 mm; mass: 6.216 kg).



Figure 2. Float-zone crystal ingot Si28-33Pr11: schematic cross section. The measured samples (cubic shape with approx. 500 mg each) bracketing the sphere areas (P and U) are taken from parts N and V.

2. Theoretical Background

The silicon material described in this article requires a special methodology for the measurement of the molar mass and isotopic composition, because of the extreme enrichment in ²⁸Si and thus the ultra-low abundances of ²⁹Si and ³⁰Si. For this reason, typical mass spectrometric methods used for the determination of M and/or x('Si) might fail or will lead to large uncertainties. Details of these procedures have been published elsewhere [14–16]. Briefly, a modified isotope-dilution mass spectrometry method (virtual-element isotope dilution mass spectrometry: VE-IDMS) was applied in combination with isotope ratio mass spectrometry (high resolution multicollector inductively-coupled plasma mass spectrometer MC-ICP-MS). Mass bias correction of the measured isotope ratios was performed using a gravimetric mixtures method yielding the necessary calibration (K) factors [15]. The measurement of the isotope ratios will give accesses to the respective $x(^{i}Si)$. The extremely high enrichment will generate too large uncertainties if ratios e.g., ³⁰Si/²⁸Si are measured. Therefore, the silicon material is treated as consisting of (theoretically) ²⁹Si and ³⁰Si only (the virtual element which can be regarded as an impurity) in the matrix of ²⁸Si (an excess amount). The measurements require mainly the determination of the isotope ratios $R({}^{30}\text{Si}/{}^{29}\text{Si}) = x({}^{30}\text{Si})/(x({}^{29}\text{Si}))$ and the knowledge of the masses (m_{yx} and m_x) of components in the blend bx of the sample material x (Si enriched in ²⁸Si) and a "spike" material y (Si enriched in ³⁰Si). Finally, the amount-of-substance fractions $x(^{i}Si)$ and the molar mass M will be derived, the latter with relative uncertainties in the 10^{-9} range. The VE-IDMS method has been applied and validated by several national metrology institutes (NMIs) and serves as a primary method [17–20].

3. Materials and Experimental Methods

The silicon samples (each with a mass of approximately 500 mg) were cut from two axial positions (parts N and V) of the original ingot (compare Figure 2). From each part, two samples (adjacent to the axis and with a small distance) were used, bracketing the intended area of the two spheres. The crystal has been produced in Russia (isotopic enrichment at the Stock Company Production Association Electrochemical Plant (Sc "PA ECP") in Zelenogorsk and the production of the polycrystal in the G.G. Devyatykh Institute of Chemistry of High-Purity Substances of the Russian Academy of Sciences (IChHPS RAS) in Nizhny Novgorod, and finally at the Leibniz-Institute for Crystal Growth (IKZ) in Berlin in the framework of a joint project aiming at manufacturing several silicon crystal-spheres highly enriched in ²⁸Si [12,21,22]. The sample notation is: Si28-33Pr11 N.2.1, Si28-33Pr11 N.2.3, Si28-33Pr11 V.2.1, and Si28-33Pr11 V.2.3. Prior to the preparation of the sample solutions used for the mass spectrometric measurements, the solid samples were carefully cleaned and etched to remove possible surface layers of e.g., oxides [23]. The rather large size of the individual samples was necessary, because of the extremely high enrichment in the ²⁸Si isotope and thus the respectively very small abundances in ²⁹Si and ³⁰Si with the latter being the analytes of interest. The cleaned and etched samples were weighed (with buoyancy correction) dissolved in aqueous tetramethylammonium hydroxide (TMAH)(Electronic Grade, 99.9 999 %, Alfa Aesar, Thermo Fisher GmbH, Kandel, Germany) with a mass fraction of the final sample solution w(TMAH) = 0.0006 g/g. This yields the following mass fractions of the solutions to be measured with the MC-ICP-MS: sample $w_x(Si) \approx 4000 \ \mu g/g$, blend $w_{\rm bx}({\rm Si}) \approx 3000 \ \mu {\rm g/g}$, and natural silicon for mass bias correction $w_{\rm w}({\rm Si}) = 4 \ \mu {\rm g/g}$. All mass spectrometric measurements were performed with a Neptune XT™ MC-ICP-MS (Thermo Fisher Scientific GmbH, Bremen, Germany) using the operation parameters listed in Table 1.

Table 1. Summar	y of the main	operation	parameters and	l instrument	settings	of the MC	C-ICP-MS.
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Argon gas (cooling, auxiliary, sample)/L min $^{-1}$	16, 0.8, 0.9 1.2
power (radio frequency)/W	1175
torch, bonnet	sapphire
nebulizer (PFA ¹ ; flow rate/ μ L min ⁻¹)	50
spray chamber (PFA ¹ , PEEK ²)	cyclonic/Scott
sampler, skimmer (orifice/mm)	nickel (1.1), nickel (0.8; XT type)
mass resolution $M/\Delta M$	8000 (high resolution)
slit size/µm	25
autosampler	CETAC ASX 110 FR
Faraday detectors	С, НЗ
operation mode	static
virtual amplifier™	left rotation
integration time/s	4
number of integrations (cycles) per block	1 (3)
number of blocks	6

¹ PFA: perfluoroalkoxy alkane, ² PEEK: polyether ether ketone.

The isotope ratio measurements were carried out in exactly the same way for the samples x, the blends bx, the natural material w, and the blank solutions. Prior to each silicon solution, a blank solution was measured to enable the signal correction for blank and carry-over effects. Each silicon solution was measured four times in the order sample x, blend bx, and natural silicon w yielding the uncorrected intensity ratios (in V/V) of ${}^{30}\text{Si}/{}^{29}\text{Si}$.

The natural silicon solution w was measured at the end of each sequence in order to avoid a contamination of the isotopic composition of the sample and blend solution. Moreover, the measured intensity ratio $R_{\text{meas}}({}^{30}\text{Si}/{}^{29}\text{Si})$ in w was used to calculate the respective *K* factor applying the "true" values of R_{w} given elsewhere [24]. With that *K* factor, each measured ratio $R_{\text{meas}}({}^{30}\text{Si}/{}^{29}\text{Si})$ was converted to a corrected isotope ratio $R({}^{30}\text{Si}/{}^{29}\text{Si})$ of that sequence.

4. Results and Discussion

4.1. Molar Mass of Si28-33Pr11

In this study, four samples were measured aiming at a first glance overview of the behavior/distribution of the molar mass (isotopic composition) along the crystal axis acting as a first decision guidance for the cutting regions of the two spheres. It is the first study on the molar mass of enriched silicon in our group using a new further development of the NeptuneTM MC-ICP-MS, the new Neptune XTTM. Each sample was measured in exactly the same way using the same sequences and operating conditions. Four to six sequences per samples were measured (in total 21 sequences, see Supplementary Materials). The average molar mass values of the respective samples are shown in Figure 3 (with associated uncertainties, k = 1). The respective data as well as the amount-of-substance fractions *x* are listed in Table 2. In contrast to comparable studies performed with other crystals of enriched silicon, the average uncertainty of the average molar mass of all four crystals measured in this study is slightly increased yielding $M(Si) = 27.976\ 950\ 48\ (16)\ g/mol\ with\ u_{rel}(M) = 5.7 \times 10^{-9}$ (including data scattering) [21,22,24].



Figure 3. Molar masses *M* of the four crystal samples (Si28-33Pr11) investigated in this study. For each average value, the combined uncertainty (k = 1) is given by error bars. The average value (arithmetic mean) of all measurements is $M(Si) = 27.976\ 950\ 48\ (16)\ g/mol\ (solid\ line)$. The average relative uncertainty is $u_{\rm rel}(M) = 5.7 \times 10^{-9}$ including the contributions of data scattering.

Table 2. Average molar masses and amount-of-substance fractions (isotopic composition) of different samples (Si28-33Pr11). Numbers in brackets denote uncertainties in the last digits. Uncertainties (k = 1) do not cover data scattering.

Sample	M g mol $^{-1}$	x(²⁸ Si) mol/mol	x(²⁹ Si) mol/mol ×10 ^{−5}	x(³⁰ Si) mol/mol ×10 ^{−7}
N.2.1	27.976 950 371 (71)	0.999 976 461 (64)	2.3232 (60)	3.07 (17)
N.2.3	27.976 950 390 (86)	0.999 976 266 (85)	2.3602 (85)	1.312 (47)
V.2.1	27.976 950 655 (99)	0.999 976 061 (98)	2.3747 (96)	1.926 (86)
V.2.3	27.976 950 519 (76)	0.999 976 161 (74)	2.3683 (74)	1.562 (74)
average	27.976 950 484 (84)	0.999 976 237 (81)	2.3566 (80)	1.97 (10)

The reason for this increase is suggested to originate from data scattering between the different measurements as will be shown below. At a first glance, the molar masses of the measured samples agree within the limits of uncertainty and thus the crystal can be treated as homogeneous along the main axis which is supported by the general manufacturing process of the float-zone crystal as has been described previously [12]. The relative uncertainties associated with *M* of the single measurements range in the lower 10^{-9} region not including data scattering as reported in [22]. Figure 4 displays the detailed measurement results of *M* of the crystal sample V.2.3. Here, the error bars indicate the respective uncertainties without including data scattering. It is evident that some data points are not included in the k = 1 range. Since this behavior is observed when measuring a single sample, it is clear that this kind of fluctuation cannot be attributed to inhomogeneities of the material (e.g., disordering or impurities in the crystal lattice). The scattering is a combined result of the experimental conditions (plasma stability, decrease of sensitivity due to strong depositions of Si components on the sampler and skimmer cones during the measurement of the highly concentrated Si solutions, general low signal abundance).



Figure 4. Single measurements of molar masses *M* of the sample Si28-33Pr11 part V.2.3 (error bars for k = 1 without scattering contribution). The solid line represents the average molar mass *M* of all sequences (including the measurements of all the other samples). The dashed lines denote the respective upper and lower average uncertainties (k = 1) without the contribution of scattering.

A consistency analysis calculating the degrees of equivalence (d_i) has been performed for the molar mass results of the four samples (Figure 5) with $d_i = M_i - M$ (differences of the single samples values and average value of the molar mass). Within the limits of uncertainty, all d_i enclose the zero line, clearly showing the consistency of the molar masses of the crystal samples. A representative uncertainty analysis (single measurement of sample N.2.1) is given in Table 3. The uncertainty analysis was performed using the GUM Workbench ProTM software (version 2.4.1 392, Metrodata GmbH, Braunschweig, Germany) according to the model equation of the molar mass of the VE-IDMS principle e.g., [21]. As in previous studies on other crystals highly enriched in ²⁸Si, one of the main contributions to the uncertainty associated with M is the measured intensity ratio (index 2 denotes the ratio ³⁰Si/²⁹Si) $R_{bx,2}^{meas}$ in the blend of the sample and the "spike" material (Si enriched in ³⁰Si); here with 61%. The second main contribution (24.5%) is the corrected isotope ratio $R_{w,2}$ of the natural silicon material w measured for the K factor determination. The measured intensity ratio $R_{x,2}^{meas}$ in the sample contributes with

another 13%. The masses of the components in the blend bx as well as the molar masses of the individual silicon isotopes do not contribute to the uncertainty at all.



Figure 5. Degrees of equivalence d_i of the four samples of the crystal Si28-33Pr11 (average molar mass without scattering). Uncertainties for k = 2. All data are consistent due to the enclosure of the zero line.

Quantity	Unit	Best Estimate (Value)	Standard Uncertainty	Sensitivity Coefficient	Index
X_i	$[X_i]$	x _i	$u(x_i)$	ci	
M(²⁸ Si)	g/mol	27.976926534940	540×10^{-12}	1.0	0.0%
$m_{\rm yx}$	g	$5.611000 imes 10^{-6}$	704×10^{-12}	4.2	0.0%
m _x	g	0.062474995	569×10^{-9}	-380×10^{-6}	0.0%
<i>M</i> (²⁹ Si)	g/mol	28.976494669090	610×10^{-12}	23×10^{-6}	0.0%
M(³⁰ Si)	g/mol	29.9737701360	27.0×10^{-9}	-560×10^{-9}	0.0%
$R_{v,3}$	mol/mol	1.5855	0.0222	-81×10^{-9}	0.1%
$R_{\rm v.2}$	mol/mol	269.04	5.65	2.0×10^{-9}	1.4%
$R_{\rm x,2}^{\rm meas}$	V/V	0.010380	686×10^{-6}	50×10^{-6}	13.0%
$R_{bx,2}^{meas}$	V/V	3.7540	0.0116	-6.4×10^{-6}	60.9%
$R_{\rm w,2}$	mol/mol	0.66230	1.32×10^{-3}	-36×10^{-6}	24.5%
$R_{\rm w,2}^{\rm meas}$	V/V	0.7028500	73.8×10^{-6}	33×10^{-6}	0.0%
Ŷ	[Y]	y	$u_{\rm c}(y)$		
М	g/mol	27.9769502183	95.1×10^{-9}		

Table 3. Representative uncertainty budget of sample N.2.1 (single measurement).

The comparable small contribution of $R_{x,2}^{\text{meas}}$ to u(M) is unusual, because of the isotopic composition of this very crystal. Although the enrichment in ²⁸Si with $x(^{28}\text{Si}) = 0.999\,976\,24$ (19) mol/mol is not that large compared to other highly enriched silicon crystals (see Section 3), the characteristic of the crystal Si28-33Pr11 is the large ratio of $x(^{29}\text{Si})$ and $x(^{30}\text{Si})$ with two orders of magnitude. This is an additional experimental challenge: the small abundance of ²⁹Si is accompanied by a much smaller signal of ³⁰Si leading to a difficult data collection.

4.2. Comparison of the Available Highly Enriched Silicon Crystals

The realization and dissemination of the kilogram and mole via the XRCD method is based on silicon spheres highly enriched in ²⁸Si with extremely high chemical purity and an almost perfect crystal lattice [5]. Again, only an enrichment in ²⁸Si of this order of magnitude is capable to yield an uncertainty of $u_{\rm rel}(M) < 1.0 \times 10^{-8}$ which is essential to obtain $u_{\rm rel}(N_{\rm A}) < 2 \times 10^{-8}$, which was a prerquisite for the realization of $N_{\rm A}$ prior to the revision of the SI [5]. A silicon sphere matching this condition is called a "primary" sphere according the notation given in [6]. A sphere of this kind must be well characterized by the XRCD method. Due to the large amount of material (1 kg per sphere), the manufacturing is extremely expensive, but also time consuming with the need of extraordinary logistic efforts [12]. This is the reason why only a small pool of spheres has been manufactured yet, each a kind of an individual material artefact with properties of its own. Currently, the production of ten spheres has been completed/is under way according to the original crystals listed in Table 4. Each of the spheres can be used as a primary mass standard with lowest associated uncertainty u(m) on the metrological top level suitable for the calibration/comparison of other weights on the next lower metrological level. Therefore, the spheres are interchanged in part for the reason of laboratory intercomparisons on the highest level. Additionally, they are object of basic metrological research (XRCD properties and time-dependent changes of surface characteristics). The spheres with the highest enrichment in ²⁸Si are originating from the crystal Si24-Pr11 (the second crystal manufactured during the "kilogram-2 project" [12]) with an amount-of-substance fraction $x(^{28}Si) > 0.999$ 99 mol/mol, followed by the spheres from Si28-31Pr11 (obtained during the "kilogram-3 project"), the latter not yet fully characterized. All available crystals show an enrichment of at least $x(^{28}Si) > 0.999 9 \text{ mol/mol.}$ In Figure 6, both the average molar masses and $x(^{28}Si)$ of the respective crystals are compared. It is evident that there is a strong correlation between *M* and $x(^{28}Si)$.

Table 4. Comparison of *M* and $x(^{i}Si)$ of the available silicon spheres highly enriched in ²⁸Si used for the XRCD experiment (uncertainties for k = 1).

	Crystal Si28-	Mg mol ⁻¹	x(²⁸ Si) mol/mol	x(²⁹ Si) mol/mol ×10 ⁻⁵	<i>x</i> (³⁰ Si) mol/mol ×10 ^{−7}	Year	Ref
	10Pr11	27.976 970 12 (12)	0.999 957 52 (12)	4.136 (11)	11.21 (14)	2015	[24]
	23Pr11	27.976 942 666 (40)	0.999 984 470 (39)	1.492 1 (38)	6.095 (48)	2017	[21]
	24Pr11	27.976 933 787 (77)	0.999 993 104 (66)	0.653 6 (51)	3.60 (17)	2019	[22]
	31Pr11	27.976 941 260 (42)	0.999 985 501 (40)	1.426 4 (39)	2.338 (75)	2018	1
	33Pr11	27.976 950 48 (16)	0.999 976 24 (19)	2.357 (24)	1.97 (78)	2020	2
-			1 0				

¹ Preliminary results; ² this work.

The error bars (uncertainties) of both *M* and $x(^{28}Si)$ are not shown in Figure 6, because of their comparable small range which is covered by the data points itself. On an absolute scale, the "abundance" of ²⁹Si and ³⁰Si is "tiny" yielding ranges of approximately $6 \times 10^{-6} < x(^{29}Si) < 4 \times 10^{-5}$ mol/mol. The range of $x(^{30}Si)$ is lowered by up to two orders of magnitude: $2 \times 10^{-7} < x(^{30}Si) < 1 \times 10^{-6}$ mol/mol. In fact, the measurement of the ³⁰Si isotopes is challenging, and the more difficult, the smaller $x(^{30}Si)$. This experimental problem is not influencing the uncertainty associated with *M* because of the absence of any input values of amount-of-substances in the conditional equation of *M* given in [24].



Figure 6. Left scale (filled circles): Average molar masses *M* of the available silicon crystals highly enriched in ²⁸Si. Right scale (filled squares): Amount-of-substance fractions $x(^{28}Si)$ displaying the "enrichment" of the respective crystal. Uncertainties for both *M* and $x(^{28}Si)$ are not displayed, because of their extremely small values being hidden by the data points. Data for the crystal Si28-31Pr11 are yet preliminary due to the limited number of samples.

5. Conclusions

This work presents latest results of the molar mass and amount-of-substance fractions of a new chemically ultrapure silicon crystal (Si28-33Pr11), highly enriched in ²⁸Si, to be used for the preparation of two additional spheres in the very limited pool of primary reference standards for the dissemination of the kilogram and the mole. For the correct estimation of Si atoms, it is necessary to determine chemical impurities like C, N, and O (in the lower ranges of 10^{15} cm³, 10^{13} cm³, and 10^{14} – 10^{15} cm³, respectively) via IR spectroscopy most exactly. The reported crystal produced during the "kilogram-3-project" serves as the origin of two new unique spheres. The isotopic composition expressed by the molar mass M has been determined at several crystal positions yielding an average M = 27.97695048(16) g/mol with $u_{rel}(M) = 5.7 \times 10^{-9}$. Now, crystals highly enriched in ²⁸Si enable the use of 10 respective spheres, characterized by the XRCD method, which can be compared worldwide acting as the highest standards for the mass and amount-of-substance. However, the silicon crystals differ in their absolute compositions of ²⁸Si, ²⁹Si, and ³⁰Si aiming first at the high enrichment in ²⁸Si. The uncertainty associated with M is correlated at a first glance with the enrichment in ²⁸Si. In parallel, the measurability of the isotopes ²⁹Si and ³⁰Si—which are the main target measurands using the VE-IDMS principle—is a limiting factor. Due to the extremely tiny abundance of both isotopes, $u_{rel}(M)$ might increase although $x(^{28}Si)$ increases. Thus, care must be taken that for future productions of silicon spheres highly enriched in ²⁸Si ($x(^{28}Si) > 0.9999$ mol/mol), there should be a proper balance between high enrichment and a reasonable ratio ²⁹Si/³⁰Si on a measurable scale.

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