

## Open Access Repository eprint

Terms and Conditions: Users may access, download, store, search and print a hard copy of the article. Copying must be limited to making a single printed copy or electronic copies of a reasonable number of individual articles or abstracts. Access is granted for internal research, testing or training purposes or for personal use in accordance with these terms and conditions. Printing for a for-fee-service purpose is prohibited.

Title: The isotopic composition of enriched Si: a data analysis

Author(s): Bulska, E.; Drozdov, M. N.; Mana, G.; Pramann, A.; Rienitz, O.; Sennikov, P.; Valkiers, S.

Journal: Metrologia

Year: 2011, Volume: 48, Issue: 2

DOI: doi:10.1088/0026-1394/48/2/S05

Funding programme: iMERA-Plus: Call 2007 SI and Fundamental Metrology

Project title: T1.J1.2: NAH: Avogadro and molar Planck constants for the redefinition of the kilogram

Copyright note: This is an author-created, un-copyedited version of an article accepted for publication in Metrologia. IOP Publishing Ltd is not responsible for any errors or omissions in this version of the manuscript or any version derived from it. The definitive publisher-authenticated version is available online at doi:10.1088/0026-1394/48/2/S05

# The isotopic composition of enriched Si: a data analysis

E. Bulska<sup>||</sup>, M. N. Drozdov<sup>‡</sup>, G. Mana<sup>†§</sup>, A. Pramann<sup>‡</sup>, O. Rienitz<sup>‡</sup>, P. Sennikov<sup>‡</sup>, and S. Valkiers<sup>‡</sup>

<sup>||</sup> University of Warsaw, Faculty of Chemistry, Pasteura 1, 02-093 Warsaw, Poland

<sup>‡</sup> IPM-RAS – Institute for Physics of Microstructures, Russian Academy of Sciences, GSP-105, 603950 Nizhny Novgorod, Russia

<sup>†</sup> INRIM – Istituto Nazionale di Ricerca Metrologica, Str. delle Cacce 91, 10135 Torino, Italy

<sup>‡</sup> PTB – Physikalisch-Technische-Bundesanstalt, Bundesallee 100, D-38116 Braunschweig, Germany

<sup>‡</sup> IChHPS-RAS – Institute of High Purity Substance Chemistry, Russian Academy of Sciences, 49 Tropinin St., GSP-75, Nizhny Novgorod 603950, Russia

<sup>‡</sup> IRMM – Institute for Reference Materials and Measurements, Retieseweg 111, B-2440 Geel, Belgium

**Abstract.** To determine the Avogadro constant by counting the atoms in quasi-perfect spheres made of a silicon crystal highly enriched with  $^{28}\text{Si}$ , the isotopic composition of the crystal was measured in different laboratories by different measurement methods. This paper examines the consistency of the measurement results.

Submitted to: *Metrologia*

PACS numbers: 06.20.-f, 06.20.Jr, 82.80.Ms, 07.05.Kf

## 1. Introduction

The mass of the Pt-Ir kilogram artefact may have changed by about  $50\ \mu\text{g}$  since its manufacturing, in 1889. An accurate measurement of the Avogadro constant,  $N_{\text{A}}$ , by counting the number of atoms in 1 kg spheres made of Si single-crystals will make it possible to obtain a kilogram on the basis of an atom mass, thus allowing the prototype drift to be monitored. Owing to the smallness of drift, the uncertainty associated with  $N_{\text{A}}$  must not exceed  $2 \times 10^{-8}$  kg; therefore, according to  $N_{\text{A}} = 8M/(\rho a^3)$ , the molar mass,  $M$ , density,  $\rho$ , and unit cell volume,  $a^3$ , must be measured to relative accuracies close to  $10^{-8}$ .

To cope with the difficulty of determining the molar mass of natural Si, we resorted to a silicon crystal highly enriched with  $^{28}\text{Si}$  [1, 2]. In order to measure density, two slices were taken from the  $^{28}\text{Si}$  boule – whose centers are at 229 mm and 367.5 mm distance from the seed crystal – and shaped as quasi-perfect spheres. To determine

§ To whom correspondence should be addressed (g.mana@inrim.it)

the molar mass, a number of samples were cut before and after each sphere and all around them. The usual way of measuring the molar mass is by determining isotopic composition via gas mass spectrometry after converting the silicon into  $\text{SiF}_4$ . These measurement was carried out at the IRMM. Since crystal enrichment made the calibration of the mass spectrometer relatively unimportant [3], the PTB used multi collector-inductively coupled plasma mass-spectrometry of aqueous Si solutions in NaOH and developed a measurement method based on isotope dilution [4, 5, 6]. The isotopic composition of the  $^{28}\text{Si}$  crystal was determined also by secondary ion mass spectrometry, at the IPM-RAS.

## 2. Summary of measurement methods

### 2.1. Gas mass spectrometry

At the IRMM, each sample, of about 70 mg, was etched in a concentrated  $\text{HNO}_3$ , HF, and  $\text{CH}_3\text{COOH}$  solution to remove about 22 mg of contaminated surface material. Each sample was subsequently dissolved in a solution of 1.8 mL of HF and 0.3 mL of  $\text{HNO}_3$  in 20.0 mL of ultrapure water, according to



and subsequently precipitated by adding 3.9 mL of a 0.1% solution of  $\text{BaCl}_2$ , according to



Eventually, the washed and dried  $\text{BaSiF}_6$  was decomposed at 540 °C in high vacuum yielding the  $\text{SiF}_4$  gas.

The measured quantities were the ratios between  $^{29}\text{SiF}_3^+$  and  $^{30}\text{SiF}_3^+$  currents and the  $^{28}\text{SiF}_3^+$  current. The ion currents were measured by a single Faraday cup in peak jumping mode; the subsequent demodulation with respect to the peak index removed any linear drift. The  $\text{SiF}_4$  gas changes isotopic composition because of the isotope fractionation process in the molecular gas flow from the inlet system to the ion source. Therefore, the current ratios were extrapolated to the start time via a non-linear least-squares regression. To obtain the isotope amount-ratios, calibration factors are required [7], which were obtained by measuring deliberately adjusted amount ratios embodied in mixtures of enriched Si isotopes. The natural Si contaminations of the solutions were measured by graphite furnace atomic absorption spectrometry at the University of Warsaw; the results indicate that 8.040(56)  $\mu\text{g}$  of natural Si were added in the preparation of  $\text{SiF}_4$ . Accordingly, the measured ratios were corrected for this contamination.

### 2.2. Secondary ion mass spectrometry

At the IPM-RAS, the isotopic composition of two samples, one from the polycrystal (before purification and crystallization) and the other from the float-zone crystal, was determined by a secondary ion mass spectrometer equipped with a time-of-flight mass analyzer [8]. The ion guns for sputtering and mass analysis were used in pulsed mode. Sputtering was made by both  $\text{O}_2^+$  and  $\text{Cs}^+$  ions with energies from 0.5 keV to 2 keV; the pulse current was hundreds of nanoamperes, the scan area was from  $(0.2 \times 0.2)$   $\text{mm}^2$  to  $(0.5 \times 0.5)$   $\text{mm}^2$ . Mass analysis was carried out by 25 keV  $\text{Bi}^+$  ions; the pulse current was 1 pA and the pulse duration was 1 ns. The detector idle time for

the strong  $^{28}\text{Si}^+$  signal was corrected for, thus providing a linear relationship between the  $^{28}\text{Si}^+$  current and the  $^{28}\text{Si}$  fraction in the sample. In this way, the quantitative analysis of isotope concentration was possible without reference-samples.

The samples were etched in a  $\text{HNO}_3$  and HF solution. This removed the electropositive elements, but H, O, and F remained on the surface. Hydrogen originated a strong  $^{28}\text{SiH}$  signal, which increased the reading of the  $^{29}\text{Si}$  signal by one or two orders of magnitude. The second problem was surface contamination by natural Si. Chemical etching does not completely remove this contamination; natural Si dilutes in the interface between the surface and bulk. With a rough surface, the depth of this interface is few  $\mu\text{m}$ ; better results may be obtained by a combination of surface polishing and chemical etching. In this case, the interface depth is less than  $0.1 \mu\text{m}$ . To solve these problems a profiling was made to a depth of few micrometers; only when the H concentration attained its bulk value the natural Si contamination and  $^{28}\text{SiH}$  signal did not affect the measurement.

### 2.3. Multi collector-inductively coupled plasma mass-spectrometry

The very high isotopic enrichment, larger than 99.99%, turned out to be a big challenge; ion-current ratios larger by more than five orders of magnitude than the unity had to be measured. To overcome this difficulty and the natural Si contamination, a novel measurement procedure was developed by the PTB, which does not require measurement of the  $^{28}\text{Si}$  fraction [6]. It is based on isotope dilution combined with multi collector-inductively coupled plasma mass spectrometry – the samples were digested by means of an aqueous NaOH solution. Only the  $^{29}\text{Si}^+$  and  $^{30}\text{Si}^+$  currents were measured; to recover the  $^{28}\text{Si}$  fraction, the crystal samples were blended with a spike, a crystal highly enriched with  $^{30}\text{Si}$ . In addition to the masses of the blended samples, the ratios between the  $^{30}\text{Si}^+$  and  $^{29}\text{Si}^+$  currents were measured in the sample, spike, and blend; the ratio between the  $^{28}\text{Si}^+$  and  $^{29}\text{Si}^+$  currents was measured only in the spike. The missing ratio between the  $^{28}\text{Si}^+$  and  $^{29}\text{Si}^+$  current in the sample was obtained by data analysis. The spectrometer was calibrated on-line by mixtures of natural Si and two crystals enriched with the  $^{29}\text{Si}$  and  $^{30}\text{Si}$  isotopes [5, 7]. Natural Si contamination, memory effects, and offsets were monitored on-line by having the NaOH solutions remeasured before each sample, spike, blend, or mixture. In this way, each individual set of ion-current measured-values was corrected.

## 3. Analysis of measurement results

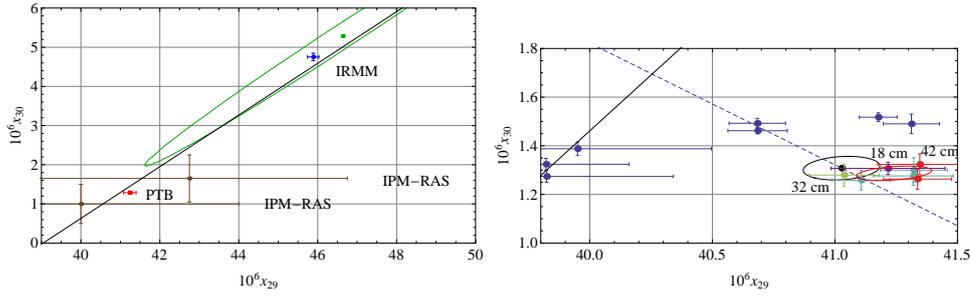
By indicating with  $x_k$  the amount fraction of the  $^k\text{Si}$  isotope, and since  $\sum_k x_k = 1$ , the isotopic composition can be represented by a point in the  $x_{29} - x_{30}$  plane. Therefore, all the measured amount ratios were converted into amount fractions. Figure 1 (left) summarizes the input data.

By indicating with  $x_k^0$  the isotope fractions of the  $^{28}\text{Si}$  crystal, if contamination by natural Si occurs, the isotope fractions of the contaminated sample will be

$$x_k = (1 - \alpha)x_k^0 + \alpha x_k^{\text{nat}}, \quad (3)$$

where  $x_k^{\text{nat}}$  are the isotope fractions of natural Si and  $\alpha$  is the molar contamination. By solving (3) with respect to  $x_k^0$ , we obtain

$$x_k^0 = \frac{x_k - \alpha x_k^{\text{nat}}}{1 - \alpha} \approx (1 + \alpha)x_k - \alpha x_k^{\text{nat}}. \quad (4)$$



**Figure 1.** Left: isotopic compositions of the  $^{28}\text{Si}$  crystal determined by the PTB, IPM-RAS, and IRMM. The error bars indicate the standard deviation of the data sets. The dot (green) indicates the composition obtained via a least-squares adjustment of the IRMM data. Right: zoom of the PTB data; the rainbow colors indicate the sample location, from the nearest (18 cm, violet) to the farthest (42 cm, red) from the seed crystal. The data (blue) on the left of the solid line are the non-corrected data. The error bars indicate the uncertainty of each individual datum. The lines indicate the locus of samples contaminated or depleted by natural Si (solid) and of samples having the same molar mass (dashed); the dot (black) at their intersection is the least-squares adjustment of the isotopic composition. The ellipses indicate 68% confidence region.

Therefore, if  $|\alpha| \ll 1$ , (3) accounts both for enrichment, when  $\alpha \geq 0$ , or depletion of natural Si, when  $\alpha \leq 0$ . For all practical purposes, the locus of a contaminated or depleted material is a line through  $(x_{29}^0, x_{30}^0)$  and parallel to  $[x_{29}^{\text{nat}} - x_{29}^0, x_{30}^{\text{nat}} - x_{30}^0]^T$ . Figure 1 (left) indicates that all the determinations of isotopic composition are reasonably consistent, provided natural Si contaminations occurred during measurements.

Let the sampling distributions of the isotope fractions  $y_k^i$  determined by the PTB, IPM-RAS, and IRMM be Gaussian and independent. Therefore,  $y_k^i \in N(x_k^i, u_k^i)$ , where

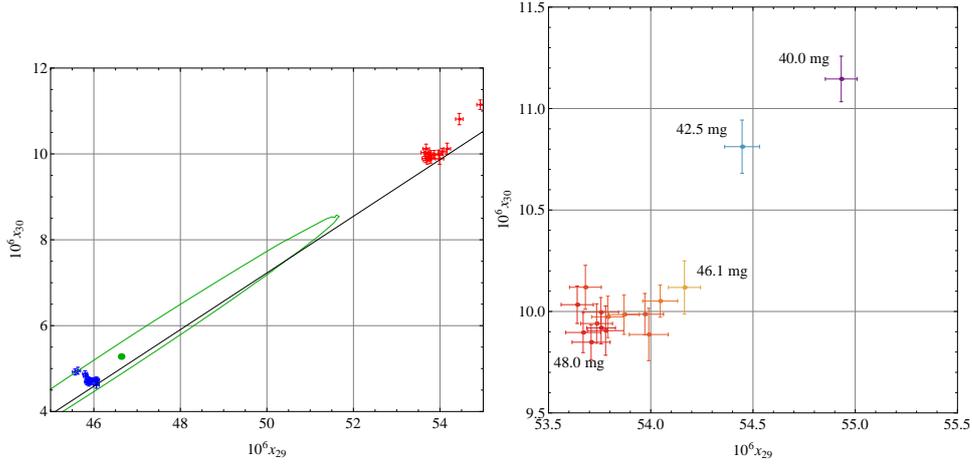
$$x_k^i = \begin{cases} x_k^0 & \text{if } i = \text{PTB and IPM-RAS} \\ (1 - \alpha_i)x_k^0 + \alpha_i x_k^{\text{nat}} & \text{if } i = \text{IRMM} \end{cases}, \quad (5)$$

are the isotope fractions of the contaminated samples,  $\alpha_i$  are the relevant molar contaminations,  $x_k^0$  are the isotope fractions of the  $^{28}\text{Si}$  crystal, and  $u_k^i$  are the measurement uncertainties.  $y_k^i$  is the average  $^k\text{Si}$  fraction determined by the  $i$ -th laboratory, but, as a precaution,  $u_k^i$  is the standard deviation of the relevant data set, not that of the average. It is to be noted that, since the relevant measurement procedures either correct or exclude contamination,  $\alpha_i = 0$  for the PTB and the IPM-RAS data.

In (5),  $x_{29}^0$ ,  $x_{30}^0$ , and  $\alpha_{\text{IRMM}}$  are model parameters to be determined. If no prior information about the parameters is available, their most probable values minimize [9]

$$\chi^2 = \frac{1}{2} \sum_{\substack{k=29,30 \\ i=\text{PTB,IPM-RAS,IRMM}}} \left( \frac{y_k^i - x_k^i}{u_k^i} \right)^2. \quad (6)$$

The result is shown in Fig. 1 (right). The most probable fractions are indicated by the black dot. The ellipse is the relevant 68% confidence region calculated as the inverse of the Hessian matrix of (6) evaluated at the  $\chi^2$  minimum [9].



**Figure 2.** Left: the IRMM data before (top, red) and after (bottom, blue) the correction for the natural-Si contamination. Right: zoom of the non-corrected IRMM data. The rainbow colors indicate the sample mass, from the lightest (40.0 mg, violet) to the heaviest (48.0 mg, red). Some of the sample mass is also indicated. The error bars indicate the uncertainty of each individual datum. The line is the locus of samples contaminated or depleted by natural Si.

### 3.1. Correction of natural Si contamination

**3.1.1. IRMM data.** The molar contamination of natural Si of the  $\text{BaSiF}_6$  is  $\alpha \approx \mu M/m$ , where  $\mu = 2.863(20) \times 10^{-7}$  mol is the amounts of natural Si added in its preparation – as measured by University of Warsaw – and  $m$  and  $M$  are the mass and molar mass of the crystal samples. The average shown in Fig. 1 (left) has been obtained by using these  $\alpha$  values and (4) to correct each of the raw data. The raw and the corrected data are shown in Fig. 2 (left).

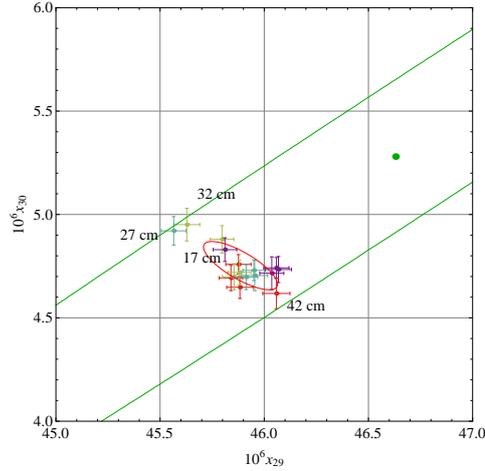
Figure 2 (right) shows that the non-corrected data are consistent with a contamination increasing with a decreasing sample mass. Let the sampling distributions of the measured  $y_k^i$  fractions, where, now,  $i$  labels the samples, be Gaussian and independent. Therefore,  $y_k^i \in N(x_k^i, u_k^i)$ , where  $x_k^i$  – given by (3) – is the  $k$ Si fraction of the contaminated sample and  $u_k^i$  are the measurement uncertainties. Additionally, let no prior information about the unknown parameters  $\mu$ ,  $x_{29}^0$ , and  $x_{30}^0$  be available. Hence, their most probable parameter values minimize [9]

$$\chi^2 = \frac{1}{2} \sum_{\substack{k=29,30 \\ i=1,N}} \left( \frac{y_k^i - x_k^i}{u_k^i} \right)^2. \quad (7)$$

By using (3), the dependence of  $\chi^2$  on  $\mu$ ,  $x_{29}^0$ , and  $x_{30}^0$  can be made explicit. Hence,

$$\chi^2(\mu, x_{29}^0, x_{30}^0) = \frac{1}{2} \sum_{\substack{k=29,30 \\ i=1,N}} \left[ \frac{y_k^i - (1 - \mu/n_i)x_k^0 - \mu x_k^{\text{nat}}/n_i}{u_k^i} \right]^2, \quad (8)$$

where  $n_i = m_i/M$  are the Si moles in the  $i$ -th sample,  $m_i$  and  $M$  – which is a function of  $x_{29}^0$  and  $x_{30}^0$  – being the sample mass and molar mass. The result is  $\mu = 2.6(1.4) \times 10^{-7}$  mol, to be compared with  $\mu = 2.863(20) \times 10^{-7}$  mol obtained by the University of Warsaw. The most probable fractions are indicated by the green



**Figure 3.** Zoom of the corrected IRMM data. The rainbow colors indicate the sample location, from the nearest (17 cm, violet) to the farthest (42 cm, red) from the seed crystal. Some of the sample location is also indicated. The error bars indicate the uncertainty of each individual datum. The black line is the locus of samples contaminated or depleted by natural Si. The ellipses are the 68% confidence regions.

dot in Figs. 1 and 2, the ellipse being the relevant 68% confidence region. The  $\mu$  uncertainty and the fraction confidence-region have been calculated as the inverse of the Hessian matrix of (8) evaluated at the  $\chi^2$  minimum.

*3.1.2. PTB data.* The contamination by natural Si, as well as offsets and memory effects, were corrected by measuring the ion currents of the blank, the aqueous NaOH solution plus the spectrometer background-current. In brief, the measurement procedure was as follows [10]. The solutions of the two blends for the spectrometer calibration (prepared from the  $^{29}\text{Si}$ ,  $^{30}\text{Si}$ , and natural Si materials), of the IDMS-blend (prepared from the  $^{28}\text{Si}$  and  $^{30}\text{Si}$  materials), and of the parent materials themselves were filled into separate vials of the auto-sampler tray. Each solution measurement was preceded by a blank measurement under exactly the same conditions. In total, seven solution measurements and seven blank measurements were performed in a sequence. The solution currents were corrected by subtracting the previously measured blank ones. Eventually, the ratios of the corrected currents were used to calculate the calibration factors and, together with these so determined factors, the isotope amount ratios of the  $^{28}\text{Si}$  material. It is worth noting that an individual spectrometer calibration is carried out for each measurement of a different sample of the  $^{28}\text{Si}$  crystal.

Since natural Si contamination and background currents originate an inextricable contribution to the measured values of the  $^{28}\text{Si}$  crystal isotope-fractions, and since they affect the spectrometer calibration as well, no simple model like (3) is available to correct the measurement results (Fig. 1). Consequently, the measured fractions are not corrected ex-post according to an estimate of the natural Si contamination. Therefore, under- and over-correction are equally likely and the correction uncertainty accounts for both possibilities. Figure 1 (right) shows that the isotopic compositions determined without subtraction of the blank currents are much more scattered than

**Table 1.** Comparison between the expected and observed standard deviations and correlation of the measured isotope fractions.

laboratory	expected value			observed value		
	$10^6 u_{29}$	$10^6 u_{30}$	$\rho_{29,30}$	$10^6 u_{29}$	$10^6 u_{30}$	$\rho_{29,30}$
IRMM	0.059	0.063	0.00	0.14	0.095	-0.77
PTB	0.16	0.041	0.31	0.12	0.024	0.37

expected by their individual uncertainties. When the same isotopic compositions are recalculated after subtraction of the blank currents, they group together and their scattering is consistent with what expected.

### 3.2. Homogeneity of isotopic composition

In order to identify gradients of the isotopic composition, in Fig. 3, the IRMM data are shown by rainbow colors indicating the sample location, from the nearest to the boule seed-crystal (violet) to the farthest (red). The same color code has been used to display the PTB data in Fig. 1 (left). No significant correlation between the isotopic composition and the sample location can be identified.

### 3.3. Statistical properties of data

Figure 3 (left) shows the IRMM data, corrected according to the University of Warsaw determination of the natural Si contamination; they are inside the 68% confidence region of the most probable composition estimated from the correlation between the raw data and the sample mass. However, the isotope fractions are still insufficiently corrected; this suggests that some contamination mechanism has not yet been identified.

The table 1 compares the standard deviations and correlations associated to the individual measured fractions with those estimated from the sets of repeated measurements shown in Figs. 1 and 3. The scattering of the fractions measured by the IRMM is larger than the uncertainty associated to each single datum. In addition, though no correlation is expected, the fractions measured by the IRMM display a 77% negative correlation, as also shown by the 68% confidence region in Fig. 3. The PTB data show a good agreement between the expected and observed uncertainties and correlation.

## 4. Conclusions

The isotopic composition of the  $^{28}\text{Si}$  crystal used to determine  $N_A$  was measured in different laboratories by means of different measurement methods. At present, only the IRMM and PTB carried out calibrated measurements of the isotope amount-ratios and only the PTB assessed the total uncertainty budget [11]. The analysis of the measurement results indicates that all the data are consistent with a model accounting for a natural Si contamination, with the PTB ones being unaffected. Additionally, the standard deviation and correlation of the PTB data-set are consistent with those associated to each individual datum. For this reasons, the  $N_A$  value given in [2] relies on the PTB molar-mass determination alone and we postponed the use of IRMM data

until a full assessment of the uncertainty budget will be completed and the measured values will be published. The consistency of the isotopic composition determined by the PTB with those determined by the IRMM and IPM-RAS is of a particular value in assessing the reliability of the  $N_A$  determination. Furthermore, no data set displays a correlation between the measured isotopic composition and the sample location; therefore, they prove the homogeneity of the  $^{28}\text{Si}$  boule.

## Acknowledgments

This research received funding from the European Community's Seventh Framework Programme, ERA-NET Plus, under the iMERA-Plus Project - Grant Agreement No. 217257.

## References

- [1] Becker P, Friedrich H, Fujii K, Giardini W, Mana G, Picard A, Pohl H-J, Riemann H, and Valkiers S 2009 The Avogadro constant determination via enriched silicon-28 *Meas. Sci. Technol.* **20** 092002
- [2] Andreas B, Azuma Y, Bartl G, Becker P, Bettin H, Borys M, Busch I, Gray M, Fuchs P, Fujii K, Fujimoto H, Kessler E, Krumrey M, Kuetsgens U, Kuramoto N, Mana G, Manson P, Massa E, Mizushima S, Nicolaus A, Picard A, Pramann A, Rienitz O, Schiel D, Valkiers S and Waseda 2011 A determination of the Avogadro constant by counting the atoms in a  $^{28}\text{Si}$  crystal *Phys. Rev. Lett.* **106** 030801
- [3] Mana G, Massa E, Valkiers S, and Willenberg G-D 2010 Uncertainty assessment of Si molar mass measurements *Int. J. Mass Spectrom.* **289** 6-10
- [4] Rienitz O, Pramann A, Schiel D, Schlote J, Guettler B, and Valkiers S 2011 Molar mass of silicon highly enriched in  $^{28}\text{Si}$  using IDMS *Metrologia* this issue
- [5] Rienitz O, Pramann A, and Schiel D 2010 Novel concept for the mass spectrometric determination of absolute isotopic abundances with improved measurement uncertainty: Part 1 Theoretical derivation and feasibility study *Int. J. Mass Spectrom.* **289** 4753
- [6] Mana G, Rienitz O, and Pramann A 2010 Measurement equations for the determination of the Si molar mass by isotope dilution mass spectrometry *Metrologia* **47** 4603
- [7] Mana G and Rienitz O 2010 The calibration of Si isotope ratio measurements *Int. J. Mass Spectrom.* **291** 55-60
- [8] Drozdov M N, Drozdov Yu N, Pryakin D A, Shashkin V I, Sennikov P G, and Pohl H-J 2010 Qualitative Sims Analysis of  $^{28,29,30}\text{Si}$  Isotope Concentration in Silicon using a Tof.Sims-5 Setup *Bulletin of the Russian Academy of Sciences: Physics* **74** 75-7. Original Russian text 2010 *Izvestiya Rossiiskoi Akademii Nauk. Seriya Fizicheskaya* **74** 84-6
- [9] Sivia DS and Skilling J 2006 *Data Analysis, A Bayesian Tutorial* (Oxford, Oxford University Press)
- [10] Pramann A, Rienitz O, Schiel D, Guettler B 2011 Novel concept for the mass spectrometric determination of absolute isotopic abundances with improved measurement uncertainty: Part 2 - Development of an experimental procedure for the determination of the molar mass of silicon using MC-ICP-MS *Int. J. Mass Spectrom.* **299** 78-86
- [11] Rienitz O, Pramann A, Schiel D, Guettler B, and Valkiers S 2011 Novel concept for the mass spectrometric determination of absolute isotopic abundances with improved measurement uncertainty: Part 3 Molar mass of silicon highly enriched in  $^{28}\text{Si}$  *Int. J. Mass Spectrom.* submitted