



## The calibration of Si isotope ratio measurements

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### 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.

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### 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 <sup>28</sup>Si crystal; isotope enrichment and crystal production were completed and a 5 kg single crystal with a <sup>28</sup>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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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  $r_{ij} = I_i/I_j$  ratios, where

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

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,  $I_{\text{Tot}} = I_{28} + I_{29} + I_{30}$  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  $\kappa_{29}$  and  $\kappa_{30}$  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,  $\kappa_{29}$  and  $\kappa_{30}$  are set to one and used to calculate the isotopic composition of the parent materials and  $R_i$ . Next,  $\kappa_i$  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

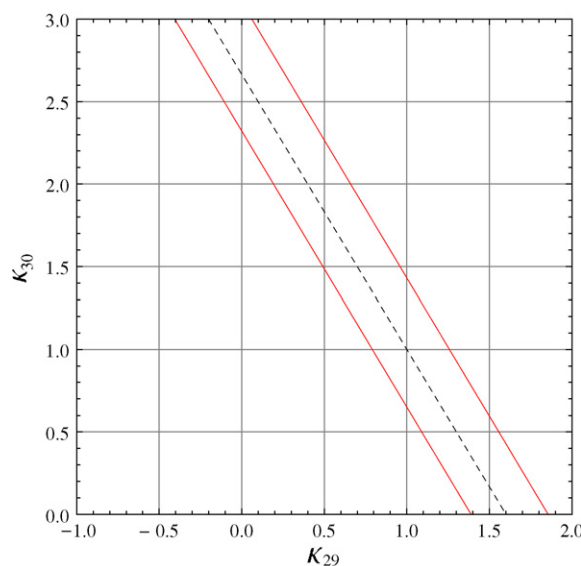
To prepare a synthetic mixture, at least two samples with a different isotopic composition are necessary. Let A, B, and S indicate the samples and mixture, respectively. Hence,  $n_A$  and  $n_B$  moles of the materials A and B are blended to obtain  $n_S = n_A + n_B$  moles of the mixture S.

The calibration equations are

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

and

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



**Fig. 1.** The root loci of the calibration Eqs. (3a) and (3b) with a mixture of enriched <sup>28</sup>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 <sup>28</sup>Si amount fractions in the parent materials. The unknown calibration factors  $\kappa_{29}$  and  $\kappa_{30}$  are hidden in  $n_A = m_A/M_A$  and  $n_B = m_B/M_B$ , where

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

and  $M_B$  – which is given by a similar equation – are the molar masses of the parent materials. Therefore,

$$n_A x_{28}^A = \frac{m_A}{M_{28} + \kappa_{29} r_{29}^A M_{29} + \kappa_{30} r_{30}^A M_{30}} \tag{5}$$

and a similar equation holds for  $n_B x_{28}^B$ .

To solve (3a) and (3b) numerically,  $n_A x_{28}^A$  and  $n_B x_{28}^B$  are eliminated by taking (5) into account; next both equations are solved with respect to  $\kappa_{30}$  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  $\kappa_{29}$  and  $\kappa_{30}$  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,

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

which implies that we can fix one of the unknown quantities, say  $\kappa_{29}$ , and solve (3a) and (3b) for the other. The meaning of (6), which was found by eliminating  $\kappa_{29}$  and  $\kappa_{30}$  from (3a) and (3b), is shown in Fig. 2; when the molar fraction of B in the blend,  $n_B/(n_A + n_B)$ , varies from zero to one, the mixture composition varies along the line joining its components, enriched <sup>28</sup>Si and <sup>nat</sup>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.

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