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Novel concept for the mass spectrometric determination of absolute isotopic abundances with improved measurement uncertainty: Part 2 – Development of an experimental procedure for the determination of the molar mass of silicon using MC-ICP-MS

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ABSTRACT

The isotopic abundances and thus molar mass $M(\mathrm{Si})$ of a silicon crystal material with natural isotopic abundances have been measured for the first time using multicollector-ICP-mass spectrometry (MC-ICP-MS) in combination with a novel concept of a modified isotope dilution mass spectrometry (IDMS)-method. This experimental work is the further development of part 1 of this series of papers. While part 1 describes the theoretical background and the mathematical derivation of the novel concept in detail, the measurements presented here serve to validate the novel concept and give experimental proof of its capability. Moreover, the also new method for the analytical calculation of calibration factors needed in the determination of absolute isotope amount ratios has been tested successfully. Silicon isotopic abundances have been measured directly from an aqueous alkaline matrix following a new sample preparation protocol developed within the framework of this study. A molar mass of $M(\mathrm{Si}) = 28.08548(13)$ g/mol with an associated relative uncertainty of $u_{\mathrm{rel}} = 4.6 \times 10^{-6}$ ($k = 1$) has been measured. This is in excellent agreement with the current IUPAC value for the molar mass of natural silicon $M(\mathrm{Si}_{\mathrm{nat}}) = 28.08550(15)$ g/mol with $u_{\mathrm{rel}} = 5.3 \times 10^{-6}$ ($k = 1$). An uncertainty budget according to the Guide to the Expression of Uncertainty in Measurement (GUM) was calculated to assess the presented results and to validate the novel concept with the help of experimental data. The development of a new experimental procedure is presented in detail and the contributions to the uncertainty are discussed in comparison to part 1 of this work.

1. Introduction

For the intended re-determination of the Avogadro constant N_A with a relative combined measurement uncertainty of $u_{\mathrm{rel}}(N_A) \leq 1 \times 10^{-8}$ – which is the task of the international Avogadro coordination (IAC) – the number of silicon atoms in a highly pure silicon single crystal material are "counted" by applying the "XRCDMM" method [1–5]. In the current schedule of the project, two silicon spheres, artificially enriched with the ^{28}Si isotope ($x(^{28}\mathrm{Si}) > 0.9999$ mol/mol) are used. A prerequisite of this approach is the determination of the isotopic abundances of Si in that material with the intention to obtain a relative uncertainty associated with the molar mass of $u_{\mathrm{rel}}(M) \leq 1 \times 10^{-8}$. Up to now, the molar mass of natural silicon crystal material for the re-determination of N_A has been measured by isotope ratio mass spectrometry (IRMS) with respect to ^{28}Si using a gas mass spectrometer with the SiF_4 starting molecule [4]. In these studies, a sequential mass scanning technique was used and calibration factors were calculated iteratively. With that set-up it is not possible to measure the content of natural silicon contamination directly as in the case of the Physikalisch-Technische Bundesanstalt (PTB) experiment, because of a very small amount of gas from a blank experiment, which is not measurable. This fact will be discussed later. In gas mass spectrometry the route of molar mass determination was the transformation of the silicon crystal into gaseous SiF_4 via several steps: the crystal was digested in HF/HNO_3; then precipitated with $BaCl_2$ as $BaSiF_6$. The latter was then thermally decomposed into SiF_4. Each of these steps is sensitive to cumulative contamination with natural silicon.

Abbreviations: IDMS, isotope dilution mass spectrometry; VE, virtual element; GUM, Guide to the Expression of Uncertainty in Measurement; MC-ICP-MS, multicollector inductively coupled plasma mass spectrometer; "Si28", silicon material artificially enriched with respect to ^{28}Si to obtain a ^{28}Si amount-of-substance fraction larger than the natural one ($x(^{28}\mathrm{Si}) > 0.99$ mol/mol); "Si29", silicon material highly enriched with respect to ^{29}Si; "Si30", silicon material highly enriched with respect to ^{30}Si; XRCDMM, X-ray crystal density molar mass.

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In contrast, at PTB a different and complementary pathway for molar mass determination was developed. The aim of the current study is to check the respective experimental procedures of the molar mass measurement applying the novel concept described in [6] and to establish the capability to measure the molar mass of the new ultra-pure silicon crystal "Si28". This principle is different from the SiF_4 –route at least in three ways: first, the mass spectrometric determination of the isotopic abundances is performed using MC-ICP-MS. The main advantage of this experimental technique is the simultaneous detection of several ion currents and thus isotope amount ratios (static mode) with a constant electric and magnetic field of the mass spectrometer. In our case the simultaneous detection of the three Si isotope channels enables a measurement of ion current ratios and thus the determination of isotope amount ratios with a relative uncertainty reduced by three orders of magnitude compared to a sequential operating ICP-mass spectrometer. In the case of the "Si28" material, the contamination by natural silicon can be corrected by measuring the blank (solvent plus instrumental background). This is one major advantage of our experiment – however not that important in the case of natural silicon molar mass measurements. Second, a new route for the chemical preparation of the analyte solutions is applied. One aim of this preparation method is to circumvent numerous chemical conversion steps from the silicon crystal into a liquid silicon solution which may be accompanied by corresponding and cumulative contaminations with natural silicon. The one step preparation ensures a chemical transfer being quantitative, corresponding to a 100% recovery – extremely difficult to realize in the case of the SiF_4 – route. Finally, a modified IDMS technique – described in detail in part 1 [6] – using a so-called *virtual element* (VE) – consisting of the minor abundant silicon isotopes ^{29}Si and ^{30}Si in their matrix namely the sum of all three Si isotopes (^{28}Si, ^{29}Si, ^{30}Si) in combination with a new analytical and non-iterative determination of calibration factors K [7] is applied. The combination of these innovations has been successfully performed at PTB for the first time using a silicon crystal material of natural isotopic abundance in order to give experimental proof of its applicability, prior to applying the new method to the extremely limited and thus expensive "Si28" Avogadro-crystal material [3].

2. Method

2.1. Molar mass

The theoretical principle and derivation of the determination of the molar mass by applying the modified IDMS using a VE is described in detail in [6]. For a better understanding, only a brief description of the basic steps is given here. IDMS is a powerful tool for the most accurate determination of the mass fraction w of an analyte in its sample matrix [8–14]. The main difference of the modified IDMS presented here in contrast to the classical one is the determination of the mass fraction w_{imp} of the VE consisting of the least abundant isotopes in the matrix consisting of all isotopes of the element with the aim to determine the molar mass of the original element. The molar mass $M(Si)$ is obtained merely from the isotope amount ratio R_{x} (definition given below) and the mass fraction w_{imp} of the VE. The molar masses of the respective isotopes $M(^{28}\mathrm{Si})$, $M(^{29}\mathrm{Si})$, and $M(^{30}\mathrm{Si})$ are given in IUPAC reference tables [15]: the molar mass of the sample is generally defined as follows:

$$M(\mathrm{Si}) = \sum_{i=28}^{30} [x_{\mathrm{x}}(^{i}\mathrm{Si}) \times M(^{i}\mathrm{Si})] \tag{1}$$

The amount-of-substance fractions $x_{\mathrm{x}}(^{30}\mathrm{Si})$, $x_{\mathrm{x}}(^{29}\mathrm{Si})$, and $x_{\mathrm{x}}(^{30}\mathrm{Si})$ are determined by the following relations:

$$x_{\mathrm{x}}(^{28}\mathrm{Si}) = \frac{(1-w_{\mathrm{imp}})/M(^{28}\mathrm{Si})}{(1-w_{\mathrm{imp}})/M(^{28}\mathrm{Si}) + (1+R_{\mathrm{x}}) \times w_{\mathrm{imp}}/(M(^{29}\mathrm{Si}) + R_{\mathrm{x}} \times M(^{30}\mathrm{Si}))} \tag{2}$$

$$\begin{aligned} x_{\mathrm{x}}(^{29}\mathrm{Si}) &= \frac{1 - x_{\mathrm{x}}(^{28}\mathrm{Si})}{1+R_x} \\ &= \frac{w_{\mathrm{imp}}/(M(^{29}\mathrm{Si}) + R_{\mathrm{x}} \times M(^{30}\mathrm{Si}))}{(1-w_{\mathrm{imp}})/M(^{28}\mathrm{Si}) + (1+R_{\mathrm{x}}) \times w_{\mathrm{imp}}/(M(^{29}\mathrm{Si}) + R_{\mathrm{x}} \times M(^{30}\mathrm{Si}))} \end{aligned} \tag{3}$$

$$\begin{aligned} x_{\mathrm{x}}(^{30}\mathrm{Si}) &= R_{\mathrm{x}} \times x_{\mathrm{x}}(^{29}\mathrm{Si}) \\ &= \frac{R_{\mathrm{x}}(w_{\mathrm{imp}}/M((^{29}\mathrm{Si}) + R_{\mathrm{x}} \times M(^{30}\mathrm{Si})))}{(1-w_{\mathrm{imp}})/M(^{28}\mathrm{Si}) + (1+R_{\mathrm{x}}) \times w_{\mathrm{imp}}/(M(^{29}\mathrm{Si}) + R_{\mathrm{x}} \times M(^{30}\mathrm{Si}))} \end{aligned} \tag{4}$$

It should be noted that Eqs. (2)–(4) are valid only in the special case of a high purity sample ($w_{\mathrm{pur}} = 1\,\mathrm{g/g}$). This is the case when applying it to the natural silicon crystal material (ultra pure single crystal material) used in our study. R_{x} is the isotope amount ratio $x_{\mathrm{x}}(^{30}\mathrm{Si})/x_{\mathrm{x}}(^{29}\mathrm{Si})$ of the sample (natural silicon). The mass fraction w_{imp} denotes that of the virtual element (VE) ($w_{\mathrm{imp}} = w_{\mathrm{x}}(^{29}\mathrm{Si}) + w_{\mathrm{x}}(^{30}\mathrm{Si})$) in the sample:

$$w_{\mathrm{imp}} = w_{\mathrm{y}} \times \frac{m_{\mathrm{yx}}}{m_{\mathrm{x}}} \times \frac{M(^{29}\mathrm{Si}) + R_{\mathrm{x}} \times M(^{30}\mathrm{Si})}{M(^{29}\mathrm{Si}) + R_{\mathrm{y}} \times M(^{30}\mathrm{Si})} \times \frac{R_{\mathrm{y}} - R_{\mathrm{bx}}}{R_{\mathrm{bx}} - R_{\mathrm{x}}} \tag{5}$$

Eq. (5) serves as the modified IDMS equation. The masses m_{x} and m_{yx} indicate the respective masses of the originally solid amounts of sample and spike, introduced into the IDMS blend bx. The isotope amount ratios $R_j = x_j(^{30}\mathrm{Si})/x_j(^{29}\mathrm{Si})$ in the sample $j = \mathrm{x}$ (natural Si), spike $j = \mathrm{y}$ ("Si30", silicon crystal highly enriched with ^{30}Si) and IDMS blend $j = \mathrm{bx}$ (mixture of natural Si and "Si30") have to be measured. w_{y} is the mass fraction of the VE in the spike material:

$$w_{\mathrm{y}} = \frac{M(^{29}\mathrm{Si}) + R_{\mathrm{y}} \times M(^{30}\mathrm{Si})}{R_{\mathrm{y},28} \times M(^{28}\mathrm{Si}) + M(^{29}\mathrm{Si}) + R_{\mathrm{y}} \times M(^{30}\mathrm{Si})} \tag{6}$$

The isotope amount ratio R_{y} corresponds to the ratio $x_{\mathrm{y}}(^{30}\mathrm{Si})/x_{\mathrm{y}}(^{29}\mathrm{Si})$ in the spike material, whereas the ratio $R_{\mathrm{y},28}$ denotes the ratio $x_{\mathrm{y}}(^{28}\mathrm{Si})/x_{\mathrm{y}}(^{29}\mathrm{Si})$ in the same material.

Meanwhile the theoretical basis of the novel concept – described in [6] is successfully checked and validated independently by INRIM (Istituto Nazionale di Ricerca Metrologica, Italy) [16]. This alternative approach for the calculation of the molar mass has been developed from the scratch ending up in the same formalism for the molar mass as given in [6].

2.2. Calibration factors

The determination of isotope amount ratios is always influenced by mass discrimination effects. These are especially evident when using plasma spectrometers [17–19]. For this reason, the measured isotope amount ratios R^{meas} (actually the ion current ratios) must be corrected applying calibration factors K to yield true isotope amount ratios R^{true}. In the current study the ratios R_{x}, R_{y}, and R_{bx} were corrected using the factor K_{30} and the ratio $R_{\mathrm{y},28}$ was corrected with the factor K_{28}:

$$R_j \equiv R_j^{\mathrm{true}} = K_{30} \times R_j^{\mathrm{meas}} \quad \text{with} \quad R_j^{\mathrm{meas}} = \frac{I_j(^{30}\mathrm{Si}^+)}{I_j(^{29}\mathrm{Si}^+)} \quad \text{and}\ j \in \{\mathrm{x, y, bx}\} \tag{7}$$

$$R_{\mathrm{y},28} \equiv R_{\mathrm{y},28}^{\mathrm{true}} = K_{28} \times R_{\mathrm{y},28}^{\mathrm{meas}} \quad \text{with} \quad R_{\mathrm{y},28}^{\mathrm{meas}} = \frac{I_j(^{28}\mathrm{Si}^+)}{I_j(^{29}\mathrm{Si}^+)} \tag{8}$$

A new mathematical closed-form method has recently been developed for the experimental determination of these K factors during the ICP-MS experiment [7]. For this purpose two blends b1 and b2 prepared from three independent isotopically different parent materials x, y and z were mixed gravimetrically. The following two expressions yield the calibration factors by determining the masses of the respective materials introduced into the blends b1 and b2 and

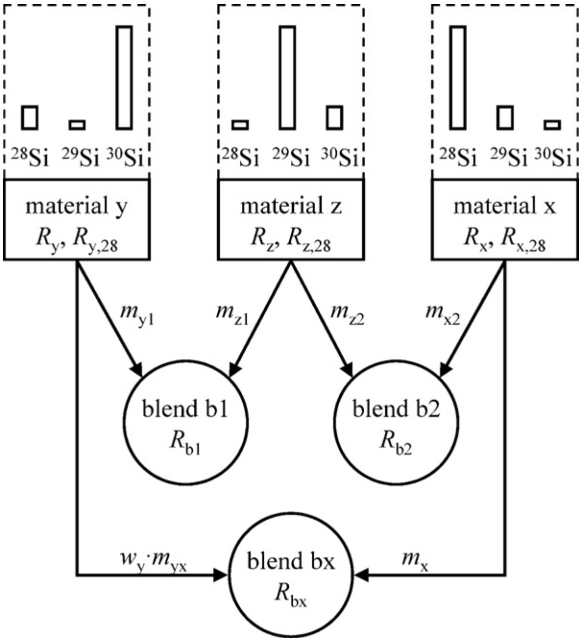

Fig. 1. Preparation of the blends b1 and b2, used to determine the calibration factors *K*, and of the IDMS blend bx, used to determine the molar mass *M*. Altogether nine isotope amount ratios *R* as well as six masses *m* are necessary to calculate the molar mass according to Eq. (1)–(10).

by measuring the isotope amount ratios both in the parent materials and in the blends b1 and b2. Fig. 1 schematically shows the principle of the *K* factor determination. Fig. 2 displays the relations between the isotope amount ratios and masses to be measured, the *K* factors, and finally the molar mass *M*. The detailed derivation of the *K* evaluation is given in [7]:

$$K_{30} = \frac{M(^{29}\text{Si}) \times N_{30}}{M(^{30}\text{Si}) \times D} \tag{9}$$

$$K_{28} = -\frac{M(^{29}\text{Si}) \times N_{28}}{M(^{28}\text{Si}) \times D} \tag{10}$$

Table 1

MC-ICP-MS operating conditions.

Instrument settings	
RF power	1200 W
Coolant Ar gas flow rate	16.0 L min^{-1}
Auxiliary Ar gas flow rate	0.8 L min^{-1}
Sample Ar gas flow	1.2 L min^{-1}
Additional Ar gas flow (applied to the Scott-type part of the spray chamber)	0.02 L min^{-1}
Sampler cone (nickel)	1.1 mm
Skimmer cone (nickel)	0.8 mm
Lens settings	optimized for intensity
Torch system	Sapphire
Data acquisition	
Operation mode	Static
Cup configuration	L3 (^{28}Si), C (^{29}Si), H3 (^{30}Si)
Resolution $M/\Delta M$	6000 (medium resolution)
Integration time	17 s
Number of integrations	1
Number of cycles per block	3
Number of blocks	6

3. Experiment

3.1. Instrumentation

All ion current measurements needed for the determination of the isotope amount ratios were performed using a commercial Thermo Finnigan Neptune double-focusing MC-ICP-MS equipped with nine Faraday detectors [20,21]. The mass spectrometer is located in a clean laboratory ($\nu = 21\,^\circ$C with $\dot{\vartheta} < 0.1$ K/h) equipped with a laboratory lock and an additional air laminar flow filter system (Spetec Laminar Flow Box FBS-V 75, class H14, efficiency ≥99.995%) for the sample introduction area. Table 1 summarizes the main instrumental settings and data acquisition parameters. For silicon measurements three Faraday cups (L3, C, and H3) were used. In the very beginning of the experiments the instrumental parameters were optimized with a 100 μg/g solution of Pb in 0.15 mol/kg HNO_3 solution (NIST SRM 981), because the Pb standard was established to keep track of the long-term instrumental behaviour. During the experiments presented here, the optimization was performed with a

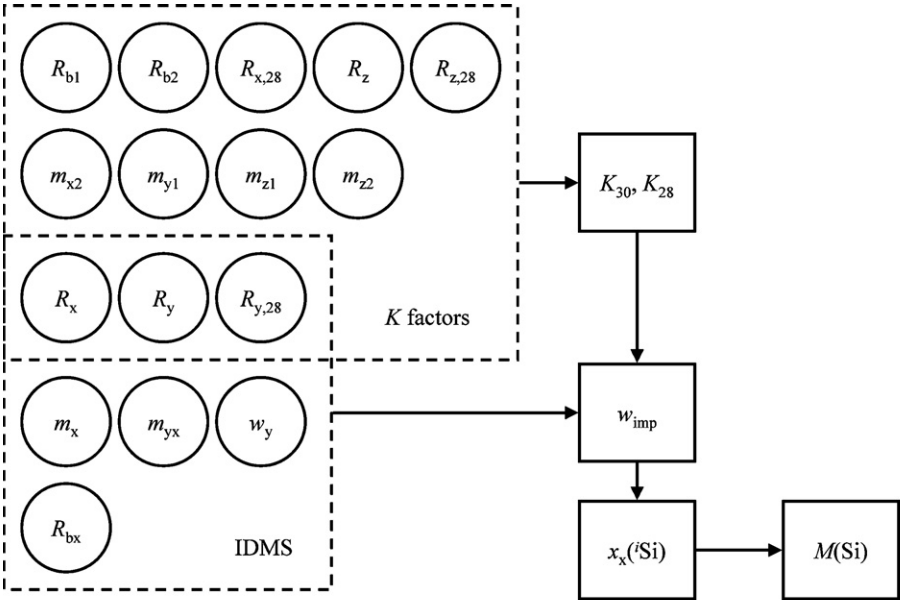

Fig. 2. Relation between isotope amount ratios *R* and masses *m* for *K* factor determination, modified IDMS and the resulting amount of substance and molar mass determination.

solution of natural silicon ($w(\mathrm{Si}) = 4\,\mu\mathrm{g/g}$ in NaOH ($w(\mathrm{NaOH}) = 0.0001\,\mathrm{g/g}$)). Because of potential contaminations, the measurements require an equipment which is as Si-free as possible. For this reason a specially constructed sapphire torch with an additional boron nitride shield (AHF analysentechnik AG, Germany) was used instead of a quartz torch. Also the standard spray chamber was replaced with a spray chamber (combination of cyclonic and Scott type) made of PEEK and PFA (AHF analysentechnik AG, Germany) equipped with a PFA 50 type nebulizer (Elemental Scientific Inc., $50\,\mu\mathrm{L\,min^{-1}}$ flow rate). The experiments were performed at medium resolution ($M/\Delta M = 6000$) in static mode. During the experiments a sensitivity of $(1 \pm 0.1)\,\mathrm{V}/(\mu\mathrm{g/g})$ in medium resolution was obtained for the ^{28}Si signal. This relatively low sensitivity compared to [22] was probably a consequence of the use of aqueous NaOH as the matrix, the use of a self-aspirating $50\,\mu\mathrm{L/min}$ nebulizer, and the use of a standard cone instead of an X-cone. Moreover, preliminary experiments using several monoelemental standard solutions showed decreased sensitivity (at least by a factor of two) when using the sapphire torch instead of the standard quartz torch (for yet unknown reasons). The stability of the signals with respect to the uncertainty of the isotope amount ratios had higher priority than enhancement of intensity. Main experimental parameters were: $-10\,\mathrm{kV}$ acceleration voltage, 1200 W RF power, 16, 0.8, and $1.2\,\mathrm{L\,min^{-1}}$ coolant, auxiliary and sample gas argon flow rates. All tubings were made of PFA, inert to a large extent and Si-free. Samples were injected from a computer-driven auto sampler (ASX-100, CETAC Technologies, USA) equipped with PFA vials (AHF analysentechnik AG, Germany).

3.2. *Materials and reagents*

All chemical reagents were of the highest purity commercially available (see the respective details). All samples and solutions were prepared gravimetrically applying an air buoyancy correction (ambient conditions air pressure, temperature, and humidity measured using a calibrated testo 650 equipped with the sensors 0638.1645 and 0636.9741; balances specified later on) to guarantee the metrological uplink to the mass with the SI unit kilogram. The silicon single crystals used for investigations (natural silicon, “Si29”, and “Si30”) were slices of approximately 50...70 mg each, cut from residual parts of the original float-zone ingot of the respective crystal. The chemical purity of these materials has been tested by infrared spectroscopy. Typical values of the dominant contaminations of carbon, oxygen, and nitrogen were in the range of $w = 3 \times 10^{-8}\,\mathrm{g/g}$ [23] which is more than 6 orders of magnitude below the value of the sum of $w(^{29}\mathrm{Si})$ and $w(^{30}\mathrm{Si})$. In general, the magnitudes of these contaminations are insignificant for the determination of the molar mass. Thus, all silicon materials used were treated as ideal pure samples with a mass fraction of $w = 1\,\mathrm{g/g}$. The surfaces of the samples were pre-cleaned with acetone (Merck p.a.: 99.8%) and ethanol (Merck p.a.: 99.9%) to get rid of organic surface contaminations and washed with purified water. Subsequently the samples were etched in an ultrasonic bath (Sonorex RK103H, Bandelin electronic, Germany) at 70 °C for 50 min. The etching solution was a mixture of 0.380 g/g HF (Fluka TraceSELECT Ultra, 49 g/g), 0.070 g/g H_2O_2 (Merck Ultrapur 0.31 g/g), 0.086 g/g HNO_3 (Merck Ultrapur, 0.60 g/g) and 0.464 g/g purified H_2O. The total etching procedure can be summarized by the following steps [24,25]:

$$SiO_2 + 6HF \rightarrow SiF_6 + H_2 + 2H_2O \tag{11}$$

$$Si + HNO_3 + 6HF \rightarrow H_2SiF_6 + HNO_2 + H_2 + H_2O \tag{12}$$

Eq. (11) describes how in the first step residual oxide layers are removed from the silicon surface. Eq. (12) can be divided into separate reactions (13)–(16) showing that subsequently, the upper silicon surface layers are removed as well in order to guarantee a surface, unaffected by implantations or any inhomogeneities.

$$HNO_3 + HNO_2 \rightarrow 2NO_2 + H_2O \tag{13}$$

$$2NO_2 + Si \rightarrow Si^{2+} + 2NO_2^{-} \tag{14}$$

$$Si^{2+} + 2OH^{-} \rightarrow SiO_2 + H_2 \tag{15}$$

$$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O \tag{16}$$

After washing with ultrapure water and drying, the silicon samples were initially weighed by the PTB mass laboratory (balances: Mettler Toledo UMT5, resolution: $0.1\,\mu\mathrm{g}$; Sartorius MC210S, resolution: $10\,\mu\mathrm{g}$). Stock solutions of silicon were prepared by dissolving the weighed sample crystals in aqueous sodium hydroxide ($NaOH{\cdot}1H_2O$, Merck Suprapur 99.99%, $w(\mathrm{NaOH}) = 0.17\,\mathrm{g/g}$) followed by gravimetrical dilution steps with $NaOH_{aq}$ ($w(\mathrm{NaOH}) = 0.0001\,\mathrm{g/g}$) using a Mettler H315 balance (resolution: 0.1 mg). The ultrapure water ($\sigma = 18\,\Omega\,\mathrm{cm}$) was generated by a Millipore water purification system (ELIX 5 UV, Milli-Q Element A10, Millipore Corporation, USA). The silicon under investigation was transformed within one single chemical conversion step from the crystal into the aqueous solution:

$$Si + 4OH^{-} \rightarrow SiO_4^{4-} + 2H_2 \tag{17}$$

The dissolving process (Eq. (17)) was performed using the already mentioned ultrasonic bath at a temperature of $\vartheta \approx 50\,^{\circ}\mathrm{C}$ within approximately 10 days. This is an additional and definitive advantage to avoid cumulative contaminations of silicon in comparison to a multi-step chemical conversion needed for gas phase mass spectrometry using the sequence: SiS (dissolving, digestion) $\rightarrow H_2SiF_6$ (precipitation) $\rightarrow BaSiF_6$ (decomposition) $\rightarrow SiF_4$ [26]. In our experiments, all vials, vessels and bottles were made of purified PFA. The sequential cleaning steps of those PFA devices are listed in Table 2. The total procedure took 4–5 days. Only chemicals of highest commercial purity were used (see above). The cleaning procedure was validated using X-ray-induced fluorescence in the PTB-laboratory of X-ray optics. No significant contamination has been found. Sample preparation was performed in a silicon-free cleanbench area with a 99.995% efficiency air filter system (AstroCel II, A99C9S2R3/H14). The stock solutions of natural silicon, “Si29”, and “Si30” had contents in the range of $w(\mathrm{Si}) = 600\,\mu\mathrm{g/g}$ in an aqueous matrix containing $w(\mathrm{NaOH}) = 0.005\,\mathrm{g/g}$. The final solutions were obtained after three additional dilution steps resulting in alkaline aqueous solutions of $w(\mathrm{Si}) = 4\,\mu\mathrm{g/g}$ in $w(\mathrm{NaOH}) = 0.0001\,\mathrm{g/g}$. The latter was used as the respective blank solution for the reported measurements. Alkaline digestion (in solid NaOH) of silicon samples has been recently described [27–29],

Table 2
Cleaning steps of PFA bottles and vials prior to experiments.

Step	Cleaning steps		
	Action	Reagent	Duration
1	Rinsing, flat shaker	Purified H_2O	1 day
2	Drying, cabinet dryer		6 h
3	Washing, flat shaker	HNO_3 ($w = 0.0015\,\mathrm{g/g}$)	6 h
4	Rinsing, flat shaker	Purified H_2O	6 h
5	Drying, cabinet dryer		6 h
6	Washing	HF ($w = 0.1\,\mathrm{g/g}$)	30 min
7	Rinsing, flat shaker	Purified H_2O	1 day
8	Washing, flat shaker	NaOH ($w = 0.0001\,\mathrm{g/g}$)	1 day
9	Rinsing, flat shaker	Purified H_2O	6 h
10	Drying, cabinet dryer		6 h

Table 3
Molecular interferences affecting the signals of $^{28}Si^+$, $^{29}Si^+$, and $^{30}Si^+$ [15]. The mass resolutions $M/\Delta M$ necessary to separate the interferences from the silicon signals were calculated using the respective silicon isotope mass in the denominator.

		M in g/mol	$M/\Delta M$
Isotope	$^{28}Si^+$	27.9769265	
Interference	$^{12}C^{16}O^+$	27.9949146	1555
	$^{14}N_2^+$	28.0061480	957
Isotope	$^{29}Si^+$	28.9764947	
Interference	$^{28}Si^1H^+$	28.9847515	3509
	$^{13}C^{16}O^+$	28.9982695	1331
	$^{12}C^{17}O^+$	28.9991315	1280
	$^{12}C^{16}O^1H^+$	29.0027397	1104
	$^{14}N^{15}N^+$	29.0031830	1086
	$^{14}N_2\,^1H^+$	29.0139730	773
Isotope	$^{30}Si^+$	29.9737702	
Interference	$^{29}Si^1H^+$	29.9843197	2841
	$^{14}N^{16}O^+$	29.9979886	1238
	$^{12}C^{18}O^+$	29.9991604	1181
	$^{15}N_2^+$	30.0002179	1133
	$^{13}C^{17}O^+$	30.0024863	1044
	$^{13}C^{16}O^1H^+$	30.0060945	927
	$^{12}C^{17}O^1H^+$	30.0069565	903
	$^{14}N^{15}N^1H^+$	30.0110080	805

but the respective subsequent ICP-MS measurements have been performed in acidic media. In the present study we have the advantage of combining the smooth, simple digestion method in aqueous NaOH for quantitative purposes with the subsequent ICP-MS measurements in an alkaline medium, which – to our knowledge has been performed for the first time. In this context it must be mentioned that the choice of measuring under alkaline plasma conditions was a consequence of previously performed long-term studies concerning the highest stabilitiy of the ion currents as a function of the pH and nature of the solvent ($SiCl_4$ in NaOH, Si in HF, $(NH_4)_2SiF_6$, Si in NaOH)[30]. The digestion with aqueous NaOH gave the most stable signals and plasma conditions.

3.3. Mass spectrometry

Prior to every measurement the mass range of the multicollector mass spectrometer was checked thoroughly especially in the range between $^{28}Si^+$ and $^{30}Si^+$ to discover possible interferences and to check the mass accuracy. When carrying out measurements under so-called *pseudo-high resolution* it is important to prove the absence of interferences and to ensure to measure on the plateau representing the isotope to be measured. This was done by scanning the respective mass window using several solutions of natural silicon ranging from $w(Si) = 50$ ng/g to 400 ng/g in aqueous sodium hydroxide ($w(NaOH) = 100$ µg/g). The silicon signals were related directly proportional to their concentrations. Molecular interferences – however are not affected by these changes of mass fractions. Because the three silicon isotopes suffer from molecular interferences, extreme care must be taken to identify them. Table 3 summarizes a majority of molecular interferences in the mass range of interest. As can be seen, all three silicon isotopes have the lowest masses in their respective interference pattern. All those relevant interferences are clearly resolved. As described in detail in [20,21] a proper criterion for a parameter-independent resolution is the so-called *resolving power* R_{power} (5, 95%):

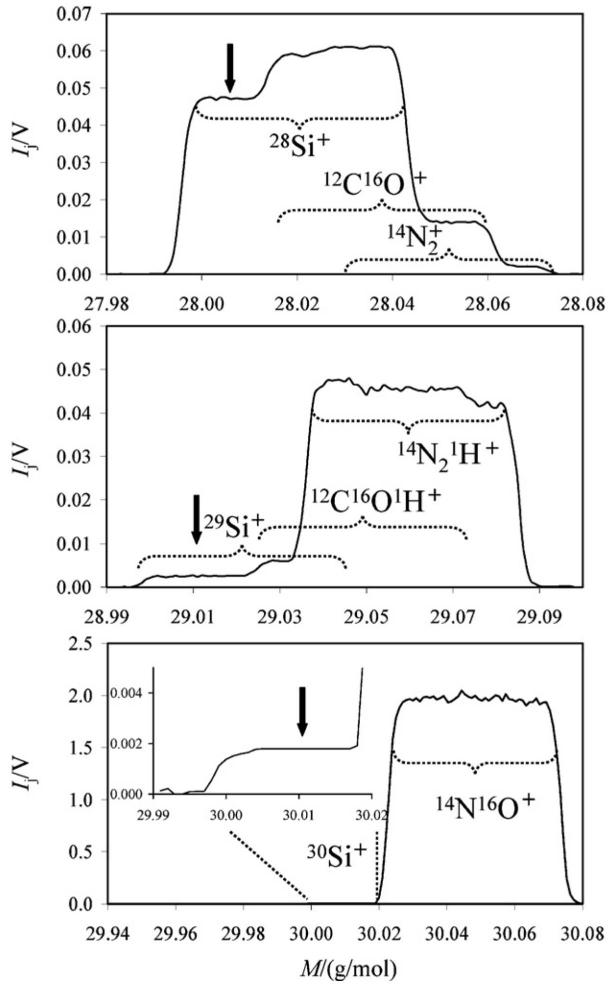

Fig. 3. High resolution mass scans ($M/\Delta M = 8000$) of natural silicon crystal material ($w = 100$ ng/g in 100 µg/g NaOH) using the Neptune's central Faraday cup. The ranges of the ^{28}Si, ^{29}Si, and ^{30}Si isotopes and molecular interferences are shown by dotted curly brackets. The bold downward arrows indicate the respective center of the resolved, uninterfered $^{28}Si^+$, $^{29}Si^+$, and $^{30}Si^+$ signal plateaus.

$$R_{power}(5, 95\%) = \frac{M}{M(95\%) - M(5\%)} \qquad (18)$$

$M(95\%)$ is the mass at 95% of the peak height, $M(5\%)$ is the mass at 5% of the peak height, and M is the mass of the peak (center of the plateau). Generally, the resolving power should be larger than the standard resolution $M/\Delta M$ by a factor of about 2 in order to guarantee an interference-free peak plateau. Fig. 3 shows mass scans (ion signal vs. molar mass) of a natural silicon sample ($w(Si) = 100$ ng/g) acquired in high resolution mode ($M/\Delta M = 8000$) with the Thermo Finnigan Neptune MC-ICP-MS. The $^{28}Si^+$ isotope can be clearly resolved as the first plateau, followed by a $^{12}C^{16}O^+$ -interference, and a signal from molecular nitrogen ($^{14}N_2^+$). The pattern in the ^{29}Si range displays in the low mass range a clear plateau of $^{29}Si^+$, followed by intense interferences of $^{12}C^{16}O^1H^+$ and $^{14}N_2^1H^+$. The $^{30}Si^+$ signal plateau is accompanied by a subsequent very intense $^{14}N^{16}O^+$ signal. In the case of separating $^{28}Si^+$ from $^{12}C^{16}O^+$ a resolution of $M/\Delta M \approx 1555$ is required. The respective R_{power} (5, 95%) is approx. 5600. For $^{29}Si^+$ and $^{12}C^{16}O^1H^+$ $M/\Delta M$ is 1104 (R_{power} (5, 95%) ≈ 6200) and for $^{30}Si^+$ and the subsequent $^{14}N^{16}O^+$ signal $M/\Delta M$ is 1238 (R_{power} (5, 95%) ≈ 4000). For

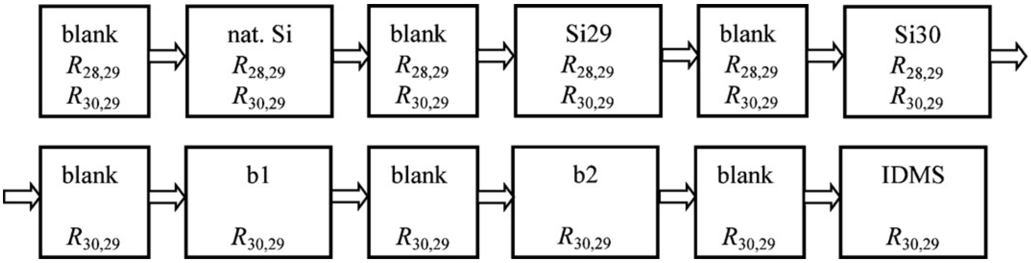

Fig. 4. Schematic sequence of the measurement of silicon samples bracketed by blank measurements (NaOH; $w(\text{NaOH}) = 0.0001$ g/g). The shown sequence is performed twice in the forward direction and twice in the reverse direction. Total duration of the experimental run is approx. 7 h.

this reason, the silicon isotopes were measured directly without corrections.

A crucial merit of the used mass spectrometer is the ability to choose between three different fixed resolution modes. Hydride formation ($^{28}\text{Si}^{1}\text{H}^{+}$ and $^{29}\text{Si}^{1}\text{H}^{+}$), which indeed is an important issue during the ongoing measurements of "Si28", which will be discussed in detail in part 3 of this series of papers, was of no significance in the case of the nearly natural silicon material and cannot be observed in the natural material. For the sake of higher transmission and thus a proper repeatability in isotope amount ratio determinations, the reported experiments were performed in medium resolution ($M/\Delta M = 6000$) which is sufficient to separate the molecular interferences but yields increased intensities, approximately by a factor of 2 compared to high resolution mode. The measurement procedure was arranged as follows: all the solutions of the original materials y, z, and x ("Si30", "Si29", and natural silicon), the two blends b1 and b2 (prepared from "Si30" and "Si29", and from natural silicon and "Si29", resp.) for *K*-factor determination, and the IDMS-blend bx (natural silicon and "Si30") were subdivided each into three aliquots. Each aliquot was filled into a separate vial of the autosampler tray. Every sample was measured four times. A sample measurement was bracketed by two blank measurements under exactly equal conditions (compare Fig. 4). In total, 24 sample measurements and 25 blank measurements were performed in one single sequence (total time to run one sequence: approx. 7 h). The Neptune software (version 3.2.0.14) was used to run these sequences automatically overnight. One sample (or blank) measurement consisted of 60 s take up time, the isotope amount ratio determination itself (configured as a *method*), and subsequently a 40 s wash time. The baseline is retrieved after approximately 15 s. The so-called *method* in the Neptune software contains the respective cup configuration and controls the number of *blocks* and *cycles*. The cycle denotes a single measurement of the sample or blank and defines the applied ion current integration time (17 s), as well as the idle time (3 s). The blocks pool a certain number of consecutive cycles (here: 3). The number of blocks (here: 6) was a multiple of the number of Faraday cups (selected in the cup configuration for the measurement) in order to take advantage of the Neptune's *Virtual Amplifier concept* [20]. This unique feature allows to exchange the amplifiers between the cups used after every block. This helped to reduce statistical influences due to gain fluctuations as well as it helped to detect inconsistencies of the gain calibration. The acquired signal raw data of the samples were corrected numerically afterwards with the corresponding previously measured blank data (blank signal versus silicon sample signal: below 1%). The corrected intensities of the three silicon isotopes were used to calculate the average raw isotope amount ratios ($^{30}\text{Si}/^{29}\text{Si}$ and $^{28}\text{Si}/^{29}\text{Si}$). These isotope amount ratio data of the four individual measurements – evenly arranged throughout the sequence – were averaged and yielded the best estimates of the respective isotope amount ratios and their associated standard uncertainties.

4. Results and discussion

The distribution of five independent measurement results of the molar mass $M(\text{Si})$ of the investigated natural silicon crystal is shown in Fig. 5. The measurements were carried out within a period of two weeks. The single data (filled circles) are accompanied by error bars displaying the respective combined measurement uncertainty $u(M(\text{Si}))$ with $k = 1$. The mean value of $M(\text{Si})$ is plotted as a bold dashed line. The numerical values of $M(\text{Si})$ and amount-of-substance fractions $x(^{i}\text{Si})$ of the silicon crystal are additionally listed in Table 4. The mean molar mass of the investigated natural silicon material is $M(\text{Si}) = 28.08548(13)$ g/mol with an associated relative uncertainty of $u_{\text{rel}} = 4.6 \times 10^{-6}$ for $k = 1$. The relative standard deviation of the mean of the measurements is $s_{\text{rel}} = 4 \times 10^{-7}$. This result is in excellent agreement with the current IUPAC value $M(\text{Si}) = 28.08550(15)$ g/mol with an associated relative uncertainty of $u_{\text{rel}} = 5.3 \times 10^{-6}$ for $k = 1$ [15]. The aim of the present study performed at PTB is to show and prove the general application of the novel method using a modified IDMS presented in detail in [6] in order to determine the absolute molar mass of a high purity single crystal of silicon. Moreover, to our knowledge it is the first time, an MC-ICP-MS technique was applied for the determination of the molar mass of silicon. The advantages of the novel method are at least two-fold: one merit should be the reduction of the measurement uncertainty associated with the isotope amount ratios $R_j = x(^{30}\text{Si})/x(^{29}\text{Si})$ in the sample solution and in the IDMS blend (consisting of the sample and a silicon crystal material ("Si30") highly enriched with ^{30}Si). Second, the masses of gravimetrically prepared solutions are known accurately. However, in the previ-

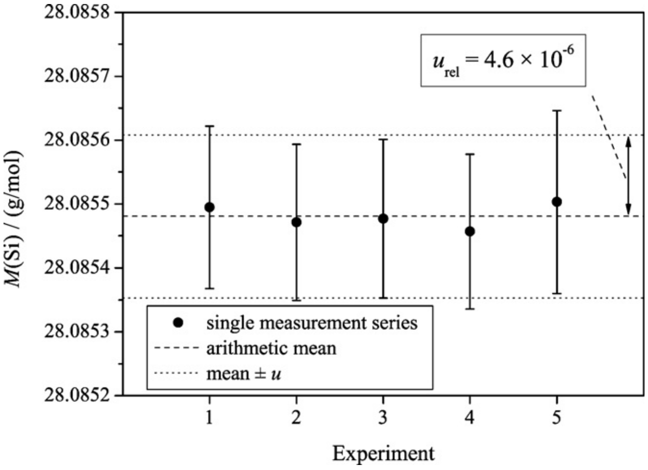

Fig. 5. Molar mass distribution of natural silicon crystal material (5 independent measurement sequences: filled circles). Error bars indicate the respective combined measurement uncertainty ($k = 1$). Bold dashed line: mean value; dotted lines: associated standard uncertainty of the mean value.

Table 4
Molar mass M and isotopic abundances (amount-of-substance fractions) $x(^{i}\mathrm{Si})$ of the natural silicon crystal determined during five measurements. Their respective combined measurement uncertainties u are given in brackets (last digits).

Molar mass and isotopic composition: natural silicon crystal Experiment	M, g/mol	$x(^{28}\mathrm{Si})$, mol/mol	$x(^{29}\mathrm{Si})$, mol/mol	$x(^{30}\mathrm{Si})$, mol/mol
1	28.08549(13)	0.922265(96)	0.046784(70)	0.030951(35)
2	28.08547(12)	0.922282(93)	0.046774(67)	0.030944(33)
3	28.08548(13)	0.922281(94)	0.046769(67)	0.030950(34)
4	28.08546(12)	0.922288(92)	0.046776(66)	0.030936(32)
5	28.08550(14)	0.922261(100)	0.046783(71)	0.030956(47)
Mean	28.08548(13)	0.922275(96)	0.046777(68)	0.030948(36)

ous paper [6] – part 1 of the presentation of the novel concept – the resulting predicted measurement uncertainty of the molar mass is two orders of magnitude smaller than in this experimental study. This apparent contradiction can easily be resolved and is no limitation of the application of the novel method on the "Si28" material. The theoretical prediction of $u(M)$ was calculated assuming a silicon sample which is artificially enriched with respect to the ^{28}Si isotope ($x_x(^{28}\mathrm{Si}) > 0.9998$ mol/mol). That kind of material is used at present for the re-determination of the Avogadro-constant. Its relative measurement uncertainty associated with M needs to be in the lower 10^{-8} range [31]. Unfortunately, a reference value for the molar mass of that new highly enriched material is not yet available. Therefore, in part 1 of this series of papers we examined theoretically whether it is possible to determine the molar mass with that low uncertainty and we started the experiment – as described in this part – with natural silicon material available in a larger extent. Another crucial point why we started with natural silicon in the present study for validating the method experimentally is the circumstance of the very high costs of the "Si28"-material: ≈1,000,000 €/kg. For that reason the method must be very well characterized and well-proven before measuring the new "Si28" material routinely. The disadvantage of this natural silicon crystal material is the respectively lower enrichment in ^{28}Si with $x_x(^{28}\mathrm{Si}) = 0.922$ mol/mol which was proven to limit the uncertainty associated with the molar mass by at least two orders of magnitude. Therefore, this was the initial very reason to switch to the "Si28" material in the case of the re-determination of the Avogadro constant [31]. The explanation of the larger $u(M)$ in the case of natural silicon material can be found in the respective uncertainty budget. Table 5 shows a representative uncertainty budget of the molar mass $M(Si)$ of natural silicon of the present study according to the Guide to the Expression of Uncertainty in Measurement [32]. Three main contributions to the overall uncertainty of M(Si) can be observed: The first is the uncertainty of the mass mx of the solid sample material x (natural silicon) in the final solution used for the measurements. About 89% of this uncertainty results from the original weighing of the solid silicon sample crystal prior to dissolving ($u_{\mathrm{rel}}(m_x) = 2.2 \times 10^{-4}$). The subsequent dilution steps of

Table 5
Uncertainty budget of the molar mass of the natural silicon crystal material (exemplarily experiment 3) measured with a Thermo Finnigan Neptune MC-ICP-MS. The uncertainty budget has been calculated with the aid of the *GUM-Workbench* software [33]. Quantities are defined and named according to [34]. The isotopic abundances resemble an almost natural composition with $x_x(^{28}\mathrm{Si}) = 0.922$ mol/mol. The budget can be directly compared to that of the hypothetical silicon crystal highly enriched with the ^{28}Si isotope discussed in [6]. The quantities are explained in detail in section 2. $m_{y,f}$ and $w_{y,f}$ are the masses and corresponding mass fractions of the spike (y) solution used for the preparation of the IDMS blend bx (e.g., $m_y = m_{y,f} \times w_{y,f}$). The standard uncertainties are given for $k = 1$. The sensitivity coefficients c_i have the unit $[c_i] = \mathrm{g/mol}/[X_i]$ which is not displayed to support clarity. The right column (Index) displays the relative uncertainty contribution (in %) of the respective input quantity X_i to the molar mass M(Si) which is the final output quantity Y. Intermediate results being no real input quantities of the molar mass budget are resulting in blank cells for c_i and Index. Displayed isotope amount ratios R are already corrected for background through subtracting the blank values gathered during the measurement sequence. The combined measurement uncertainty u_c is given for $k = 1$.

Quantity X_i	Unit $[X_i]$	Best estimate (value) x_i	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Index
$x_x(^{28}\mathrm{Si})$	mol/mol	0.9222813	9.38×10^{-5}		
$x_x(^{29}\mathrm{Si})$	mol/mol	0.0467691	6.68×10^{-5}		
$x_x(^{30}\mathrm{Si})$	mol/mol	0.0309496	3.40×10^{-5}		
$M(^{28}\mathrm{Si})$	g/mol	27.97692649	1.10×10^{-7}	9.30×10^{-1}	0.0
$M(^{29}\mathrm{Si})$	g/mol	28.97649468	1.10×10^{-7}	4.70×10^{-2}	0.0
$M(^{30}\mathrm{Si})$	g/mol	29.97377018	1.10×10^{-7}	2.70×10^{-2}	0.0
w_{imp}	g/g	0.0812834	9.75×10^{-5}		
w_y	g/g	0.9945808	1.41×10^{-4}		
R_x	mol/mol	0.69384	2.43×10^{-4}	1.00×10^{-1}	4.2
R_y	mol/mol	204.742	8.62×10^{-1}	2.60×10^{-5}	3.4
R_{bx}	mol/mol	7.75558	2.12×10^{-3}	-1.60×10^{-2}	7.4
K_{30}	1	0.953755	9.38×10^{-4}	-4.80×10^{-2}	13.1
$R_{y,28}$	mol/mol	1.0931	2.82×10^{-2}	-5.40×10^{-2}	1.5
K_{28}	1	1.047978	2.07×10^{-3}	-5.60×10^{-4}	0.0
m_{yx}	g	1.65×10^{-4}	10.8×10^{-8}		
m_x	g	4.69×10^{-4}	32.8×10^{-8}	-7.60×10^{-5}	37.6
k_{conv}	(g/g)/(μg/g)	1.00×10^{-6}			
$w_{y,f}$	g/g	13.29060	8.64×10^{-3}	-8.20×10^{-3}	32.4
$m_{y,f}$	g	12.445897	8.71×10^{-4}	8.80×10^{-3}	0.4
Y	$[Y]$	y	$u_c(y)$	$u_{\mathrm{rel}}(y)$	
M(Si)	g/mol	28.08548	0.00013	4.5×10^{-6}	

the sample *x* will add an uncertainty in m_x of only 11%. The second contribution is the mass fraction $w_{y,f}$ of the solid spike material "Si30" in the final spike solution used to prepare the IDMS blend bx of the sample x and spike y: this adds another 32% which is also mainly influenced by the uncertainty of the mass of initially dissolved "Si30" crystal material (spike). A reduction of the uncertainty of the weighings of the initial solid samples m_x and m_y by a factor of 2 will change the uncertainty in M(Si) by a factor of 3 or 4 (this can be simulated by using the *GUM-workbench software* [33]). A final relative measurement uncertainty of $U_{rel}(M)$ of 2×10^{-6} of natural silicon might then be achievable. A further reduction in $U(M)$ of the natural material will be restricted by the uncertainty of the isotope ratio measurements only. However, in the case of the "Si28" material, these crystal weighings do not influence the uncertainty in such a way as in the case of natural silicon. This has been demonstrated in [6]. There, only the uncertainties of $M(^{28}\text{Si})$ and R_{bx} restrict the uncertainty. This dramatic difference in uncertainty associated with M by two orders of magnitude is a direct consequence of the grade of enrichment of ^{28}Si of the respective sample (natural Si vs. "Si28"). Therefore, increasing the enrichment of ^{28}Si will directly reduce the uncertainty associated with the molar mass, as predicted in [6]. Since the material intended to be used for the re-determination of the Avogadro constant exhibits an enrichment much larger than that of the material in this study and even larger than the hypothetical one used to calculate the prediction in [6], the novel concept derived in part 1 was proven to be suitable for the measurements of "Si28" within the Avogadro project.

5. Conclusions

The present study demonstrates the experimental applicability of the novel concept for the determination of the molar mass using IDMS, described in part 1 of the current work. The IDMS-technique can indeed be applied experimentally for the determination of the "virtual element" – the mass fraction of ^{29}Si and ^{30}Si in the matrix of the entire element containing also ^{28}Si. Thus, the molar mass of a silicon material has been measured for the first time using an ICP-MS technique. In this context, a new and elegant preparation technique for the transformation of silicon into an aqueous alkaline silicate solution in one single chemical step has been successfully tested. This might strongly reduce the possibility of contaminating the "Si28" material used in the ongoing re-determination of the Avogadro-constant. As a third main result of this study it has been shown and proven experimentally for the first time that the calibration factors needed to correct for mass discrimination in order to yield the isotope amount ratios can be determined according to the theoretical prediction [7]. The larger relative measurement uncertainty of M(Si) in the 10^{-6} range of the present study compared to that of the hypothetical material in part 1 [6] has its origin in the "low" enrichment of the ^{28}Si isotope (92.2%) in the natural silicon material. This affects the uncertainty budget through larger sensitivity coefficients and finally the overall measurement uncertainty. Preliminary experiments using the "Si28" silicon crystal material performed in our laboratory indicate a reduction of $U_{rel}(M)$ by two orders of magnitude compared to $U_{rel}(M(\text{Si}))$ in the present study, which is in excellent agreement or even beyond with the theoretically predicted uncertainty.

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