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Measurement of the molar mass of ^{28}Si-enriched silicon crystal（AVO28） with HR-ICP-MS

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Abstract

Accurate molar mass measurement of the highly ^{28}Si-enriched crystal (AVO28) plays a crucial role in the accurate determination of the Avogadro constant and thus the new definition of the kilogram. At the National Institute of Metrology (NIM), a high resolution inductively coupled plasma mass spectrometer (HR-ICP-MS) combined with the 'virtual element' isotope dilution mass spectrometry (VE-IDMS) method was used to determine the molar mass of the AVO28 material. The key advantage of this approach is that it can separate the interferences, such as ^{28}Si^{1}H, completely from silicon ions when using medium mass resolution mode ($M/\Delta M$~5000). During the sample preparation, AVO28, WASO 04, enriched ^{29}Si and ^{30}Si materials were dissolved with 25% (mass fraction) tetramethylammonium hydroxide (TMAH), and the amounts of TMAH in prepared sample solutions were finally diluted to 0.025% to maximally reduce the potential interferences of nitrogen or carbon based polyatomic species on silicon isotopes. Dead time correction and mass bias correction were also studied and performed. As a result, an average molar mass of four pieces of the AVO28 material was determined to be 27.97696905 g mol^{-1} with an associated relative standard uncertainty of 9.4×10^{-9} (k = 1). This result is in between the reported results of the Physikalisch-Technische Bundesanstalt (PTB,

Germany), the National Metrology Institute of Japan (NMIJ, Japan), the National Institute of Standards and Technology (NIST, USA) and the National Research Council (NRC, Canada), with its uncertainty level very close to that of PTB and NRC.

Introduction

The silicon molar mass measurement reported in this paper is part of the international effort to redefine the kilogram (kg). The kilogram is the only base unit of the International System of Units (SI) defined in terms of an artificial material, namely, the international prototype of the kilogram. Although the prototype has served science and technology well, it has a number of important limitations, with one of the most significant being that its mass is not explicitly linked to an invariant of nature and in consequence its long-term stability is not assured.[1, 2] Driven by a consensus on limitations of the current definition, the General Conference on Weights and Measures (CGPM) at its 24th meeting in 2011 adopted a resolution to revise the SI, where definition of the kilogram is proposed to be linked to the exact numerical values of the Planck constant (*h*).[2] Given the importance of the kilogram as a critical base unit which the definitions of the ampere (A), mole (mol) and candela (cd) all depend on, its redefinition has been deemed by the international metrology community as one of the most important cutting-edge basic research topics and has involved tremendous efforts of many laboratories over the past decades.

At present there are two independent and mutually comparable ways to redefine the kilogram, besides the direct measurement of the Plank constant (*h*) by Watt-balance experiments,[3-5] measurement of the Avogadro constant (N_A) by silicon crystal experiment is another promising method.[6-8] Considering the continuity of mass metrology, the relative uncertainty of N_A must not exceed 2×10^{-8}.[9] To enable the silicon crystal experiment, a highly ^{28}Si-enriched (AVO28) crystal was grown and two ^{28}Si spheres with perfect shape were manufactured under the organization of the International Avogadro Coordination (IAC).[10] Then the Avogadro constant can be obtained using equation (1), in which each parameter of the silicon sphere needs to be determined accurately.

$$N_A = nM/(\rho a^3) \qquad (1)$$

where n is the number of atoms per unit cell of a silicon crystal, equal to 8, ρ is the density and a is the lattice parameter, M is the molar mass. For silicon, the molar mass can be calculated by equation (2).

$$M(Si) = \frac{m_{28} \times R_{28/29} + m_{29} + m_{30} \times R_{30/29}}{R_{28/29} + 1 + R_{30/29}} \qquad (2)$$

where m_{28}, m_{29}, m_{30} are the nuclide mass of Si isotopes, $R_{28/29}$ and $R_{30/29}$ are the isotope ratios of $n(^{28}\text{Si})/n(^{29}\text{Si})$ and $n(^{30}\text{Si})/n(^{29}\text{Si})$.

In order to achieve a redetermination of N_A with an uncertainty target of $u_{rel}(N_A) \leq 2 \times 10^{-8}$, the relative uncertainty of molar mass of AVO28 crystal should be less than 1×10^{-8}. [9] As nuclide masses have been determined precisely enough to meet the requirement of molar mass measurement,[11] the isotope ratio becomes the main uncertainty contributor to the molar mass.

Initially, molar mass of the AVO28 crystal was measured with gas mass spectrometry and multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS), but a large discrepancy was found between their measurement results.[12] The natural Si contamination in the enriched ^{28}Si material, which was difficult to correct on-line when using gas mass spectrometry, was thought to be the main reason. However, influences from natural Si contamination and instrumental memory effect can be eliminated with the matrix matching method when using MC-ICP-MS.

In the AVO28 crystal, the abundance of ^{28}Si is extremely high (>99.99%), and the isotope ratio of $n(^{28}\text{Si})/n(^{29}\text{Si})$ is over 200000,[13] which is almost impossible to measure directly with mass spectrometry by now. To solve this problem, a novel approach called ‘virtual element’ isotope dilution mass spectrometry (VE-IDMS) was developed by the Physikalisch-Technische Bundesanstalt (PTB, Germany).[13-18] In this approach, the isotopes ^{29}Si and ^{30}Si with minor abundances in the AVO28 crystal consist of the so called ‘virtual element’, and the mass fraction w_{imp} of the virtual element is determined by a modified IDMS technique, with which the absolute isotope ratios can be obtained and then the molar mass is calculated by equation (3).[13, 14] PTB's research showed that a standard uncertainty of $R_{30/29}$ in the AVO28 crystal high to 4% could still enable the molar mass measurement when applying the modified IDMS method.[13] Thereafter, the VE-IDMS approach was also adopted by the National Research Council (NRC, Canada) [19], the National Metrology Institute of Japan (NMIJ, Japan) [20] and the National Institute of Standards and Technology (NIST, USA) [21] in their molar mass measurements of AVO28 crystal.

$$M\text{（}Si\text{）}= \frac{m_{28}}{1+(m_y/m_x)((m_{28}(1+R^x_{30/29})-m_{29}-R^x_{30/29}m_{30})/(R^y_{28/29}m_{28}+m_{29}+R^y_{30/29}m_{30}))((R^y_{30/29}-R^{yx}_{30/29})/(R^{yx}_{30/29}-R^x_{30/29}))} \quad (3)$$

where m_y and m_x denote the mass of isotopically enriched ^{30}Si material and the mass of AVO28 material used to prepare the spiked ^{28}Si solution; $R^x{}_{30/29}$ is the corrected isotope ratio of $n(^{30}\mathrm{Si})/n(^{29}\mathrm{Si})$ in AVO28 material, $R^y{}_{30/29}$ and $R^y{}_{28/29}$ are the corrected isotope ratios of $n(^{30}\mathrm{Si})/n(^{29}\mathrm{Si})$ and $n(^{28}\mathrm{Si})/n(^{29}\mathrm{Si})$ in enriched ^{30}Si material, $R^{yx}{}_{30/29}$ is the corrected isotope ratio of $n(^{30}\mathrm{Si})/n(^{29}\mathrm{Si})$ in the spiked ^{28}Si solution.

Nevertheless, to measure Si isotope ratios with MC-ICP-MS still has two major technical problems. One is the mass bias effect caused by different transmission efficiency of different isotopes, so that deviation to the true value becomes nonnegligible and must be corrected.[22, 23] Due to the lack of appropriate certified reference materials (CRMs), correction solutions need to be gravimetrically prepared with isotopically enriched silicon materials.[13, 19-21] The other problem lies in the isobaric interferences produced in the ICP ion source like NO^+, CO^+, $N_2{}^+$, N_2H^+, SiH^+, and so on. There was once an attempt to use the collision cell technique to eliminate these interferences. However, Si ions especially the $^{30}Si^+$ were still heavily interfered by these polyatomic ions and signal intensities of Si ions were reduced greatly when collision gases were used.[24] The high mass resolution mode was adopted to solve this problem by Pramann et al.[13] Under 8000 mass resolution, $^{29}Si^+$ and $^{30}Si^+$ could be partly separated from interferences, a small plateau of $^{29}Si^+$ was observed, and data could be properly collected when the instrument was stable enough during the entire measurement process.[13]

In this study, a high resolution inductively coupled mass spectrometer (HR-ICP-MS) was selected to measure the molar mass of the AVO28 crystal, based upon four key considerations. Firstly, as the abundances of ^{29}Si and ^{30}Si in AVO28 crystal are low to about 0.004% and 0.0001% respectively,[13] the signal intensity of $^{29}Si^{+}$ might be comparable to that of the interference caused by hydride silicon ($^{28}Si^{1}H^{+}$), and the signal intensity of $^{30}Si^{+}$ might be at only 1-2 mV, two orders of magnitude lower than that of $^{14}N^{16}O^{+}$.[13] Secondly, as is different to MC-ICP-MS (Neptune), HR-ICP-MS (Element2) has a truly high mass resolution, by which all silicon isotopes can be measured free from interferences. Thirdly, although there is only one collector equipped in Element2 HR-ICP-MS, uncertainties of measured isotope ratios are still able to meet the requirement of molar mass measurement according to the uncertainty evaluation by PTB's work.[13] Finally, as the four national metrology institutes (NMIs) have all used the same type of instrument (Neptune) to measure the molar mass of AVO28 crystal, and an obvious discrepancy was found between results of the NRC and other three NMIs, it is reasonable and necessary to conduct an independent molar mass measurement using a different technique.

This paper describes the development, application and evaluation of a new HR-ICP-MS method for the molar mass measurement of the AVO28 crystal at the National Institute of Metrology (NIM, China). The VE-IDMS approach developed by PTB was adopted. Tetramethylammonium hydroxide (TMAH) was used to dissolve the solid silicon materials and the amount of TMAH in sample solutions was set to 0.025%. Measurement precision of isotope ratios, dead time correction, mass bias correction and detection system linearity were all investigated and their effects on the molar mass of AVO28 materials were also evaluated. Finally, the molar masses of four AVO28 samples were measured. Data were analyzed in comparison with data obtained by the other four NMIs.

Experiment

Materials and reagents

All solid silicon materials used in this experiment were provided by the IAC and distributed by the PTB, which included four pieces of AVO28 samples (X) respectively named 5B1.2.2.3, 5B1.2.2.4, 8B3.2.2.2 and 8B3.2.2.4, one isotopically enriched ^{30}Si sample (Y), one isotopically enriched ^{29}Si sample (Z) and one natural silicon sample (WASO 04)(W). All samples were carefully cleaned and etched individually before use.

25% (mass fraction) tetramethylammonium hydroxide (TMAH) solution (TraceSELECT®, Ultra, Fluka) and hydrofluoric acid (HF, 49%, for trace analysis, Fluka) were purchased from Sigma-Aldrich Trading Co., Ltd. Nitric acid was purified in-house by sub-boiling distillation in a PFA still. Fresh 18 MΩ cm deionized water was made with a Millipore water purification system (Elix 5 UV, Milli-Q Element A10, Millipore Corporation, USA). All vessels including bottles and tubes were made of PFA to avoid contamination from natural silicon during the material preparation process. They were firstly washed with acetone and ethanol to clean the organics, then washed with 10% (volume fraction) HNO_3 for 24h, 0.1% (volume fraction) HF for 2h, 0.25% (mass fraction) TMAH for 24h and finally rinsed with water. The cleaned vessels were stored in a clean fume hood and were air-dried.

Sample preparation

Figure 1 illustrates the seven different sample solutions that are required for a completely calibrated measurement of the molar mass of one AVO28 sample (see the bottom of Figure 1, solutions encircled by a dash box). The stock solutions were firstly prepared by dissolving the solid materials in TMAH. Then these stock solutions were used to respectively prepare the blend solutions for IDMS and the blend solutions for mass bias correction. All the solutions were prepared in a 1000 class clean room. Air buoyancy correction was made to all weighing data. In order to accurately correct the effect of blank on isotope ratio measurement, the corresponding procedure blank solution for each sample solution was prepared in the same way. The solution preparation process was described in details as below.

Stock solutions. Solid materials were initially weighed separately with a UMX2 balance (Mettler Toledo, the balance permits estimation to 0.1μg). After dissolved in

25% (mass fraction) TMAH, the stock solution was transferred into the PFA bottle and a certain amount of 25% (mass fraction) TMAH solution was added into the corresponding bottle. Then these bottles were transferred into the oven and the temperature was kept at 60℃ for 3-4 days.[20] During the reaction process, caps were loosely covered on PFA bottles for the purpose of releasing the gas generated. After complete dissolution, samples X were gravimetrically diluted with water to produce stock X solutions (w_{Si}=2400 μg g^{-1}, 0.1% (mass fraction) TMAH) and then X solutions (w_{Si}=600 μg g^{-1}, 0.025% (mass fraction) TMAH); samples of WASO 04, ^{29}Si and ^{30}Si were respectively gravimetrically diluted with water to produce the 600 μg g^{-1} stock solutions (2.5% (mass fraction) TMAH), which were then gravimetrically diluted with water to separately produce the W solution, the Z solution and the Y solution through two steps.

Blend solutions for IDMS. Giving consideration to the extreme isotopic composition of AVO28 crystal, 6 μg g^{-1} ^{30}Si (Y solution) was chosen to be the spike for IDMS method. According to the classical theory of IDMS, the blend solutions with the optimum dilution ratio[25], $r(^{30}Si/^{29}Si) = 4.9$ were prepared to minimize the measurement uncertainty of isotope ratio. About 17.25 g ^{28}Si-enriched solution (X solution) and 2 g Y solution were accurately weighed in a clean 100 mL PFA bottle. The spiked solution was diluted with water to produce the YX solution, and all four YX solutions were prepared in the same way.

Blend solutions for K factors. Two series of blend solutions were gravimetrically prepared to correct the mass bias effect in this work. Three WZ blend solutions were prepared with WASO 04 solution (W solution) and ^{29}Si solution (Z solution), the value of $^{28}Si/^{29}Si$ in these solutions was 5 (WZ1 solution), 2 (WZ2 solution) and 1 (WZ3 solution) respectively. Three YZ blend solutions were prepared with ^{30}Si solution (Y solution) and ^{29}Si solution (Z solution), the value of $^{30}Si/^{29}Si$ in these solutions was 5 (YZ1 solution), 2 (YZ2 solution) and 1 (YZ3 solution) respectively.

Finally, the silicon concentration in prepared W solution, Z solution, Y solution and all blend solutions for K factors was 6 μg g^{-1}, in blend solutions for IDMS was

600 μg g^{-1}, and the matrix of each sample solution was finally diluted to be 0.025% (mass fraction) TMAH (See Figure 1).

Procedure blank solutions. To enable a proper conducting of blank correction, which was critical to the molar mass measurement of AVO28 crystal, a corresponding procedure blank solution was prepared for each sample solution in the same way, which means that, they were prepared through the same serial dilutions and a same amount of 25% TMAH, calculated based on the Si material weight and the TMAH concentration in prepared sample solution, was used. The concentration of TMAH in each procedure blank solution was showed in Figure 2. Because there was no Si material to react with TMAH in the blank solution, the concentration of TMAH in the blank solution was higher than that in the corresponding sample solution (compare the w_{TMAH} shown in Figure 1 and Figure 2). However, the quantity of silicon contamination induced from sample preparation was the same.

Instrumentation

The mass spectrometer used for silicon isotope ratio measurement in this work was a double focusing sector field SF-ICP-MS (Element2 HR-ICP-MS, Thermo Scientific; Bremen, Germany) with electrostatic and magnetic scanning analyzers, which are configured in a reverse Nier-Johson geometry. Predefined resolution settings of 300, 4000 and 10000 allow three different mass resolutions. The instrument was equipped with one platinum sampler cone and one platinum skimmer cone (1.1 and 0.8 mm orifice diameters, respectively), a cyclonic spray chamber with a self-aspirating PFA nebulizer (50 μL min^{-1}), a quartz torch with a sapphire injector (AHF analysentechnik AG, Germany), a platinum guard electrode and a secondary electron multiplier with conversion dynode. The instrument was placed in a 10000 class clean room with constant temperature and humidity conditions.

All isotope ratio measurements were performed in a medium mass resolution setting ($M/\Delta M$~5000) using the electrostatic scanning (E-Scan) mode. Under this mode, the accelerating voltage was scanned while the magnetic field was kept constant. This mode allowed a very rapid switching between peaks and therefore an isotope ratio with much higher precision could be attained compared to the magnetic scanning mode (B-Scan).[26, 27]

Isotope ratio measurement

Prior to a measurement sequence, mass calibration was carried out carefully and the instrumental settings were optimized by using a 1 ng ml^{-1} multi-element standard solution to produce a stable and acceptable intensity. Additionally, both sampler cone and skimmer cone were changed on a daily basis to keep the instrumental background at a low level. In the seven sample solutions, for W solution, Z solution, Y solution, WZ solution and YZ solution, ion signals of ^{28}Si, ^{29}Si and ^{30}Si were all collected, and ^{28}Si/^{29}Si, ^{30}Si/^{29}Si were determined, whereas only ^{30}Si/^{29}Si was determined for YX solution and X solution. Because the seven sample solutions differed a lot in the Si isotopic compositions, both analog and pulse counting mode ('Both' mode) was adopted to collect the Si ion signals. The typical operating parameters were listed in Table 1. Under this condition, the instrument sensitivity was about 1×10^{7} counts per second (cps) / (μg g^{-1}) for ^{28}Si^{+} in natural silicon, and approx 10 cps / (μg g^{-1}) for ^{30}Si^{+} in AVO28 sample.

The seven sample solutions and their corresponding procedure blank solutions were analyzed following the sequence shown in Figure 2. Before analyzing each procedure blank solution, 0.025% (mass fraction) TMAH and deionized water were used to rinse the sample introducing system at least 20 min to avoid potential cross contamination between different samples. The ion signals of silicon isotopes obtained from the procedure blank solution were measured under the same conditions and were subtracted automatically from the corresponding sample solution by setting the measurement program. Normally, the Si concentration in blank solution was proved to be similar to that obtained by NIST[21] and lower than that obtained by NMIJ[20] with Neptune. The complete list of data for all blank solutions is contained in the extended supplement.

Results and discussion

Spectral interferences

Measurement of Si with ICP-MS will be complicated by spectral interferences to all its three isotopes. These interferences include polyatomic ions, doubly charged ions or isobaric interferences. Table 2 lists the main spectral interferences relating to each Si isotope and the evaluated mass resolutions used to separate Si isotopes from the corresponding interferences. Because the enrichment of ^{28}Si in the AVO28 material was extremely high, a very strong signal of hydride silicon $^{28}Si^{1}H^{+}$ might be produced during the measurement. In this study, an experiment was designed to estimate the yield of hydride silicon: a 6 μg g^{-1} ^{30}Si solution was introduced into the instrument, and the isotope ratio of $^{30}Si^{1}H^{+}/^{30}Si^{+}$ was measured under the same conditions shown in Table 1. The value was approximately 0.0004%, equivalent to the value of $^{29}Si^{+}/^{28}Si^{+}$ in the AVO28 material, [13] which meant that the intensity of produced $^{28}Si^{1}H^{+}$ was similar to that of $^{29}Si^{+}$. A typical mass scan of X solution with Element2 HR-ICP-MS under the medium resolution (MR) mode is shown in Figure 3. It was obvious that the MR mode was sufficient to separate the silicon isotopes completely from the polyatomic species, and was preferable than the HR mode as a higher level of sensitivity could be obtained. In order to minimize the production of nitrogen and/or carbon based interferences, concentration of TMAH in the solutions was further diluted to 0.025%. Additionally, both sample cone and skimmer cone were changed to Pt cones instead of Ni cones to avoid generation of Ni^{2+}.

Measurement precision of isotope ratios

Although the Element2 HR-ICP-MS has a worse measurement precision than the MC-ICP-MS due to their structural difference, it is still a feasible approach for the molar mass measurement of AVO28 crystal because a relative uncertainty of 4% for $^{30}Si/^{29}Si$ in AVO28 crystal has been proved to be sufficient when the VE-IDMS method is adopted.[13] In this work, the measurement uncertainties of Si isotope ratios in all seven sample solutions were investigated under the same instrumental condition shown in Table 1, 0.16~1.5% relative standard deviation (RSD) were obtained and measurement results were listed in Table 3.

As measuring all the seven sample solutions in one sequence normally takes about 5 hrs, stability of the instrument is quite important and needs to be tested as well. A replicate analysis of WASO 04 solution was carried out over 5 hrs. 0.15% RSD (n=5) was obtained for $^{28}Si^{+}/^{29}Si^{+}$, which were illustrated in Figure 4. The experiment indicated that no obvious systematic drift of instrument was observed over the entire measurement period.

Dead time correction

The time from the beginning of an incoming pulse till the time when a new pulse can be registered is called dead time.[28, 29] When the counting rates are at a high level (from 10^6 to 5×10^7 counts s^{-1}), the registered events may be less than those actually occurring, which will cause the ion signals to be non-linear, and affect the determination of the isotope ratios, especially for the ratio far from unit. Therefore, dead time correction is very crucial to an accurate determination of isotope ratio. Considering that dead time is independent of analyte mass number when using Element2 HR-ICP-MS,[26, 30, 31] a natural uranium solution was used to measure the dead time in this work following instructions provided by the instrument company. In short, four solutions with 0.5, 1.0, 1.5 and 2.0 μg L^{-1} of uranium were prepared, in which the count rates of ^{238}U were no more than 4×10^6 counts s^{-1}. Data were collected for the $^{235}U^+$ and $^{238}U^+$ isotopes in these samples without dead time correction (uncheck the box “dead time correction active” via the software), and then the measured signal intensities of $^{235}U^+$ and $^{238}U^+$ were corrected based on equation (4). The corrected isotope ratios of $^{235}U^+/^{238}U^+$ were calculated with the corrected signal intensities, and were plotted as a function of the uranium concentrations. The dead time value was optimized until the slope of the line was close to zero, and this optimized value was used to correct the detector’s dead time effect. Figure 5 compared the changes of $^{235}U^+/^{238}U^+$ caused by different U concentration obtained with different dead time values. When dead time was set 3 ns, the corrected results of $^{235}U^+/^{238}U^+$ did not vary with the changes of U concentration.

$$I_{corr} = \frac{I_{meas}}{1 - I_{meas} \times \tau_{dead}} \qquad (4)$$

Where I_{corr} is the corrected intensity (cps); I_{meas} is the measured intensity (cps); τ_{dead} is the dead time value(s).

It is necessary to point out that the measured dead time could be changeable and the true dead time is difficult to determine with a high accuracy.[28, 30, 31] In order to assess the impact of dead time change on molar mass value, the seven solutions were repeatedly measured under different dead time settings. The obtained molar masses of sample '8B3.2.2.2' were shown in Figure 6. We can see that there is no obvious change in the molar mass no matter the dead time correction is inadequate or over-estimated. Theoretically, there will be a bias on the corrected isotope ratios if the dead time used is different from the true value. One reasonable explanation is that this bias could be interpreted as part of and be corrected by the mass bias correction, [31] which leads to the agreement among the molar masses measured under different dead time settings.

Linearity test

As mentioned before, isotopic compositions in the seven sample solutions are very different, and signal intensities of one isotope ions may range from several thousand counts s^{-1} to over ten million counts s^{-1}. Therefore, the linearity of detection system in Element2 HR-ICP-MS was tested to ensure that no bias would be caused by different signal intensities. A series of W solutions were prepared and measured under the same condition, with Si concentrations ranging from 0.3 μg g^{-1} to 15 μg g^{-1}. Figure 7 showed the signal intensities of $^{28}Si^{+}$ plotted as a function of Si concentrations. Obviously, the signal intensities were linear to the Si concentrations within this range. The external precision of measured isotope ratios of $^{28}Si^{+}/^{29}Si^{+}$ in the ten solutions was less than 1%.

Mass Bias Correction

Mass bias is another important effect causing deviations of measured isotope ratios from true values. In order to investigate the influence of variations of isotope ratios on correction factors (*K* factors), three YZ blend solutions and three WZ blend solutions were prepared and measured under the same instrumental condition. Results were shown in Figure 8, where no obvious discrepancy was observed. Thereafter, only YZ1 and WZ1 solutions were used to correct the mass bias effect for the molar mass measurement of AVO28 crystal. The typical values of K factors obtained with YZ1 and WZ1 solutions in different days were compared and listed in Table 4.

Compared to the mass bias effect caused in MC-ICP-MS, the effect caused in Element2 HR-ICP-MS was much less.[20, 21]

Molar mass of AVO28 crystal

Molar masses of the four AVO28 materials were repeatedly measured for several times and were calculated by equation (3) with the corrected isotope ratios and samples' weights, the 34 values obtained so far were summarized in Figure 9. The data were classified into four groups in correspondence to the four AVO28 samples. Each data point was obtained individually in one sequence as shown in Figure 2. These data obeyed a normal distribution according to the statistic analysis. The average molar mass and isotopic compositions of the four AVO28 materials as well as their grand average values are listed in Table 5. Comparing the data obtained by 5B and 8B samples, we know that materials cut from different parts of the ^{28}Si crystal are homogeneous within the standard uncertainty. The average molar mass of the AVO28 crystal obtained in this work is M(Si) = 27.97696905g mol^{-1} with an associated relative standard uncertainty of 9.4×10^{-9} (k = 1). The uncertainty level is similar to that of PTB[13] and NRC[19] but higher than that of NIST[21] and NMIJ[20].

Uncertainty evaluation

Uncertainties for all measurement results were evaluated basically according to the Guide to Expression of Uncertainty in Measurement of ISO/BIPM.[32] The individual parameters and their contributions to the uncertainty budget of the results were calculated using the GUM Workbench program.[33] Taking sample 5B1.2.2.3 as an example, a representative uncertainty budget is shown in Table 6. Similar to other NMIs' results, the isotope ratios of ^{30}Si/^{29}Si in the solutions are the dominating uncertainties to the molar mass of AVO28 crystal. Considering that different NMIs adopted different measurement methods or data dealing processes, the proportion of different items in the combined uncertainty could be different. In this work, major uncertainty contributors included ^{30}Si/^{29}Si in the blend solution YZ (67%), the spiked solution YX (27%) and the ^{28}Si solution X (5%). As shown in Table 3, the uncertainty of ^{30}Si/^{29}Si in X solution and Y solution measured with Element2 HR-ICP-MS is comparable to that measured with MC-ICP-MS, but its uncertainty in the YZ and the

YX solution measured with Element2 HR-ICP-MS is tens of times of that measured with MC-ICP-MS, especially for the $^{30}Si/^{29}Si$ in YZ solution.[13, 21] This reveals the main reason why the predominant contributor to the uncertainty of the molar mass of AVO28 crystal obtained in this work was the measurement of $^{30}Si/^{29}Si$ in YZ solution.

Discussion

Figure 10 summarizes the molar mass of AVO28 crystal obtained by PTB[13], NRC[19], NMIJ[20], NIST[21] and NIM (this work). The value obtained in this work is lower than the values reported by PTB, NMIJ and NIST, but higher than the value of NRC. Table 7 lists the corrected $^{29}Si/^{30}Si$, the isotope abundances and the molar mass of the 'virtual element' obtained by PTB[13], NRC[19], NMIJ[20], NIST[21] and NIM (this work). Comparing these data, NIM is much closer to NIST in both $^{29}Si/^{30}Si$ value and molar mass of 'virtual element', but is much closer to NRC in molar mass of AVO28 crystal. Comparing the isotope abundances of ^{28}Si, ^{29}Si and ^{30}Si, we can find that discrepancies among the obtained molar masses are mainly caused by the different isotope abundances of ^{30}Si. So how to separate the extremely low $^{30}Si^+$ from interferences and collect it precisely is still a big challenge.

Conclusions

This work measured the molar mass of four AVO28 samples provided by the IAC, with a view to contribute to the accurate determination of the Avogadro constant N_A, one of the prerequisites for redefining the kilogram. Compared with the other four NMIs that have reported measurement results for this aim by now, NIM has for the first time applied a HR-ICP-MS combined with the VE-IDMS approach to the measurement, which has a prominent advantage that it can enable an interference-free measurement when using medium mass resolution mode. During the experiment, 25% (mass fraction) TMAH was used to dissolve solid materials and solutions were finally diluted to be 0.025% (mass fraction) TMAH in order to minimize the potential interferences of nitrogen or carbon based polyatomic species to silicon isotopes. Uncertainties of measured isotope ratios, instrument stability and linearity were all studied and the results had all testified to the feasibility of applying HR-ICP-MS to molar mass measurement. Correction of dead time effect and mass bias effect were also carefully considered with influence on molar mass evaluated. Finally, an average molar mass of four pieces of AVO28 material was determined to be 27.97696905 g mol^{-1} with an associated relative standard uncertainty of 9.4×10^{-9} ($k = 1$). This work established a new approach for the AVO28 molar mass measurement and provided a verification to the existing measurement results that were all obtained using the MC-ICP-MS method.

An online supplementary data file is available, in which the equations, raw and reduced data reported in this paper are contained along with some relevant equations.

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Tables

Table 1 HR-ICP-MS operating conditions and signal measurement parameters

Parameters	
RF power (W)	1300
Cool gas (L·min^{-1})	16.0
Auxiliary gas (L·min^{-1})	0.80
Sample gas (L·min^{-1})	1.020
Sampler cone (Pt)	1.1 mm
Skimmer cone (Pt)	0.8 mm
Resolution (m/Δm)	5000
Acquisition mode	Electrostatic scanning
Number of isotopes	^{28}Si/^{29}Si and ^{30}Si/^{29}Si
Detection mode	Both
Sample time (ms)	10
Samples per peak	20
Mass window	120%
Peak search window	50%
Integration window	60%
Dead time (ns)	3

Table 2 Spectral interferences on natural silicon isotopes

Isotope	Abundance (%)	Interference	Resolution^{a}
$^{28}Si^{+}$	92.2223(9)	$^{12}C^{16}O^{+}$	1557
		$^{14}N_2^{+}$	958
$^{29}Si^{+}$	4.6853(6)	$^{28}Si^{1}H^{+}$	3509
		$^{58}Ni^{2+}$	3282
		$^{13}C^{12}O^{+}$	1332
		$^{12}C^{16}O^{1}H^{+}$	1105
		$^{14}N_2{}^{1}H^{+}$	774
$^{30}Si^{+}$	3.0924(7)	$^{29}Si^{1}H^{+}$	2839
		$^{14}N^{16}O^{+}$	1239
		$^{60}Ni^{2+}$	3577

a The resolution is defined as $M/\Delta M$ with overlap at 10% of maximum peak height.

Table 3 Internal precision of silicon isotope ratios in the seven sample solutions measured with HR-ICP-MS under MR mode.

Solutions	$^{28}Si^+/^{29}Si^+$	RSD (%)	$^{30}Si^+/^{29}Si^+$	RSD (%)
WZ	4.678	0.21	-	-
Z	0.01526	1.43	0.002522	0.37
YZ	-	-	4.656	0.28
Y	1.889	0.87	274.50	0.70
WASO	19.39	0.21	0.6547	0.37
YX	-	-	6.609	0.16
X (5B1.2.2.3)	-	-	0.02576	1.48

Table 4. K factors of $^{28}Si/^{29}Si$ and $^{30}Si/^{29}Si$ obtained by YZ1 and WZ1 solutions in different days

Day	$K_{28/29}$	$K_{30/29}$
1	1.0326	0.9775
2	1.0225	0.9839
3	1.0179	0.9895
4	1.0169	0.9864

Table 5. Molar mass and isotopic composition of the four AVO28 samples. The standard uncertainties are given in parentheses (k = 1).

Sample	$x(^{28}Si)$	$x(^{29}Si)$ ($\times10^{-5}$)	$x(^{30}Si)$ ($\times10^{-6}$)	Molar mass (g mol^{-1})	u_{rel}
5B1.2.2.3	0.99995841(26)	4.059(26)	1.005(15)	27.97696911(27)	9.5×10^{-9}
5B1.2.2.4	0.99995839(22)	4.063(22)	0.972(10)	27.97696909(23)	8.1×10^{-9}
Avg of 5B	0.99995840(24)	4.061(24)	0.988(13)	27.97696910(25)	8.8×10^{-9}
8B3.2.2.2	0.99995851(25)	4.051(24)	0.983(9)	27.97696899(26)	9.1×10^{-9}
8B3.2.2.4	0.99995849(25)	4.051(25)	0.994(11)	27.97696900(30)	1.1×10^{-8}
Avg of 8B	0.99995850(25)	4.051(25)	0.989(10)	27.97696900(28)	1.0×10^{-8}
Grand Avg	0.99995845(25)	4.056(24)	0.989(12)	27.97696905(26)	9.4×10^{-9}

Table 6 Uncertainty budget of the molar mass of AVO28 material (sample 5B1.2.2.3, originating from part 5 of the crystal).

Quantity[a] X_i	Unit $[X_i]$	Value estimate x_i	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Index
$M\ (^{28}Si)$	g/mol	27.976926534694	4.4×10^{-10}	1.0	0.0%
$M\ (^{29}Si)$	g/mol	28.976494664901	5.23×10^{-10}	3.9×10^{-6}	0.0%
$M\ (^{30}Si)$	g/mol	29.9737701360	2.3×10^{-8}	9.6×10^{-7}	0.0%
r_x	V/V	0.02576	3.8×10^{-4}	8.7×10^{-5}	5.4%
r_{yx}	V/V	6.609	1.1×10^{-2}	-6.6×10^{-6}	26.9%
r_y	V/V	274.5	1.9	1.4×10^{-9}	0.0%
r_{y28}	V/V	1.889	1.6×10^{-2}	-6.9×10^{-9}	0.0%
r_z	V/V	0.002522	9.3×10^{-5}	-5.0×10^{-5}	0.1%
r_{z28}	V/V	0.0153	2×10^{-4}	-4.0×10^{-5}	0.3%
r_w	V/V	0.655	2×10^{-3}	3.3×10^{-8}	0.0%
r_{w28}	V/V	19.39	4×10^{-2}	-1.4×10^{-8}	0.0%
r_{yz}	V/V	4.656	1.3×10^{-2}	8.9×10^{-6}	67.2%
r_{wz}	V/V	4.678	1.0×10^{-2}	1.9×10^{-7}	0.0%
m_z	g	0.0481583	4×10^{-7}	8.6×10^{-4}	0.0%
m_w	g	0.0586830	2×10^{-7}	-1.2×10^{-6}	0.0%
m_y	g	0.0522018	5×10^{-7}	3.8×10^{-5}	0.0%
m_x	g	0.2637198	4×10^{-7}	-1.6×10^{-4}	0.0%
f_{28}	mol/mol	0.99995833	1.4×10^{-7}		
f_{29}	mol/mol	0.00004064	1.4×10^{-7}		
f_{30}	mol/mol	0.00000103	1.5×10^{-7}		
Y	$[Y]$	y	$u_c(y)$		$u_{rel}(y)$
M(Si)	*g/mol*	27.97696922	1.4×10^{-7}		5.0×10^{-9}

The uncertainties were calculated by *GUM Workbench* software. The uncertainties are all standard uncertainties with a coverage factor of k =1.

[a]*M* prefix denotes the relative atomic mass of silicon isotope, data are taken from [9], *r* prefix denotes a measured isotope ratio, *m* prefix denotes a mass, *f* prefix denotes a isotope abundance. r_x: ^{30}Si/^{29}Si in 5B1223 sample; r_{yx}: ^{30}Si/^{29}Si in spiked 5B1223 solution YX; r_y: ^{30}Si/^{29}Si in ^{30}Si spike; r_{y28}: ^{28}Si/^{29}Si in ^{30}Si spike; r_z: ^{30}Si/^{29}Si in ^{29}Si spike; r_{z28}: ^{28}Si/^{29}Si in ^{29}Si spike; r_w: ^{30}Si/^{29}Si in WASO; r_{w28}: ^{28}Si/^{29}Si in WASO; r_{yz}: ^{30}Si/^{29}Si in blend solution YZ; r_{wz28}: ^{28}Si/^{29}Si in blend solution WZ; m_z: mass of ^{29}Si solid material to prepare solution Z; m_w: mass of WASO solid material to prepare solution W; m_y: mass of ^{30}Si solid material to prepare solution Y; m_x: mass of ^{28}Si solid material to prepare solution X.

Table 7 Comparison of the corrected ^{29}Si/^{30}Si ratios and isotope abundances of ^{28}Si, ^{29}Si and ^{30}Si in the AVO28 crystal measured by NIM (this work), NIST[20], NMIJ[19], NRC[18] and PTB[12]. And also the molar mass of the virtual element (M_{VE}, ^{29}Si+^{30}Si in the crystal[13]).

NMI	^{29}Si/^{30}Si	$x(^{28}$Si)	$x(^{29}$Si) ($\times 10^{-5}$)	$x(^{30}$Si) ($\times 10^{-6}$)	M_{VE}
PTB	31.95	0.99995750(17)	4.121(15)	1.29(4)	29.006765
NMIJ	34.92	0.99995763(3)	4.120(7)	1.180(3)	29.004262
NIST	38.58	0.99995770	4.123	1.069	29.001693
NIM	41.01	0.99995845(25)	4.056(24)	0.989(12)	29.000233
NRC	60.81	0.9999588	4.05	0.666	28.992629

Figures

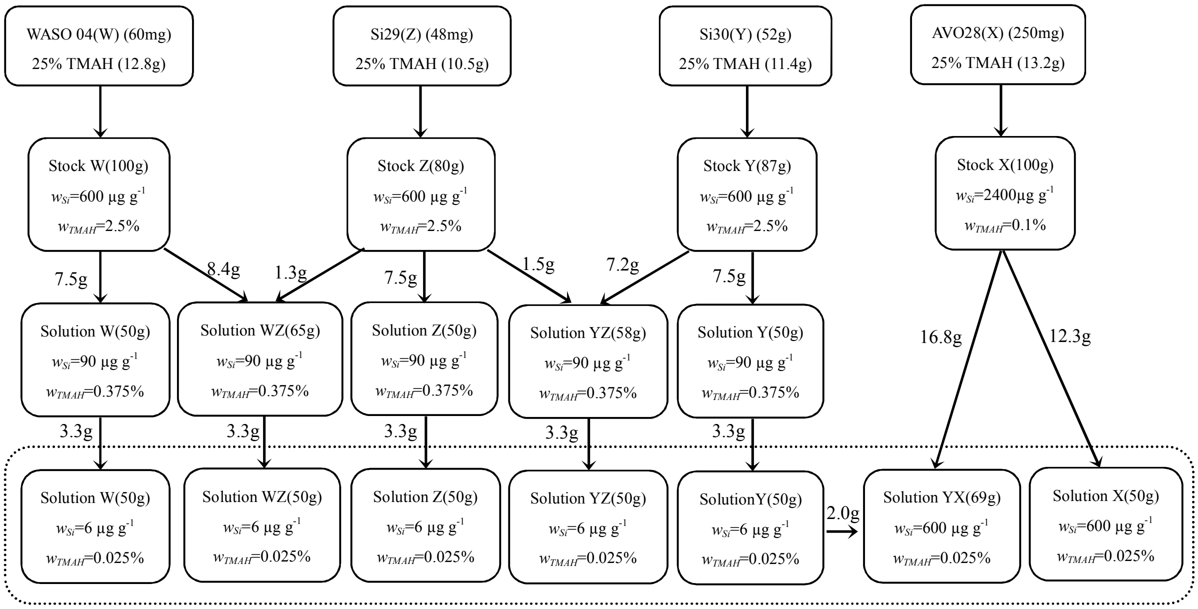


Figure 1 Procedure to prepare the solutions for molar mass measurement of AVO28 material with VE-IDMS approach

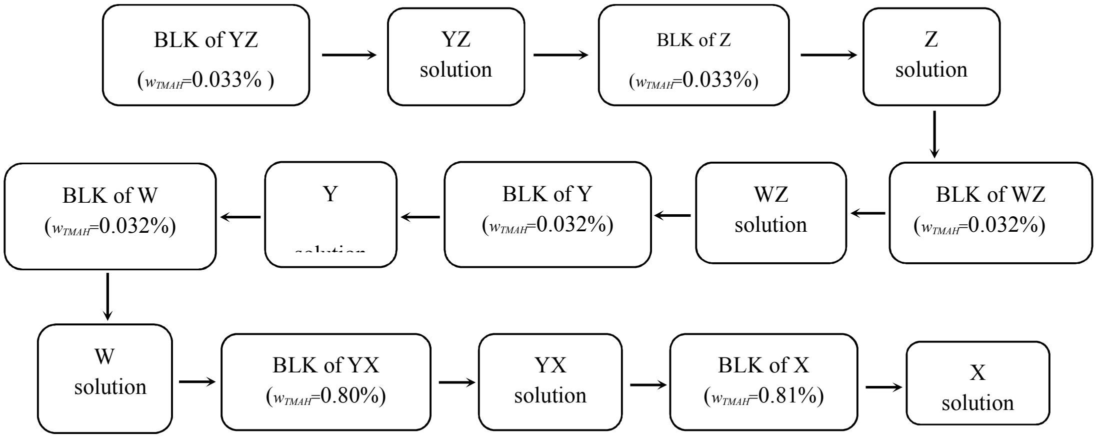


Figure 2 Optimized sequence of the molar mass measurement of AVO28 material

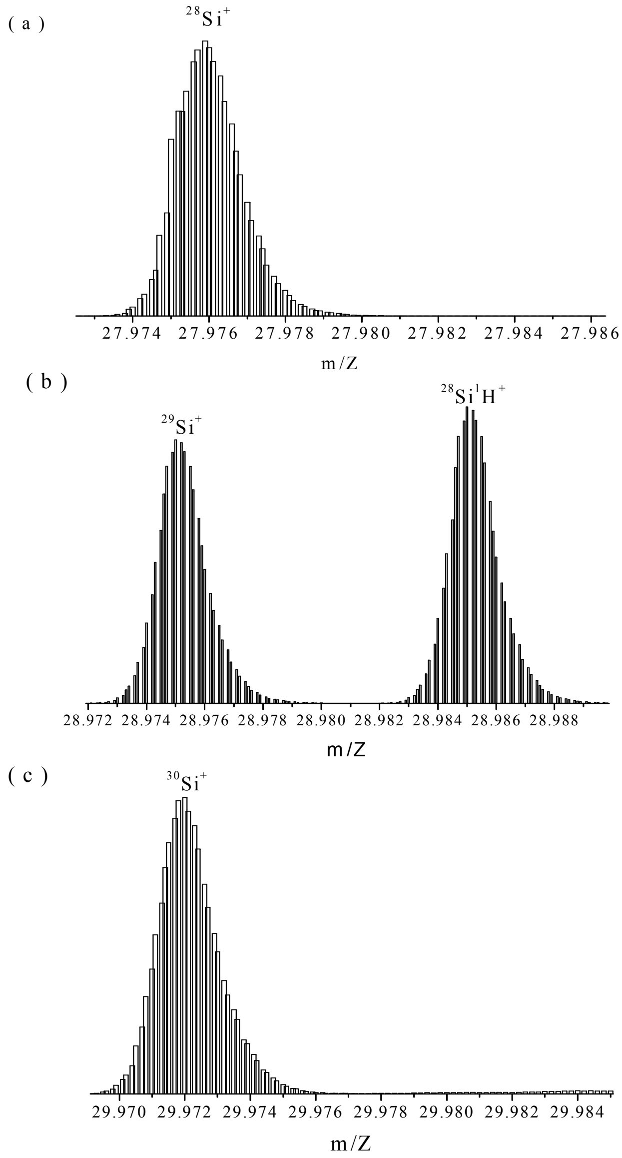


Figure 3 Spectra of ^{28}Si-enriched material obtained with Element2 HR-ICP-MS under medium resolution mode ($M/\Delta M$~5000). The width of the mass window for each of the three isotopes is about 0.016 amu. No obvious interference is observed for ^{28}Si^{+} (a) and ^{30}Si^{+} (c), and ^{28}Si^{1}H^{+} is totally separated from ^{29}Si^{+} (b).

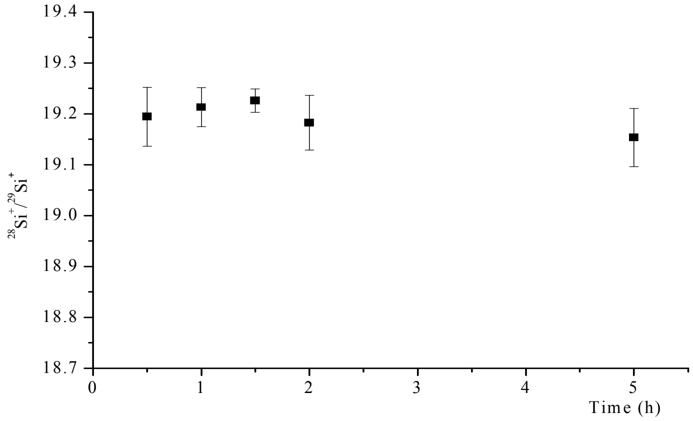


Figure 4 Stability test of Element2 HR-ICP-MS. Error bars represent the standard deviation of measured isotope ratios.

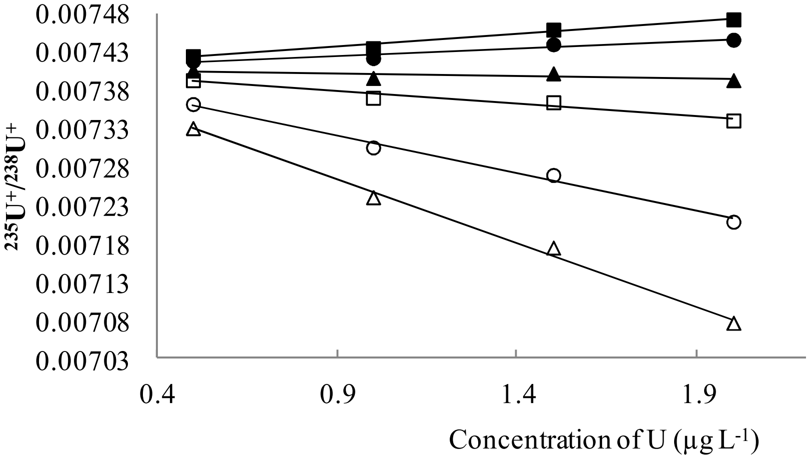


Figure 5 Effect of dead time correction on isotope ratios of $^{235}U^+/^{238}U^+$ without mass bias correction. Ratios corrected using dead times of 0ns (filled squares), 1ns (filled circles), 3ns (filled triangles), 5ns (open squares), 10ns (open circles) and 15ns (open triangles) are plotted at different concentrations (0.5, 1.0, 1.5 and 2.0 μg L^{-1}). The optimum dead time is defined by the point at which the slope is near to be zero, corresponding to $\tau = 3$ ns.

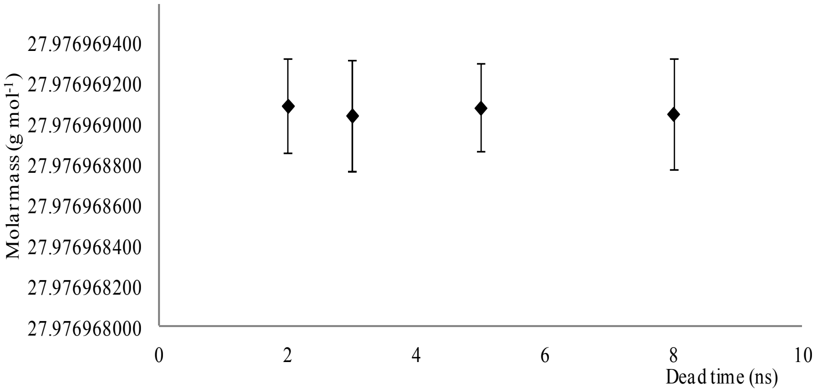


Figure 6 Measurement results of molar mass of AVO28 sample "8B3.2.2.2" under different dead time settings. The corresponding combined uncertainty is evaluated with GUM workbench software ($k = 1$).

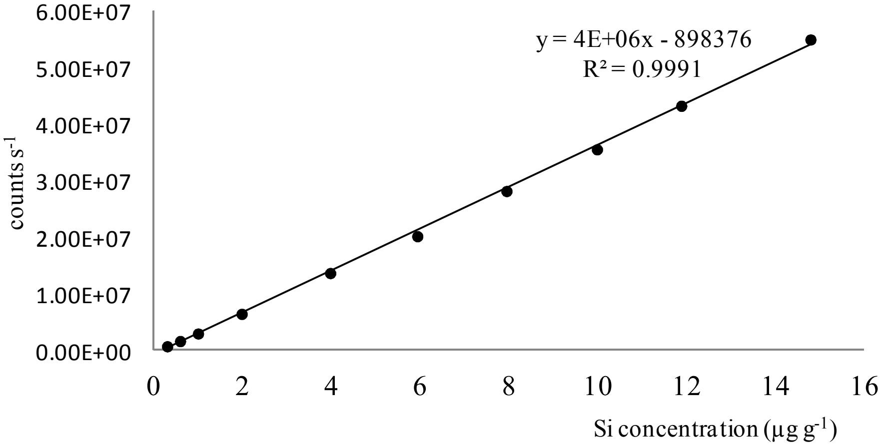


Figure 7 Testing result of linearity obtained with natural silicon solutions under "Both" mode. Data were collected for the $^{28}Si^{+}$ at Si concentrations of 0.3, 0.6, 1, 2, 4, 6, 8, 10, 12, 15 µg g^{-1}.

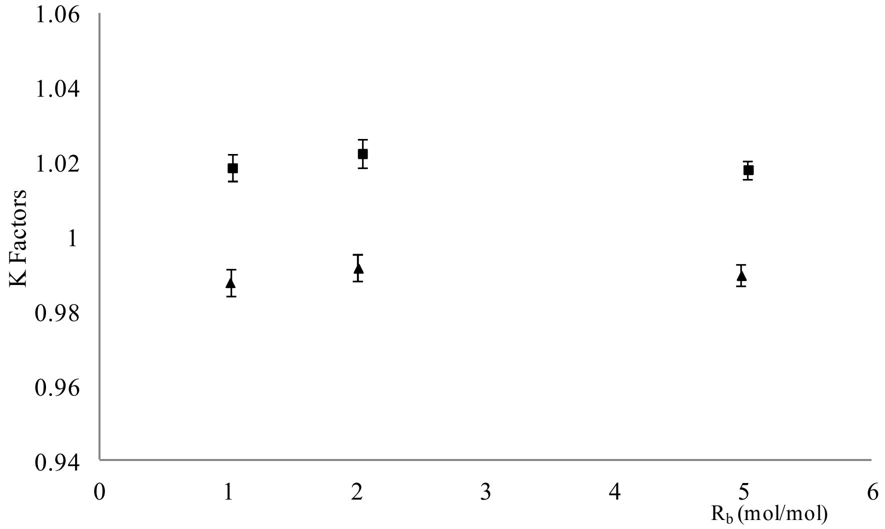


Figure 8 Correction factors of $K_{28/29}$ (filled squares) and $K_{30/29}$ (filled triangles) obtained with three WZ blend solutions and three YZ blend solutions. Error bars represent the combined standard uncertainty (u) ($k = 1$).

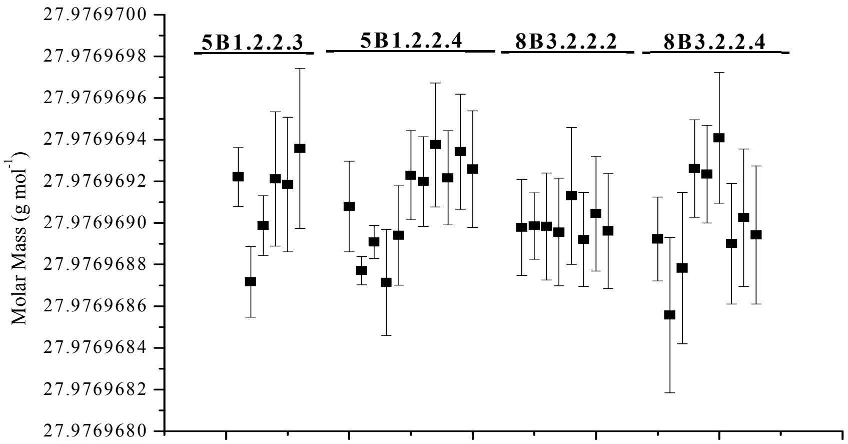


Figure 9 Summary plots of the molar mass of four AVO28 samples measured with HR-ICP-MS. Each data was obtained by one sequence and the corresponding combined uncertainty was evaluated with GUM workbench software ($k = 1$).

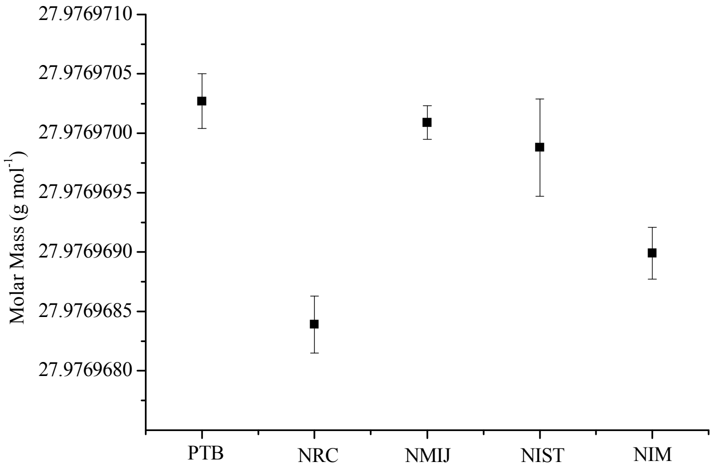
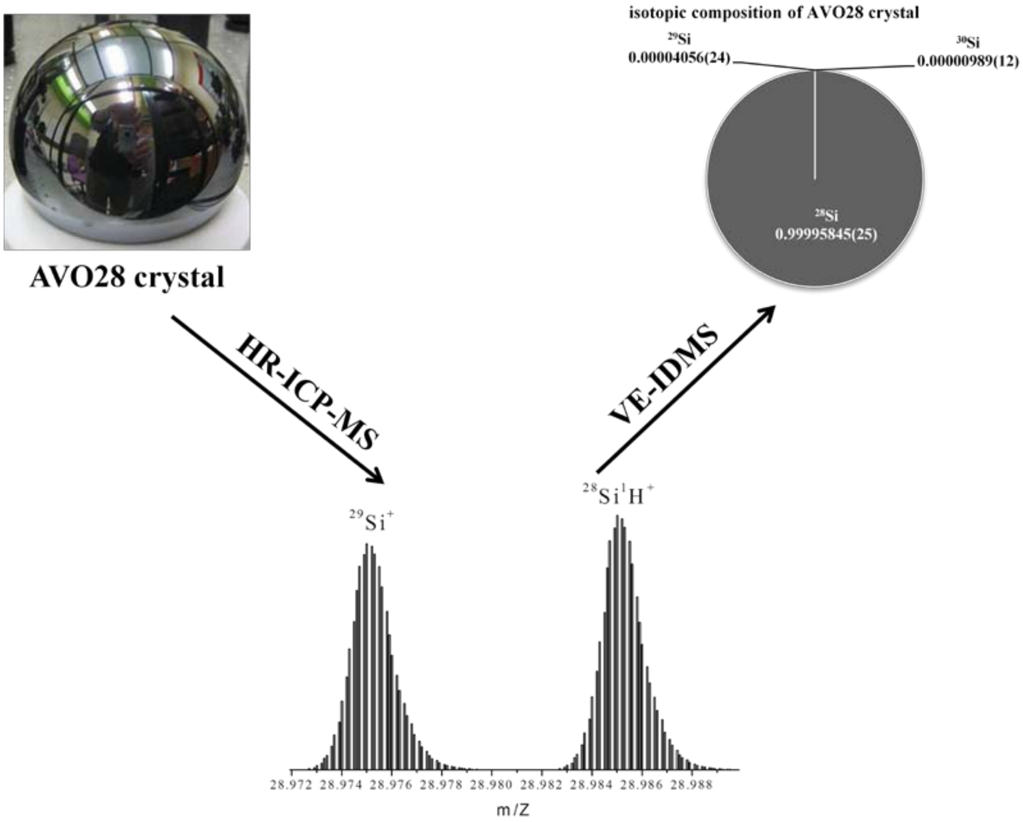


Figure 10 Comparison of the molar mass of the AVO28 crystal determined by NIST[20], NMIJ[19], NRC[18], PTB[12] and NIM (this work) with VE-IDMS approach. Error bars represent the combined standard uncertainty (*u*) (*k* = 1).


isotopic composition of AVO28 crystal
^{29}Si 0.00004056(24)
^{30}Si 0.00000989(12)
^{28}Si 0.99995845(25)
AVO28 crystal
HR-ICP-MS
VE-IDMS
$^{29}Si^+$
$^{28}Si^1H^+$
28.972
28.974
28.976
28.978
28.980
28.982
28.984
28.986
28.988
m/Z