International Journal of Mass Spectrometry 291 (2010) 55–60

Contents lists available at ScienceDirect

International Journal of Mass Spectrometry

journal homepage: www.elsevier.com/locate/ijms

The calibration of Si isotope ratio measurements

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ARTICLE INFO

Article history:
Received 29 November 2009
Received in revised form 15 January 2010
Accepted 15 January 2010
Available online 25 January 2010

PACS:
82.80.Ms
07.75.+h
06.20.−f
06.20.Dk

MSC:
62P35
92E99

Keywords:
Si molar mass
Metrology
Isotopic composition
Isotopic abundance
Atomic weight

ABSTRACT

The determination of absolute isotope amount ratios requires the calibration of mass spectrometric measurements. In this paper, for the first time, the relevant calibration factors are given via exact analytical equations. It extends the results of a previous investigation, based on a simple two-isotope model, to a three-isotope system. Particular emphasis is given to silicon, because of its role in the determination of the Avogadro constant. The conditions ensuring the existence and uniqueness of the calibration-equation solutions are related as well.

1. Introduction

The determination of absolute isotope amount ratios (or abundance ratios) is essential in areas of chemistry and geology such as provenance testing (for instance, health-care, forensics, nutrition), geochronology, and the determination of molar masses. An important application is to determine the molar mass of silicon to an accuracy allowing to redefine the kilogram [1–4]. With this in view, several metrology institutes are participating in an international research project (International Avogadro Coordination, IAC) using a highly enriched ^{28}Si crystal; isotope enrichment and crystal production were completed and a 5 kg single crystal with a ^{28}Si enrichment higher than 99.99% is available for measurements [5].

Regardless of the particular task, the calibration of the mass spectrometric measurements is inevitable; three ways to obtain the relevant calibration factors are known and accepted. The first is to use an external standard [6]; if necessary, in conjunction with semi-empirical fractionation laws [7,8]. The second is to use an internal correction based on the already mentioned fractionation laws [9]. Both methods need one or more consensus values; therefore, the determined ratios are not truly absolute but rather they depend on the accepted reference. The third method overcomes this limitation through gravimetrically prepared blends (or mixtures) of isotopically enriched materials. From the measured ratios in the parent materials and blends, the calibration factors are calculated. Since the relevant calibration equations are non-linear, it is commonly accepted that either an approximate solution can be obtained [10,11] or recursive algorithms are necessary [12–19]. Both methods offer no truly exact solution. Additionally, the numeric methods shows poor convergence under certain circumstances [20].

In a previous paper [21] the issues of measurement uncertainty and calibration in a two-isotope system were addressed; here the results are extended to the real three-isotope system. For the very first time, the calibration factors are given explicitly by means of exact formulae; accordingly, they are straightforwardly calculated in one step from the measured ratios. No approximation or numeric method is necessary. Additionally, stating the model equation explicitly allows the associated calibration uncertainty to be estimated according to the Guide to the Expression of Uncertainty in Measurement [22,26]. Different synthetic mixtures have been

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doi:10.1016/j.ijms.2010.01.008

considered and the extensive algebraic manipulations have been carried out with the aid of *Mathematica* [23]. It is demonstrated that with a two-component mixture, a calibration is impossible. Subsequently, three-component mixtures are considered and the concept of components and mixture independence is introduced, which ensures the uniqueness of calibration. Blending three parent materials in pairs is particularly attractive because the calibration equations reduce to a system of two linear equations. Additionally, this resembles separate calibrations of two two-isotope systems, so that an approximate uncertainty analysis based on the simpler two-isotope model is possible.

2. Calibration of mass spectrometric measurements

Converting the measured ion-current ratios into the isotope amount ratios requires calibration factors, which are close to one and are obtained by measuring synthesized ratios generated by means of mixtures of enriched-Si isotopes. When considering a three-isotope system, only two of the $r_{i/j} = I_i/I_j$ ratios, where

$$I_i = a_i x_i I_{\mathrm{Tot}}, \tag{1}$$

are independent. The basic model to relate the ion currents and isotope amount fractions is given in [24,25]; in the present paper, the relationship (1) is assumed, where x_i are isotope amount fractions, a_i accounts for fractionation and ammeter calibration, $I_{\mathrm{Tot}} = I_{28} + I_{29} + I_{30}$ being the total ion current, and $i = 28$, 29, and 30.

Let $r_{29} = I_{29}/I_{28}$ and $r_{30} = I_{30}/I_{28}$ be the ratio pair chosen; hence, molar mass is

$$M = \frac{M_{28} + R_{29}M_{29} + R_{30}M_{30}}{1 + R_{29} + R_{30}}, \tag{2}$$

where the isotope amount ratios R_{29} and R_{30} are related to the measured ion-current ratios by $R_i = \kappa_i r_i$ and $\kappa_i = a_i/a_{28}$ are calibration factors.

As for the two-isotope system [21], the determination of the calibration factors requires blending weighed amounts of Si with different isotopic compositions and measuring the isotope amount ratios in the blend and parent materials. The usual way to determine κ_{29} and κ_{30} is by comparing the measured and expected ratios – r_i and R_i, respectively – in the synthetic mixture; in a formula, $\kappa_i = R_i/r_i$. However, to calculate R_i for the gravimetrically prepared mixture, the isotopic composition of the parent materials must be measured and, in turn, this requires that the calibration factors are known in advance. Therefore, a recursive procedure is used; initially, κ_{29} and κ_{30} are set to one and used to calculate the isotopic composition of the parent materials and R_i. Next, κ_i is recalculated and used to update the isotopic composition of the parent materials and the mixture ratios. This procedure is iterated until the calibration factors converge to well-defined values.

3. Two-component mixture

To prepare a synthetic mixture, at least two samples with a different isotopic composition are necessary. Let A, B, and S indicate the samples and mixture, respectively. Hence, n_{A} and n_{B} moles of the materials A and B are blended to obtain $n_{\mathrm{S}} = n_{\mathrm{A}} + n_{\mathrm{B}}$ moles of the mixture S.

The calibration equations are

$$r_{29}^{\mathrm{S}} = \frac{n_{\mathrm{A}} r_{29}^{\mathrm{A}} x_{28}^{\mathrm{A}} + n_{\mathrm{B}} r_{29}^{\mathrm{B}} x_{28}^{\mathrm{B}}}{n_{\mathrm{A}} x_{28}^{\mathrm{A}} + n_{\mathrm{B}} x_{28}^{\mathrm{B}}} \tag{3a}$$

and

$$r_{30}^{\mathrm{S}} = \frac{n_{\mathrm{A}} r_{30}^{\mathrm{A}} x_{28}^{\mathrm{A}} + n_{\mathrm{B}} r_{30}^{\mathrm{B}} x_{28}^{\mathrm{B}}}{n_{\mathrm{A}} x_{28}^{\mathrm{A}} + n_{\mathrm{B}} x_{28}^{\mathrm{B}}}, \tag{3b}$$

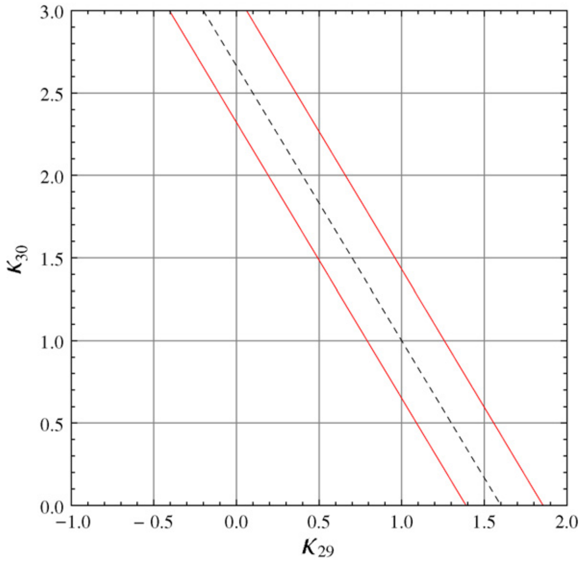

Fig. 1. The root loci of the calibration Eqs. (3a) and (3b) with a mixture of enriched ^{28}Si and natural silicon are the same (dashed line). When the measurements of the ion-current ratios are uncertain, the root loci split into parallel lines, for example, the red (solid) ones. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

where x_{28}^{A} and x_{28}^{B} are the ^{28}Si amount fractions in the parent materials. The unknown calibration factors κ_{29} and κ_{30} are hidden in $n_{\mathrm{A}} = m_{\mathrm{A}}/M_{\mathrm{A}}$ and $n_{\mathrm{B}} = m_{\mathrm{B}}/M_{\mathrm{B}}$, where

$$M_{\mathrm{A}} = (M_{28} + \kappa_{29} r_{29}^{\mathrm{A}} M_{29} + \kappa_{30} r_{30}^{\mathrm{A}} M_{30}) x_{28}^{\mathrm{A}} \tag{4}$$

and M_{B} – which is given by a similar equation – are the molar masses of the parent materials. Therefore,

$$n_{\mathrm{A}} x_{28}^{\mathrm{A}} = \frac{m_{\mathrm{A}}}{M_{28} + \kappa_{29} r_{29}^{\mathrm{A}} M_{29} + \kappa_{30} r_{30}^{\mathrm{A}} M_{30}} \tag{5}$$

and a similar equation holds for $n_{\mathrm{B}} x_{28}^{\mathrm{B}}$.

To solve (3a) and (3b) numerically, $n_{\mathrm{A}} x_{28}^{\mathrm{A}}$ and $n_{\mathrm{B}} x_{28}^{\mathrm{B}}$ are eliminated by taking (5) into account; next both equations are solved with respect to κ_{30} to obtain $\kappa_{30} = f_1(\kappa_{29})$ and $\kappa_{30} = f_2(\kappa_{29})$. Each equation identifies a line in the $\kappa_{29}\kappa_{30}$ plane and the sought calibration factors are the coordinates of the line intersection. However, the two equations represent the same line, as shown in Fig. 1, and any κ_{29} and κ_{30} pair on it is a legitimate solution. The uncertainty of the ion-current measurements makes the equations inconsistent, so that no solution exists any more. Careless attempts to solve the calibration equations recursively could seemingly produce a solution. However, the lack of a satisfactory convergence – the numerical solution diffuses in the gap between the two lines in Fig. 1 – reveals the non-existence of solutions.

We cannot solve the calibration equations uniquely because they are not independent; in fact, the following identity holds,

$$r_{29}^{\mathrm{S}}(r_{30}^{\mathrm{A}} - r_{30}^{\mathrm{B}}) - r_{30}^{\mathrm{S}}(r_{29}^{\mathrm{A}} - r_{29}^{\mathrm{B}}) - r_{29}^{\mathrm{B}} r_{30}^{\mathrm{A}} + r_{29}^{\mathrm{A}} r_{30}^{\mathrm{B}} = 0, \tag{6}$$

which implies that we can fix one of the unknown quantities, say κ_{29}, and solve (3a) and (3b) for the other. The meaning of (6), which was found by eliminating κ_{29} and κ_{30} from (3a) and (3b), is shown in Fig. 2; when the molar fraction of B in the blend, $n_{\mathrm{B}}/(n_{\mathrm{A}} + n_{\mathrm{B}})$, varies from zero to one, the mixture composition varies along the line joining its components, enriched ^{28}Si and $^{\mathrm{nat}}$Si. The blend locus, together with r_{29}^{S}, uniquely determines r_{30}^{S}. The identity (6) is nothing else than the algebraic translation of this constraint. Similarly, the blend locus and r_{29}^{S} uniquely determine the ion-current ratio of any additional two-component mixture. Consequently, with two components only, calibration is impossible.

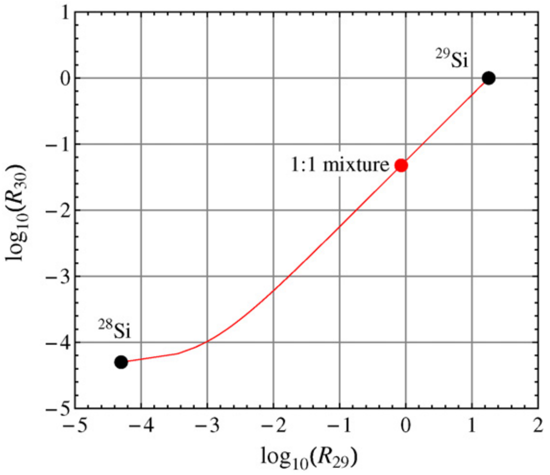

Fig. 2. Locus of a two-component mixture; the isotopic composition of the parent materials (A and B) is given in Table 1. The 1:1 mixture is also shown (red dot). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

4. Three-component mixtures

4.1. Single mixture

The next to minimal number of blend components is three. Hence, $n_A + n_B + n_C = n_S$, where A, B, and C are three materials with different isotopic compositions. The calibration equations are

$$r_{29}^{S} = \frac{n_A r_{29}^{A} x_{28}^{A} + n_B r_{29}^{B} x_{28}^{B} + n_C r_{29}^{C} x_{28}^{C}}{n_A x_{28}^{A} + n_B x_{28}^{B} + n_C x_{28}^{C}} \qquad (7a)$$

and

$$r_{30}^{S} = \frac{n_A r_{30}^{A} x_{28}^{A} + n_B r_{30}^{B} x_{28}^{B} + n_C r_{30}^{C} x_{28}^{C}}{n_A x_{28}^{A} + n_B x_{28}^{B} + n_C x_{28}^{C}}, \qquad (7b)$$

where $n_A = m_A/M_A$, n_B, and n_C (which are given by similar equations) are the amounts of substance of the parent materials in the mixtures.

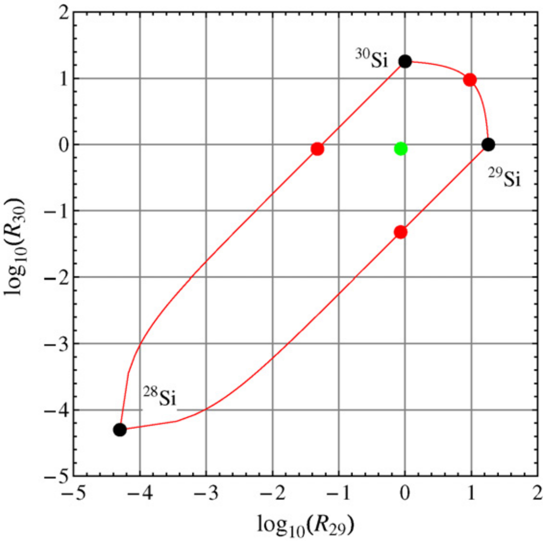

Fig. 3. Locus of a three-component mixture. Some two- and three-component mixtures are also shown (red and green dots, respectively). The isotopic composition of the parent materials is given in Table 1. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

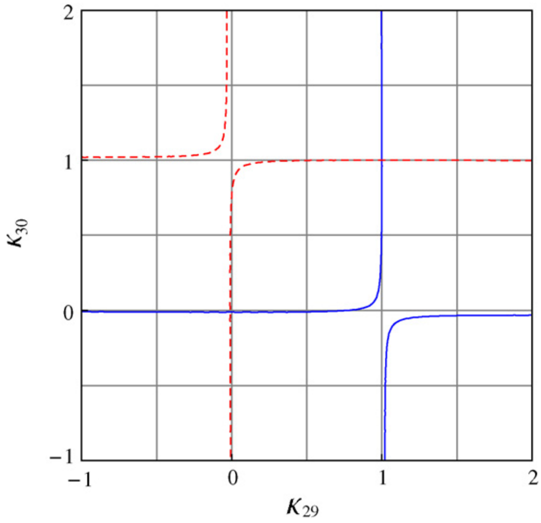

Fig. 4. Root loci of the calibration equations for a three-component mixture; red (dashed) is (8a) and blue (solid) is (8b). The isotopic compositions of the parent material and the and their mixed amounts are given in Table 1. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

The mixture locus is shown in Fig. 3; when the molar fractions n_A/n_S, n_B/n_S, and n_C/n_S vary from zero to one, the mixture is in the area enclosed by the lines whose vertices are the parent materials. According to the results related in the previous section, a necessary condition for (7a) and (7b) to be independent is the independency of the mixture's parents. This means that no parent material must itself be a mixture of the others; in contrast, the mixture locus shown in Fig. 3 collapses into a line and r_{29} uniquely determines r_{30}. In addition, the mixture itself must not be a degenerate one, that is, it must not be a blend of two components alone.

To solve the calibration equations, $n_A x_{28}^{A}$, $n_B x_{28}^{B}$, and $n_C x_{28}^{C}$ are eliminated from (7a) and (7b) taking (5) into account. After some simplifications, this leads to the system of quadratic equations,

$$\begin{pmatrix} M_{28}^2 & M_{28}M_{29}\kappa_{29} & M_{29}^2\kappa_{29}^2 \end{pmatrix} \mathbf{A}^{29} \begin{pmatrix} M_{28}^2 \\ M_{28}M_{30}\kappa_{30} \\ M_{30}^2\kappa_{30}^2 \end{pmatrix} = 0 \qquad (8a)$$

and

$$\begin{pmatrix} M_{28}^2 & M_{28}M_{29}\kappa_{29} & M_{29}^2\kappa_{29}^2 \end{pmatrix} \mathbf{A}^{30} \begin{pmatrix} M_{28}^2 \\ M_{28}M_{30}\kappa_{30} \\ M_{30}^2\kappa_{30}^2 \end{pmatrix} = 0, \qquad (8b)$$

where the elements of the matrices $\mathbf{A}^{29}$ and $\mathbf{A}^{30}$ are Appendix A. In (8a) and (8b), each equation identifies the two branches of a hyperbola, as shown in Fig. 4, and the sought κ_{29} and κ_{30} values are the coordinates of the hyperbola intersection nearest to $\{\kappa_{29} = 1, \kappa_{30} = 1\}$. Handling of this polynomial system is a tour de force of algebraic computation; closed form solutions have been found with the aid of *Mathematica* [23], but, since a very large output was generated, they are not given here.

When the uncertainty of the current ratio determinations is considered, the (8a) and (8b) hyperbolae move out of their ideal position and no more intersect in $\{\kappa_{29}, \kappa_{30}\}$. The intersection angle indicates the sensitivity of the calibration factors to the current ratios; the more perpendicular the intersection, the less sensitive the calibration factors. In the limit when the mixture is a blend of only two materials, the calibration equations identify the same hyperbola and, in the presence of measurement errors, no solution exists any more.

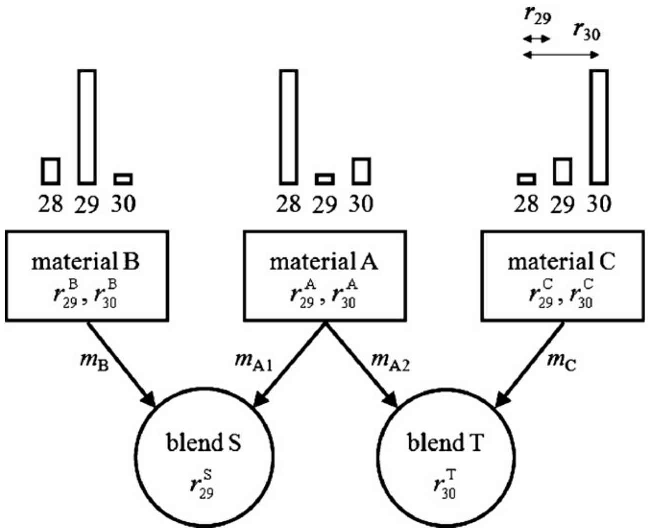

Fig. 5. Preparation of two isotopic mixtures S and T from three independent parent materials A, B and C.

4.2. Two mixtures

A second way to work around the difficulties of a dependent mixture, is to blend the materials A, B, and C pair-wise, as shown in Fig. 5. Two mixtures – S, obtained blending m_{A1} grams of A and m_{B} grams of B, and T, obtained blending m_{A2} grams of A and m_{C} grams of C – are sufficient to make the calibration possible. If A, B, and C are differently enriched-Si materials, this procedure is qualitatively equivalent to calibrating the r_{29} and r_{30} ratios in two separate two-isotope systems. We thus expect that the results of the propagation-of-uncertainty analysis based on the simpler two-isotope model investigated in [21] are approximately valid. In this case, the calibration equations are

$$r_{29}^{\mathrm{S}} = \frac{n_{\mathrm{A1}} r_{29}^{\mathrm{A}} x_{28}^{\mathrm{A}} + n_{\mathrm{B}} r_{29}^{\mathrm{B}} x_{28}^{\mathrm{B}}}{n_{\mathrm{A1}} x_{28}^{\mathrm{A}} + n_{\mathrm{B}} x_{28}^{\mathrm{B}}} \tag{9a}$$

and

$$r_{30}^{\mathrm{T}} = \frac{n_{\mathrm{A2}} r_{30}^{\mathrm{A}} x_{28}^{\mathrm{A}} + n_{\mathrm{C}} r_{30}^{\mathrm{C}} x_{28}^{\mathrm{C}}}{n_{\mathrm{A2}} x_{28}^{\mathrm{A}} + n_{\mathrm{C}} x_{28}^{\mathrm{C}}}, \tag{9b}$$

where $n_{\mathrm{A1}} = m_{\mathrm{A1}}/M_{\mathrm{A}}$, n_{A2}, n_{B}, and n_{C} (which are given by similar equations) are the amounts of substance of the parent materials in the mixtures.

The first step to solve (9a) and (9b) is to use equations similar to (5) to eliminate $n_{\mathrm{A1}} x_{28}^{\mathrm{A}}$, $n_{\mathrm{A2}} x_{28}^{\mathrm{A}}$, $n_{\mathrm{B}} x_{28}^{\mathrm{B}}$, and $n_{\mathrm{C}} x_{28}^{\mathrm{C}}$. Hence, after some simplifications, we obtain the system of linear equations

$$\mathbf{A} \begin{pmatrix} M_{28} \\ M_{29}\kappa_{29} \\ M_{30}\kappa_{30} \end{pmatrix} = 0, \tag{10}$$

where

$$A_{11} = m_{\mathrm{A1}}(r_{29}^{\mathrm{S}} - r_{29}^{\mathrm{A}}) + m_{\mathrm{B}}(r_{29}^{\mathrm{S}} - r_{29}^{\mathrm{B}}), \tag{11a}$$

$$A_{12} = m_{\mathrm{A1}} r_{29}^{\mathrm{B}}(r_{29}^{\mathrm{S}} - r_{29}^{\mathrm{A}}) + m_{\mathrm{B}} r_{29}^{\mathrm{A}}(r_{29}^{\mathrm{S}} - r_{29}^{\mathrm{B}}), \tag{11b}$$

$$A_{13} = m_{\mathrm{A1}} r_{30}^{\mathrm{B}}(r_{29}^{\mathrm{S}} - r_{29}^{\mathrm{A}}) + m_{\mathrm{B}} r_{30}^{\mathrm{A}}(r_{29}^{\mathrm{S}} - r_{29}^{\mathrm{B}}), \tag{11c}$$

$$A_{21} = m_{\mathrm{A2}}(r_{30}^{\mathrm{T}} - r_{30}^{\mathrm{A}}) + m_{\mathrm{C}}(r_{30}^{\mathrm{T}} - r_{30}^{\mathrm{C}}), \tag{11d}$$

$$A_{22} = m_{\mathrm{A2}} r_{29}^{\mathrm{C}}(r_{30}^{\mathrm{T}} - r_{30}^{\mathrm{A}}) + m_{\mathrm{C}} r_{29}^{\mathrm{A}}(r_{30}^{\mathrm{T}} - r_{30}^{\mathrm{C}}), \tag{11e}$$

$$A_{23} = m_{\mathrm{A2}} r_{30}^{\mathrm{C}}(r_{30}^{\mathrm{T}} - r_{30}^{\mathrm{A}}) + m_{\mathrm{C}} r_{30}^{\mathrm{A}}(r_{30}^{\mathrm{T}} - r_{30}^{\mathrm{C}}). \tag{11f}$$

To solve (10) yields the formulae giving the calibration factors:

$$\kappa_{29} = \frac{M_{28} E_{29}}{M_{29} D} \tag{12a}$$

and

$$\kappa_{30} = -\frac{M_{28} E_{30}}{M_{30} D}, \tag{12b}$$

where

$$\begin{aligned} E_{29} = {} & m_{\mathrm{A1}} m_{\mathrm{A2}}(r_{29}^{\mathrm{S}} - r_{29}^{\mathrm{A}})(r_{30}^{\mathrm{T}} - r_{30}^{\mathrm{A}})(r_{30}^{\mathrm{C}} - r_{30}^{\mathrm{B}}) \\ & + m_{\mathrm{A1}} m_{\mathrm{C}}(r_{29}^{\mathrm{S}} - r_{29}^{\mathrm{A}})(r_{30}^{\mathrm{T}} - r_{30}^{\mathrm{C}})(r_{30}^{\mathrm{A}} - r_{30}^{\mathrm{B}}) \\ & + m_{\mathrm{A2}} m_{\mathrm{B}}(r_{29}^{\mathrm{S}} - r_{29}^{\mathrm{B}})(r_{30}^{\mathrm{T}} - r_{30}^{\mathrm{A}})(r_{30}^{\mathrm{C}} - r_{30}^{\mathrm{A}}), \end{aligned} \tag{12c}$$

$$\begin{aligned} E_{30} = {} & m_{\mathrm{A1}} m_{\mathrm{A2}}(r_{29}^{\mathrm{S}} - r_{29}^{\mathrm{A}})(r_{30}^{\mathrm{T}} - r_{30}^{\mathrm{A}})(r_{29}^{\mathrm{C}} - r_{29}^{\mathrm{B}}) \\ & + m_{\mathrm{A1}} m_{\mathrm{C}}(r_{29}^{\mathrm{S}} - r_{29}^{\mathrm{A}})(r_{30}^{\mathrm{T}} - r_{30}^{\mathrm{C}})(r_{29}^{\mathrm{A}} - r_{29}^{\mathrm{B}}) \\ & + m_{\mathrm{A2}} m_{\mathrm{B}}(r_{29}^{\mathrm{S}} - r_{29}^{\mathrm{B}})(r_{30}^{\mathrm{T}} - r_{30}^{\mathrm{A}})(r_{29}^{\mathrm{C}} - r_{29}^{\mathrm{A}}), \end{aligned} \tag{12d}$$

and

$$\begin{aligned} D = {} & m_{\mathrm{A1}} m_{\mathrm{A2}}(r_{30}^{\mathrm{T}} - r_{30}^{\mathrm{A}})(r_{29}^{\mathrm{A}} - r_{29}^{\mathrm{S}})(r_{29}^{\mathrm{B}} r_{30}^{\mathrm{C}} - r_{29}^{\mathrm{C}} r_{30}^{\mathrm{B}}) \\ & + m_{\mathrm{A1}} m_{\mathrm{C}}(r_{30}^{\mathrm{T}} - r_{30}^{\mathrm{C}})(r_{29}^{\mathrm{A}} - r_{29}^{\mathrm{S}})(r_{29}^{\mathrm{B}} r_{30}^{\mathrm{A}} - r_{29}^{\mathrm{A}} r_{30}^{\mathrm{B}}) \\ & + m_{\mathrm{A2}} m_{\mathrm{B}}(r_{30}^{\mathrm{T}} - r_{30}^{\mathrm{A}})(r_{29}^{\mathrm{B}} - r_{29}^{\mathrm{S}})(r_{29}^{\mathrm{A}} r_{30}^{\mathrm{C}} - r_{29}^{\mathrm{C}} r_{30}^{\mathrm{A}}). \end{aligned} \tag{12e}$$

The choice of the ratio pair to be measured is not unique. Other possibilities are to measure the $\{r_{29}^{\mathrm{S}}, r_{29}^{\mathrm{T}}\}$, $\{r_{30}^{\mathrm{S}}, r_{30}^{\mathrm{T}}\}$, or $\{r_{30}^{\mathrm{S}}, r_{29}^{\mathrm{T}}\}$ ratios. Each choice results in a different set of calibration equations, which has the same structure as (9a) and (9b) with the relevant sub- and superscript permutations. An attractive feature is that, provided all the r_{29}^{S}, r_{30}^{S}, r_{29}^{T}, and r_{30}^{T} ratios are measured, they provide redundancy and consistency checks through the constraints

$$r_{29}^{\mathrm{S}}(r_{30}^{\mathrm{A}} - r_{30}^{\mathrm{B}}) - r_{30}^{\mathrm{S}}(r_{29}^{\mathrm{A}} - r_{29}^{\mathrm{B}}) - r_{29}^{\mathrm{B}} r_{30}^{\mathrm{A}} + r_{29}^{\mathrm{A}} r_{30}^{\mathrm{B}} = 0 \tag{13a}$$

which is the same Eq. (6), and

$$r_{29}^{\mathrm{T}}(r_{30}^{\mathrm{A}} - r_{30}^{\mathrm{C}}) - r_{30}^{\mathrm{T}}(r_{29}^{\mathrm{A}} - r_{29}^{\mathrm{C}}) - r_{29}^{\mathrm{C}} r_{30}^{\mathrm{A}} + r_{29}^{\mathrm{A}} r_{30}^{\mathrm{C}} = 0. \tag{13b}$$

Finally, additional blends can be considered; for instance, B + C and A + B + C, which bring us three additional independent equations and one additional constraint. The resulting over-determined system of equations can be used to improve calibration and molar mass determination via a least squares solution and to identify model and measurement inconsistencies, if any.

5. Measurement uncertainty

The uncertainty estimate of the Si molar mass measurement on the basis of the real three-isotope model cannot be summarized in a simple formula. For this reason, we test here an approximation based on a simpler two-isotope model, which was reported in [21]. The basic result was that, if the measured currents are strictly proportional to the isotope amount fractions and their uncertainty is

$$u_i = (u_1 + u_2 x_i) I_{\mathrm{Tot}}, \tag{14}$$

where u_1 accounts for the detection limit and systematic errors and u_2 accounts for the ion-source noise, the molar mass uncertainty is

$$\frac{u_M}{M} = 0.08 u_1, \tag{15}$$

which holds when x_{29} and x_{30} tend to zero.

This prediction has been tested numerically for the actual three-isotope system by a Monte Carlo simulation; the parameter values

Table 1
Parameters used in Figs. 2–4 and the Monte Carlo simulation.

$\kappa_{29} = 1$	$\kappa_{30} = 1$
$R^{\mathrm{A}}_{29} = 5 \times 10^{-4}$	$R^{\mathrm{A}}_{30} = 5 \times 10^{-4}$
$R^{\mathrm{B}}_{29} = 18$	$R^{\mathrm{B}}_{30} = 1$
$R^{\mathrm{C}}_{29} = 1$	$R^{\mathrm{C}}_{30} = 18$
$m_{\mathrm{A}} = m_{\mathrm{A1}} = m_{\mathrm{A2}} = m_{\mathrm{B}} = m_{\mathrm{C}} = 1\,\mathrm{g}$	
$u_1 = 2 \times 10^{-7}$	$u_2 = 1 \times 10^{-4}$

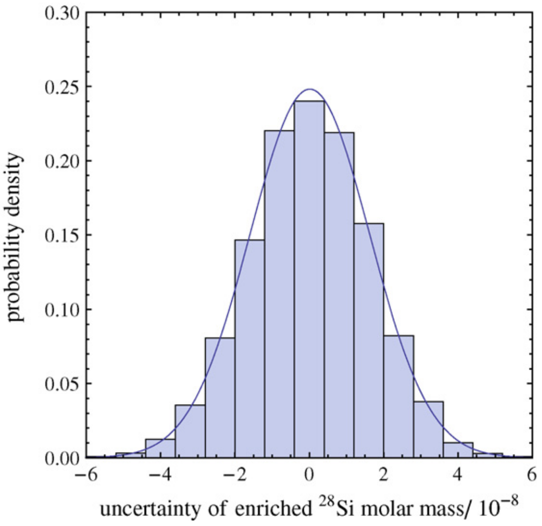

Fig. 6. Monte Carlo histogram of molar mass uncertainty. The values of the parameters used are in Table 1, weighing uncertainty has been neglected. The solid line is the best Gaussian fit to the frequencies.

used are listed in Table 1. A pair a two-isotope mixtures was considered and the calibration factors were determined according to (12a) and (12b). Next, the ion-current ratios were converted into the R_i isotope amount ratios and the molar mass of the enriched ^{28}Si sample (in the simulation, the material A) was calculated according to (2). The simulation result is given in Fig. 6; the standard deviation of the Monte Carlo sample, $u_M/M = 1.61 \times 10^{-8}$, agrees with the $u_M/M = 1.60 \times 10^{-8}$ value predicted by (15).

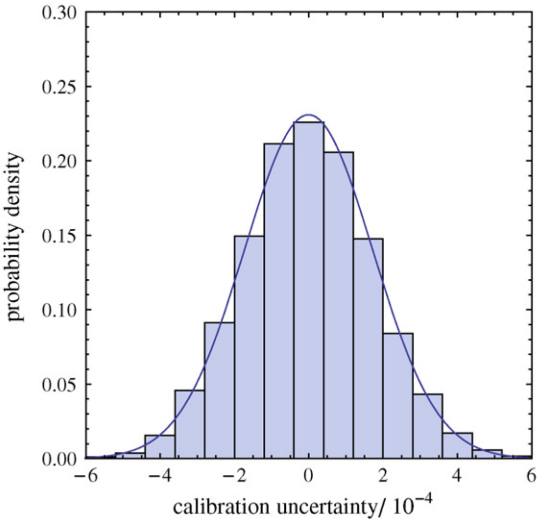

Fig. 7. Monte Carlo histogram of calibration uncertainty. The values of the parameters used are in Table 1, weighing uncertainty has been neglected. The solid line is the best Gaussian fit to the frequencies.

According to [21], the result of (12a) and (12b) should be insensitive to offsets $I_{0n} = c_n I_{\mathrm{Tot}}$ in the

$$I_n = (a_n x_n + c_n) I_{\mathrm{Tot}} \tag{16}$$

model linking the isotope fraction x_n to the relevant ion current I_n. This invariance of (12a) and (12b) with respect to arbitrary translations of the ion-current zeroes can be understood by observing that (16) can be rewritten as $I_n = a_n(x_n + x_{0n}) I_{\mathrm{Tot}}$, where $c_n = a_n x_{0n}$. Therefore, apart from insignificant clues arising from weighing, offsets cannot be discriminated from variations of the isotopic compositions of the parent materials, which do not have any effect on the calibration. Also this prediction has been tested by a Monte Carlo simulation; the result is given in Fig. 7. With highly enriched parent materials, the Monte Carlo estimate of the calibration uncertainty, $u_\kappa/\kappa = 1.67 \times 10^{-4}$, is in good agreement with the minimum uncertainty,

$$\frac{u_\kappa}{\kappa} \approx 2\sqrt{2}\left(u_1 + \frac{u_2}{2}\right) = 1.42 \times 10^{-4}, \tag{17}$$

predicted in [21].

6. Conclusions

We investigated the calibration of Si molar mass measurements by means of synthesized isotope ratios generated by blending silicon samples with different isotopic compositions. The mathematical structure of the relevant measurement equations delivered useful information about calibration. With a single two-component blend, since the mixture and its parents are not independent, the calibration is impossible. Calibration requires us to blend three materials, of which none is a mixture of the remaining two. It has been demonstrated that the calibration factors can be exactly obtained by solving systems of quadratic or linear equations; therefore, there is no need to stick to recursive calculations. With the use of two two-component blends calibration is particularly simple, because the calibration factors are solutions of a system of two linear equations.

Acknowledgment

This work received funds from the European Community's Seventh Framework Programme ERA-NET Plus—grant 217257.

Appendix A. Coefficients of the calibration equations

The list of the coefficients of powers of κ_{29} and κ_{30} in (8a) is

$$A^{29}_{11} = m_{\mathrm{A}}(r^{\mathrm{S}}_{29} - r^{\mathrm{A}}_{29}) + m_{\mathrm{B}}(r^{\mathrm{S}}_{29} - r^{\mathrm{B}}_{29}) + m_{\mathrm{C}}(r^{\mathrm{S}}_{29} - r^{\mathrm{C}}_{29}) \tag{18a}$$

$$\begin{aligned} A^{29}_{21} = {} & m_{\mathrm{A}}(r^{\mathrm{B}}_{29} + r^{\mathrm{C}}_{29})(r^{\mathrm{S}}_{29} - r^{\mathrm{A}}_{29}) + m_{\mathrm{B}}(r^{\mathrm{A}}_{29} + r^{\mathrm{C}}_{29})(r^{\mathrm{S}}_{29} - r^{\mathrm{B}}_{29}) \\ & + m_{\mathrm{C}}(r^{\mathrm{A}}_{29} + r^{\mathrm{B}}_{29})(r^{\mathrm{S}}_{29} - r^{\mathrm{C}}_{29}) \end{aligned} \tag{18b}$$

$$A^{29}_{31} = m_{\mathrm{A}} r^{\mathrm{B}}_{29} r^{\mathrm{C}}_{29}(r^{\mathrm{S}}_{29} - r^{\mathrm{A}}_{29}) + r^{\mathrm{A}}_{29}[m_{\mathrm{B}} r^{\mathrm{C}}_{29}(r^{\mathrm{S}}_{29} - r^{\mathrm{B}}_{29}) + m_{\mathrm{C}} r^{\mathrm{B}}_{29}(r^{\mathrm{S}}_{29} - r^{\mathrm{C}}_{29})] \tag{18c}$$

$$\begin{aligned} A^{29}_{12} = {} & m_{\mathrm{A}}(r^{\mathrm{B}}_{30} + r^{\mathrm{C}}_{30})(r^{\mathrm{S}}_{29} - r^{\mathrm{A}}_{29}) + m_{\mathrm{B}}(r^{\mathrm{A}}_{30} + r^{\mathrm{C}}_{30})(r^{\mathrm{S}}_{29} - r^{\mathrm{B}}_{29}) \\ & + m_{\mathrm{C}}(r^{\mathrm{A}}_{30} + r^{\mathrm{B}}_{30})(r^{\mathrm{S}}_{29} - r^{\mathrm{C}}_{29}) \end{aligned} \tag{18d}$$

$$\begin{aligned} A^{29}_{22} = {} & m_{\mathrm{A}}(r^{\mathrm{S}}_{29} - r^{\mathrm{A}}_{29})(r^{\mathrm{C}}_{29} r^{\mathrm{B}}_{30} + r^{\mathrm{B}}_{29} r^{\mathrm{C}}_{30}) + m_{\mathrm{B}}(r^{\mathrm{S}}_{29} - r^{\mathrm{B}}_{29})(r^{\mathrm{C}}_{29} r^{\mathrm{A}}_{30} + r^{\mathrm{A}}_{29} r^{\mathrm{C}}_{30}) \\ & + m_{\mathrm{C}}(r^{\mathrm{S}}_{29} - r^{\mathrm{C}}_{29})(r^{\mathrm{B}}_{29} r^{\mathrm{A}}_{30} + r^{\mathrm{A}}_{29} r^{\mathrm{B}}_{30}) \end{aligned} \tag{18e}$$

$$A^{29}_{32} = 0 \tag{18f}$$

$$A^{29}_{13} = m_{\mathrm{C}} r^{\mathrm{A}}_{30} r^{\mathrm{B}}_{30}(r^{\mathrm{S}}_{29} - r^{\mathrm{C}}_{29}) + r^{\mathrm{C}}_{30}[m_{\mathrm{B}} r^{\mathrm{A}}_{30}(r^{\mathrm{S}}_{29} - r^{\mathrm{B}}_{29}) + m_{\mathrm{A}} r^{\mathrm{B}}_{30}(r^{\mathrm{S}}_{29} - r^{\mathrm{A}}_{29})] \tag{18g}$$

$$A^{29}_{23} = 0 \tag{18h}$$

$$A^{29}_{33} = 0 \tag{18i}$$

By inspecting (5), (7a) and (7b), it is clear that the coefficients of powers of κ_{29} and κ_{30} in (8b) can be obtained from the previous list by exchanging everywhere the subscript 30 for the 29 one and vice versa. In a formula $\mathrm{A}^{30} = \mathrm{A}^{29}(29 \rightleftharpoons 30)$.

Appendix B. List of main symbols

a	calibration factor (ion current) (1)
κ	calibration factor (ion-current ratios)
I	ion current (A)
m	mass (g)
M	molar mass (g/mol)
n	amount-of-substance (mol)
r	ion-current ratio (A/A)
R	isotope amount ratio (mol/mol)
u	standard uncertainty
x	amount-of-substance fraction (mol/mol)

Appendix C. List of main sub- and super-scripts

A, B, C	parent materials
S, T	synthetic mixtures
28, 29, 30	^{28}Si, ^{29}Si, ^{30}Si
Tot	total ion current

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