



Novel concept for the mass spectrometric determination of absolute isotopic abundances with improved measurement uncertainty: Part 1 – theoretical derivation and feasibility study

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ABSTRACT

The development of a new method for the experimental determination of absolute isotopic abundances using a modified isotope dilution mass spectrometry (IDMS) technique is described. The intention and thus main application will be the quantification of molar masses M of highly enriched materials with improved measurement uncertainty ($U_{\text{rel}}(M) \approx 10^{-8}$ with $k=2$). In part 1 of the current work, the theoretical foundation of the new method and its mathematical derivation is shown in detail, while part 2 will cover the experiments based on the new method described. Its core idea is the introduction of a *virtual element* (VE) consisting of all isotopes but the one having the largest or smallest abundance. IDMS is used to determine the mass fraction of this VE in its matrix, namely the element itself. A new set of equations serve to calculate all isotopic abundances (even the large one omitted with the introduction of the VE) merely from the mass fraction of the VE. A comprehensive uncertainty budget according to the *Guide to the Expression of Uncertainty in Measurement* (GUM) was set up in order to discuss and validate the novel concept. The hypothetical input data of the uncertainty budget were estimated to resemble a silicon material highly enriched with respect to ^{28}Si used in the context of the international *Avogadro Project*. Considering the calculated results, the experimental determination of the molar mass of the above mentioned silicon seems very promising. As far as the authors know, this will be the first time IDMS was applied to determine a molar mass.

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1. Introduction

Isotope dilution mass spectrometry (IDMS) is widely accepted for its ability to determine analyte contents in nearly all possible matrices both highly precise and accurate (in other words with a small measurement uncertainty). Meanwhile, IDMS is established as a primary method in analytical chemistry [1]. Only isotope ratios and masses have to be measured. The IDMS model equation is highly symmetric and therefore, mass bias effects, sample losses, matrix effects or recovery problems virtually have no impact on the final result [2–8].

The intention of the International Avogadro Project is the redefinition of the SI unit of the mass – the kilogram – by the exact determination of fundamental constants: the Avogadro constant

(N_A) and the Planck constant (h). To achieve this the relative measurement uncertainty of N_A has to be reduced below 2×10^{-8} . The history and methods in this context are well described [9–16]. The latest approach to determine N_A on the desired level of uncertainty is related to the exact measurement of the molar mass of an artificial silicon material, which is highly enriched in the ^{28}Si isotope ($x(^{28}\text{Si}) > 99.98\%$). A relative measurement uncertainty in the order of magnitude of 10^{-8} associated with this very molar mass is required. The molar mass determination is done by measuring the absolute isotope ratios using mass spectrometry. Doing it the established usual way, in the enriched silicon material isotope ratios far away from unity in the order of 10^{-5} have to be determined which causes a lot of difficulties, due to several issues like detector linearity, dynamic range etc., and which therefore eventually limits improvements regarding the measurement uncertainty.

To exclude the most abundant isotope ^{28}Si from all considerations is the fundamental idea to overcome this problem, because this way the range in which isotope ratios have to be determined becomes much narrower ($10^{-1} \leq x(^i\text{Si})/x(^{29}\text{Si}) \leq 7 \times 10^1$ instead of $2 \times 10^{-5} \leq x(^i\text{Si})/x(^{28}\text{Si}) \leq 1$). This leads directly to the introduction of a “new” virtual element (VE) consisting of only two instead of three isotopes. In the case of the silicon crystal, highly enriched with ^{28}Si only the isotopes ^{29}Si and ^{30}Si with minor abundances have to

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 highly enriched with respect to ^{28}Si ; “Si30”, silicon material highly enriched with respect to ^{30}Si .

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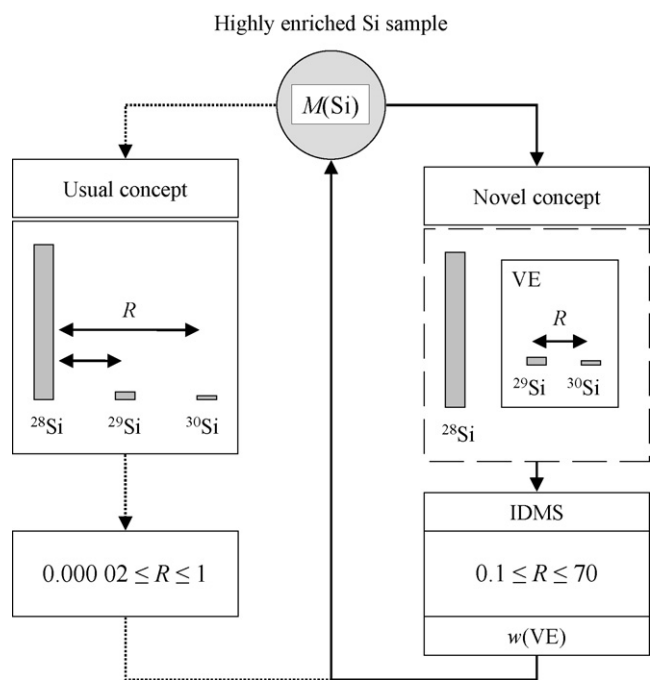


Fig. 1. Schematic comparison of the usual vs. novel concept (introduction of a virtual element VE) to determine the isotopic abundances (and eventually the molar mass M) in a highly enriched silicon material. The novel concept applying IDMS narrows the range in which isotope ratios R have to be measured, what reduces the combined uncertainty of the desired molar mass significantly.

be measured. It is evident that the isotope ratios comparably closer to unity will lead to a much smaller measurement uncertainty. But to simply ignore the existence of ^{28}Si is of no help when it comes to calculating the molar mass of the highly enriched silicon material, because the isotopic abundance of ^{28}Si is still unknown.

At this point applying IDMS comes in handy to determine the mass fraction $w(\text{VE})$ of the virtual element. New equations were derived to calculate the isotopic abundances of the “real” silicon (not only of ^{29}Si and ^{30}Si , but also ^{28}Si) merely from the mass fraction of the virtual element (Fig. 1). These abundances are essential to calculate the molar mass. This is the first time IDMS was applied to determine a molar mass. To check the applicability of this novel concept and to compare it to the usual one, typical performance parameters of the mass spectrometer intended to be used for the measurements were included in an uncertainty budget according to the GUM [17]. This uncertainty budget provided a most comprehensive description of the measurements needed to determine the molar mass of a silicon material containing approximately 99.98% ^{28}Si . The advantages of the new method are manifested in the uncertainty calculated of the estimated data and underpinned by first experimental [18].

2. Method

2.1. Modified isotope dilution mass spectrometry using a virtual element

Generally, IDMS is performed by preparing a blend bx of a sample x and a spike material y . The latter providing a non-natural isotope distribution which is preferably inverse with respect to that of the sample (Fig. 2):

$$w_x = w_y \frac{m_{yx} M_x R_y - R_{\text{bx}}}{m_x M_y R_{\text{bx}} - R_x} \frac{\sum_i R_{x,i}}{\sum_i R_{y,i}} \quad (1)$$

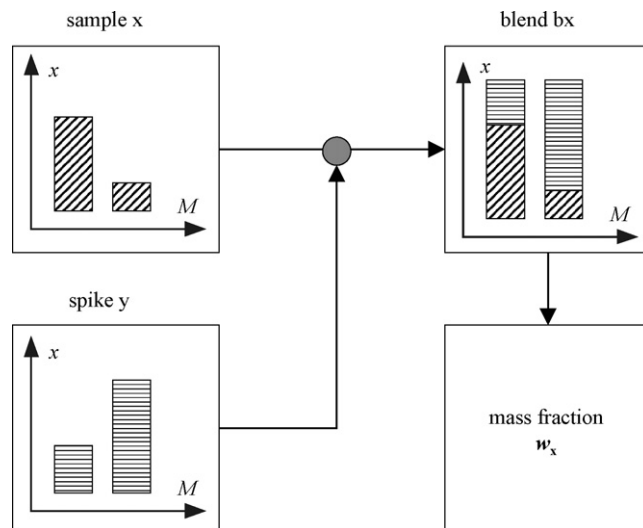


Fig. 2. Scheme of isotope dilution mass spectrometry (IDMS) applied to a two-isotope element. Sample x and spike y with inverse isotopic abundances of the same element are mixed to yield a blend bx . Practically from the knowledge of the mixed amounts of sample and spike and the isotope ratios in the blend, sample and spike, the mass fraction w_x of the element in the sample matrix results.

Eq. (1) shows the relation between the mass fraction w_x of the element in the sample matrix and the mass fraction w_y of the element in the spike material. R are the respective isotope ratios in the sample, spike and blend. The masses m express the amounts of sample and spike used to prepare the blend, while M are the molar masses of the element of interest in the sample and spike. When measuring the isotope ratios of the sample R_x , spike R_y and blend R_{bx} , the mass fraction w_x of the element of interest in the sample can be determined with highest accuracy. In the framework of the novel concept this mass fraction w_x is the mass fraction $w(\text{VE})$ of the virtual element. It describes to which degree the silicon in whole is “contaminated” with ^{29}Si and ^{30}Si , therefore in the following it will be named w_{imp} .

However, despite of the advantages of IDMS, it is generally difficult to measure isotope ratios smaller than 0.01 or larger than 100, resp., or spread over a range larger than three orders of magnitude with sufficient accuracy. As mentioned in section 1, very pure materials consisting of several isotopes having very low abundances ($\ll 1\%$) can be measured with the modified IDMS method. Table 1 shows the amount-of-substance fractions x and the corresponding isotope ratios R of the highly enriched hypothetical silicon sample “Si28”. It is evident that the merits of introducing a VE are twofold: the smallest isotope ratio to be measured increases by four orders of magnitude from 10^{-5} to 10^{-1} and additionally, only one isotope ratio – $^{30}\text{Si}/^{29}\text{Si}$ – has to be measured. The advantage of having to measure isotope ratios within a range not larger than two orders of magnitude applies also for the spike material “Si30” needed for the IDMS method (Table 2), although concerning the spike both isotope ratios have to be measured (Eq. (3)).

The IDMS formula Eq. (1) reduces in the case of Si and after introducing the VE to the following form, which is very convenient, because neither the molar mass of the VE in the sample M_x nor that in the spike M_y has to be known (see Appendix B):

$$w_{\text{imp}} = w_y \frac{m_{yx} M(^{29}\text{Si}) + R_x M(^{30}\text{Si}) R_y - R_{\text{bx}}}{m_x M(^{29}\text{Si}) + R_y M(^{30}\text{Si}) R_{\text{bx}} - R_x} \quad (2)$$

The mass fraction of VE is given by the masses of sample m_x and spike m_{yx} mixed to yield the blend bx , the molar masses M of ^{29}Si and ^{30}Si [19], the isotope ratios $R = x(^{30}\text{Si})/x(^{29}\text{Si})$ in x , y and bx , and by the mass fraction w_y of VE in the spike. In case the sample x

Table 1

Approximate amount-of-substance fractions x (isotopic abundances) and resulting isotope ratios of the hypothetical “Si28” sample applying the usual concept (three isotopes) and after introduction of the virtual element consisting of two isotopes (novel concept).

Sample $x = \text{“Si28”}$				
i	Usual concept		Novel concept	
	$x(^i\text{Si})$ in mol/mol $\times 10^{-2}$	$R = x(^i\text{Si})/x(^{28}\text{Si})$	$x(^i\text{Si})$ in mol/mol $\times 10^{-2}$	$R = x(^i\text{Si})/x(^{29}\text{Si})$
28	99.983	1	0.00	–
29	0.015	1.5×10^{-4}	88.24	1
30	0.002	2.0×10^{-5}	11.76	1.3×10^{-1}

Table 2

Approximate amount-of-substance fractions x (isotopic abundances) and resulting isotope ratios of the “Si30” spike necessary for the modified IDMS method. Isotope ratio $x(^{28}\text{Si})/x(^{29}\text{Si})$ in brackets necessary for VE mass fraction in the spike, Eq. (3).

Spike $y = \text{“Si30”}$			
i	Usual concept		Novel concept
	$x(^i\text{Si})$ in mol/mol $\times 10^{-2}$	$x(^i\text{Si})$ in mol/mol $\times 10^{-2}$	$R = x(^i\text{Si})/x(^{29}\text{Si})$
28	0.5	0.00	(3.3×10^{-1})
29	1.5	1.51	1
30	98.0	98.49	6.5×10^1

was dissolved and diluted before mixing with the possibly also dissolved and diluted spike y , the masses m_x and m_{yx} are the masses of the originally solid, undiluted amounts of sample and spike introduced in the blend bx . The advantage of deriving Eq. (2) this way is that the mass fractions w_x and w_y become automatically those in the original sample and spike and that the mathematics remains untouched whatever dissolving and dilution steps lie between the sample/spike and the blend. The mass fraction of VE in the spike was derived from its definition (see Appendix A):

$$w_y = \frac{M(^{29}\text{Si}) + R_y M(^{30}\text{Si})}{R_{y,28} M(^{28}\text{Si}) + M(^{29}\text{Si}) + R_y M(^{30}\text{Si})} \quad \wedge \quad R_{y,28} = \frac{x_y(^{28}\text{Si})}{x_y(^{29}\text{Si})} \quad (3)$$

The novel relationship Eq. (4) (see Appendix C) links the amount-of-substance fraction $x_x(^{28}\text{Si})$ of ^{28}Si in the sample “Si28” to the mass fraction of VE calculated using Eqs. (2) and (3). Eq. (4) is restricted to the special case of a high purity sample ($w_{\text{pur}} = 1 \text{ g/g}$), because the two new silicon spheres intended to be used for the re-determination of the Avogadro number will meet this requirement:

$$x_x(^{28}\text{Si}) = \frac{(1 - w_{\text{imp}})/(M(^{28}\text{Si}))}{(1 - w_{\text{imp}})/(M(^{28}\text{Si})) + (1 + R_x)(w_{\text{imp}})/(M(^{29}\text{Si}) + R_x M(^{30}\text{Si}))} \quad (4)$$

The result from Eq. (4) yields – inserted in Eq. (5) – the amount-of-substance fraction $x_x(^{29}\text{Si})$ of ^{29}Si in the sample “Si28”, that of Eq. (5) inserted in Eq. (6) yields $x_x(^{30}\text{Si})$:

$$x_x(^{29}\text{Si}) = \frac{1 - x_x(^{28}\text{Si})}{1 + R_x} = \frac{(w_{\text{imp}})/(M(^{29}\text{Si}) + R_x M(^{30}\text{Si}))}{(1 - w_{\text{imp}})/(M(^{28}\text{Si})) + (1 + R_x)(w_{\text{imp}})/(M(^{29}\text{Si}) + R_x M(^{30}\text{Si}))} \quad (5)$$

$$x_x(^{30}\text{Si}) = R_x x_x(^{29}\text{Si}) = \frac{(R_x w_{\text{imp}})/(M(^{29}\text{Si}) + R_x M(^{30}\text{Si}))}{(1 - w_{\text{imp}})/(M(^{28}\text{Si})) + (1 + R_x)w_{\text{imp}}/(M(^{29}\text{Si}) + R_x M(^{30}\text{Si}))} \quad (6)$$

The desired molar mass $M(\text{“Si28”})$ of the hypothetical material is calculated from the amount-of-substance fractions $x_x(^{28}\text{Si})$, $x_x(^{29}\text{Si})$, and $x_x(^{30}\text{Si})$ of all silicon isotopes (Eqs. (4)–(6)). The molar mass of the respective silicon isotopes $M(^i\text{Si})$ are the IUPAC reference values [19]:

$$M(\text{“Si28”}) = \sum_{i=28}^{30} x_x(^i\text{Si}) M(^i\text{Si}) \quad (7)$$

2.2. Calibration factors

Isotope ratio measurements are accompanied by a mass bias [20,21]. Therefore, a correction for mass discrimination effects must be applied to the measured ratios of – for example – ion currents I . Calibration factors (K) are used to convert the measured ratios into “true” values. For the determination of the molar mass (Eqs. (2)–(7)), basically one calibration factor – namely K_{30} – is needed to correct the measured values R_j^{meas} of the $^{30}\text{Si}/^{29}\text{Si}$ -ratios (R_x , R_y , and R_{bx}) in order to calculate their respective “true” values R_j^{true} :

$$R_j \equiv R_j^{\text{true}} = K_{30} R_j^{\text{meas}} \quad \text{with} \quad R_j^{\text{meas}} = \frac{I_j(^{30}\text{Si})}{I_j(^{29}\text{Si})} \quad \text{and} \quad j \in \{x, y, bx\} \quad (8)$$

Eq. (3) also requires the calibration factor K_{28} to correct the measured $^{28}\text{Si}/^{29}\text{Si}$ -ratio in the spike material to yield $R_{y,28}$:

$$R_{y,28} \equiv R_{y,28}^{\text{true}} = K_{28} R_{y,28}^{\text{meas}} \quad \text{with} \quad R_{y,28}^{\text{meas}} = \frac{I_y(^{28}\text{Si})}{I_y(^{29}\text{Si})} \quad (9)$$

Within the framework of the *Avogadro Project* analytic solutions (instead of numerical ones) for these calibration factors were derived for the first time [22]. The basic idea is to prepare gravimetrically two blends S and T from three independent isotopically different parent materials A, B and C. For example the $^{30}\text{Si}/^{29}\text{Si}$ -ratio in blend S can be written:

$$r_{30}^S K_{30} = \frac{n_{30}^S}{n_{29}^S} = \frac{x_{30}^A n_A + x_{30}^B n_B}{x_{29}^A n_A + x_{29}^B n_B} \quad (10)$$

Substituting the amount-of-substance fractions with the corresponding isotope ratios and the amounts-of-substance with the masses of the blended materials results in the following expression:

$$r_{30}^S = \frac{(m_{A,1} r_{30}^A)/(K_{28} r_{28}^A M(^{28}\text{Si}) + M(^{29}\text{Si}) + K_{30} r_{30}^A M(^{30}\text{Si})) + m_B r_{30}^B/(K_{28} r_{28}^B M(^{28}\text{Si}) + M(^{29}\text{Si}) + K_{30} r_{30}^B M(^{30}\text{Si}))}{(m_{A,1})/(K_{28} r_{28}^A M(^{28}\text{Si}) + M(^{29}\text{Si}) + K_{30} r_{30}^A M(^{30}\text{Si})) + (m_B)/(K_{28} r_{28}^B M(^{28}\text{Si}) + M(^{29}\text{Si}) + K_{30} r_{30}^B M(^{30}\text{Si}))} \quad (11)$$

Solving equation (11) and its analogue expression for blend T simultaneously yields Eqs. (12)–(16). In the case of silicon eight isotope ratios r have to be measured. From the particular masses m of the parent materials used to prepare the blends and the measured raw ratios (not corrected for mass bias) the desired calibration factors K are calculated:

$$K_{30} = \frac{M(^{29}\text{Si}) \cdot N_{30}}{M(^{30}\text{Si}) \cdot D} \tag{12}$$

$$K_{28} = -\frac{M(^{29}\text{Si}) \cdot N_{28}}{M(^{28}\text{Si}) \cdot D} \tag{13}$$

$$D = m_{A,1}m_{A,2}(r_{30}^A - r_{30}^S)(r_{30}^T - r_{30}^A)(r_{28}^B r_{30}^C - r_{28}^B r_{30}^C) + m_{A,1}m_C(r_{30}^A - r_{30}^S)(r_{30}^T - r_{30}^C)(r_{28}^A r_{30}^B - r_{28}^A r_{30}^B) + m_{A,2}m_B(r_{30}^B - r_{30}^S)(r_{30}^T - r_{30}^A)(r_{28}^A r_{30}^C - r_{28}^A r_{30}^C) \tag{14}$$

$$N_{30} = m_{A,1}m_{A,2}(r_{30}^S - r_{30}^A)(r_{30}^T - r_{30}^A)(r_{28}^C - r_{28}^B) + m_{A,1}m_C(r_{30}^S - r_{30}^A)(r_{30}^T - r_{30}^C)(r_{28}^A - r_{28}^B) + m_{A,2}m_B(r_{30}^S - r_{30}^B)(r_{30}^T - r_{30}^A)(r_{28}^C - r_{28}^A) \tag{15}$$

$$N_{28} = m_{A,1}m_{A,2}(r_{30}^S - r_{30}^A)(r_{30}^T - r_{30}^A)(r_{30}^C - r_{30}^B) + m_{A,1}m_C(r_{30}^S - r_{30}^A)(r_{30}^T - r_{30}^C)(r_{30}^A - r_{30}^B) + m_{A,2}m_B(r_{30}^S - r_{30}^B)(r_{30}^T - r_{30}^A)(r_{30}^C - r_{30}^A) \tag{16}$$

These “closed form”-solutions allow to implement them straightforward into the uncertainty budget of the modified IDMS described here. It is reasonable to collect the necessary data to determine K_{30} and K_{28} within the IDMS experiment. In this case the parent material B corresponds to the spike y . As material C either the sample x or an additional silicon material with natural isotopic

abundances is suitable. Merely material A, a silicon enriched with respect to ^{29}Si has to be incorporated into the experiment beyond the materials needed for the IDMS measurements.

3. Results and discussion

The modified IDMS method described here is mainly intended to be applied for the determination of the molar mass of the hypothetical “Si28” material, highly enriched with the ^{28}Si isotope with a relative measurement uncertainty in the range of 10^{-8} . To study the feasibility of this novel concept, Eqs. (2)–(9) were applied to calculate the measurement uncertainty associated with the desired molar mass and also to estimate the particular uncertainty contributions of all input quantities according to the GUM [17]. The calculations were carried out with the GUM workbench software [23]. The estimated isotopic abundances assigned to the “Si28” sample and the “Si30” spike are given in Table 1. The uncertainties associated with these input quantities are based on conservatively estimated performance values ($u_{\text{rel}}(R_x) = u_{\text{rel}}(R_y) = 0.5\%$, $u_{\text{rel}}(R_{\text{bx}}) = 0.1\%$). These values are typical for the multicollector inductively coupled plasma mass spectrometer (MC-ICP-MS) Thermo Finnigan Neptune intended to be applied for future measurements. Estimations for the calibration factors along with their associated uncertainties were taken from a preliminary measurement and its according uncertainty budget made use of Eqs. (12)–(16). The uncertainties associated with the masses of sample and spike were calculated from the certified uncertainties usual for analytical balances and from the uncertainties arising from the air buoyancy correction. Molar masses and their respective uncertainties were taken from [19]. The results are given in Table 3. The sensitivity coefficients c_i are the partial derivatives of the molar mass of “Si28” with respect to the input quantities and can be considered as “weighting” factors of the respective standard uncertainty. The last column of Table 3 shows the relative contribution of all input quantities to the expanded measurement

Table 3 Uncertainty budget of the molar mass of a silicon material (“Si28”) highly enriched with the ^{28}Si isotope [23] mainly using estimated data. Quantities X_i are explained in section 2.1, except for $m_{x,f}$, $m_{y,f}$, $w_{x,f}$ and $w_{y,f}$. These are the masses and respective mass fractions of the final solutions of sample and spike, resp., used to prepare the blend bx . E.g., $m_x = m_{x,f}w_{x,f}$. Standard uncertainties u are displayed for $k=1$. Index (right column) gives the relative uncertainty contribution (in %) of the respective input quantity to the molar mass M (“Si28”), the output quantity Y . Units of the sensitivity coefficient [c_i] omitted for the sake of clarity. [c_i] = $\text{g/mol}/[X_i]$. The resulting combined uncertainty associated with the molar mass $u_c(y)$ can be converted using a coverage factor of $k=2$ into the quoted relative expanded uncertainty of 3.3×10^{-8} . Blank cells for c_i and Index indicate intermediate results being no real input quantities of the molar mass. Best estimates for the ratios R are chosen in a way to yield the values shown in tab. 1 and tab. 2 after multiplication with their according calibrator factor.

Quantity X_i	Unit $[X_i]$	Best estimate (Value) x_i	Standard Uncertainty $u(x_i)$	Sensitivity Coefficient c_i	Index
$x_x(^{28}\text{Si})$	mol/mol	0.999829653	358×10^{-9}		
$x_x(^{29}\text{Si})$	mol/mol	150.750×10^{-6}	276×10^{-9}		
$x_x(^{30}\text{Si})$	mol/mol	19.597×10^{-6}	117×10^{-9}		
$M(^{28}\text{Si})$	g/mol	27.976926490	110×10^{-9}	1.0	5.5
$M(^{29}\text{Si})$	g/mol	28.976494680	110×10^{-9}	150×10^{-6}	0.0
$M(^{30}\text{Si})$	g/mol	29.973770180	110×10^{-9}	13×10^{-6}	0.0
w_{imp}	g/g	177.131×10^{-6}	375×10^{-9}		
w_y	g/g	0.9953292	33.9×10^{-6}		
R_x	mol/mol	0.137244	686×10^{-6}	510×10^{-6}	54.7
R_y	mol/mol	68.974	0.345	93×10^{-9}	0.5
R_{bx}	mol/mol	1.00000	1.00×10^{-3}	-220×10^{-6}	22.6
K_{30}	1	0.947221	874×10^{-6}	-160×10^{-6}	8.4
$R_{y,28}$	mol/mol	0.31522	1.58×10^{-3}	-2.8×10^{-6}	0.0
K_{28}	1	1.05746	1.82×10^{-3}	-840×10^{-9}	0.0
m_{yx}	g	14.72000×10^{-6}	7.40×10^{-9}		
m_x	g	0.1078000	54.0×10^{-6}		
$w_{x,f}$	g/g	3500.00	1.75	-54×10^{-9}	4.1
$m_{x,f}$	g	30.800000	800×10^{-6}	-6.2×10^{-6}	0.0
$w_{y,f}$	g/g	1.000000	500×10^{-6}	190×10^{-6}	4.1
$m_{y,f}$	g	14.720000	800×10^{-6}	13×10^{-6}	0.0
Y	[Y]	y	$u_c(y)$	$u_{\text{rel}}(y)$	
M (“Si28”)	g/mol	27.97711631	469×10^{-9}	1.68×10^{-8}	

uncertainty of the final result, the molar mass M . The simulation yielded a molar mass of $M(^{28}\text{Si}) = 27.9771163 \text{ g mol}^{-1}$. The expanded uncertainty associated with this value was found to be $U(M(^{28}\text{Si})) = 0.94 \times 10^{-6} \text{ g mol}^{-1}$ (along with a coverage factor of $k = 2.0$ valid on a confidence level of $p \approx 95\%$). This corresponds to a relative uncertainty of $U_{\text{rel}} = 3.3 \times 10^{-8}$.

Table 3 shows three main contributions to $U(M(^{28}\text{Si}))$: The largest contributions with 54.7% and 22.6% are related to the isotope ratios R_x – namely the ratio of the $^{30}\text{Si}/^{29}\text{Si}$ in the sample $x(^{28}\text{Si})$ – and R_{bx} (the ratio $^{30}\text{Si}/^{29}\text{Si}$ in the blend prepared from the sample and the spike). These define indeed the bottleneck of the total procedure, because the absolute amounts of the ^{30}Si and ^{29}Si isotopes in the hypothetical sample which is highly enriched with the isotope ^{28}Si (Table 1) ranges between 10^{-2} and $10^{-3}\%$. The calibration factor K_{30} together with the mass fractions $w_{x,f}$ and $w_{y,f}$ of the gravimetrically prepared solutions contribute another 16.6%. It is clear that due to the large effects of the isotope ratios R_x and R_{bx} , these must be measured with lowest possible measurement uncertainty. Experimentally, this might be achieved by using an MC-ICP-MS as mentioned above [24].

To compare the simulated results describing the performance and suitability of the modified IDMS method, also the uncertainty of the usually applied direct method was calculated using the input quantities and associated uncertainties in the same performance range. The values used for this second simulation were estimated even more conservatively. Using relative uncertainties associated with $R_{x,29/28} = 1.5 \times 10^{-4}$ and $R_{x,30/28} = 2.0 \times 10^{-5}$ of 1% and 2%, resp., a relative expanded uncertainty of $U_{\text{rel}} = 12 \times 10^{-8}$ was calculated. Therefore, the use of the modified IDMS method should be suitable to improve the uncertainty associated with the desired molar mass by a factor larger than three at least under the constraints mentioned above.

4. Conclusions

The described novel concept combining the modified IDMS method with a “virtual element” – here silicon consisting of two isotopes ^{29}Si and ^{30}Si instead of three – is a well appropriate tool to measure the molar mass of the hypothetical “Si28” material with an uncertainty improved compared to the uncertainty obtained using the usual concept. At least when the same mass spectrometer will be used. Furthermore the calculations basing on conservatively estimated preliminary performance data indicate that to reach a relative expanded uncertainty in the range of 10^{-8} seems feasible. Conveniently, only one isotope ratio – $R_{30,29}$ – in the sample and blend has to be measured. However, these two input quantities cause almost three quarters of the measurement uncertainty associated with the molar mass. Therefore, suitable experimental methods have to be applied to determine them with lowest possible measurement uncertainty. Generally, the new method is not restricted to enriched silicon, but it can also be applied to any other element (containing one isotope having a considerably smaller or larger abundance in comparison to the other isotopes). In these cases the novel concept helps minimizing the uncertainty of isotope ratio measurements.

Furthermore, introducing the virtual element helps narrowing the range in which isotope ratios have to be measured, what also brings them closer to unity. The first issue makes this method applicable also on less “sophisticated” mass spectrometers, while the second reduces the influence of systematic errors like detector dead time or linearity and therefore reduces the measurement uncertainty even more.

At the moment the experimental verification of the novel concept is in progress as a consequence of these very encouraging results.

The next step will be the determination of the molar mass of the two silicon spheres highly enriched with ^{28}Si in the framework of the *Avogadro Project* [12]. The results presented demonstrate the chance to meet or even exceed the requirements of the *Avogadro Project*.

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Appendix A. Mass fraction of VE in the spike

Definition of the mass fraction [25] considering that the virtual element represents the sum of ^{29}Si and ^{30}Si :

$$w_y = \frac{m_y(^{29}\text{Si}) + m_y(^{30}\text{Si})}{m_y(^{28}\text{Si}) + m_y(^{29}\text{Si}) + m_y(^{30}\text{Si})} \quad (\text{A.1})$$

Inserting in Eq. (A.1) the definition of the molar mass [25]:

$$w_y = \frac{n_y(^{29}\text{Si})M(^{29}\text{Si}) + n_y(^{30}\text{Si})M(^{30}\text{Si})}{n_y(^{28}\text{Si})M(^{28}\text{Si}) + n_y(^{29}\text{Si})M(^{29}\text{Si}) + n_y(^{30}\text{Si})M(^{30}\text{Si})} \quad (\text{A.2})$$

Eq. (A.2) can be rewritten using the definition of the amount-of-substance fraction [25]:

$$w_y = \frac{x_y(^{29}\text{Si})M(^{29}\text{Si}) + x_y(^{30}\text{Si})M(^{30}\text{Si})}{x_y(^{28}\text{Si})M(^{28}\text{Si}) + x_y(^{29}\text{Si})M(^{29}\text{Si}) + x_y(^{30}\text{Si})M(^{30}\text{Si})} \quad (\text{A.3})$$

Multiplying both numerator and denominator by $1/x_y(^{29}\text{Si})$ and replacing the resulting fractions with isotope ratios:

$$w_y = \frac{M(^{29}\text{Si}) + R_y M(^{30}\text{Si})}{R_{y,28} M(^{28}\text{Si}) + M(^{29}\text{Si}) + R_y M(^{30}\text{Si})} \quad (\text{3})$$

Appendix B. Mass fraction of VE in the sample

Expressing the molar masses of VE in the sample and in the spike in terms of isotope ratios starting from their definitions [19]:

$$M_x = x_x(^{29}\text{Si})M(^{29}\text{Si}) + x_x(^{30}\text{Si})M(^{30}\text{Si}) \quad (\text{B.1})$$

$$M_y = x_y(^{29}\text{Si})M(^{29}\text{Si}) + x_y(^{30}\text{Si})M(^{30}\text{Si}) \quad (\text{B.2})$$

$$M_x = \frac{1}{1 + R_x} M(^{29}\text{Si}) + \frac{R_x}{1 + R_x} M(^{30}\text{Si}) \quad (\text{B.3})$$

$$M_y = \frac{1}{1 + R_y} M(^{29}\text{Si}) + \frac{R_y}{1 + R_y} M(^{30}\text{Si}) \quad (\text{B.4})$$

Replacing the molar masses in the well-known IDMS formula Eq. (1) with eqs. (B.3)–(B.4), expanding the sum considering the exclusion of ^{28}Si and renaming w_x yields Eq. (2):

$$w_x = w_y \frac{m_{yx}}{m_x} \frac{M_x}{M_y} \frac{R_y - R_{\text{bx}}}{R_{\text{bx}} - R_x} \sum_i R_{x,i} \quad (\text{1})$$

$$w_{\text{imp}} = w_y \frac{m_{yx}}{m_x} \frac{1/(1 + R_x)M(^{29}\text{Si}) + R_x/(1 + R_x)M(^{30}\text{Si})}{1/(1 + R_y)M(^{29}\text{Si}) + R_y/(1 + R_y)M(^{30}\text{Si})} \frac{R_y - R_{\text{bx}}}{R_{\text{bx}} - R_x} \frac{1 + R_x}{1 + R_y} \quad (\text{B.5})$$

$$w_{\text{imp}} = w_y \frac{m_{yx}}{m_x} \frac{M(^{29}\text{Si}) + R_x M(^{30}\text{Si})}{M(^{29}\text{Si}) + R_y M(^{30}\text{Si})} \frac{R_y - R_{\text{bx}}}{R_{\text{bx}} - R_x} \quad (\text{2})$$

Appendix C. Amount-of-substance fractions of all Si isotopes in the sample

The mass fraction of VE in the sample w_{imp} (measured by IDMS Eq. (2)) is equal to the sum of the mass fractions of the isotopes ^{29}Si and ^{30}Si in the silicon sample in whole:

$$w_{imp} = w_x(^{29}\text{Si}) + w_x(^{30}\text{Si}) \tag{C.1}$$

Introducing the definition of mass fractions [25]:

$$w_{imp} = \frac{m_x(^{29}\text{Si})}{m_x(^{28}\text{Si}) + m_x(^{29}\text{Si}) + m_x(^{30}\text{Si})} + \frac{m_x(^{30}\text{Si})}{m_x(^{28}\text{Si}) + m_x(^{29}\text{Si}) + m_x(^{30}\text{Si})} \tag{C.2}$$

$$w_{imp} = \frac{m_x(^{29}\text{Si}) + m_x(^{30}\text{Si})}{m_x(^{28}\text{Si}) + m_x(^{29}\text{Si}) + m_x(^{30}\text{Si})} = \frac{m_x(^{29}\text{Si}) + m_x(^{30}\text{Si})}{m} \tag{C.3}$$

Substituting in Eq. (C.3) the unknown masses of the individual isotopes with their respective amount of substance and at the same time restricting the number of isotopes by introducing the definition of their particular ratio yields the link between the amount of substance of ^{29}Si and the mass fraction of VE (Eq. (C.7)):

$$w_{imp} = \frac{n_x(^{29}\text{Si})M(^{29}\text{Si}) + n_x(^{30}\text{Si})M(^{30}\text{Si})}{m} \tag{C.4}$$

$$R_x = \frac{x_x(^{30}\text{Si})}{x_x(^{29}\text{Si})} = \frac{n_x(^{30}\text{Si})}{n_x(^{29}\text{Si})} \Rightarrow n_x(^{30}\text{Si}) = R_x n_x(^{29}\text{Si}) \tag{C.5}$$

$$w_{imp} = \frac{n_x(^{29}\text{Si})M(^{29}\text{Si}) + R_x n_x(^{29}\text{Si})M(^{30}\text{Si})}{m} \tag{C.6}$$

$$w_{imp} = n_x(^{29}\text{Si}) \frac{M(^{29}\text{Si}) + R_x M(^{30}\text{Si})}{m} \Rightarrow n_x(^{29}\text{Si}) = \frac{w_{imp} m}{M(^{29}\text{Si}) + R_x M(^{30}\text{Si})} \tag{C.7}$$

Combining Eqs. (C.5) and (C.7) links also the amount of substance of ^{30}Si with the mass fraction of VE:

$$n_x(^{30}\text{Si}) = R_x \frac{w_{imp} m}{M(^{29}\text{Si}) + R_x M(^{30}\text{Si})} \tag{C.8}$$

The mass fraction of VE and the mass fraction of ^{28}Si sum up to the mass fraction of total silicon in the sample $w_x(\text{Si})$:

$$w_x(\text{Si}) = w_{imp} + w_x(^{28}\text{Si}) \tag{C.9}$$

$$x_x(^{29}\text{Si}) = \frac{1}{1 + R_x} \left(1 - \frac{(1 - w_{imp}) / (M(^{28}\text{Si}))}{(1 - w_{imp}) / (M(^{28}\text{Si})) + (1 + R_x) (w_{imp}) / (M(^{29}\text{Si}) + R_x M(^{30}\text{Si}))} \right) \tag{C.19}$$

$$x_x(^{30}\text{Si}) = \frac{1}{1 + R_x} \left(\frac{(1 - w_{imp}) / (M(^{28}\text{Si})) + (1 + R_x) (w_{imp}) / (M(^{29}\text{Si}) + R_x M(^{30}\text{Si})) - (1 - w_{imp}) / (M(^{28}\text{Si}))}{(1 - w_{imp}) / (M(^{28}\text{Si})) + (1 + R_x) (w_{imp}) / (M(^{29}\text{Si}) + R_x M(^{30}\text{Si}))} \right) \tag{C.20}$$

Assuming a pure material ($w_x(\text{Si}) = 1$) – justified in case of the silicon dealt with here – everything apart from VE has to be ^{28}Si :

$$w_x(^{28}\text{Si}) = 1 - w_{imp} \tag{C.10}$$

Introducing the definition of the mass fraction and replacing the mass of ^{28}Si with the amount of substance results in the link between this amount of substance and the mass fraction of VE:

$$w_x(^{28}\text{Si}) = \frac{m_x(^{28}\text{Si})}{m} = \frac{n_x(^{28}\text{Si})M(^{28}\text{Si})}{m} \tag{C.11}$$

$$1 - w_{imp} = \frac{n_x(^{28}\text{Si})M(^{28}\text{Si})}{m} \Rightarrow n_x(^{28}\text{Si}) = \frac{(1 - w_{imp})m}{M(^{28}\text{Si})} \tag{C.12}$$

The desired expression Eq. (4) for the amount-of-substance fraction of ^{28}Si results from replacing the amounts of substance with Eqs. (C.7), (C.8) and (C.12) in its definition and reducing by dividing numerator and denominator by m :

$$x_x(^{28}\text{Si}) = \frac{n_x(^{28}\text{Si})}{n_x(^{28}\text{Si}) + n_x(^{29}\text{Si}) + n_x(^{30}\text{Si})} \tag{C.13}$$

$$x_x(^{28}\text{Si}) = \frac{(1 - w_{imp})m / (M(^{28}\text{Si}))}{(1 - w_{imp})m / (M(^{28}\text{Si})) + (w_{imp}m) / (M(^{29}\text{Si}) + R_x M(^{30}\text{Si})) + R_x (w_{imp}m) / (M(^{29}\text{Si}) + R_x M(^{30}\text{Si}))} \tag{C.14}$$

$$x_x(^{28}\text{Si}) = \frac{(1 - w_{imp}) / (M(^{28}\text{Si}))}{(1 - w_{imp}) / (M(^{28}\text{Si})) + (1 + R_x) (w_{imp}) / (M(^{29}\text{Si}) + R_x M(^{30}\text{Si}))} \tag{4}$$

The definition of the amount-of-substance fraction implies that the sum of all amount-of-substance fractions of the isotopes of a certain element is equal to unity:

$$\sum_i x_{x,i} = 1 \tag{C.15}$$

In the case of silicon Eq. (C.15) reads:

$$x_x(^{28}\text{Si}) + x_x(^{29}\text{Si}) + x_x(^{30}\text{Si}) = 1 \tag{C.16}$$

Replacing the amount-of-substance fraction of ^{30}Si with Eq. (C.5) and rearranging to isolate the amount-of-substance fraction of ^{29}Si :

$$x_x(^{28}\text{Si}) + x_x(^{29}\text{Si}) + R_x x_x(^{29}\text{Si}) = x_x(^{28}\text{Si}) + (1 + R_x) x_x(^{29}\text{Si}) = 1 \tag{C.17}$$

$$x_x(^{29}\text{Si}) = \frac{1 - x_x(^{28}\text{Si})}{1 + R_x} \tag{C.18}$$

Replacing the amount-of-substance fraction of ^{28}Si with Eq. (4) yields Eq. (5):

$$x_x(^{29}\text{Si}) = \frac{(w_{imp}) / (M(^{29}\text{Si}) + R_x M(^{30}\text{Si}))}{(1 - w_{imp}) / (M(^{28}\text{Si})) + (1 + R_x) (w_{imp}) / (M(^{29}\text{Si}) + R_x M(^{30}\text{Si}))} \tag{5}$$

Combining Eq. (5) and Eq. (C.5) leads to the amount-of-substance fraction of ^{30}Si :

$$x_x(^{30}\text{Si}) = R_x x_x(^{29}\text{Si}) \\ = \frac{(R_x w_{\text{imp}})/(M(^{29}\text{Si})) + (R_x M(^{30}\text{Si}))}{(1 - w_{\text{imp}})/(M(^{28}\text{Si})) + (1 + R_x)w_{\text{imp}}/(M(^{29}\text{Si})) + R_x M(^{30}\text{Si})} \quad (6)$$

In a more general case of a not perfectly pure sample ($w_x(\text{Si}) < 1$) Eqs. (4) and (5) have to be modified by replacing the expression $(1 - w_{\text{imp}})$ with $(w_x(\text{Si}) - w_{\text{imp}})$.

References

- [1] Bureau International des Poids et Mesures. Consultative Committee for Amount of Substance (CCQM). Report of the 4th meeting, 1998.
- [2] P. De Bièvre, Isotope dilution mass spectrometry: What can it contribute to accuracy in trace analysis? *Fresenius J. Anal. Chem.* 337 (1990) 766–771.
- [3] K.G. Heumann, Isotope Dilution Mass Spectrometry, in: F. Adams, R. Gijbels, R. van Grieken (Eds.), *Inorganic Mass Spectrometry*, John Wiley & Sons, New York, 1988, pp. 301–376.
- [4] K.G. Heumann, Isotope dilution mass spectrometry, *Int. J. Mass Spectrom. Ion Processes* 118/119 (1992) 575–592.
- [5] K.G. Heumann, Isotope dilution mass spectrometry (IDMS) of the Elements, *Mass Spectrom. Rev.* 11 (1992) 41–67.
- [6] W. Riepe, H. Kaiser, Massenspektrometrische Spurenanalyse von Calcium, Strontium und Barium in Natriumazid durch Isotopenverdünnungstechnik, *Z. Anal. Chem.* 223 (1966) 321–335.
- [7] P. Klingbeil, J. Vogl, W. Pritzkow, G. Riebe, J. Müller, Comparative Studies on the Certification of Reference Materials by ICPMS and TIMS Using Isotope Dilution Procedures, *Anal. Chem.* 73 (2001) 1881–1888.
- [8] M.J.T. Milton, J. Wang, High accuracy method for isotope dilution mass spectrometry with application to the measurement of carbon dioxide, *Int. J. Mass Spectrom.* 218 (2002) 63–73.
- [9] P. Becker, H. Bettin, H.-U. Danzebrink, M. Gläser, U. Kuetgens, A. Nicolaus, D. Schiel, P. De Bièvre, S. Valkiers, P. Taylor, Determination of the Avogadro constant via the silicon route, *Metrologia* 40 (2003) 271–287.
- [10] P. Becker, Tracing the definition of the kilogram to the Avogadro constant using a silicon single crystal, *Metrologia* 40 (2003) 366–375.
- [11] P. Becker, History and progress in the accurate determination of the Avogadro constant, *Rep. Prog. Phys.* 64 (2001) 1945–2008.
- [12] P. Becker, D. Schiel, H.-J. Pohl, A.K. Kaliteevski, O.N. Godisov, M.F. Churbanov, G.G. Devyatykh, A.V. Gusev, A.D. Bulanov, S.A. Adamchik, V.A. Gaava, I.D. Kovalev, N.V. Abrosimov, B. Hallmann-Seiffert, H. Riemann, S. Valkiers, P. Taylor, P. De Bièvre, E.M. Dianov, Large-scale production of highly enriched ^{28}Si for the precise determination of the Avogadro constant, *Meas. Sci. Technol.* 17 (2006) 1854–1860.
- [13] K. Fujii, M. Tanaka, Y. Nezu, K. Nakayama, H. Fujimoto, P. De Bièvre, S. Valkiers, Determination of the Avogadro constant by accurate measurement of the molar volume of a silicon crystal, *Metrologia* 36 (1999) 455–464.
- [14] P. De Bièvre, G. Lenaers, T.J. Murphy, H.S. Peiser, S. Valkiers, The chemical preparation and characterization of specimens for “absolute” measurements of the molar mass of an element, exemplified by silicon, for redeterminations of the Avogadro constant, *Metrologia* 32 (1995) 103–110.
- [15] P. Seyfried, P. Becker, A. Kozdon, F. Lüdicke, F. Spieweck, J. Stümpel, H. Wagenbreth, D. Windisch, P. De Bièvre, H.H. Ku, G. Lenaers, T.J. Murphy, H.S. Peiser, S. Valkiers, A determination of the Avogadro Constant, *Z. Phys. B* 87 (1992) 289–298.
- [16] P. Becker, P. De Bièvre, K. Fujii, M. Glaeser, B. Inglis, H. Luebbig, G. Mana, Considerations on future redefinitions of the kilogram, the mole and of other units, *Metrologia* 44 (2007) 1–14.
- [17] Guide to the expression of uncertainty in measurement, International Organization for Standardization ISO, Geneva, 1993.
- [18] H. Bettin, private communication, PTB Braunschweig.
- [19] J.R. de Laeter, J.K. Böhlke, P. De Bièvre, H. Hidaka, H.S. Peiser, K.J.R. Rosman, P.D.P. Taylor, Atomic Weights of the Elements: Review 2000 (IUPAC Technical Report), *Pure Appl. Chem.* 75 (2003) 683–800.
- [20] A. Montaser (Ed.), *Inductively Coupled Plasma Mass Spectrometry*, Wiley-VCH, New York, 1998.
- [21] J. Vogl, Calibration Strategies and Quality Assurance, in: S.M. Nelms (Ed.), *Inductively Coupled Plasma Mass Spectrometry Handbook*, Blackwell Publishing Ltd, Oxford, 2005, pp. 146–181.
- [22] G. Mana, O. Rienitz, The calibration of Si isotope-ratio measurements, *Int. J. Mass Spectrom.*, submitted.
- [23] GUM-Workbench™, Version 1.2.11.56 Win32 © ‘96-99 by Metrodata GmbH.
- [24] M.E. Wieser, J.B. Schwieters, The development of multiple collector mass spectrometry for isotope ratio measurements, *Int. J. Mass Spectrom.* 242 (2005) 97–115.
- [25] I. Mills, T. Cvitaš, K. Homann, N. Kallay, K. Kuchitsu (Eds.), *International Union of Pure and Applied Chemistry: Quantities, Units and Symbols in Physical Chemistry*, Blackwell Science Ltd., Oxford, 1993.