



Uncertainty assessment of Si molar mass measurements

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ABSTRACT

The uncertainty of the Si molar mass measurement is theoretically investigated by means of a two-isotope model, with particular emphasis to the role of this measurement in the determination of the Avogadro constant. This model allows an explicit calibration formula to be given and propagation of error analysis to be made. It also shows that calibration cannot correct for non-linearity.

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1. Introduction

The Avogadro constant, $N_A = 6.02214179(30) \times 10^{23} \text{ mol}^{-1}$ [1,2], is the molar number of entities. It expresses the ^{12}C mass in kilograms according to $m(^{12}\text{C}) = M(^{12}\text{C})/N_A$, where $M(^{12}\text{C}) = 12 \text{ g mol}^{-1}$ is the molar mass, and connects the atomic and macroscopic scales. A method to derive it from the density ρ , the molar mass M , and the unit cell volume V_0 of a crystal – namely, in all experiments, silicon – was suggested by Bragg in 1913 [3]; it relies on $N_A = nM/(\rho V_0)$, where n is the number of atom per unit cell. Since the comparisons between the official copies and the international prototype of the kilogram show a divergence with time as large as $5 \times 10^{-8} \text{ kg}$ since their first calibration in 1889, to determine N_A to an accuracy allowing the kilogram definition to be based on the ^{12}C mass [4–6], the relative uncertainty of the silicon molar mass measurement must be reduced to at least $2 \times 10^{-8} M(\text{Si})$. With

this in view, several metrology institutes are participating in an international research project (International Avogadro Coordination, IAC) for the determination of N_A using a highly enriched ^{28}Si crystal. Isotope enrichment and crystal production were completed and a 5 kg crystal with ^{28}Si enrichment higher than 99.99% is now available for measurements [7].

The isotope amount ratios are measured by gas mass spectrometry; the measured quantities being ion-current ratios [8–12]. Only in the ideal case can the measured ratios be identified with the isotope amount ratios; in practice, conversion factors are required, which are close to unity and are obtained by measuring synthesized amount ratios embodied in mixtures of enriched Si isotopes.

By application of concepts suggested by De Bièvre's [13] and Friedrich [14], we have investigated the uncertainty of the molar mass measurement with the aid of a two-isotope model and *Mathematica* [15]. This model allows an explicit calibration formula to be obtained. In addition, we examine how the molar mass of highly enriched ^{28}Si could be obtained, in a way similar to isotope dilution, simultaneously to calibration. The measurement accuracy depends on the ion-current uncertainty and on how the ion currents relate to the isotope amount fractions. An important result is the demon-

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stration that by calibration it is impossible to correct offsets in the ion-current measurements. A strict proportionality between the isotope amount fractions and the ion currents is essential to calibration, whatever the composition of the mixture used might be.

2. Two-isotope model

For the sake of simplicity, let us consider silicon as composed by two isotopes only, namely, ^{28}Si and ^{29}Si . Hence, the molar mass is

$$M = \frac{M_{28} + RM_{29}}{1 + R}, \quad (1)$$

where M_{28} and M_{29} are the molar masses of ^{28}Si and ^{29}Si and $R = x/(1-x)$ is the ratio between the isotope amount fractions $x_{29} = x$ and $x_{28} = 1-x$ of ^{29}Si and ^{28}Si . By leaving off the M_{28} and M_{29} uncertainties, which are irrelevant, the relative uncertainty of the molar mass is

$$\frac{u_M}{M} = Cx(1-x)\frac{u_R}{R}, \quad (2)$$

where u_R is the R uncertainty and the C coefficient accounts for effective mass difference between the Si isotopes. To examine to the extend to which this approximation supplies useful information, let us re-evaluate (2) in the actual three-isotope case. Therefore,

$$M = \frac{M_{28} + R_{29}M_{29} + R_{30}M_{30}}{1 + R_{29} + R_{30}}, \quad (3)$$

where the symbols have their usual meaning. Provided the R_{29} and R_{30} uncertainties are equal, at least approximately, the relative uncertainty of the molar mass is still given by (2), where $R = R_{29} + R_{30}$,

$$C \approx \frac{\Delta M \sqrt{(1 - R_{30})^2 + (2 + R_{29})^2}}{M}, \quad (4)$$

and $\Delta M \approx 1$ g/mol. The C coefficient ranges from 0.08 (when $R_{29} \approx R_{30} \approx 0$) to 0.11 (when $R_{29} \approx R_{30} \approx 1$); in the following, since we are mostly interested in the natural silicon and enriched ^{28}Si , we will use $C = 0.08$.

The isotope amount ratio is related to the measured $r = I_{29}/I_{28}$ ratio between the ion currents by $R = \kappa_0 r$, where κ_0 is a calibration factor. Consequently,

$$\frac{u_R}{R} = \sqrt{\left(\frac{u_{\kappa_0}}{\kappa_0}\right)^2 + \left(\frac{u_r}{r}\right)^2}, \quad (5)$$

where u_{κ_0} and u_r are the calibration and current-ratio uncertainties.

To complete the analysis of the propagation of uncertainty, we need a model to relate the ion currents and isotope amount fractions. The basic model is given in [16]; in the present paper, a proportional relationship is assumed. To compensate for source noise and drift, measurements are performed by using a single Faraday cup in peak jumping mode. The jumping mode and the subsequent data analysis, a demodulation of the data with respect to the peak indexing, remove any linear drift. In this way a set of current ratios is obtained, where the dividend and divisor are as simultaneous as possible. The sample in the expansion vessel changes isotopic composition because of the isotope fractionation process in the molecular gas flow from the inlet system to the ion source. Extrapolation of the current ratios to the start time of the measurement via a non-linear least-squares regression is thus required. Let the extrapolated values of the ion currents be proportional to the isotope amount fractions, that is,

$$I_n = a_n x_n I_T, \quad (6)$$

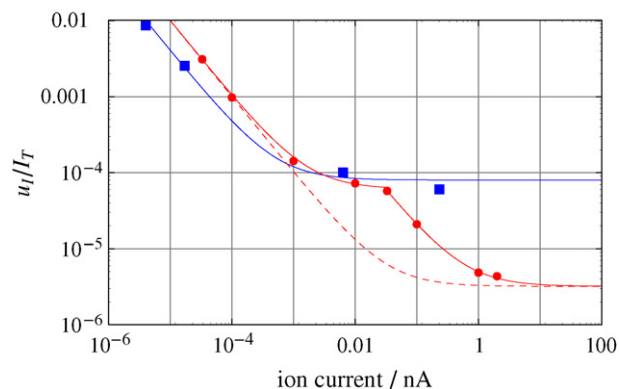


Fig. 1. Uncertainty of the ion-current. Squares (blue) indicate the ion-current noise, bullets (red) the calibration uncertainty of the ammeter electronics. Different feedback resistors are used for currents below and above 0.03 nA; typically, 400 G Ω and 3 G Ω , respectively. This explains the discontinuous character of the calibration uncertainty. The u_1 and u_2 parameters for the solid (blue) and dashed (red) lines are given in Table 1 (cases a and b), $I_T = 1$ nA. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

where $n = 28$ and 29 , a_n accounts for fractionation, and $I_T = I_{28} + I_{29} \approx 1$ nA is the total ion-current, and let

$$u_n = (u_1 + u_2 x_n) I_T \quad (7)$$

be the equivalent current uncertainty after ratio extrapolation.

The $u_{1,2}$ contributions were investigated experimentally. In a first test, performed by the IRMM, the ion-current noise was considered; the ratios – expected to be one by definition – obtained from typical sequences (100 data, with 8 s integration time) of the same current were extrapolated to the time zero and the equivalent current uncertainties were estimated backward. In a second test, performed by the Physikalisch-Technische Bundesanstalt, it was investigated the calibration uncertainty of the detection electronics, a feedback ammeter with a transimpedance amplifier which converts the input current into a voltage [17]. Results are shown in Fig. 1. In the low current regime, the limiting factor is the ammeter calibration; in the high current one, it is the ion-source noise. It must be noted that this analysis does not consider the residual contributions of systematic effects after they have been identified and corrected for—for instance, background signal, cross talk between ion currents, non-linearity. These uncertainty contributions must be included in the u_1 term and will be further discussed in Section 4.

The relative uncertainty of the current-ratio is

$$\frac{u_r}{r} = \sqrt{\left[\frac{u_1 + u_2(1-x)}{1-x}\right]^2 + \left[\frac{u_1 + u_2 x}{x}\right]^2}, \quad (8)$$

which is shown in Fig. 2; the parameter values used are listed in Table 1. By putting (2), (5) and (8) together, the relative uncertainty

Table 1

Detection limit, u_1 , and ion-source, u_2 , contributions to the ion-current uncertainty used in numerical examples. Values are expressed in relative units, with respect to the total ion-current, see Eq. (6).

Case	u_1	u_2
a	4×10^{-8}	0.8×10^{-4}
b	1×10^{-7}	3.2×10^{-6}
c	8×10^{-7}	2.0×10^{-4}
d	2×10^{-7}	1.0×10^{-4}

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