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A new generation of 99.999% enriched ^{28}Si single crystals for the determination of Avogadro's constant

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Abstract

A metrological challenge is currently underway to replace the present definition of the kilogram. One prerequisite for this is that the Avogadro constant, N_A , which defines the number of atoms in a mole, needs to be determined with a relative uncertainty of better than 2×10^{-8} . The method applied in this case is based on the x-ray crystal density experiment using silicon crystals. The first attempt, in which silicon of natural isotopic composition was used, failed. The solution chosen subsequently was the usage of silicon highly enriched in ^{28}Si from Russia. First, this paper reviews previous efforts from the very first beginnings to an international collaboration with the goal of producing a ^{28}Si single crystal with a mass of 5 kg, an enrichment greater than 0.9999 and of sufficient chemical purity. Then the paper describes the activities of a follow-up project, conducted by PTB, to produce a new generation of highly enriched silicon in order to demonstrate the quasi-industrial and reliable production of more than 12 kg of the ^{28}Si material with enrichments of five nines. The intention of this project is also to show the availability of ^{28}Si single crystals as a guarantee for the future realisation of the redefined kilogram.

Keywords: Avogadro constant, silicon, isotope enrichment, XRCD method, kilogram, redefinition, revised SI

(Some figures may appear in colour only in the online journal)

⁷ Deceased in 2014



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1. Introduction

The kilogram is the only base unit of the International System of Units (SI) still defined by a material prototype as stated by the 1st General Conference on Weights and Measures in 1889. The mass of the international prototype of the kilogram (IPK) expressed in terms of the SI unit kilogram is invariable by definition, but since 1889 the mass differences between the IPK and its official and national copies have drifted by about 50 μg , or 5×10^{-8} in relative terms, on the average. A sufficiently accurate determination of the drift is not yet possible, but it is evident that there is a need for a new definition of the mass unit. It has now been more than 40 years ago since the first attempts were started to find a way of defining the kilogram based on an atomic or fundamental physical constant. Since then, two methods have advanced sufficiently far to make it likely that there will be a new definition within the coming years, namely the watt balance experiment to determine the Planck constant h and the so-called x-ray crystal density (XRCD) method [1] which is used in the Avogadro experiment for determining the Avogadro constant N_A .

Using the Avogadro experiment for a new definition of the mass unit, the kilogram, can be understood as the mass of a specific number of silicon atoms. The number of atoms in a perfect mono-crystal can be determined by measuring the volume V of a macroscopic sample and its lattice parameter a_0 . In the case of silicon, the unit cell (with the edge length a_0) contains 8 atoms; thus the number N of atoms in the sample is

$$N = 8V/a_0^3. \quad (1)$$

When also measuring the mass m of the sample, the (mean) mass of one silicon atom, $m_{\text{Si-atom}}$, can be calculated by

$$m_{\text{Si-atom}} = m/N = ma_0^3/(8V). \quad (2)$$

A real silicon sample does not only contain one type of atom; it contains three different silicon isotopes of differing mass and additionally some impurities of other chemical elements. When the kilogram is newly defined, a relative measuring uncertainty of N_A at the level of 10^{-8} is needed. This means, with 6×10^{23} entities in one mole, the ‘counting’ uncertainty should be of the order of 6×10^{15} atoms! Therefore, all kinds of atoms with a content higher than this limit must be identified and taken into consideration.

Natural silicon consists of three isotopes with differing masses. Therefore, the isotopic composition of the sample has to be determined with high precision. From the isotopic composition the molar mass M and the amount of substance (=number of moles) in the silicon sample, $n = m/M$, can be determined. Then the Avogadro constant N_A can be calculated

$$N_A = N/n = 8M/(\rho a_0^3) \quad (3)$$

with the density of the sample, $\rho = m/V$.

Unfortunately, the molar mass of natural silicon cannot be determined better than 1×10^{-7} , relatively, by using gas mass spectrometry. Relative uncertainties below the 10^{-8} level can only be achieved if isotopically enriched silicon with an enrichment better than 0.9999 is used (see sections 4.2 and 4.3).

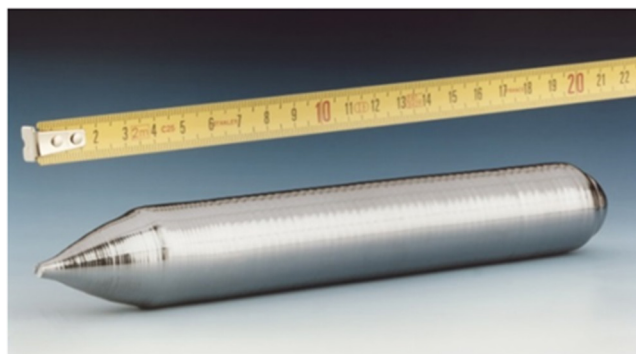


Figure 1. The first ^{28}Si single crystal approx. 215 mm in length and 30 mm in diameter. The crystal is of $\langle 111 \rangle$ —orientation [12]. John Wiley & Sons. [Copyright © 2010 WILEY-VCH Verlag]

Even the purest silicon crystal still contains some atoms of different chemical elements which change the mass of the sample with respect to a pure sample of the same volume. The concentrations of these elements have to be determined and their influence on the Avogadro constant has to be corrected. The elements carbon (C), oxygen (O) and nitrogen (N) have the largest impurity concentrations in the ^{28}Si crystals used for the determination of the Avogadro constant, and their contents must be carefully reduced and measured (section 4.4). Carbon additionally disturbs the lattice parameter measurement since it is not homogeneously distributed in the crystal but causes so-called striations [2]. To minimize this effect the concentration of carbon should be below $2 \times 10^{15} \text{ cm}^{-3}$.

In order to improve the already published results for the Avogadro constant, the availability of almost ideal ^{28}Si crystals is an essential precondition. The aim of the project named ‘kg-2’ was therefore to increase the isotopic enrichment and to reduce the impurity content in the final crystals. Last but not least, it is envisaged to test and provide reliable and reproducible ^{28}Si production at a quasi-industrial level with a quantity that allows making available a sufficient number of 1 kg spheres to the metrological community. As the XRCD or Avogadro method is one of the accepted methods of the *mise en pratique* on the kilogram to realize the mass unit after redefinition, the ^{28}Si spheres can be used for the realization of the new mass unit.

2. Historical background

Since Avogadro’s findings in 1811, the determination of the number of entities in a mole of substance has fascinated generations of scientists. With the discovery of x-rays and the decoding of crystal structures, the counting of atoms in a silicon crystal has become the basis of the search for a new mass standard, according to the published ‘Phantasies on a natural unity of mass’ in 1963 by Egidi [3]. Two years later, Bonse and Hart [4] implemented from a silicon crystal an x-ray interferometer, an important tool to measure the silicon lattice parameter extremely accurately in the length unit ‘meter’. Nine years later, 1974, Deslattes [5] from the former National Bureau of Standards, USA, published his pioneering article about the first precise Avogadro constant based on Bonse’s idea. Other national metrology institutes started similar projects, among

Table 1. Properties of ^{28}Si crystals produced from 2000 to 2007, extended compared to [12].

Charge No.	1 + 2	3	4	5	6	7	10
^{28}Si enrichment	0.99896	0.9987	0.9993	0.9944	0.9994	0.9998	0.99995
Ingot mass (g)	20	50	46	32	46	190	5964
Crystal mass (g)	6	13	19	10.5	32	75	4530
Date (month/yr)	02/2000	04/2001	09/2001	11/2001	12/2001	06/2002	05/2007

them also the Physikalisch-Technische Bundesanstalt (PTB, Germany), which was able to follow with corrected data in 1992 [6]. All relevant data were measured with silicon of natural isotopic composition, namely 92% ^{28}Si , 5% ^{29}Si and 3% ^{30}Si . But the measurement uncertainty of the molar mass M was eventually the limiting factor.

Zosi [7] outlined a way out of this problem in 1983: He proposed using perfect silicon spheres manufactured from enriched ^{28}Si crystals for the determination of N_A . An initial attempt was started in 1990 at PTB when two sources of enriched material were made available from the Oak Ridge National Laboratory (ORNL), USA, and from the National Institute of Metrology (NIM), Russia. The enrichment of both sources of ^{28}Si material was similar: 0.9989 and 0.9988, respectively. As the material delivered by NIM in the form of 590 g of Si powder was found to be contaminated by an undesirably high amount of impurities, only the ORNL material—about 1284 g of $^{28}\text{SiO}_2$ grains—has been converted into a silicon single crystal in collaboration with the Wacker-Chemitronic company in Germany [8]. The final product, the first ^{28}Si single crystal, has a mass of about 300 g and an enrichment of 0.9902 (figure 1). The enrichment was unexpectedly diluted and the impurity contents of boron (B) and aluminium (Al) were very high. The derived data for the Avogadro constant were about $10^{-5} N_A$ larger than the data of previous measurements and not in accordance with the CODATA value published in 1986, possibly due to the imperfection of the crystal.

But in the 1990s, scientific interest and the technological promise of highly enriched isotopes led to a sharp rise in the number of experimental and theoretical studies dealing with isotopically controlled semiconductor crystals. In 1994, Tarbejev *et al* presented the selection of appropriate working gases, the development of gas centrifuges, their arrangement for the effective separation of the isotopes and the optimization of the production process. A resulting mole fraction of better than 0.9999 seemed to be feasible. The requirements for the production process in growing ^{28}Si single crystals and the related problems were also discussed. They also estimated the uncertainties necessary for the check measurements during production [9].

A contract for a feasibility study was signed between PTB and former nuclear technologists in St. Petersburg and Nizhny Novgorod (Russia) to produce highly enriched silicon based on improved technologies for purification, enrichment and analytical methods [10]. The enrichment of the material was more than 0.999 ^{28}Si and the concentration of the main impurities B, N, C, O, and Al was some orders of magnitude smaller than in the first attempt described above. Since 2000, in several feasibility studies on the production of high-purity ^{28}Si in accordance with the Avogadro project, the enrichment

of ^{28}Si could be increased from 0.99896 to finally 0.9998 in charge No. 7, see table 1. The final product of charge 7 is shown in figure 2. The central part was dislocation-free and was used for investigations connected with the Avogadro project [11]. The impurity concentration was $8.2 \times 10^{14} \text{ cm}^{-3}$ for oxygen and $3.4 \times 10^{15} \text{ cm}^{-3}$ for carbon.

Based on these studies, the fabrication of a 1 kg silicon single crystal sphere of 0.9999 enriched ^{28}Si seemed to be feasible. The International Avogadro Coordination (IAC) was founded in 2004 by several national metrological institutes with the aim to finance a new project for the production of a ^{28}Si crystal (charge 10, see table 1). This project was planned again with partners from Nizhny Novgorod and St. Petersburg, with the target of producing a 5 kg single crystal with an enrichment of more than 0.9999 [13].

The final crystal was of p-type with a mass of 4530 g and an enrichment of—surprisingly—about 0.99995, shown in figure 3. Only a small end part of about 200 g was disturbed by back-gliding dislocations. Most of the impurities had accumulated in other residual parts with a total mass of approx. 1 kg, the ^{28}Si isotopic enrichment was not affected. The impurity concentration could be reduced significantly and was in the order of $0.4 \times 10^{15} \text{ cm}^{-3}$ for oxygen and of $2 \times 10^{15} \text{ cm}^{-3}$ for carbon. This material was used for the accurate determination of the Avogadro constant in 2010 [14] and for improvements in the measurement uncertainty in 2014: With two ^{28}Si spheres shaped and polished first in Australia and later repolished at PTB, a relative uncertainty of 2×10^{-8} was reached [15].

3. Realisation of improved ^{28}Si crystals: the kg-2 project

The redefinition of the kilogram is expected for 2018—a great challenge for the metrological community. It will be the starting point for a new era of mass metrology, which will have an impact not only in the near future. Therefore, for the redefinition of the kilogram and its realisation by the XRCD method, the experiments within the framework of the IAC based on two ^{28}Si spheres can be considered as a feasibility study. Experiments on a multitude of ^{28}Si spheres are necessary to form the new definition on a solid basis. Simultaneously, the quality of the material should be improved with respect to enrichment and chemical purity, in order to push the measuring uncertainty towards the 10^{-9} region before the definition of the kilogram can be changed. Through enrichments higher than five nines and impurity concentrations smaller than 10^{15} cm^{-3} , the perfection of the silicon material would come very close to an ideal one. In spite of the enormous costs for the material and the financial shortages in most of the metrology institutes, PTB decided to shoulder the material procurement

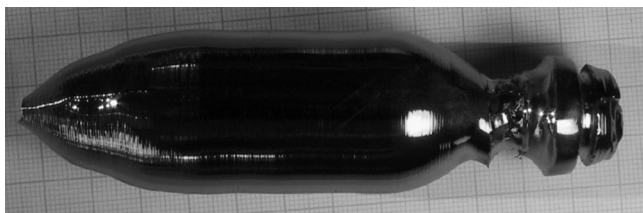


Figure 2. Final ^{28}Si crystal of charge 7, mass about 75 g [12]. John Wiley & Sons. [Copyright © 2010 WILEY-VCH Verlag]



Figure 3. Final single crystal of the IAC Project, grown in 2007 (charge 10) [12]. John Wiley & Sons. [Copyright © 2010 WILEY-VCH Verlag]

alone. The aim of this new project named ‘kg-2’ is therefore (1) to demonstrate the availability of ^{28}Si crystal material at a quasi-industrial level with finally two ^{28}Si single crystals of about 6 kg each and the manufacture of four 1 kg spheres, (2) to reduce the carbon content by an additional cleaning of the SiF_4 gases by centrifugation and by using high purity chemical substances, and (3)—by the way—to accentuate the need of the so-called silicon path to the new kilogram.

How are these ambitious plans to be realised? How is the production process to reduce the impurity content and to simultaneously increase the isotopic enrichment to be improved? The first ^{28}Si mono-crystals were still made on a laboratory scale. Now the Stock Company ‘Production Association Electrochemical Plant’ (SC ‘PA ECP’) in Zelenogorsk (near Krasnoyarsk, Russia), PTB’s main project partner and one of the most important suppliers for isotopes worldwide, was elected to be responsible for the $^{28}\text{SiF}_4$ gas production. The chemical conversion into silane and the deposition as a polycrystal was again performed at the G.G. Devyatikh Institute of Chemistry of High-Purity Substances of the Russian Academy of Sciences (IChHPS RAS) in Nizhny Novgorod, Russia. The final growth to perfect mono-crystals was carried out at the Leibniz Institute for

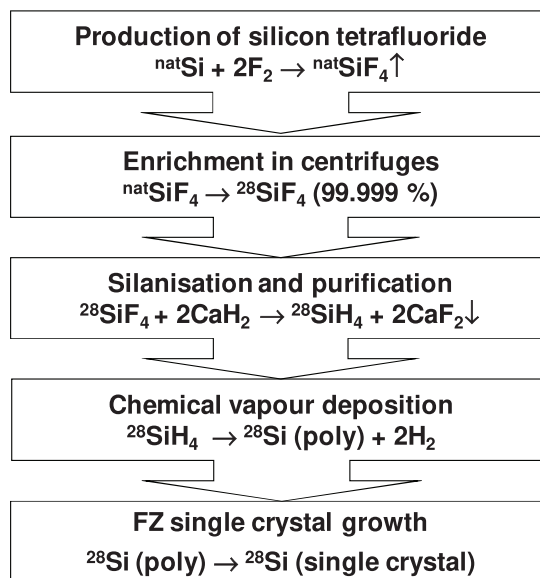


Figure 4. Main technological steps of the ^{28}Si crystal production ($^{\text{nat}}\text{Si}$: silicon of natural isotopic composition).

Crystal Growth (Leibniz-Institut für Kristallzüchtung, IKZ) in Berlin-Adlershof, Germany. The kg-2 project was administratively conducted in Russia by the ISOTOPE company, a Russian governmental organization.

The production of ^{28}Si single crystals from silicon of natural isotopic composition to the highly enriched single crystal consists of 5 main steps, as shown in figure 4.

3.1. Enrichment of ^{28}Si in centrifuges

According to figure 4, solid silicon granulates with natural isotope composition were converted to SiF_4 gas in the first step. SiF_4 is used as a process gas for the centrifugal separation of Si for two reasons: there exists only one isotope of fluorine, namely ^{19}F , and SiF_4 has a sufficiently high vapour pressure at room temperature.

In contrast to the previous projects, SiF_4 was obtained by direct fluorination of high-purity natural silicon in order to significantly reduce the boron and carbon impurities. SiF_4 was synthesized from the element according to the chemical reaction



The natural abundance silicon ($^{28}\text{Si} \approx 92.23\%$) of electronic grade quality was manufactured and supplied by Wacker Polysilicon Europe, Wacker Chemie AG, Germany. SC ‘PA ECP’ produced high-purity fluorine (F_2) by itself. A special installation with a reactor was constructed and used for the synthesis of the initial SiF_4 and for silicon isotope separation in centrifugal cascades. Gas centrifugation is the only effective method of isotope separation with a high enrichment level. Other methods, such as magnetic mass separation, ion exchange and laser technology, are more expensive. These methods do not allow a high isotopic enrichment to be reached.

In order to fulfil the requirements for a very high enrichment of ^{28}Si along with the high chemical purity, the separation

Table 2. Comparison of Si isotopic composition measurements from the enriched gas $^{28}\text{SiF}_4$, in the solid state as polycrystalline material and finally as single crystal. The number in parenthesis denotes the associated expanded uncertainty of the last digits ($k = 2$).

	$x(^{28}\text{Si})$ in mol mol $^{-1}$	$x(^{29}\text{Si})$ in mol mol $^{-1}$	$x(^{30}\text{Si})$ in mol mol $^{-1}$	$x(^{29}\text{Si})/x(^{30}\text{Si})$
Charge 22				
ECP, $^{28}\text{SiF}_4$	0.999974	0.000022	0.000004	5.5
ICHPS, $^{28}\text{SiF}_4$	0.999962(18)	0.000033(15)	<0.000005	>6.6
PTB, polycrystal	0.99998003(22)	0.00001821(20)	0.00000176(4)	10.3
Charge 23				
ECP, $^{28}\text{SiF}_4$	0.9999825	0.0000151	0.0000024	6.3
ICHPS, $^{28}\text{SiF}_4$	0.9999827(41)	0.0000165(35)	0.0000009(5)	18.3
PTB, polycrystal	0.99998590(12)	0.00001354(11)	0.00000056(3)	24.2
PTB, final crystal	0.999984472(78)	0.000014919(76)	0.000000609(10)	24.5
Charge 24				
ECP, $^{28}\text{SiF}_4$	0.9999957	0.0000037	0.0000005	7.4
ICHPS, $^{28}\text{SiF}_4$	0.999995(2)	0.000005(2)	0.0000005(2)	10.0
ICHPS (ICP-MS), polycrystal	0.9999946(16)	0.0000052(16)	0.0000002(1)	26.0
PTB, polycrystal	0.999994751(41)	0.000004815(32)	0.000000434(19)	11.1
PTB, final crystal	0.999993039(33)	0.000006583(31)	0.000000378(10)	17.4

of the SiF_4 gas was performed in three centrifugal cycles (the second step in figure 4).

In cycle 1, an enrichment of about 99.9% $^{28}\text{SiF}_4$ was achieved. The 99.9% $^{28}\text{SiF}_4$ gas was used in a next step as input gas for cycle 2, where the centrifuge cascade was specially designed in order to reduce the carbon-containing impurities in the gas. Values smaller than 100 ppm in the case of CO_2 and smaller than 30 ppm for CO , CH_4 , C_2H_2 , C_2H_4 , and C_2H_6 were targeted. The purified gas was then enriched up to 99.999% in cycle 3.

Using ECP's gas centrifuge cascades made it possible to produce high-enriched $^{28}\text{SiF}_4$ with the required low content of carbon impurities. Gas centrifuge method using allows producing enriched stable and radioactive isotopes of various chemical elements with high chemical purity [16].

The entire amount of material was produced in three charges numbered 22, 23 and 24. Charge 22 was used for the production of slim rods, which acted as deposition rods for the two 6 kg polycrystals (charges 23 and 24). Si isotopes in the final $^{28}\text{SiF}_4$ gas were analyzed at SC 'PA ECP' and at the ICHPS RAS by mass spectrometry. ICHPS RAS also measured the polycrystalline product of charge 24 by ICP-MS (see section 4.3). The results were also compared with PTB's measurement results (for method, see section 4.2) of the polycrystalline and the final single crystal material produced from this $^{28}\text{SiF}_4$ (see table 2).

3.2. Silanisation and purification of silane

During the third technological step the $^{28}\text{SiF}_4$ gas was converted into silane, $^{28}\text{SiH}_4$. For the production of high-purity silane the hydride method was used [17]. First, the synthesis of silane was carried out by the reaction of high-purity silicon tetrafluoride with calcium hydride



The synthesis was performed in the flow-through mode. A mixture of isotopically enriched silicon tetrafluoride with hydrogen of special grade B purity was passed through a

Table 3. Content of some hydrocarbon impurities in $^{28}\text{SiH}_4$ before and after purification.

Impurity	$^{28}\text{SiH}_4$ after synthesis 10 $^{-8}$ mol mol $^{-1}$	Purified $^{28}\text{SiH}_4$ 10 $^{-8}$ mol mol $^{-1}$
Methane (CH_4)	$(2.2 \pm 0.2) \times 10^3$	<4
Ethylene (C_2H_4)	130 ± 10	<0.5
Ethane (C_2H_6)	42 ± 4	<2
Propylene (C_3H_6)	23 ± 3	<0.6
Propane (C_3H_8)	5 ± 2	<0.5
n-butane ($n\text{-C}_4\text{H}_{10}$)	3 ± 1	<0.7
Iso-butane ($iso\text{-C}_4\text{H}_{10}$)	27 ± 3	<0.7

layer of mechanically dispersed calcium hydride. The reactor was made of high-purity Si-free stainless steel to prevent the diffusion of boron compounds and natural Si into the highly enriched gas. It was found in [18] that the reaction between silicon tetrafluoride and calcium hydride occurs in the form of propagating waves. The yield of ^{28}Si during the silanisation process was between 92% and 94%.

The content of hydrocarbon impurities in silane after synthesis was at the level of 10^{-5} mol mol $^{-1}$ (see second column of table 3). The content of polysilanes and disiloxanes is the largest component according to the data of a gas-chromatographic-mass-spectrometric (GC-MS) analysis at a level of 10^{-3} mol mol $^{-1}$. Calcium hydride seems to be the main source of impurities, in particular carbon [19].

3.2.1. Technical details of the purification in brief. The produced $^{28}\text{SiH}_4$ was freed from impurities by the methods of cryofiltration and periodic low-temperature rectification [20, 21]. Cryofiltration of silane was performed using a Petryanov tissue at a temperature of 163 K (-110 °C). The flow rate of silane was about 100 g h^{-1} (volume flow rate about 1 l min^{-1}). Rectification was carried out in a packed metal rectification column with a middle feeding tank—operating in the mode of discrete extraction of impurities from the lower to the upper separating sections. The height of rectifying sections of the column was 100 cm and 170 cm with a cross-section of

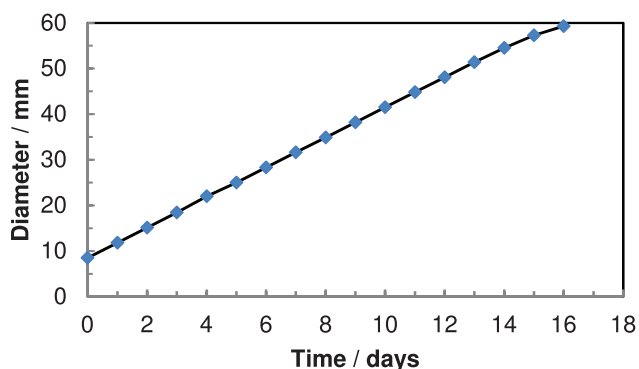


Figure 5. Diameter of the ^{28}Si polycrystal as a function of deposition time (slim rod diameter: 8.5 mm).

4.9 cm^2 . A fine spiral prismatic packing of Nichrome wire was used ($3 \times 3 \times 0.2\text{ mm}$). The column load was 1000 g; the degree of extraction was 0.003–0.006. The low-volatile impurities were methane, carbon dioxide and hydrogen, and the semi-volatile impurities C_2 – C_9 hydrocarbons, alkylsilanes, polysilanes, and polysiloxanes. Ethylene is the most difficult to remove impurity in $^{28}\text{SiH}_4$ (reduction factor $\alpha = 1.28$). The duration of the rectification process is determined by the starting concentration and the reduction factor of this impurity at the bottom of the column. The on-line analysis of the fractions enriched by ethylene was performed by gas chromatography. With the aim to free the product mainly from carbon-containing impurities, the purification process was stopped after reaching the content of ethylene at a concentration level of a few $10^{-7}\text{ mol mol}^{-1}$ in the concentrate of the impurities. The yield of the high-purity product during purification was 80%. The content of chemical impurities in the purified $^{28}\text{SiH}_4$ is given in table 3. High-purity $^{28}\text{SiH}_4$ was prepared with the content of C_1 – C_9 hydrocarbons and of alkylsilanes with less than $4 \times 10^{-8}\text{ mol mol}^{-1}$ of disiloxane and of higher silanes at the level of $10^{-7}\text{ mol mol}^{-1}$.

3.3. Chemical vapour deposition of ^{28}Si

The process of depositing the ^{28}Si from the $^{28}\text{SiH}_4$ is the fourth step in figure 4 which was carried out by chemical (or better, pyrolytic) vapour deposition (CVD) in a single-rod set-up particularly designed for this purpose. A ^{28}Si rod with an enrichment of more than 0.9999 with a diameter of 8.5 mm and a length of 850 mm was used as a substrate for the deposition ('slim rod'). The rod was heated up to $800\text{ }^\circ\text{C}$ by passing an electric current. The method of so-called high-voltage start was used for heating the rod from room temperature up to the operating value. The temperature of the rod was PID controlled within $\pm 2\text{ K}$. Deposition was carried out in a stainless steel reactor with cooled walls.

To meet the requirements for the final crystal with respect to the carbon content ($< 2 \times 10^{15}\text{ cm}^{-3}$), all possible sources of this impurity had to be avoided during the installation of the set-up. Therefore, carbon-containing materials were not used to manufacture the internal components of the reactor. The reactor surface was cleaned without using carbon-containing solvents.



Figure 6. Polycrystalline silicon rod of charge 23 in the deposition apparatus (length of the rod about 85 cm).

Compared to previous projects, the whole set-up was modernized with the aim of increasing its operational stability. The characteristics of the power supply circuit were improved. An uninterruptible power supply of 30 kW was used to provide a stable power supply. Besides, a flattening filter was installed in the power supply circuit to reduce the start-up current. The program for changing the parameters of the temperature regulator was modernized to allow an on-line correction of the parameters during the deposition process.

The deposition procedure of polycrystalline silicon was optimized in order to increase the rate from $0.010\text{ g (cm}^2\text{ h)}^{-1}$ up to $0.018\text{ g (cm}^2\text{ h)}^{-1}$ without a noticeable change in the yield. The specific deposition rate per unit area of the rod surface was kept constant by increasing the feeding rate of $^{28}\text{SiH}_4$ proportional to the surface area of the growing rod. The dependence of the diameter of the polycrystal on the deposition time is given in figure 5. It takes about 2 weeks to deposit 6 kg of ^{28}Si . A higher deposition rate provides a decrease in the background contamination of the polycrystalline silicon from the apparatus material and a decrease of the exposure time of $^{28}\text{SiH}_4$ in the reactor. The yield of the product, determined by comparison of the mass of the ^{28}Si in the consumed $^{28}\text{SiH}_4$ with the mass of the polycrystalline silicon produced on this basis, was 95%. The final polycrystalline rod of charge 23 just after the deposition is shown in figure 6.

4. FZ single crystal growth

The last step in the technological process of figure 4 is the growth of the dislocation-free ^{28}Si single crystal. The crucible-free floating zone (FZ) technique was used to achieve the

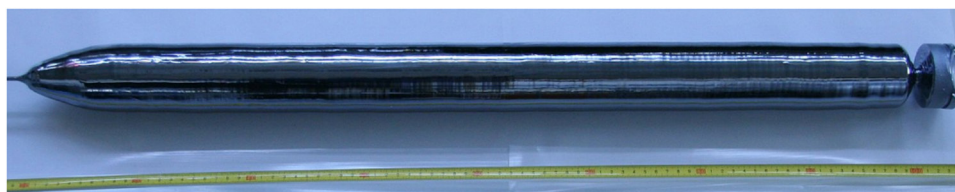


Figure 7. Crystal of charge 23 after the first FZ run (length about 80 cm, diameter 6.0 cm).

chemical purity needed and to save the isotopic enrichment from the polycrystalline starting material (poly-Si). Before the FZ growth, the polycrystalline rod was prepared by cutting off the electrical contacts and by preparing a cone on one side and a groove for the holder on the other side. This preparation leads to fragmentary losses of material. Due to the high initial oxygen and carbon concentrations in the polycrystalline rod, several growth runs had to be performed, also leading to loss of original (as-deposited) material. This is the reason why additional procedures on the way from the starting material to the final crystal of high perfection were necessary to optimize the growth process and to minimize the loss of material.

At the beginning, the number of FZ runs had to be estimated based on the oxygen and carbon concentrations in the poly-Si. As-deposited polycrystalline samples were annealed before the measurement for over 10 h at a temperature of about 1350 °C to make them transparent for IR beams [22]. The contents of C and O were measured using Fourier-transform infrared (FTIR) absorption spectroscopy (see chapter 4.4) both in the polycrystalline material and at the end of the crystal after the first FZ growth run (figure 7). Both measurements resulted in nearly the same carbon concentration: $N_C = 3.5 \times 10^{15} \text{ cm}^{-3}$ for charge 23. Due to oxygen evaporation during the first FZ growth process, the oxygen concentration measured in the FZ crystal was one order less than in the polycrystal, measured as $N_O = 5.2 \times 10^{17} \text{ cm}^{-3}$.

For a further decrease of the oxygen concentration in the crystal, two growth runs were made in vacuum. The next runs were carried out in an argon atmosphere while saving the low oxygen concentration by previously desorbing the water layers in vacuum.

Carbon was further reduced by the segregation effect of multiple FZ passing. The number of growth runs was estimated using the theory of zone refining for many passes [23] on the basis of the carbon concentration in the starting material and on the target concentration (smaller than $2.0 \times 10^{15} \text{ cm}^{-3}$) over the whole crystal length, and was determined to be 6 runs.

However, even though the freeze-off technique was used at the end of each run to avoid a new preparation of the grown crystal for the next run, some additional material is lost by freezing-off and is missing in the final crystal. That is why—using experience from the past [12]—all cut fragments of polycrystalline silicon were regrown by a Czochralski (Cz) technique resulting in a crystal 50 mm in diameter that was joined to the FZ crystal just after the first run. To avoid isotope dilution during Cz growth, the quartz crucible was coated before the growth process with a $^{28}\text{SiO}_2$ layer of about 100 μm in thickness [24]. Thus, no isotope dilution could be detected in the Cz crystal.



Figure 8. The final FZ mono-crystals of the kg-2 project (charge 23 (left) and 24 (right)), grown in 2015 and in 2016, respectively. The crystals have a $\langle 100 \rangle$ crystallographic orientation.

A $\langle 100 \rangle$ oriented ^{28}Si crystal grown in a previous step of the project by a crucible-free pedestal technique was used as a seed crystal. At the end of the growth process the crystal was grown tapered down to a diameter of 79 mm by using the automatic diameter control system in order to protect the cylindrical part of the crystal from back-gliding dislocations. The final mono-crystals of charges 23 and 24 shown in figure 8 have the following specifications: mass 5.12 kg and 5.64 kg, respectively, maximal diameter 100.3 mm and n-type conductivity except for the first 50 mm in the cone. The cylindrical part of charge 24 crystal is 20 mm longer than that of the charge 23 crystal.

4.1. Crystal quality

The main parameters representing the quality of the final crystals are isotopic enrichment, carbon concentration and their spatial homogeneity. An indispensable precondition for the determination of N_A with further reduced measurement uncertainty is the determination of the molar mass $M(\text{Si})$ of the new silicon material highly enriched in the ^{28}Si isotope with reduced associated uncertainty ($u_{\text{rel}}(M(\text{Si})) < 5 \times 10^{-9}$), a challenge for any mass spectrometry.

Samples from different parts of the crystal were cut for the analysis. The isotopic analysis was made by laser mass spectrometry (LIMS) and high-resolution inductively coupled plasma mass spectrometry (HR ICP-MS) at the IChHPS RAS and by isotope dilution mass spectrometry (IDMS) at PTB. The oxygen and carbon concentration in the ^{28}Si single crystal was measured by IR spectroscopy (IChHPS RAS and PTB, see section 4.4). Additionally, the instrumental neutron activation analysis was used to check the purity with respect to many other chemical elements [25].

4.2. Molar mass measurements at PTB

The molar mass $M(\text{Si})$ —and thus the enrichment—was determined by using the modified isotope dilution mass spectrometry virtual-element (VE-IDMS) method applying high-resolution multicollector-inductively coupled plasma mass spectrometry (MC-ICP-MS) which is described in detail elsewhere [26–28]. In brief, $M(\text{Si})$ can be expressed using the relation

$$M(\text{Si}) = \sum_{i=28}^{30} [x(^i\text{Si}) \cdot M(^i\text{Si})] \quad (6)$$

with amount-of-substance fractions $x(^i\text{Si})$ and molar masses $M(^i\text{Si})$ of the i th silicon isotope [29]. The $x(^i\text{Si})$ are accessible via the measurement of isotope ratios R applying state-of-the-art isotope ratio mass spectrometry using the VE-IDMS method. In summary, the enriched silicon is regarded as consisting of ^{29}Si and ^{30}Si (=the virtual element) in the matrix of all three Si isotopes. By measuring predominantly the isotope ratios $R(^{30}\text{Si}/^{29}\text{Si})$ in the enriched silicon sample ('Si28') and in an IDMS blend consisting of the 'Si28' material and a silicon crystal material highly enriched in the ^{30}Si isotope ('Si30', spike), $x(^{28}\text{Si})$, $x(^{29}\text{Si})$, and $x(^{30}\text{Si})$ can be determined with associated uncertainties sufficient to obtain $u_{\text{rel}}(M(\text{Si})) < 5 \times 10^{-9}$. This method has been successfully applied and approved by several leading NMIs in the past few years by measuring $M(\text{Si})$ of the silicon material used to determine N_A [26–28, 30–32]. As an additional check, the ^{30}Si mole fraction was measured by the instrumental neutron activation analysis [33, 34].

Another main outcome within the context of the determination of $M(\text{Si})$ is the development and application of an analytically closed-form method for the determination of calibration (K) factors necessary for correcting measured isotope ratios for mass bias effects [35]. These K factors are accessible experimentally and described in detail elsewhere [28]. All quantities measured and applied were treated by a respective uncertainty analysis according to the guide to the expression of uncertainty in measurement (GUM) [36].

The VE-IDMS method needs both a high enrichment (expressed in $x(^{28}\text{Si})$) and a large ratio $x(^{29}\text{Si})/x(^{30}\text{Si})$ to reach an uncertainty $u_{\text{rel}}(M(\text{Si}))$ below 5×10^{-9} [27, 28].

For the experimental procedure, the silicon crystal samples (approx. 300 mg each)—either polycrystalline or monocrystalline—were carefully cleaned, etched, and weighed applying air buoyancy correction. After dissolution in aqueous tetramethylammonium hydroxide (TMAH) and further dilution, the isotopic composition of the samples was determined using a

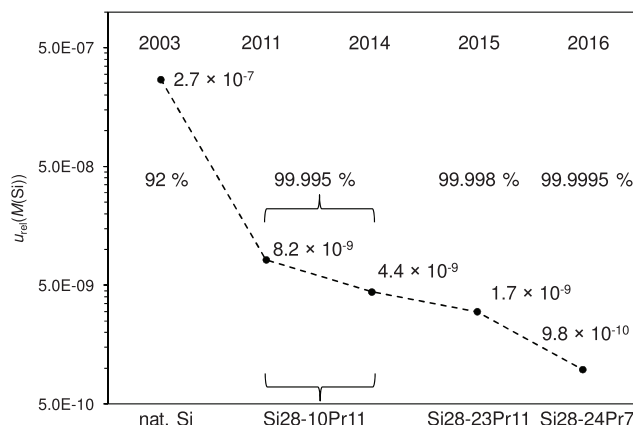


Figure 9. History of the uncertainty associated with the molar mass of silicon highly enriched in the ^{28}Si isotope measured via the VE-IDMS principle. In 2016, the second crystal of the kg-2 project provided $u_{\text{rel}}(M(\text{Si})) = 1 \times 10^{-9}$, which is a milestone in the Avogadro project. For comparison, $u_{\text{rel}}(M(\text{Si}))$ of silicon with natural isotopic composition measured using gas phase isotope ratio mass spectrometry is also displayed [38].

high resolution (HR) MC-ICP-MS (NeptuneTM, Thermo Fisher Scientific) with resolution $M/\Delta M = 9000$. The main advantage of TMAH over sodium hydroxide (NaOH) is a strongly increased signal intensity due to the absence of sodium acting as an energy sink as well as overcoming any scattering effects in the vicinity of the ion detectors [37]. The results for the charges 23 and 24 (single crystal) are given in table 2.

The outstanding reduction of the uncertainty associated with $M(\text{Si})$ during the past decade as a consequence of the increasing enrichment in ^{28}Si (expressed in $x(^{28}\text{Si})$) is demonstrated in figure 9.

4.3. Isotopic composition measurements at IChHPS RAS

All steps of the chemical process are related to a high risk of isotopic dilution by natural silicon from reagents and apparatus materials. This is in particular important for the gas $^{28}\text{SiF}_4$ which is a highly aggressive compound in the presence of moisture traces. The isotopic composition in the technological process of converting $^{28}\text{SiF}_4$ to polycrystalline ^{28}Si in the former Avogadro project was controlled by a double focusing laser ionization mass spectrometer with photographic registration of the mass spectrum. To increase the measurement precision, an internal isotopic standard was used [39]: Potassium with natural isotopic abundance: 0.932581(44) ^{39}K , 0.000117(1) ^{40}K , and 0.067302(44) ^{41}K [40]. The $^{28}\text{SiF}_4$ samples were bubbled through KOH solution, whereas polycrystalline ^{28}Si was dissolved in a KOH melt in carbon glass beakers. The prepared solution was transferred onto a substrate of high-purity germanium and then dried. The concentrate was scanned by a laser beam layer-by-layer analysis. The content of ^{28}Si was measured with respect to ^{39}K and the contents of the isotopes ^{29}Si and ^{30}Si were measured with respect to ^{40}K . The total measurement uncertainty was limited by the uncertainty of the table values for the isotopic abundances of potassium. This technique provided the prompt control of the technological process of converting $^{28}\text{SiF}_4$ into polycrystalline ^{28}Si .

While increasing the enrichment in the kg-2 project, the isotopic composition of silicon in the $^{28}\text{SiF}_4$ gas and in the crystalline ^{28}Si was measured at IChHPS RAS also by HR ICP-MS (Element 2 of Finnigan, Bremen) using the method of inverse IDMS [41]. Thus, the IChHPS RAS was able to measure both gaseous and solid samples. The measurements were carried out at an average resolution (4500) with the aim to exclude the $^{28}\text{SiH}^+$ interference with $^{29}\text{Si}^+$. For the analysis, the $^{28}\text{SiF}_4$ samples were hydrolyzed with a 0.5% solution of hydrofluoric acid HF. Hydrolysis was accompanied by the formation of a gel which was later dissolved in excess of HF. The samples of polycrystalline ^{28}Si were dissolved in the mixture of hydrofluoric and nitric acids.

Four series of solutions were prepared:

1. Solutions with a ^{28}Si concentration in the range from 1 ppm to 20 ppm.
2. Solutions with a ^{28}Si concentration in the range from 2000 ppm to 3000 ppm.
3. Solutions of silicon of natural isotopic composition ($^{\text{nat}}\text{Si}$) with concentrations in the 5 ppm to 20 ppm range.
4. Mixtures of 2000 ppm to 3000 ppm ^{28}Si with 5 ppm to 20 ppm $^{\text{nat}}\text{Si}$.

In the solutions of the first series only the content of ^{28}Si was measured. A calibration curve of intensity versus ^{28}Si concentration was plotted and the calibration parameters were determined graphically. In the solutions of the other series only the contents of ^{29}Si and ^{30}Si were measured, since the ^{28}Si signal was overamplified.

The third and the fourth series of the solutions were used to determine the coefficients of mass discrimination and of the matrix effect which could suppress the intensity of lines including the matrix element, i.e. silicon. Since the coefficient of the matrix effect is determined for each isotope, it also includes the coefficient of mass discrimination. The intensity of the signals of the ^{28}Si isotope in the second series of ^{28}Si solutions was calculated by the parameters of the calibration chart accounting for the solution concentration.

Despite the fact that the measurement uncertainty of the isotopic composition on single-collector instruments is substantially higher than in the MC-ICP-MS, this technique allowed providing prompt control of the isotopic composition in the technological process of silicon conversion. The results of the measurement carried out at the IChHPS RAS for the average value of the isotopic composition of $^{28}\text{SiF}_4$ in five containers of charge 24, and for the prepared polycrystalline material, are in good agreement with the PTB results of the final FZ crystal (see table 2). The data indicate also that the chemical treatment at the IChHPS RAS is on an excellent high purity level: Between input gas and output solid material no significant dilution of the enrichment can be detected.

4.4. Chemical impurity determination at PTB

Low-temperature infrared absorption spectroscopy was performed at PTB using a continuous-flow cryostat system

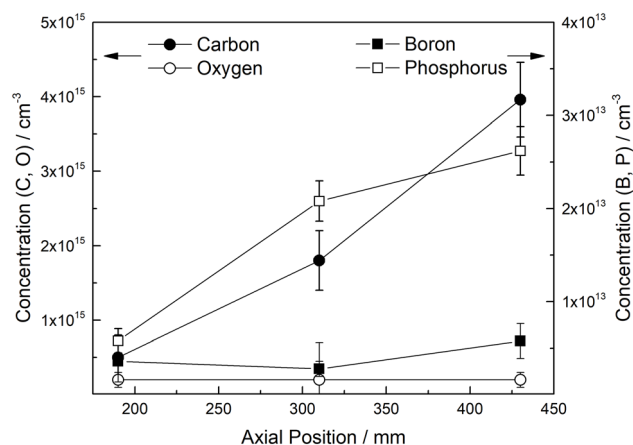


Figure 10. Axial distribution of O, C, B and P impurities in samples from the ^{28}Si single crystal of charge 23.

equipped with a multiple sample holder and a vacuum FTIR spectrometer (Bruker VERTEX 80V). Measurements could be performed with a small aperture size leading to measurement spots smaller than 3 mm in the mid-infrared range. The limiting diameter of the sample holder is then 5 mm. In the far-infrared range the loss of intensity leads to a slight increase of the detection limit, but the method was found in preliminary experiments to be sensitive enough to measure shallow impurities below the order of 10^{13} cm^{-3} which still meets the requirements for the determination of the Avogadro constant. Since the sample size for IR measurements can now be reduced from $14 \text{ mm} \times 14 \text{ mm} \times 3 \text{ mm}$ down to $7.5 \text{ mm} \times 7.5 \text{ mm} \times 3 \text{ mm}$, measurements with a higher spatially resolved radial distribution are possible, in order to get a more detailed picture of the radial impurity profile caused by striations during the growth process.

Substitutional carbon, interstitial oxygen as well as shallow impurities from the boron and nitrogen families were measured at temperatures below 10 K in the mid- and far-infrared according to standard procedures [42–44] which have been adapted to highly enriched ^{28}Si according to [45]. An automatic beam splitter changer as well as various radiation sources and detectors allow the aforementioned impurities to be measured within a single cooling cycle.

FTIR measurements were performed on samples at three different axial positions from the final single crystal of charge 23. Only C, O and the shallow impurities B and P were found in the silicon crystal whereas signals from other shallow impurities such as Al, As, Sb and Ga were below the detection limit. The results are given in figure 10. While the impurity concentrations of O and B remain predominantly constant along the crystal axis, a significant increase of the concentrations of C and P occurs at the back end of the silicon crystal. Multiple FZ runs have thus reduced the relatively high carbon content measured in the polycrystalline material by a factor of ~ 4 in the front part of the crystal. Nevertheless, the C concentration at the back end of the crystal is comparable to that of the polycrystalline material. Similar results at the front and back end were obtained at IChHPS RAS.

5. Conclusion

With charge 24, the ^{28}Si enrichment exceeds the barrier of 5 nines! In contrast to previous charges, no significant dilution by natural silicon during the whole technical process could be observed in the kg-2 project, even though the enrichment is much higher. In other words: also a further increase of enrichment would be easily exploitable. The realisation of five nines in enrichment and the production of an isotopically almost pure Si single crystal of 0.99999 enriched ^{28}Si is a challenge for all analysing methods used. Thus, with this material the current detection limit in molar mass determination is nearly reached. The main problem for further improvements of ^{28}Si single crystals is a reduction of the carbon concentration by a factor of 5. This would help to also reduce 3D lattice defects (striations).

With enriched material from the former IAC project a measurement uncertainty of $2 \times 10^{-8} N_A$ could be reached. For a further reduction of the relative uncertainty of N_A towards 1×10^{-8} and below, an improvement in the enrichment and in the molar mass determination seems to be no longer necessary. A further reduction of the measurement uncertainty is now mainly limited by the unroundness of the spheres and its influence on the diameter measurements.

The new definition of the mass unit, the kilogram, is envisaged for the year 2018. Although it would be more obvious, intrinsic and easy to explain by defining the kilogram as a specified number of atomic particles, such as the mass of a ^{28}Si or a ^{12}C atom, the new definition of the kilogram will fix the numerical value of the Planck constant. The link between the Planck constant and the mass of a silicon atom is possible with very high accuracy by other measurements like the fine-structure constant [46]. Thus, the XRCD method using ^{28}Si crystals is one accepted method for the realisation of the new kilogram. This will cause stimulation worldwide of the demand for ^{28}Si crystal spheres for primary mass standards.

The availability of enough ^{28}Si material for the determination of the Avogadro constant and the realisation of the new kilogram is an existential and necessary requirement for the redefinition. The project described here and also the already started follow-up project ('kg-3' for three more crystals and 6 spheres) impressively target increasing the number of ^{28}Si spheres in the near future and helping to disseminate ^{28}Si spheres worldwide. Measuring the relevant parameters on a large number of crystals will also lead to a significant reduction in uncertainty. To reach this ambitious goal successfully at the end of 2018, the work on N_A at PTB and in partner laboratories must be based on continuous interaction between physics and technology at their highest levels, and it would contribute to strengthening the edifice of the fundamental physical constants.

Also many other scientific ideas exist for applications of highly enriched silicon material; there is certainly a need for more and further production of this material. It should be noted that—besides the application for a new kilogram definition—the combination of highly pure and highly enriched ^{28}Si crystals with high-resolution laser-photoluminescence spectroscopy at low temperatures has opened the door for a new

understanding of fundamental problems in solid state physics. The ultra-narrow linewidth of the donor-bound transitions in ^{28}Si has also activated new research in semiconductor quantum information processing which seems to be more promising than that based on conventional quantum dots. It seems that the silicon era will not be over yet for a long time [47, 48].

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