



# The Uncertainty Paradox: Molar Mass of Enriched Versus Natural Silicon Used in the XRCD Method

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**Abstract:** The X-ray crystal density method uses silicon spheres highly enriched in <sup>28</sup>Si as a primary method for the dissemination of the SI base unit kilogram yielding smallest possible uncertainties associated with the mass *m* within a few parts in 10<sup>-8</sup>. This study compares different available and newly developed analytical methods and their results for the determination of the molar mass *M* of silicon highly enriched in <sup>28</sup>Si (*M<sub>e</sub>*) and of silicon (*M<sub>x</sub>*) with an almost natural isotopic distribution. While for *M<sub>e</sub>* relative uncertainties *u<sub>rel</sub>*(*M<sub>e</sub>*) in the lower 10<sup>-9</sup> range are obtained routinely, it was not possible to fall below a value of *u<sub>rel</sub>*(*M<sub>x</sub>*) < 4 × 10<sup>-6</sup> in the case of natural silicon, which is approximately three orders of magnitude larger. The application of the state-of-the-art isotope ratio mass spectrometry accompanied with sophisticated thoroughly investigated methods suggests an intrinsic cause for the large uncertainty associated with the molar mass of natural silicon compared to the enriched material.

**Keywords:** Silicon; Molar mass; Isotope ratios; SI; Kilogram; Mole; XRCD method

## 1. Introduction

After the revision of the International System of Units in 2019, the seven base units are defined via fixed fundamental constants [1–4]. The most far-reaching change was the new definition of the kilogram, the base unit of the mass, previously defined via a single artefact, a Pt-Ir cylinder, now defined via the Planck constant *h*. Since the revision, the dissemination of the SI units is still a challenge and an ongoing duty of the metrology community. The two most suitable methods—in metrological terms “primary methods”—for the realization and dissemination of the kilogram are the “Kibble balance” approach and the XRCD method [5, 6]. The first method directly determines the Planck constant *h* via a comparison of mechanical and electrical power; the XRCD method uses a combination of experiments for “counting” the number of silicon atoms in an Si sphere yielding the Avogadro constant *N<sub>A</sub>* as a direct

result. Since both *N<sub>A</sub>* and *h* can be converted into each other [7, 8].

$$N_A = \frac{c\alpha^2 A_r(e) M_u}{2R_\infty h} \quad (1)$$

(with the Rydberg constant *R<sub>∞</sub>*, the fine structure constant *α*, the speed of light in vacuum *c*, the relative atomic mass of an electron *A<sub>r</sub>*(*e*), and the molar mass constant *M<sub>u</sub>*), the two primary methods have a complementary character. Briefly, in the XRCD method a silicon sphere is characterized according to

$$N_A = \frac{8VM}{a^3 m} = \frac{8M}{a^3 \rho} = \frac{N}{n} \quad (2)$$

with the macroscopic volume *V* of a single crystalline sphere with eight atoms in the unit cell, a nominal mass *m* of approximately 1 kg, the lattice parameter *a*, the molar mass *M*, and the density *ρ*. After the revision of the SI, *N<sub>A</sub>* is fixed, and the measurement of the parameters given in Eq. (2) yields the mass *m* of the respective sphere with a very low uncertainty. Once characterized, a respective sphere can be used as a primary mass standard with an associated uncertainty *u<sub>rel</sub>*(*m*) < 2 × 10<sup>-8</sup>. Contributions to *m* of the surface layers and other impurities have to be determined from time

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to time [6]. Equation (2) indicates a proportional relation between  $N_A$  and  $M$ . Thus, during the efforts for the realization of  $N_A$  using the XRCD method (“Avogadro Project”), the relative uncertainty associated with  $M$  must be smaller than  $2 \times 10^{-8}$ , because one of the accompanying preconditions of the revision was  $u_{\text{rel}}(N_A) \leq 2 \times 10^{-8}$  [8]. Initially, the XRCD method aimed at the determination of  $N_A$  only, finally leading to a redefinition of the kilogram [9, 10]. Prior to 2007, silicon spheres made of silicon with almost natural isotopic composition have been used. However, it was not possible to undercut a limit of  $u_{\text{rel}}(M_x) \approx 3 \times 10^{-7}$ , which was at least one order of magnitude too large for the intended redefinition of the kilogram [11]. During the first years of the “Avogadro-Project”, the molar mass of the natural silicon crystals has been determined by pioneering gas-phase isotope ratio mass spectrometric measurements [12, 13]. At that time, the solid silicon samples had to be converted via several chemical steps into gaseous silicon tetrafluoride  $\text{SiF}_4$  [12]. Additionally, the molar mass of natural silicon delivered the largest contribution to the uncertainty associated with  $N_A$  [13]. Therefore, it was of utmost importance to reduce the impact of the molar mass  $M$  to  $u(N_A)$  and to reduce  $u(M)$  by more than at least one order of magnitude. For this reason, both theoretical and experimental problems had to be solved. The availability of a silicon crystal highly enriched in  $^{28}\text{Si}$  in 2007 was a milestone in the XRCD method: a new extremely pure and highly enriched silicon crystal with an amount-of-substance fraction  $x(^{28}\text{Si}) = 0.999\,957\,52(12)$  mol/mol [14]. The extremely low abundance of both  $^{29}\text{Si}$  and  $^{30}\text{Si}$  in these enriched crystals required new theoretical methods for the determination of the molar mass which led to the invention of the virtual element-isotope dilution mass spectrometry (VE-IDMS) method [15] which is based on the measurement of isotope ratios,  $R_j^{\text{true}}$  in Eq. (7). The intensity ratios  $R_j^{\text{meas}}$  actually measured by mass spectrometry deviate from the isotope ratios due to several unavoidable processes in the mass spectrometer starting from the ion source. The calibration or the so-called  $K$  factors convert the intensity ratios to yield the corrected isotope ratios (Eq. (7)). Usually,  $K$  factors can be determined by measuring an isotopic reference material. In case of the enriched silicon used for the XRCD method, no suitable isotopic reference material with a sufficiently low uncertainty associated with the isotope ratios exists. Therefore, an analytical closed-form approach has been developed for the determination of the  $K$  factors necessary for the correction of the measured intensity ratios [16]. The application of this primary method for the determination of the molar mass in combination with high-resolution multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) yields also for the subsequent highly enriched silicon crystals relative uncertainties in the  $10^{-9}$  range [17, 18]. The combination of these methods applied to the

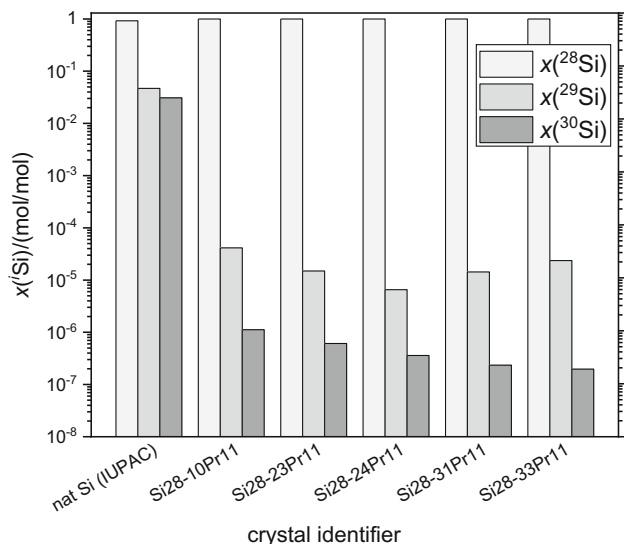
enriched silicon material reduced the relative uncertainty associated with the molar mass by two orders of magnitude within one decade. Additionally, the contribution of the molar mass to the uncertainty of  $N_A$  was reduced to  $< 10\%$  [19].

In the meantime, a small pool of silicon spheres highly enriched in  $^{28}\text{Si}$  and characterized by the XRCD method is available and guarantees the dissemination of the kilogram on the top level of traceability yielding  $u(m) < 2 \times 10^{-8}$  [18, 20]. Usually, national metrology institutes (NMIs) can use the spheres for laboratory intercomparison programmes of the mass. However, for industrial and economic purposes, this high level of enrichment is not necessary. PTB initiated a concept for the use of silicon spheres of three different categories (and thus uncertainty ranges associated with  $m$ ) for the dissemination of the mass [20]: (a)  $^{28}\text{Si}$ -primary Si spheres (highly enriched in  $^{28}\text{Si}$  as described), which are extremely expensive and need a time-consuming production, (b)  $^{\text{nat}}\text{Si}_{\text{qp}}$ -quasi-primary Si spheres, made of silicon with natural isotopic composition, and (c)  $^{\text{nat}}\text{Si}_{\text{sc}}$ -secondary Si spheres, the latter industrially manufactured. The uncertainties  $u(m)$  of the natural silicon spheres are in principal larger compared to the enriched spheres. One limiting factor of this increased uncertainty is the larger uncertainty associated with the molar mass of natural silicon  $M_x$  as outlined before. This was the motivation for the search and development of new analytical methods for the determination of the molar mass of silicon with the intention to further reduce the uncertainty using isotope ratio mass spectrometry. In this work, the current status of the different methods for the determination of  $M_x$  is described and compared with the aid of uncertainty calculations based on the “Guide to the Expression of Uncertainty in Measurement” (GUM) [21]. Figure 1 displays the isotopic composition in terms of  $x(^i\text{Si})$  of the different available silicon crystals highly enriched in  $^{28}\text{Si}$  in comparison with the distribution of natural silicon (according to IUPAC [22]).

Although the  $x(^{28}\text{Si})$  of both enriched ( $> 0.999\,9$  mol/mol) and natural ( $\approx 0.92$  mol/mol) silicon seem to be similar, the respective  $x(^{29}\text{Si})$  and  $x(^{30}\text{Si})$  of the enriched materials differ by several orders of magnitude from those of natural silicon.

## 2. Experiment and Materials

The determination of the molar mass  $M_x$  of crystalline silicon with natural isotopic composition is similar in sample preparation and isotope ratio mass spectrometry to the enriched material as described in detail elsewhere [14, 18, 23]. The different analytical methods are described in Sect. 3. Here, only a short summary of the main procedures is given.



**Fig. 1** Amount-of-substance fractions  $x(^{28}\text{Si})$ ,  $x(^{29}\text{Si})$ , and  $x(^{30}\text{Si})$  of different silicon crystals used for the XRCD method [18] compared to the isotopic composition of natural silicon [22]. The data of Si28-31Pr11 are of preliminary character

### 2.1. Reagents and Materials

The different methods—if experimentally tested—are carried out using a sample (500 mg) from a silicon single crystal with the code V3182 (PTB, Germany) with natural-like isotopic composition. This crystal was also used as calibration material for neutron activation analysis (NAA) for the measurement of  $x(^{30}\text{Si})$  in enriched silicon [24]. Calibration factors were always derived from the measurement of isotope ratios in samples of the WASO04 material with natural isotopic composition characterized in [14]. The characterization itself is extremely complex and time-consuming. It requires gravimetrically prepared solutions of highly enriched silicon materials of all three isotopes (so-called parent materials). From these, at least two binary blends need to be prepared. The intensity ratios  $^{30}\text{Si}/^{29}\text{Si}$  and  $^{28}\text{Si}/^{29}\text{Si}$  in all the blends and enriched parent materials have to be measured over several weeks to reach the necessary precision. These intensity ratios together with the accurate (buoyancy corrected) masses of the parent materials blended yielded the  $K$  factors needed to correct the above-mentioned ratios. This way, the isotope ratios in the WASO04 material were determined without any isotopic reference material, turning the WASO04 material itself into an isotopic reference material. The resulting uncertainties associated with the isotope ratios in WASO04 are low enough to determine the  $K$  factor needed for the molar mass measurement via the VE-IDMS method but too large for the direct measurement of the molar mass of any other natural silicon material. The WASO04 sample was cleaned and etched prior to weighing and dissolution in

aqueous tetramethylammonium hydroxide (TMAH), yielding a final mass fraction of the silicon sample solution  $w(\text{Si}) = 4 \mu\text{g/g}$  in  $w(\text{TMAH}) = 0.0006 \text{ g/g}$ .

### 2.2. Instrumentation

The molar mass measurements were performed using a high-resolution MC-ICP-MS (Neptune<sup>TM</sup>, Thermo Fisher Scientific GmbH, Bremen, Germany) with typical operating conditions given in [14, 17]. The samples are aqueous solutions which are introduced into the ion source as aerosols. An argon plasma serves as the ion source running at approximately 10 000 K. The necessary power of around 1200 W is inductively coupled into the plasma through a radio frequency generator running at 27 MHz. The ions are accelerated into the mass spectrometer and separated according to their mass over charge ratio by an electrostatic and subsequently a static magnetic field. The ion currents of the different masses are then simultaneously measured using an array of up to nine detectors. Prior to each sample measurement, a blank solution ( $w(\text{TMAH}) = 0.0006 \text{ g/g}$ ) was measured to correct for carryover effects. In a respective sequence, the sample ( $x$ ) was measured four times, then the blend(s) ( $bx$ ) is/are measured four times, and finally the WASO04 sample for the  $K$  factor determination was measured four times.

## 3. Analytical Methods for Molar Mass Determination

### 3.1. Classical Approach (MM A)—Direct Measurement of all three isotopes

The isotopic distribution in natural silicon is roughly:  $x(^{28}\text{Si}) = 0.92 \text{ mol/mol}$ ,  $x(^{29}\text{Si}) = 0.05 \text{ mol/mol}$ , and  $x(^{30}\text{Si}) = 0.03 \text{ mol/mol}$ . Therefore, a direct measurement of all three isotopes should yield reasonable signals and sensitivity. The molar mass is defined via

$$M_x = x_x(^{28}\text{Si})M(^{28}\text{Si}) + x_x(^{29}\text{Si})M(^{29}\text{Si}) + x_x(^{30}\text{Si})M(^{30}\text{Si}) \quad (3)$$

The index  $x$  denotes the respective sample (here: natural silicon V3182); the  $M(^i\text{Si})$  are the molar masses of the respective isotope taken from [25]. By measuring the intensity ratios and correcting them using the  $K$  factors measured within the same sequence, the following isotope ratios were determined

$$R_x = \frac{x_x(^{30}\text{Si})}{x_x(^{29}\text{Si})}; R_{x,28} = \frac{x_x(^{28}\text{Si})}{x_x(^{29}\text{Si})} \quad (4)$$

yielding

$$x(^i\text{Si}) = \frac{R_i}{\sum_{j=28}^{30} R_j} \tag{5}$$

3.2. Virtual Element VE-IDMS (MM B)—  
Measurement of <sup>29</sup>Si and <sup>30</sup>Si, One Blend  
with <sup>30</sup>Si-Enriched Silicon

This method is adopted from the molar mass determination developed for silicon highly enriched in <sup>28</sup>Si, where only the isotopes <sup>29</sup>Si and <sup>30</sup>Si (the virtual element) are measured [15]:

$$M_x = \frac{M(^{28}\text{Si})}{1 + \frac{m_y}{m_x} \times \frac{M(^{28}\text{Si}) \times (1+R_x) - M(^{29}\text{Si}) - R_x M(^{30}\text{Si})}{R_{y,28} M(^{28}\text{Si}) + M(^{29}\text{Si}) + R_y M(^{30}\text{Si})}} \times \frac{R_y - R_{bx}}{R_{bx} - R_x} \tag{6}$$

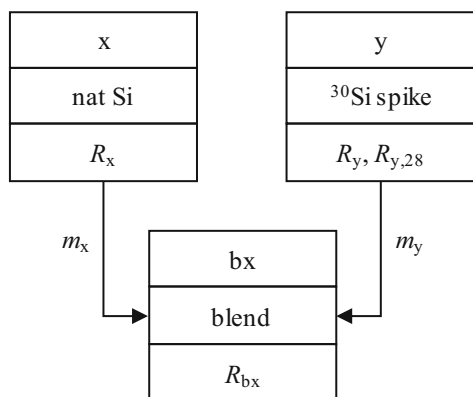
Here,  $m_y$  and  $m_x$  are the respective masses of the solid spike material y and sample material x (natural silicon) in the blend bx;  $R_j = x_j(^{30}\text{Si})/x_j(^{29}\text{Si})$  and  $R_{j,28} = x_j(^{28}\text{Si})/x_j(^{29}\text{Si})$ .

The measured intensity ratios  $R_j^{\text{meas}}$  of the materials x (natural silicon), y (silicon enriched in <sup>30</sup>Si), and bx (a blend of x and y) were corrected by the K factors  $K_{30}$  and  $K_{28}$  yielding the correct or “true” isotope ratios  $R_j^{\text{true}}$  (Fig. 2)

$$R_j^{\text{true}} = K_{30} \times R_j^{\text{meas}} \quad \text{with} \quad R_j^{\text{meas}} = \frac{I_j(^{30}\text{Si})}{I_j(^{29}\text{Si})} \quad \text{and} \tag{7}$$

$j \in \{x, y, bx\}$

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



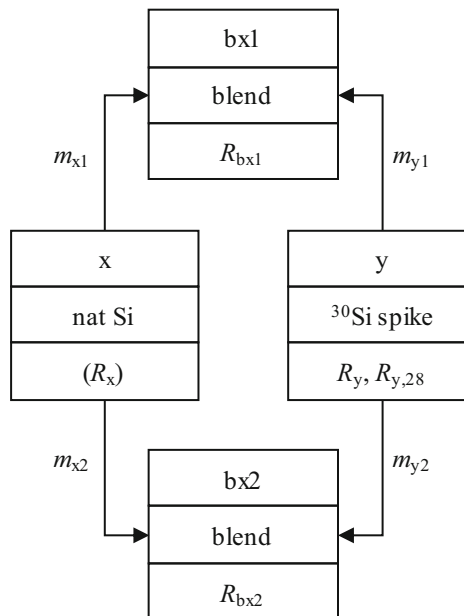
**Fig. 2** Mixing scheme in the case of the original VE-IDMS approach (MM B). For details refer to [15]

3.3. Double VE-IDMS (MM C)—Measurement of <sup>29</sup>Si  
and <sup>30</sup>Si, Two Blends with <sup>30</sup>Si-Enriched Silicon

This method is a further development of the MM B approach (3.2). When applying the VE-IDMS method using enriched silicon samples, the measurement of the isotope ratios in the sample x is difficult due to the extremely low abundance of <sup>29</sup>Si and especially <sup>30</sup>Si. Therefore, a second blend bx2 was prepared with isotope ratios  $x(^{30}\text{Si})/x(^{29}\text{Si})$  slightly different from those in bx1 and according to Eq. (9), the measurement of  $R_x$  is now obsolete.

$$M_x = \frac{M(^{28}\text{Si})}{1 + \frac{[M(^{28}\text{Si}) - M(^{29}\text{Si})] \times \left[ \frac{m_{y1}}{m_{x1}} [R_{bx1} - R_y] + \frac{m_{y2}}{m_{x2}} [R_y - R_{bx2}] \right] + [M(^{28}\text{Si}) - M(^{30}\text{Si})] \times \left[ \frac{m_{y1}}{m_{x1}} R_{bx2} [R_{bx1} - R_y] + \frac{m_{y2}}{m_{x2}} R_{bx1} [R_y - R_{bx2}] \right]}{[R_{y,28} M(^{28}\text{Si}) + M(^{29}\text{Si}) + R_y M(^{30}\text{Si})] \times [R_{bx2} - R_{bx1}]} \tag{9}$$

In contrast to approach MM B (Sect. 3.2), here two additional masses,  $m_{y2}$  and  $m_{x2}$ , have to be determined gravimetrically (the respective masses of the solid spike material y and sample material x in the second blend bx2) (Fig. 3).



**Fig. 3** Mixing scheme in the case of the double VE-IDMS approach (MM C). The preparation of a second blend bx2 renders the measurement of  $R_x$  obsolete

3.4. VE-IDMS (MM D)—Two-Step Blending of the Natural Silicon with <sup>28</sup>Si- and <sup>30</sup>Si-Enriched Silicon, Retracing  $M_x$

After the application of the VE-IDMS method to several silicon crystals with different enrichment in <sup>28</sup>Si and additional simulations (calculating  $u_{rel}(M)$  with increasing  $x(^{28}\text{Si})$ ), it became an apparent postulate that (theoretically) the higher the  $x(^{28}\text{Si})$  the smaller the  $u_{rel}(M)$ . The quintessence of this idea was to prepare a pre-mixture of the natural silicon sample (x) with silicon enriched in <sup>28</sup>Si (e) with an already known molar mass  $M_e$ . This blend was then handled as the “sample” (ex) in a subsequent VE-IDMS measurement. The “sample” (ex) consists of known amounts (masses) of natural silicon ( $m_x$ ) and silicon enriched in <sup>28</sup>Si ( $m_e$ ). Subsequently, a known mass  $m_{ex}$  of this “sample” was then mixed with the spike material (y), silicon highly enriched in <sup>30</sup>Si, to form the blend bx. The molar mass  $M_{ex}$  of the pre-blend was determined according to Eq. (10) analogue to Eq. (6).

$$M_{ex} = \frac{M(^{28}\text{Si})}{1 + \frac{m_y}{m_{ex}} \times \frac{M(^{28}\text{Si}) \times (1+R_{ex}) - M(^{29}\text{Si}) - R_{ex} \times M(^{30}\text{Si})}{R_{y,28} \times M(^{28}\text{Si}) + M(^{29}\text{Si}) + R_y \times M(^{30}\text{Si})}} \times \frac{R_y - R_{bx}}{R_{bx} - R_{ex}} \quad (10)$$

Since the masses of natural  $m_x$  and enriched silicon  $m_e$  in this blend (ex) and the molar mass  $M_e$  of the enriched silicon component are known, the molar mass of the natural silicon  $M_x$  can be calculated using the following relation (Fig. 4):

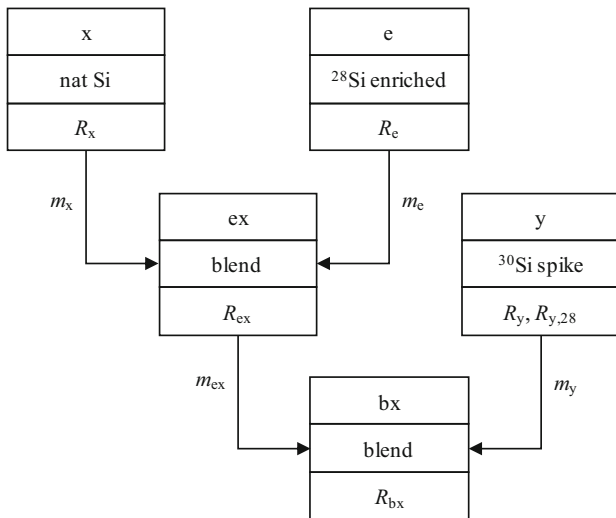


Fig. 4 Mixing scheme in the case of the VE-IDMS approach (MM D) applied to a pre-blend (ex) of the natural sample (x) and <sup>28</sup>Si-enriched silicon (e)

$$M_x = \left[ \frac{1}{M_{ex}} \times \left( \frac{m_e}{m_x} + 1 \right) - \frac{1}{M_e} \times \frac{m_e}{m_x} \right]^{-1} \quad (11)$$

3.5. Double VE-IDMS (MM E)—Two-Step Blending of the Natural Silicon with <sup>28</sup>Si- and <sup>30</sup>Si-Enriched Silicon, Retracing  $M_x$ , No Knowledge of  $M_e$  and  $R_e$  Necessary

This procedure is a combination of 3.4 and 3.3 and thus a further development of 3.4. Method MM D requires the *a priori* knowledge of the molar mass  $M_e$  of the enriched silicon material. In the method MM E, the molar mass  $M_e$  is expressed by the molar mass of a second blend  $M_{ex2}$  so that the initial knowledge of  $M_e$  and  $R_e$  becomes obsolete. Thus, two pre-blends ex1 and ex2 have to be prepared consisting of the natural silicon sample ( $M_x$ ) and a silicon material highly enriched in <sup>28</sup>Si (e) with an unknown molar mass  $M_e$ . From each of these two pre-blends, subsequently two VE-IDMS blends bx1 and bx2 have to be prepared by mixing known amounts  $m_{ex1}$  and  $m_{ex2}$  of the pre-blends with silicon enriched in <sup>30</sup>Si (with known masses  $m_{y1}$  and  $m_{y2}$ ). It is recommended to prepare blends with slightly different ratios ( $R_{bx1} < 1 < R_{bx2}$  or *vice versa*). By applying the VE-IDMS principle to these blends, the molar masses  $M_{ex1}$  and  $M_{ex2}$  in the pre-blends are determined according to Eqs. (12) and (13):

$$M_{ex1} = \frac{M(^{28}\text{Si})}{1 + \frac{m_{y1}}{m_{ex1}} \times \frac{M(^{28}\text{Si}) \times (1+R_{ex1}) - M(^{29}\text{Si}) - R_{ex1} \times M(^{30}\text{Si})}{R_{y,28} \times M(^{28}\text{Si}) + M(^{29}\text{Si}) + R_y \times M(^{30}\text{Si})}} \times \frac{R_y - R_{bx1}}{R_{bx1} - R_{ex1}} \quad (12)$$

$$M_{ex2} = \frac{M(^{28}\text{Si})}{1 + \frac{m_{y2}}{m_{ex2}} \times \frac{M(^{28}\text{Si}) \times (1+R_{ex2}) - M(^{29}\text{Si}) - R_{ex2} \times M(^{30}\text{Si})}{R_{y,28} \times M(^{28}\text{Si}) + M(^{29}\text{Si}) + R_y \times M(^{30}\text{Si})}} \times \frac{R_y - R_{bx2}}{R_{bx2} - R_{ex2}} \quad (13)$$

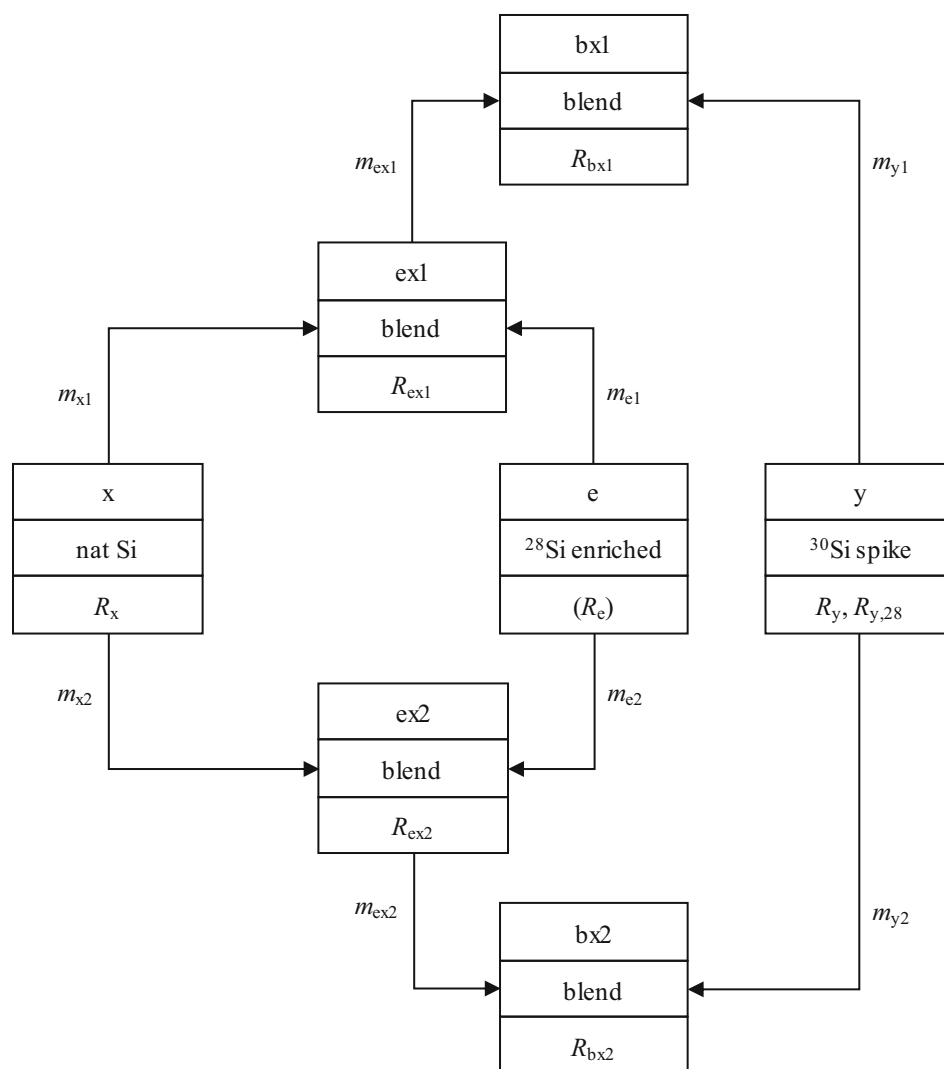
Additionally, the masses of the components of natural silicon ( $m_{x1}$ ,  $m_{x2}$ ) and silicon enriched in <sup>28</sup>Si ( $m_{e1}$ ,  $m_{e2}$ ) in the pre-blends have to be known. The molar mass  $M_x$  of the natural silicon sample is calculated according to eq. (14) using  $M_{ex1}$  and  $M_{ex2}$  from Eqs. (12) and (13) (Fig. 5):

$$M_x = \frac{\frac{m_{e2}}{m_{x2}} - \frac{m_{e1}}{m_{x1}}}{\frac{1}{M_{ex1}} \frac{m_{e2}}{m_{x2}} \left( \frac{m_{e1}}{m_{x1}} + 1 \right) - \frac{1}{M_{ex2}} \frac{m_{e1}}{m_{x1}} \left( \frac{m_{e2}}{m_{x2}} + 1 \right)} \quad (14)$$

4. Results and Discussion

The results of the different methods developed and applied for the determination of the molar mass of silicon with natural isotopic composition of the crystal V3182 are displayed in Fig. 6 and listed in Table 1. As a guideline for

**Fig. 5** Mixing scheme in the case of the double VE-IDMS approach (MM E) applied to two pre-blends (ex1 and ex2) of the natural sample (x) and  $^{28}\text{Si}$ -enriched silicon (e)



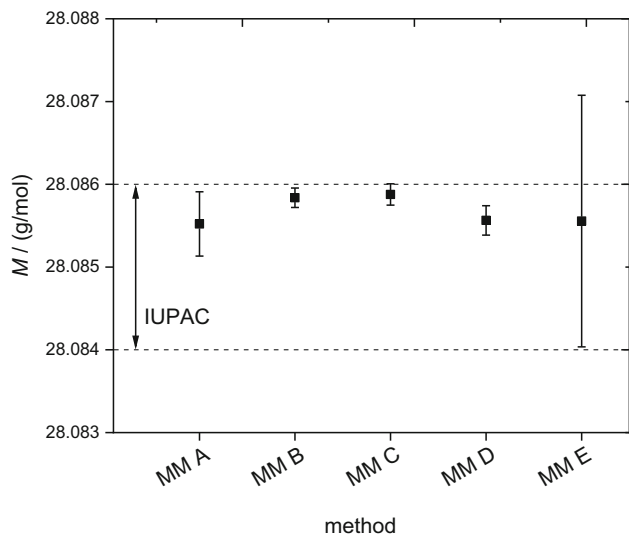
**Table 1** Molar mass results of the sample V3182 (with natural isotopic composition) determined with the several analytical methods (MM A–MM E) compared to the IUPAC range of values [26]

Method	$M/(\text{g/mol})$	$u(M)/(\text{g/mol})$	$u_{\text{rel}}(M) \times 10^{-6}$	Section
IUPAC	[28.084 ... 28.086]	–	–	Ref. [26]
MM A	28.08552	0.000 39	14	3.1
MM B	28.08584	0.000 12	4.2	3.2
MM C	28.08588	0.000 13	4.6	3.3
MM D	28.08556	0.000 18	6.3	3.4
MM E	28.085 6	0.001 5	54	3.5

the absolute order of magnitude, the range of molar mass values of natural silicon reported by IUPAC-CIAAW is plotted [26].

Within the limits of uncertainties, all results of  $M$  agree, although the respective uncertainties associated with

$M$  cover a range of more than one order of magnitude depending on the analytical method applied. The range of the molar mass reported by IUPAC was taken from the 2016 publication [26]. The IUPAC range dates back to 2009 recommended by the CIAAW (Commission on Isotopic Abundances and Atomic Weights) including long-term fractionation of silicon in natural environment which aids as an appropriate guideline for a molar mass value of an artificial silicon crystal material with almost natural composition as in the case of the V3182 crystal. The direct determination of all three amount-of-substance fractions  $x(\text{Si})$  via the measurement of the isotope ratios (MM A, classical approach, Sect. 3.1) according to Eq. (4) yields  $u_{\text{rel}}(M_x) = 1.4 \times 10^{-5}$ , which is at least three orders of magnitude too large to be suitable for the XRCD method. Table 2 contains an uncertainty budget for the V3182 sample according to MM A using the GUM Workbench Pro<sup>TM</sup> software (version 2.4.1 392, Metrodata GmbH, Germany) according to Eqs. (3)–(5).



**Fig. 6** Comparison of the molar mass results of the sample V3182 (with natural isotopic composition) determined with the several analytical methods (MM A–MM E) compared to the range of the IUPAC average molar mass of silicon (dashed black lines) [26]. The different methods are described in Sects. 3.1–3.5. Error bars denote combined uncertainties with  $k = 1$

$R_{w,28}$  and  $R_w$  (the corrected isotope ratios  $x(^{28}\text{Si})/x(^{29}\text{Si})$  and  $x(^{30}\text{Si})/x(^{29}\text{Si})$ ), in the “calibration” material (natural silicon, WASO04), have the largest impact on  $u_c(M)$  with 85.5% and 8.5%, respectively. No direct measured quantity of the sample has a significant impact on  $u_c(M_x)$ . The relative standard uncertainties  $u_{\text{rel}}(R_x^{\text{meas}})$  and  $u_{\text{rel}}(R_{x,28}^{\text{meas}})$  range in the order of 0.0003 ...0.0004 as a consequence of the high repeatability of the MC-ICP-MS measurements.

The smallest possible relative uncertainty associated with  $M_x$  was  $u_{\text{rel}}(M_x) = 4.2 \times 10^{-6}$  when using the method MM B—the VE-IDMS method—originally developed for enriched silicon directly applied on the natural silicon

sample (Sect. 3.2). This method was already validated in the long term during the determination of molar masses of enriched silicon [14, 15, 17, 18]. A representative uncertainty budget of the molar mass of the V3182 crystal determined with the VE-IDMS method is given in the left-hand side of Table 3. The main contributions originate from  $R_w$  and  $R_y$  with 69% and 27%. In this budget,  $u_{\text{rel}}(M_x)$  is  $4.2 \times 10^{-6}$ —approximately three orders of magnitude larger than in the case of Si enriched in  $^{28}\text{Si}$ . On the right-hand side of Table 3, a representative budget of the crystal Si28-23Pr11 ( $x(^{28}\text{Si}) > 0.999\ 99$  mol/mol) shows the sensitivity coefficients and indices of the respective input quantities with  $u_{\text{rel}}(M_x) = 1.4 \times 10^{-9}$  [17]. In the case of the enriched silicon, the main uncertainty contributions stem from the same or similar input quantities as in the case of the natural silicon. However, the sensitivity coefficients (partial derivatives) differ significantly by several orders of magnitude which might finally explain the strongly reduced uncertainty in the case of enriched silicon when using the VE-IDMS method (MM B).

In contrast to the original VE-IDMS method (MM B), the further developed method (MM C) did not yield a further reduced  $u_{\text{rel}}(M_x)$ . According to Table 1,  $u_{\text{rel}}(M_x) = 4.6 \times 10^{-6}$  is slightly increased, although the measurement of  $R_x$  in the sample is now obsolete. This elevated uncertainty is suggested to be induced by an increasing number of the measurands (MM B: 5 measurands; MM C: 7 measurands).

One semi-quantitative, but central result of the molar mass determinations of enriched silicon was the inverse proportionality of enrichment  $x(^{28}\text{Si})$  and  $u(M)$  when using the VE-IDMS method (MM B) [17]. Therefore, it would be necessary to investigate the relation between  $x(^{28}\text{Si})$ —the “enrichment”—and the respective  $u_{\text{rel}}(M)$  more quantitatively. A first glance simulation was carried out using

**Table 2** Uncertainty budget of a single selected molar mass determination of the sample V3182 (with natural isotopic composition) determined with the classical method MM A. Molar masses of Si isotopes are taken from [25]

Quantity	Unit	Best estimate (value)	Standard uncertainty	Sensitivity coefficient	Index
$X_i$	$[X_i]$	$x_i$	$u(x_i)$	$c_i$	
$M(^{28}\text{Si})$	g/mol	27.9769265350	$500 \times 10^{-12}$	0.92	0.0%
$M(^{29}\text{Si})$	g/mol	28.9764946653	$600 \times 10^{-12}$	0.047	0.0%
$M(^{30}\text{Si})$	g/mol	29.9737701370	$23.0 \times 10^{-9}$	0.031	0.0%
$R_x^{\text{meas}}$	V/V	0.703120	$222 \times 10^{-6}$	0.083	0.2%
$R_{x,28}^{\text{meas}}$	V/V	18.50021	$7.61 \times 10^{-3}$	$- 5.4 \times 10^{-3}$	1.1%
$R_w$	mol/mol	0.66230	$1.32 \times 10^{-3}$	0.088	8.5%
$R_w^{\text{meas}}$	V/V	0.702920	$801 \times 10^{-6}$	- 0.083	2.8%
$R_{w,28}$	mol/mol	19.7266	0.0730	$- 5.1 \times 10^{-3}$	85.5%
$R_{w,28}^{\text{meas}}$	V/V	18.4995	0.0103	$5.4 \times 10^{-3}$	1.9%
$Y$	$[Y]$	$y$	$u_c y$		
$M_x$	g/mol	28.085504	$401 \times 10^{-6}$		

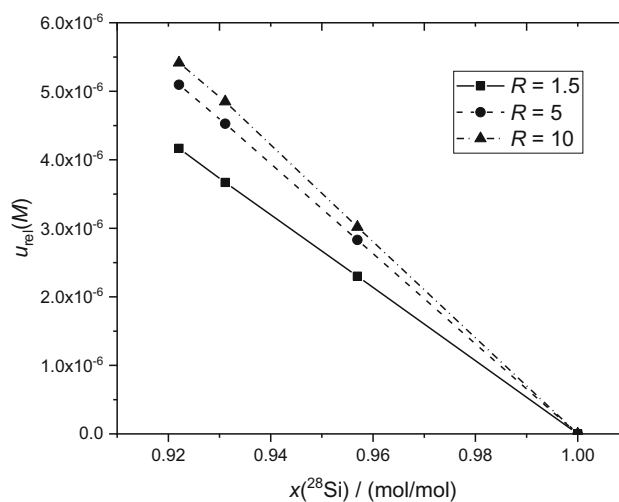
**Table 3** Uncertainty budget of a single selected molar mass determination of the sample V3182 (with natural isotopic composition) determined with the VE-IDMS method (MM B, left-hand side)

Quantity	Unit	Natural Si (V3182)				Enriched Si	
		Best estimate (value)	Standard uncertainty	Sensitivity coefficient	Index	Sensitivity coefficient	Index
$X_i$	$[X_i]$	$x_i$	$u(x_i)$	$c_i$	%	$c_i$	%
$M(^{28}\text{Si})$	g/mol	27.9769265350	$500 \times 10^{-12}$	0.93	0.0	1.0	0.0
$m_y$	g	$30.78200 \times 10^{-6}$	$3.86 \times 10^{-9}$	3600	1.3	2.4	0.3
$m_x$	g	$149.80900 \times 10^{-6}$	$1.36 \times 10^{-9}$	-730	0.0	$-120 \times 10^{-6}$	0.0
$M(^{29}\text{Si})$	g/mol	28.9764946653	$600 \times 10^{-12}$	0.047	0.0	$15 \times 10^{-6}$	0.0
$M(^{30}\text{Si})$	g/mol	29.973770137	$23.0 \times 10^{-9}$	0.028	0.0	$54 \times 10^{-9}$	0.0
$R_{y,28}$	mol/mol	1.5855	0.0222	$-380 \times 10^{-6}$	0.5	$-56 \times 10^{-9}$	0.1
$R_y$	mol/mol	269.04	5.65	$11 \times 10^{-6}$	26.8	$1.2 \times 10^{-9}$	3.1
$R_x^{\text{meas}}$	V/V	0.6976500	$98.6 \times 10^{-6}$	0.12	0.9	$33 \times 10^{-6}$	10.3
$R_{\text{bx}}^{\text{meas}}$	V/V	4.905250	$553 \times 10^{-6}$	-0.026	1.5	$-5.1 \times 10^{-6}$	23.1
$R_w$	mol/mol	0.66230	$1.32 \times 10^{-3}$	-0.074	68.8	$-23 \times 10^{-6}$	60.7
$R_w^{\text{meas}}$	V/V	0.6973100	$58.0 \times 10^{-6}$	0.070	0.1	$21 \times 10^{-6}$	2.4
$Y$	[Y]	$y$	$u_c(y)$				
$M_x$	g/mol	28.085900	$118 \times 10^{-6}$				

Molar masses of Si isotopes are taken from [25]. For comparison, the sensitivity coefficients and the “index” (relative uncertainty contribution of the respective input quantity to the uncertainty of the molar mass of the sample) of a highly enriched silicon sample (Si28-23Pr11 with  $x(^{28}\text{Si}) > 0.99999$  mol/mol [17]) are listed on the right-hand side

Excel<sup>TM</sup> and the GUM Workbench Pro<sup>TM</sup> software. In this simulation, the  $x(^{28}\text{Si})$  were changed in the range  $0.922079 \text{ mol/mol} \leq x(^{28}\text{Si}) \leq 0.999990 \text{ mol/mol}$ .  $R_w^{\text{meas}}$ ,  $R_x^{\text{meas}}$ ,  $R_{\text{bx}}^{\text{meas}}$ , and their associated standard uncertainties were kept constant. The respective molar mass and its associated uncertainty was calculated for three isotope ratios  $x(^{29}\text{Si})/x(^{30}\text{Si}) = 1.5, 5, \text{ and } 10$ . The starting values  $x(^{28}\text{Si}) = 0.922079 \text{ mol/mol}$  with  $x(^{29}\text{Si})/x(^{30}\text{Si}) = 1.5$  were chosen, because these are the respective values of natural silicon. The intention was to find a range of  $x(^{28}\text{Si})$  where the respective  $u_{\text{rel}}(M)$  falls below a value of  $1 \times 10^{-7}$ . Figure 7 shows the rough course of  $u_{\text{rel}}(M)$  vs  $x(^{28}\text{Si})$  for the ratios  $x(^{29}\text{Si})/x(^{30}\text{Si}) = 1.5, 5, \text{ and } 10$ .

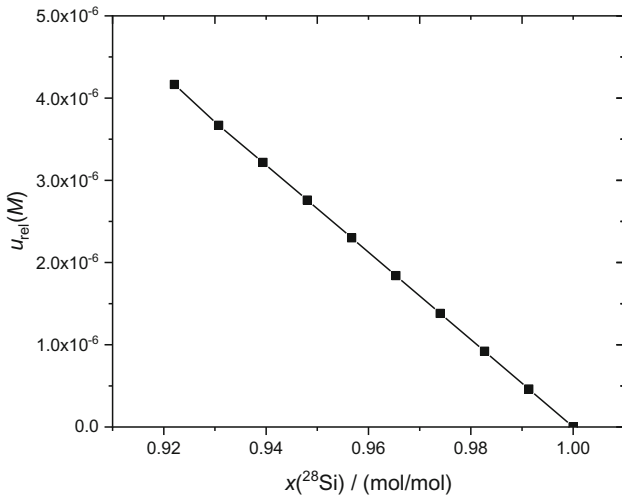
An almost linear decrease in  $u_{\text{rel}}(M)$  with  $x(^{28}\text{Si})$  can be observed. However, the ratios  $x(^{29}\text{Si})/x(^{30}\text{Si})$  do not play that important role as assumed in the past. Recent experimental investigations of enriched silicon crystals with different ratios support the finding that the enrichment and not the ratios  $x(^{29}\text{Si})/x(^{30}\text{Si})$  are mainly responsible for the small  $u_{\text{rel}}(M)$  [18]. Therefore, we concentrated on the changes of  $u_{\text{rel}}(M)$  as a function of  $x(^{28}\text{Si})$  only, using a natural-like ratio of 1.5. Figure 8 shows the development of  $u_{\text{rel}}(M)$  with a stepwise increase in  $x(^{28}\text{Si})$ . It is obvious that it is necessary to have at least an enrichment of  $x(^{28}\text{Si}) > 0.98 \text{ mol/mol}$  to fall below  $u_{\text{rel}}(M) = 1 \times 10^{-7}$ . A clearer result is shown in Fig. 9: between the two last data points ( $x(^{28}\text{Si}) = 0.991333 \text{ mol/mol}$  and  $x(^{28}\text{Si}) = 0.999990 \text{ mol/mol}$ ),  $u_{\text{rel}}(M)$  drops down drastically from  $4.6 \times 10^{-7}$  to  $5.3 \times 10^{-10}$ : three orders of magnitude.

**Fig. 7** Comparison of  $u_{\text{rel}}(M)$  vs  $x(^{28}\text{Si})$  for three different ratios  $x(^{29}\text{Si})/x(^{30}\text{Si}) = 1.5, 5, \text{ and } 10$  (for details see text)

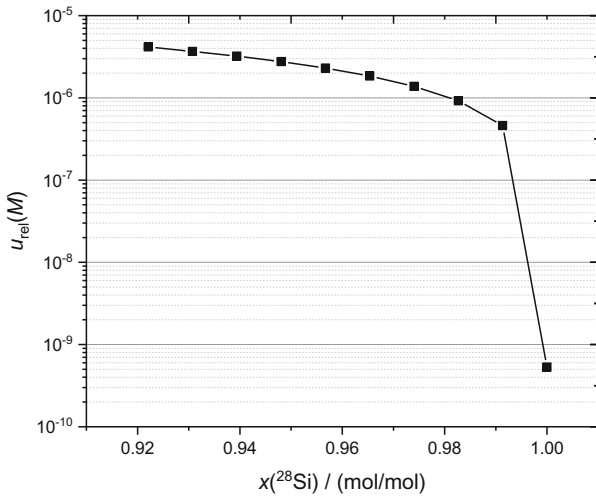
As a central result of this simulation, it can be concluded that simply an enlarged  $x(^{28}\text{Si}) (> 0.99 \text{ mol/mol})$  should be a key for  $u_{\text{rel}}(M) < 10^{-7}$  or less.

With this knowledge in mind, the idea came up to prepare a pre-blend (ex) of the sample (natural silicon) and silicon material enriched in  $^{28}\text{Si}$ . The molar mass and its associated uncertainty of this blend determined using the VE-IDMS method should be smaller than that of the pure natural silicon due to the higher enrichment of the blend. Knowing the molar mass of the enriched component ( $M_e$  in eq. (11)) from previous investigations and the masses  $m_e$





**Fig. 8** Comparison of  $u_{rel}(M)$  vs  $x(^{28}\text{Si})$  for  $x(^{29}\text{Si})/x(^{30}\text{Si}) = 1.5$  (for details see text)

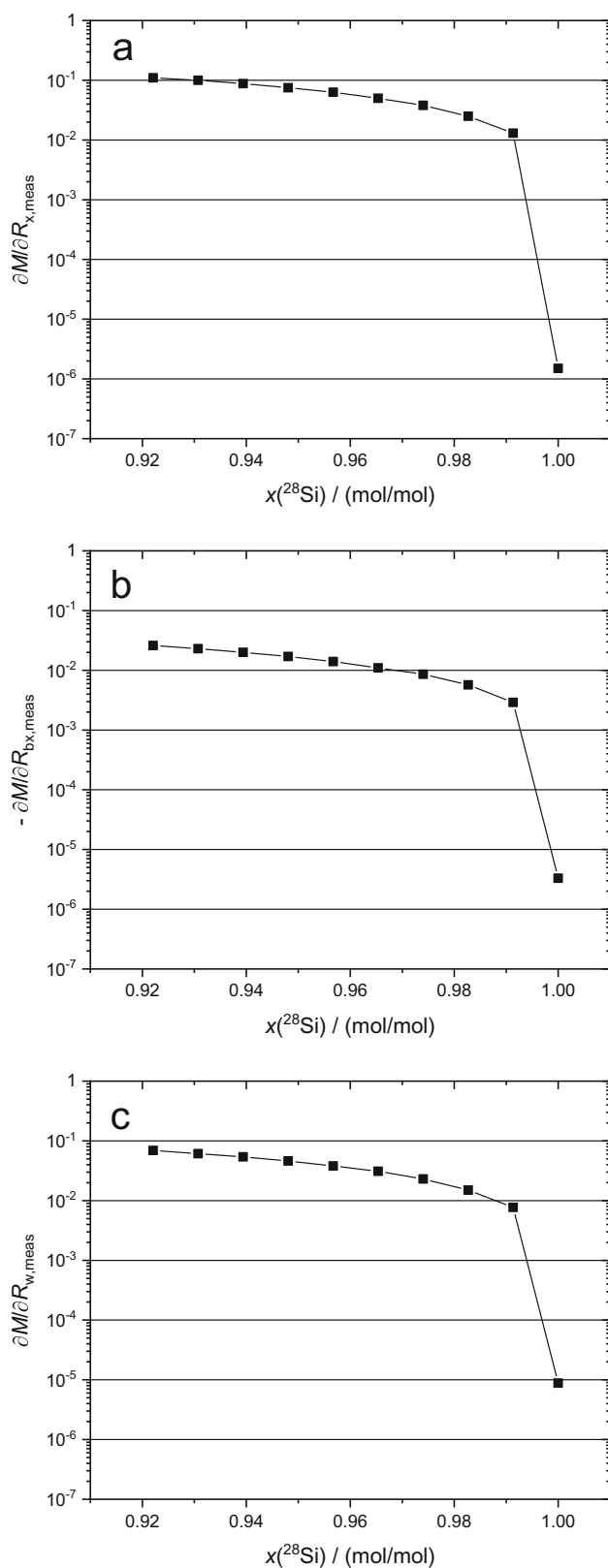


**Fig. 9** Same as Fig. 8 with  $u_{rel}(M)$  on a logarithmic scale

and  $m_x$  of the components in the pre-blend, it should be possible to recalculate the molar mass  $M_x$  of the natural silicon sample—hopefully with a reduced  $u_{rel}(M_x)$ . This is the idea behind method MM D (Sect. 3.4). Unfortunately, the application of this method (MM D, Sect. 3.4) did not succeed in a reduction of  $u_{rel}(M_x)$ . Instead,  $u_{rel}(M_x)$  increased to  $6.3 \times 10^{-6}$ , approximately 50% larger than applying the original VE-IDMS method (MM B). Table 4 shows a representative uncertainty budget of the molar mass of a natural silicon sample (V3182) using method MM D. The main contributions are  $R_{ex}^{meas}$ , the measured intensity ratio of  $x(^{30}\text{Si})/x(^{29}\text{Si})$  with 41% in the blend of natural silicon (x) and enriched silicon (e), followed by the contributions of  $R_w$  (29%) for the  $K$  factor calculation, and  $R_{bx}^{meas}$  with 26% which is measured in the blend bx of

**Table 4** Uncertainty budget of a single selected molar mass determination of the sample V3182 (with natural isotopic composition) determined with method (MM D, Sect. 3.4) according to model Eqs. (10) and (11). Molar masses of Si isotopes are taken from [25]

Quantity $X_i$	Unit $[X_i]$	Best estimate (value) $x_i$	Standard uncertainty $u(x_i)$	Sensitivity coefficient $c_i$	Index
$m_e$	g	0.13760484	$1.25 \times 10^{-6}$	0.73	0.0%
$m_x$	g	0.012395155	$113 \times 10^{-9}$	- 8.1	0.0%
$M_e$	g/mol	27.9769426664	$40.0 \times 10^{-9}$	- 11	0.0%
$M(^{28}\text{Si})$	g/mol	27.9769265350	$500 \times 10^{-12}$	12	0.0%
$m_y$	g	$17.471000 \times 10^{-6}$	$159 \times 10^{-12}$	6300	0.0%
$m_{ex}$	g	0.012267632	$112 \times 10^{-9}$	- 8.9	0.0%
$M(^{29}\text{Si})$	g/mol	28.9764946653	$600 \times 10^{-12}$	0.047	0.0%
$M(^{30}\text{Si})$	g/mol	29.9737701370	$23.0 \times 10^{-9}$	0.028	0.0%
$R_{y,28}$	mol/mol	1.5855	0.0222	- $380 \times 10^{-6}$	0.2%
$R_y$	mol/mol	269.04	5.65	$5.2 \times 10^{-6}$	2.7%
$R_w$	mol/mol	0.66230	$1.32 \times 10^{-3}$	- 0.072	28.7%
$R_w^{meas}$	V/V	0.662302	$293 \times 10^{-6}$	0.072	1.4%
$R_{ex}^{meas}$	V/V	0.660325	$272 \times 10^{-6}$	0.42	40.6%
$R_{bx}^{meas}$	V/V	1.000000	$282 \times 10^{-6}$	- 0.32	26.3%
$Y$	[Y]	y	$u_c(y)$		
$M_x$	g/mol	28.085556	$177 \times 10^{-6}$		



**Fig. 10** Evolution of sensitivity coefficients: a)  $\partial M / \partial R_{x,\text{meas}}$ , b)  $-\partial M / \partial R_{bx,\text{meas}}$ , and c)  $\partial M / \partial R_{w,\text{meas}}$ , as a function of the enrichment  $x(^{28}\text{Si})$  applied for the VE-IDMS method (MM B, Sect. 3.2, eq. (6))

natural (x) and enriched silicon (e) spiked with silicon (y) enriched in  $^{30}\text{Si}$ .

Method MM E [Sect. 3.5, Eqs. (12)–(14)] yields an even worse result:  $u_{\text{rel}}(M_x) = 5.4 \times 10^{-5}$ , which is at least one order of magnitude larger than after applying the original VE-IDMS method (MM B). Again, this degradation can be explained by an increased number of measured input quantities. At this point, the application of the VE-IDMS method (MM B) yields the smallest uncertainty associated with  $M_x$ . However,  $u_{\text{rel}}(M_x)$ —in the lower  $10^{-6}$  range—is still too large to use natural silicon as a sphere material in the XRC method on a primary dissemination level.

What are the reasons—or is the reason—for this comparable elevated uncertainty associated with  $M$  in the case of silicon with natural isotopic composition compared to silicon highly enriched in  $^{28}\text{Si}$ ? Since the VE-IDMS method (MM B) yields the smallest  $u_{\text{rel}}(M_x)$ , it was analysed in more detail. Table 3 shows that the sensitivity coefficients

$$u_c^2(y) = \sum_{i=1}^N \left( \frac{\partial M_x}{\partial x_i} \right)^2 \times u^2(x_i) \quad (15)$$

(partial derivatives, second term in Eq. (15)) are significantly different when setting up an uncertainty budget for the molar mass [according to Eq. (6)] of enriched or natural silicon. Figure 10 displays the evolution of the respective partial derivatives: (a)  $\partial M / \partial R_x^{\text{meas}}$ , (b)  $-\partial M / \partial R_{bx}^{\text{meas}}$ , and (c)  $\partial M / \partial R_w^{\text{meas}}$  with increasing enrichment  $x(^{28}\text{Si})$ .

The three intensity ratios (bias corrected: isotope ratios) are the only quantities being measured (except the masses of the blend components) in the VE-IDMS method and should thus probably be influenced by a controlled improvement in the experiment. The respective standard uncertainties  $u(R_x^{\text{meas}})$ ,  $u(R_{bx}^{\text{meas}})$ , and  $u(R_w^{\text{meas}})$  are kept constant for each  $x(^{28}\text{Si})$  in this simulation. They do not influence  $u(M)$  in a comparable way and can be neglected in this comparison. When analysing the evolution of the three sensitivity coefficients, the largest change can be observed for  $R_x^{\text{meas}}$  ranging over five orders of magnitude (Fig. 10). This is one of the key factors for the strongly decreased uncertainty associated with  $M$  when using enriched instead of natural silicon. As stated above, from the experimental point of view, the measurement of isotope ratios in natural silicon is much easier due to the significantly higher abundance of  $^{29}\text{Si}$  and  $^{30}\text{Si}$  which directly improves the respective repeatability and standard uncertainties of the measured intensity ratios. Nevertheless, from the evolution of the sensitivity coefficients of the main measurands with increasing enrichment, it is suggested at this stage that the isotopic composition itself—either in the natural or in the enriched material—influences the

sensitivity coefficients most efficiently which will finally determine the combined uncertainty associated with the molar mass.

## 5. Conclusion

One primary method of the realization and dissemination of the kilogram and mole is the XRCD method using silicon spheres highly enriched in  $^{28}\text{Si}$ . To promote a broader application of this method, the use of silicon with a natural isotopic composition would cut the costs of the spheres dramatically at the disadvantage of an elevated uncertainty. We have developed several new analytical methods based on the VE-IDMS method which is applied for enriched silicon in combination with  $K$  factor determination to reduce the uncertainty associated with the molar mass. The methods are compared by analysing the uncertainty budgets with respect to  $u(M_x)$ . Currently, the best method is still the original VE-IDMS method yielding  $u_{\text{rel}}(M_x)$  in the lower  $10^{-6}$  range, which is about three orders of magnitude larger than in the case of Si enriched in  $^{28}\text{Si}$ . Simulations were carried out to investigate the evolution of  $u_{\text{rel}}(M)$  as a function of  $x(^{28}\text{Si})$ . For the time being, it seems that an enrichment of  $x(^{28}\text{Si}) > 0.99$  mol/mol is an unconditional requirement for obtaining an uncertainty associated with the molar mass of  $u_{\text{rel}}(M) \leq 10^{-7}$ . The improvement in experimental designs to optimize the repeatability to reduce the standard uncertainties did not reduce  $u_{\text{rel}}(M_x)$ . A central observation of this study is the strong influence of the sensitivity coefficients especially of the main measurands in the VE-IDMS method when comparing natural and enriched silicon. It is suggested at this stage that the impact on the sensitivity coefficients and thus the final uncertainty  $u_{\text{rel}}(M)$  is based on intrinsic properties of the crystal material, e.g. the amount-of-substance fractions impacting the uncertainty modelling in a serious manner. Further theoretical and experimental efforts are under way.

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