Absolute measurement of the density of silicon spheres to improve the primary density standard of NMIJ

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Abstract

To improve the primary density standard of the National Metrology Institute of Japan (NMIJ), the absolute densities of two 1 kg silicon spheres, NMIJ-S4 and NMIJ-S5, were determined by measuring their masses and volumes. The volumes of the two spheres were measured by optical interferometry based on the primary length standard of NMIJ. For the accurate volume determination, the thicknesses of the surface layers on the spheres were determined by x-ray photoelectron spectroscopy (XPS). By combining the results of optical interferometry and XPS, the volumes of the two spheres at 20.000 °C and 0 Pa were determined with relative standard uncertainties of 3.0 × 10⁻⁸ and 2.9 × 10⁻⁸ for NMIJ-S4 and NMIJ-S5, respectively. From these results, the sphere volumes at 20.000 °C and 101.325 kPa were determined using the isothermal compressibility of silicon. The masses of the spheres in air were determined based on the national prototype of the kilogram of Japan. From the results of the volume and mass measurements, the densities of the two spheres at 20.000 °C and 101.325 kPa were determined with a relative standard uncertainty of 3.2 × 10⁻⁸. The density difference between the two spheres was estimated taking into account the correlation between the densities of the two spheres. The pressure-of-floatation method was also used to determine the density difference between the two spheres. The density differences determined by the two different methods agree with each other within their uncertainties.

Keywords: density measurement, volume measurement, silicon sphere, surface characterization, XPS, interferometry, mass measurement

(Some figures may appear in colour only in the online journal)
was first realized at the National Institute of Standards and Technology (NIST, USA, formerly the National Bureau of Standards) to determine the Avogadro constant by the x-ray crystal density (XRCD) method in 1974 [2]. In the XRCD method, absolute measurements of the lattice constant, density and molar mass are performed on a silicon crystal [3]. For the accurate density determination at NIST, steel spheres were prepared and their diameters were measured using an optical interferometer [4]. In 1987, a polishing technique was developed at the Commonwealth Scientific and Industrial Research Organisation (CSIRO, Australia), where a 1 kg silicon sphere with very high sphericity was fabricated [5]. This enabled the uncertainty in the volume determination to be ultimately reduced by improving the optical interferometer used to measure the sphere diameter. After the development of the polishing technique at CSIRO, several optical interferometers for measuring the diameter of silicon spheres were developed at Istituto Nazionale di Ricerca Metrologica (INRIM, Italy, formerly Istituto di Metrologia ‘G Colonetti’) [6], the National Metrology Institute of Japan (NMIJ) [7–10], Physikalisch-Technische Bundesanstalt (PTB, Germany) [11, 12] and the National Measurement Institute (NMIA, Australia) [13, 14]. They were used not only for the realization of the primary density standards of each national metrology institute but also for the determination of the Avogadro constant by the XRCD method using 28Si-enriched crystals [15–19].

At NMIJ, two 1 kg silicon spheres have been used as the primary density standard. The spheres were manufactured at CSIRO and were named NMIJ-S4 and NMIJ-S5. Details of the spheres are provided in [7]. In 1999, the volumes of the spheres were measured using a scanning-type optical interferometer [7]. The surfaces of the two silicon spheres were covered by layers mainly consisting of SiO2. The thicknesses of the surface layers (SL) were therefore determined using a spectroscopic ellipsometer for the accurate determination of the volumes of the spheres. The volumes of the spheres at 22.5 °C and 0 Pa were determined with a relative standard uncertainty of 0.99 × 10−7 for NMIJ-S4 and 1.32 × 10−7 for NMIJ-S5 [8]. From these results, the volumes of the spheres at 20 °C and 101.325 kPa were derived with a relative standard uncertainty of 0.99 × 10−7 for NMIJ-S4 and 1.32 × 10−7 for NMIJ-S5 to use the spheres as the primary density standard of NMIJ for dissemination of density standards calibrated at 20 °C in air [25].

After the density determination in 2003, a new optical interferometer with an optical frequency tuning system was developed at NMIJ and the volumes of the spheres were measured again by the new interferometer in [8]. For the accurate volume measurement, the surface of the spheres were characterized again by the spectroscopic ellipsometer. The volumes of the spheres at 22.5 °C and 0 Pa were determined with a relative standard uncertainty of 2.8 × 10−8 for NMIJ-S4 and 3.3 × 10−8 for NMIJ-S5 [8]. From these results, the volumes of the spheres at 20 °C and 101.325 kPa were evaluated using the thermal expansion coefficient and isothermal compressibility of silicon. By combining the results of the mass measurement in air [26], the densities of the spheres were derived with a relative standard uncertainty of 1.4 × 10−7. The results of the density measurements in 2003 and 2007 are summarized in Table 1 and Figure 1. The volumes of the two spheres measured in 2007 were slightly different from those measured in 2003. Taking into account that the optical interferometer used for the measurement in 2007 was developed just before the measurement, the drift of the volume was conservatively included in the estimation of the uncertainties of the densities in 2007. The relative uncertainties of the two spheres in 2007 were therefore slightly larger than those in 2003.

After the density measurement in 2007, the surfaces of other 1 kg Si spheres manufactured at CSIRO were found to be covered by a thin metallic layer (ML) and a carbonaceous contamination layer (CL) [15, 27]. The thicknesses of the two layers were analysed by an x-ray photoelectron spectroscopy (XPS) system of the Swiss Federal Institute of Metrology (METAS, Switzerland) and an x-ray fluorescence analysis system of PTB, respectively. The SL of NMIJ-S4 and NMIJ-S5 were therefore also assumed to contain the ML and the CL. However, NMIJ did not have a surface analysis system to determine the thicknesses of the two layers. The volumes of the spheres determined in 2007 were therefore re-evaluated in 2011 on the assumption that the thicknesses of the two layers on the two silicon spheres were the same as those on the other silicon spheres. The relative differences...
| Sphere   | Year | Density at 20 °C and 101.325 kPa | Relative standard uncertainty | Volume measurement (measurement condition) | Surface characterization | Corrections made to the density at measurement condition to obtain the density at 20 °C and 101.325 kPa |
|----------|------|---------------------------------|-------------------------------|---------------------------------------------|--------------------------|--------------------------------------------------------------------------------------------------|
| NMIJ-S4  | 2003 | 2329.08689(23)                  | 0.99 × 10^{-7}                | Scanning-type optical interferometer (22.5 °C and 0 Pa) [7] | Spectroscopic ellipsometry [7] | Temperature correction (from 22.5 °C to 20 °C), pressure correction (from 0 Pa to 101.325 kPa) |
|          | 2007 | 2329.08737(33)                  | 1.38 × 10^{-7}                | Optical interferometer with optical frequency tuning (22.5 °C and 0 Pa) [8] | Spectroscopic ellipsometry [8] | Temperature correction (from 22.5 °C to 20 °C), pressure correction (from 0 Pa to 101.325 kPa) |
|          | This work | 2329.087172(74)              | 0.32 × 10^{-7}                | Optical interferometer with optical frequency tuning (20 °C and 0 Pa) | XPS | Pressure correction (from 0 Pa to 101.325 kPa) |
| NMIJ-S5  | 2003 | 2329.08795(31)                  | 1.31 × 10^{-7}                | Scanning-type optical interferometer (22.5 °C and 0 Pa) [7] | Spectroscopic ellipsometry [7] | Temperature correction (from 22.5 °C to 20 °C), pressure correction (from 0 Pa to 101.325 kPa) |
|          | 2007 | 2329.08791(33)                  | 1.40 × 10^{-7}                | Optical interferometer with optical frequency tuning (22.5 °C and 0 Pa) [8] | Spectroscopic ellipsometry [8] | Temperature correction (from 22.5 °C to 20 °C), pressure correction (from 0 Pa to 101.325 kPa) |
|          | This work | 2329.087685(74)              | 0.32 × 10^{-7}                | Optical interferometer with optical frequency tuning (20 °C and 0 Pa) | XPS | Pressure correction (from 0 Pa to 101.325 kPa) |
between the density values re-evaluated in 2011 and those measured in 2007 were as small as less than $3 \times 10^{-3}$, which is much smaller than the relative standard uncertainty of the sphere densities evaluated in 2007 of $1.4 \times 10^{-2}$. The density values measured in 2007 were therefore also used for the dissemination of density standards at NMIJ after the re-evaluation in 2011.

To overcome the problem concerning the surface characterization, an XPS system was developed at NMIJ to accurately characterize the sphere surface in 2015 [28] and the thicknesses of the ML and the CL were assumed to be measured using the new XPS system. In addition, after the density measurement of the two spheres in 2007 [8], the optical interferometer with an optical frequency tuning system and the vacuum balance of NMIJ were significantly improved to accurately determine the Avogadro constant for the redefinition of the kilogram [10, 16, 29]. The densities of the two spheres were therefore measured again in this study using the new XPS system, the improved optical interferometer, and the improved vacuum balance to improve the primary density standard of NMIJ. Details of the density determination are given in this paper.

2. Optical interferometry for silicon sphere volume measurement

The sphere volumes were determined on the basis of diameter measurement by optical interferometry [9, 10]. As shown in figure 2, the surfaces of the Si spheres are covered by SL mainly consisting of SiO$_2$ [27, 30, 31]. The diameter measured by optical interferometry is therefore the apparent diameter, which is not corrected for the phase shift due to the SL on the sphere [9]. To derive the actual diameter of a sphere including the SL from the apparent diameter, the thicknesses of the SL on the sphere should be determined.

Figure 3 shows the optical interferometer with a direct optical frequency tuning system used to determine the sphere volume [9, 10]. The silicon sphere was placed in a fused-quartz Fabry–Perot etalon. The sphere and etalon were installed in a vacuum chamber equipped with an active radiation shield to control the sphere temperature. The pressure in the chamber was reduced to $1 \times 10^{-3}$ Pa. The fractional fringe order of interference for the gaps between the sphere and the etalon, $d_1$ and $d_2$, and the etalon spacing $L$ were measured by phase-shifting interferometry. The sphere diameter $D$ was calculated as $D = L - (d_1 + d_2)$. The light source of the interferometer was an external cavity diode laser with a center wavelength of 633 nm. The required phase shift for the diameter measurement was produced by tuning the optical frequency of the laser. Its optical frequency was phase-locked and controlled using a phase-stabilized frequency comb referring to the time standard UTC(NMIJ), which is used as the national length standard in Japan [32–34].

A sphere rotation mechanism installed under the sphere was used to measure the diameter from many different directions. In a set of diameter measurements, the diameter was measured from 145 directions distributed near-uniformly on the sphere surface [10]. Ten sets of diameter measurement were performed for NMIJ-S4. Between each set, the sphere was rotated to distribute the starting point of each set of measurements to the vertices of a regular dodecahedron. Because the ten directions defined by the vertices of a regular dodecahedron are uniformly distributed, the procedure for NMIJ-S4 therefore distributed all of the measurement points as uniformly as possible. On the other hand, only six sets of diameter measurement were performed for NMIJ-S5 due to the trouble of the pump to evacuate the chamber of the optical interferometer. The starting point of each set was therefore distributed to only six vertices of a regular dodecahedron. The distribution of the measurement points for NMIJ-S5 is not highly uniform compared to that for NMIJ-S4. The temperature of the sphere was measured with a standard uncertainty of 0.6 mK using small platinum resistance thermometers (PRTs) inserted in copper blocks in contact with the sphere. The copper blocks were coated by poly ether ether ketone (PEEK) to protect the sphere surface from damage during the temperature measurement. The PRTs were calibrated using the Ga melting point and the water triple point in accordance with ITS-90 [9]. The measured diameters were converted to those at 20.000 °C using the thermal expansion coefficient of Si crystal [21]. Figure 4 shows the Mollweide map projections of the distribution of the diameter based on the 145 directions.

3D plots of the diameter are shown in figure 5. The peak-to-valley value of the diameter is 79 nm for NMIJ-S4 and 124 nm for NMIJ-S5.

Figure 6 summarizes the mean apparent diameter for each set of diameter measurements from the 145 directions. The experimental standard deviation of the mean apparent diameter is 0.08 nm for NMIJ-S4 and 0.28 nm for NMIJ-S5. The average apparent diameter of the sphere was determined as the average of the mean diameter for each set of measurements. Table 2 summarizes the average apparent diameters of the two spheres at 20.000 °C and 0 Pa. Table 3 shows the uncertainty budget for the determination of the average apparent diameters of NMIJ-S4 and NMIJ-S5. Details of the uncertainty sources are given in [9, 10].
3. Surface characterization for silicon sphere volume measurement

In a vacuum, the SL consist of a metallic layer (ML), an oxide layer (OL), a carbonaceous contamination layer (CL) and a chemically absorbed water layer (CWL) as shown in figure 2. To derive the silicon sphere diameter including the SL from the apparent diameter determined by optical interferometry, the thickness of each surface layer should be determined. XPS is a surface-sensitive technique for analysing the chemical binding state. It can also be used to measure the thickness of thin films. The main component of the XPS
system of NMIJ was an ULVAC-Phi 1600C system equipped with a monochromatic Al Kα x-ray source. The pressure in the chamber was reduced to $1.5 \times 10^{-6}$ Pa. A manipulator with five-axis freedom installed in the chamber was used to rotate the sphere around the horizontal axis and vertical axis to map the entire surface. The measurement was performed at the 20 points defined by the vertices of a regular dodecahedron, which are uniformly distributed on the sphere surface. The sphere was placed on two rollers of the manipulator during the measurement. The two rollers were used to rotate the sphere around the vertical axis and were made of polyimide to protect the sphere surface from damage during the rotation. Details of the XPS system are provided in [28, 30].

### Table 2. Diameters, volumes, masses and densities of NMIJ-S4 and NMIJ-S5 at 20.000 °C.

| Quantity      | Value                  | $u_t$/$10^{-9}$ | Value                  | $u_t$/$10^{-9}$ |
|---------------|------------------------|-----------------|------------------------|-----------------|
| Vacuum Apparent diameter$^b$ | 93.61721760(61) mm | 6.6             | 93.61825327(67) mm | 7.1             |
| Actual diameter$^a$          | 93.61722388(92) mm | 9.9             | 93.61825951(91) mm | 9.7             |
| Volume          | 429.601607(13) cm³  | 30              | 429.615865(13) cm³  | 29              |
| Mass            | 1000.578573(8) g     | 8               | 1000.611996(9) g    | 9               |
| Density         | 2329.084798(71) kg m⁻³ | 31          | 2329.085302(71) kg m⁻³ | 30             |
| Air Volume      | 429.601162(13) cm³  | 30              | 429.615419(12) cm³  | 29              |
| Mass            | 1000.578586(11) g    | 11              | 1000.612006(12) g   | 12              |
| Density         | 2329.087172(74) kg m⁻³ | 32          | 2329.087685(74) kg m⁻³ | 32             |

$^a$ Relative combined standard uncertainty of each quantity.
$^b$ Average diameter observed by interferometry in vacuum.
$^c$ Average diameter including the SL in vacuum.

### Table 3. Uncertainty budget of the determination of the average apparent diameter $D_{app}$ at 20.000 °C and 0 Pa.

| Uncertainty source       | Standard uncertainty in $D_{app}$/nm |
|--------------------------|------------------------------------|
| Interferogram analysis   | 0.31                               |
| Sphere temperature       | 0.15                               |
| Diffraction effect       | 0.50                               |
| Standard deviation of the mean diameter | 0.08 |
| Relative combined standard uncertainty | 0.61 |

### Table 4. Thicknesses and optical constants of SL. Details of the values of the optical constants are provided in [15].

| Layer | Thickness/nm | NMIJ-S4 | NMIJ-S5 | Refractive index | Extinction coefficient |
|-------|--------------|---------|---------|-----------------|-----------------------|
| CWL   | 0.28(8)      | 0.28(8) | 1.332(10)| 1.54(1.00) × 10⁻⁸|
| CL    | 0.49(26)     | 0.55(20)| 1.42(14)| 0.0(1)          |
| OL    | 1.94(20)     | 1.75(18)| 1.457(1)| 0.0(1)          |
| ML    | 0.42(12)     | 0.50(14)| 2.1(1) | 2.5(1)          |

3.1 Determination of OL thickness

The thickness of the OL was determined by analysing XPS Si 2p core-level spectra, in which peaks corresponding to the SiO₂ layer and the interfacial OL (Si₃O₂, SiO and Si₂O) were observed. To ensure the traceability of the OL thickness measurement to the SI, the attenuation length for the Si 2p electrons in SiO₂ was determined by an SI-traceable x-ray
reflectometry (XRR) system at NMIJ [27] using flat Si samples with different thicknesses of thermal SiO$_2$ and the attenuation lengths for the Si 2p electrons in Si$_2$O$_3$, SiO and Si$_2$O were subsequently obtained by linear interpolation between the values for SiO$_2$ and Si. The OL thickness was determined as the sum of the thicknesses of all OL. The average OL thickness at the 20 points was estimated to be 1.94 (20) nm for NMIJ-S4 and 1.75 (18) nm for NMIJ-S5. The results are summarized in table 4.

3.2. Determination of CL thickness

In the XPS C 1s core-level spectra, peaks corresponding to the C–C/H and C–O bonds were observed. The main constituents were deduced to be both ethanol and a hydrocarbon [16]. The average thickness of the ethanol sublayer was estimated to be 0.29(25) nm for NMIJ-S4 and 0.41(19) nm for NMIJ-S5 by analysing the spectrum at the 20 measurement points. The average thickness of the hydrocarbon sublayer was estimated to be 0.20(7) nm for NMIJ-S4 and 0.14(5) nm for NMIJ-S5. Consequently, the average CL thickness $d_{CL}$ was estimated to be 0.49(26) nm for NMIJ-S4 and 0.55(20) nm for NMIJ-S5.

3.3. Determination of ML thickness

At all 20 measurement points, peaks corresponding to the silicides Ni$_2$Si and Cu$_2$Si were observed [31]. To clarify the structure of the SL, an angle-resolved XPS measurement was performed. The intensities of the peaks corresponding to the metal silicides near the bulk-silicon sphere were higher than those near the surface of the silicon spheres. From these results, the ML was assumed to lie between the bulk-silicon sphere and the OL as shown in figure 2. Details of the thickness determination of the ML and the angle-resolved XPS measurement are provided in [31].

The average thickness of the Ni$_2$Si sublayer and that of the Cu$_2$Si sublayer at the 20 points were estimated to be 0.25(10) nm and 0.17(7) nm for NMIJ-S4 and 0.27(10) nm and 0.23(10) nm for NMIJ-S5, respectively. The sum of the thicknesses of the two silicides layers was considered to be the thickness of the ML. The average thicknesses of the MLs for NMIJ-S4 and NMIJ-S5 were therefore estimated to be 0.42(12) nm and 0.55(20) nm, respectively, and are summarized in table 4.

4. Mass measurement of the silicon spheres

The masses of the two spheres in air and under vacuum were determined using the vacuum mass comparator by the method reported in [29]. A cylindrical 1 kg stainless steel standard was employed as a reference weight for the mass comparison. The masses of the spheres in air were obtained by applying buoyancy correction and center-of-gravity height correction to the results of weighing in air. The amount of buoyancy correction was determined using a pair of buoyancy artifacts with a volume difference [29]. The masses of the spheres in vacuum were obtained by applying the center-of-gravity height correction to the results of weighing in vacuum.

The mass of the 1 kg stainless steel standard was determined beforehand based on platinum-iridium standards No. 94 and E59 [35], which were calibrated with a standard uncertainty of 3.5 µg in the second phase of the Extraordinary Calibration conducted at the Bureau International des Poids et Mesures (BIPM, France) in 2015 [36, 37] and are traceable to the International Prototype of the Kilogram.

The estimated standard uncertainty of the measured mass of the spheres was approximately 12 µg in air and approximately 8 µg in vacuum. The results of the mass measurement are shown in table 2. As shown in table 2, the mass of the spheres in air is larger than that in vacuum. In air, in addition to the SL shown in figure 2, a physically adsorbed water layer (PWL) is also present. Because of the mass of the PWL, the masses in air and in vacuum are different.

### Table 5. Uncertainty budget in the determination of the phase shift correction $\Delta d$ to obtain the actual diameter.

| Uncertainty source | Standard uncertainty in $\Delta d$ (nm) |
|--------------------|--------------------------------------|
|                    | NMIJ-S4 | NMIJ-S5 |
| Refractive index   |         |        |
| CWL                | 0.00    | 0.00   |
| CL                 | 0.01    | 0.01   |
| OL                 | 0.00    | 0.00   |
| ML                 | 0.01    | 0.02   |
| Si                 | 0.00    | 0.00   |
| Extinction coefficient |      |        |
| CWL                | 0.00    | 0.00   |
| CL                 | 0.00    | 0.00   |
| OL                 | 0.00    | 0.00   |
| ML                 | 0.01    | 0.02   |
| Si                 | 0.01    | 0.01   |
| Thickness          |         |        |
| CWL                | 0.08    | 0.08   |
| CL                 | 0.24    | 0.18   |
| OL                 | 0.18    | 0.17   |
| ML                 | 0.14    | 0.16   |
| Combined standard uncertainty | 0.35    | 0.31   |

### Table 6. Relative contributions of the uncertainty sources to the density determination of NMIJ-S4 and NMIJ-S5 at 20 °C and 101.325 kPa.

| Uncertainty source | Relative contribution to density determination |
|--------------------|-----------------------------------------------|
|                    | NMIJ-S4 | NMIJ-S5 | Correlation |
| Apparent volume in vacuum | 2.0×10^{-8} | 2.2×10^{-8} | 0.16 |
| Total thickness of SL | 2.4×10^{-8} | 2.1×10^{-8} | 0.44 |
| Mass measurement in air | 1.1×10^{-8} | 1.2×10^{-8} | 0.94 |
| Total | 3.2×10^{-8} | 3.2×10^{-8} | 0.39 |

The uncertainties of the sphere diameter were calculated by applying the center-of-gravity height correction to the results of weighing in vacuum.
5. Determination of the volume and density of the Si spheres

5.1. Volume and density in vacuum

To determine the actual diameter including the SL $D_{\text{actual}}$ from the apparent diameter $D_{\text{app}}$, the total phase retardation upon reflection at the sphere surface $\delta$ was calculated in accordance with the procedure in [9]. To calculate $\delta$, the thickness and optical constants of each layer given in table 4 were used. The phase shift upon reflection $(\delta - \pi)$ was estimated to be $-0.062(7)$ rad for NMIJ-S4 and $-0.062(6)$ rad for NMIJ-S5. The effect of this phase shift on the gap measurement $\Delta d$ was 3.14(35) nm for NMIJ-S4 and 3.12(31) nm for NMIJ-S5. The average actual diameters $D_{\text{actual}}$ of the two spheres were therefore obtained using $D_{\text{actual}} = D_{\text{app}} + 2\Delta d$ and are summarized in table 2 with the actual volumes including the SL of the two spheres. The densities of the two spheres are also summarized in table 2. Table 5 shows the uncertainty budget in the determination of the phase shift correction $\Delta d$ to obtain the actual diameter.

5.2. Volume and density in air

A detailed study on the elastic properties of silicon was performed by McSkimin and Andreatch by measuring the ultrasonic velocity in a single crystal in the pressure range of 0 MPa to 200 MPa [22]. The adiabatic stiffnesses of silicon, $c_{11}$ and $c_{12}$, at 20 °C were calculated from the sound velocity data to be $1.6568 \times 10^{11}$ Pa and $0.6390 \times 10^{11}$ Pa, respectively. The adiabatic compliances of silicon, $s_{11}^a$ and $s_{12}^a$, were derived to be $7.6860 \times 10^{-12}$ Pa$^{-1}$ and $-2.1393 \times 10^{-12}$ Pa$^{-1}$, respectively, using the following equations [23]:

$$s_{11}^a = \frac{c_{11}^a + c_{12}^a}{(c_{11}^a - c_{12}^a)(c_{11}^a + 2c_{12}^a)},$$

$$s_{12}^a = \frac{-c_{12}^a}{(c_{11}^a - c_{12}^a)(c_{11}^a + 2c_{12}^a)}.$$

The relationships between the adiabatic compliances, $s_{11}$ and $s_{12}$, and the isothermal compliances, $s_{11}^i$ and $s_{12}^i$, are given by the following equations:

$$s_{11}^i - s_{11}^a = -\alpha^2 \frac{T}{\rho c_p},$$

$$s_{12}^i - s_{12}^a = -\alpha^2 \frac{T}{\rho c_p},$$

where $T$ is the temperature in K, $\alpha$ is the thermal expansion coefficient, $\rho$ is the density and $c_p$ is the isobaric specific heat. The values of $\alpha$, $\rho$ and $c_p$ at 20 °C were estimated to be $2.558 \times 10^{-6}$ K$^{-1}$, 2329 kg m$^{-3}$ and 710.4 J kg$^{-1}$ K$^{-1}$, respectively. The isothermal compliances, $s_{11}^i$ and $s_{12}^i$, were estimated using these values to be $7.6872 \times 10^{-12}$ Pa$^{-1}$ and $-2.1382 \times 10^{-12}$ Pa$^{-1}$, respectively. The isothermal compressibility of silicon, $\beta_T$, was estimated to be $1.023 \times 10^{-11}$ Pa$^{-1}$ using

$$\beta_T = \frac{1}{V} \left( \frac{\partial V}{\partial p} \right) = 3 \left( s_{11}^i + 2s_{12}^i \right).$$

The uncertainty of $\beta_T$ was estimated based on the error of the elastic moduli of silicon reported in [22] to be $1 \times 10^{-14}$ Pa$^{-1}$.

The surface of silicon spheres in air is covered by a physically adsorbed water layer (PWL) in addition to the SL shown in figure 2 [9]. The masses of the PWLs on NMIJ-S4 and NMIJ-S5 were estimated to be 13(2.6) µg and 10(2.6) µg, respectively, using the vacuum mass comparator. These correspond to PWL thicknesses of 0.47(9) nm and 0.36(9) nm, respectively.

The volumes of the spheres at 20 °C and 101.325 kPa were therefore derived from those at 20 °C and 0 Pa using the isothermal compressibility of silicon $\beta_T$ and the PWL thickness and are summarized in table 2. The density of NMIJ-S4 at 20 °C and 101.325 kPa, $\rho_{\text{NMIJ-S4}}$, and that of NMIJ-S5, $\rho_{\text{NMIJ-S5}}$, were determined by combining the masses and volumes of the two spheres in air to be

$$\rho_{\text{NMIJ-S4}} = 2329.087 \times 172(74) \text{ kg m}^{-3},$$

$$\rho_{\text{NMIJ-S5}} = 2329.087 \times 685(74) \text{ kg m}^{-3},$$

and are summarized in table 2. The standard uncertainty of the density at 20 °C and 101.325 kPa was estimated to be $3.2 \times 10^{-8}$ for the two spheres.

The correlation coefficients between the apparent volume measurements, the surface characterization and the mass measurements of the two spheres were estimated using the procedure in [16] and are summarized in table 6. Using these correlation coefficients, the correlation coefficient between the density measurements of the two spheres at 20 °C and 101.325 kPa was estimated to be 0.39 by the same procedure. From this correlation coefficient and the densities of the two spheres, the relative difference between the densities of the two spheres $\Delta \rho$ was estimated to be $2.2(4) \times 10^{-7}$ using

$$\Delta \rho = (\rho_{\text{NMIJ-S5}} - \rho_{\text{NMIJ-S4}}) / \rho_{\text{NMIJ-S4}}.$$

6. Density difference measurement by the pressure-of-floatation method

The pressure-of-floatation method [38, 39] was also used to measure the density difference between the two silicon spheres. In this method, the two spheres were placed in a closed vessel that contains a liquid mixture whose density is almost the same as that of the silicon samples. The vessel was maintained at a constant temperature. The liquid density was changed by applying additional pressure to the vessel. When the liquid had the same density as the samples, the samples floated in the liquid. The density difference between the samples was deduced from the difference in the heights of the floating samples. Details of the apparatus are provided in [38].

The relative density difference between the two spheres $\Delta \rho$ was determined using the pressure-of-floatation method to be $2.1(3) \times 10^{-7}$. Table 7 shows the uncertainty budget for
the density difference measurement. Details of the uncertainty sources are provided in [38, 39]. On the other hand, \( \Delta \rho \) was estimated from the result of the absolute density measurement of the silicon spheres to be \( 2.2(4) \times 10^{-7} \) as noted in 5.2. The consistency of the density differences obtained by the two completely different methods is supporting evidence for the reliability of the absolute density measurement.

7. Improvement of the Primary Density Standard of NMIJ

NMIJ-S4 and NMIJ-S5 have been used as the primary density standard of NMIJ. The latest determination of their densities were performed in 2007 and the relative standard uncertainty of the density determination was estimated to be \( 1.4 \times 10^{-7} \). To improve the primary density standard, the densities of the two spheres were determined in this study using the new XPS system, the improved optical interferometer and the improved vacuum balance. The densities at 20 °C and 101.325 kPa determined in this work are shown in figure 1 with those determined in 2003 and 2007. As shown in this figure, the densities determined in this work are consistent with the other data within their uncertainties. Furthermore, the uncertainties of the densities of the two spheres in this work are significantly smaller than those of the other data.

The improvement of the primary density standard was mainly introduced by the reduction of the uncertainty of the temperature correction of the sphere volumes. In 2003 and 2007, the volumes at 22.5 °C and 0 Pa were measured and those at 20 °C and 101.325 kPa were evaluated using the thermal expansion coefficient and the isothermal compressibility of silicon. In [21], the thermal expansion coefficient is represented by a quadratic function with respect to the temperature. Though the thermal expansion coefficient was accurately known, the correction of the sphere volumes at 22.5 °C to those at 20 °C was one of the large uncertainty sources in the determination of the sphere volumes at 20 °C due to the large temperature difference of 2.5 °C. To reduce the uncertainty contribution from the temperature correction, the sphere volumes were measured at 20 °C in this work. The average temperature of the volume measurement was 20.003 °C and the drift of the sphere temperature measurement during the diameter measurement from one direction was less than 0.0001 °C. The uncertainty of temperature correction was therefore negligibly small.

In addition, the surface characterization by the XPS system in this study played a crucial role to secure the reliability of the primary density standard. For the surface characterizations in 2003 and 2007, only the spectroscopic ellipsometer was used and the thicknesses of the ML and the CL on the spheres could not be measured. The thicknesses of the two layers were accurately measured using the XPS system in this study, resulting in the accurate density determination of the primary density standards.

The improvements of the optical interferometer for the volume measurement and the vacuum balance for the mass measurement also contributed to the uncertainty reduction of the primary density standard. For the volume determination in 2007, the optical interferometer was significantly improved [10, 16]. For example, the uncertainty of the sphere temperature measurement was reduced from 2.5 mK to 0.6 mK. The number of the measurement directions for the diameter measurement was increased from 280 to 1450 and the uniformity of the distribution of the measurement directions over the sphere surface was also enhanced. By these improvements, the volumes at 20 °C and 0 Pa were determined with a relative uncertainty of as small as \( 3 \times 10^{-8} \) using the improved optical interferometer in this study. This uncertainty is not so different from that in the volume determination in 2007. This situation is explained as follows. The largest uncertainty source in the volume measurement in this work is the diffraction effect as shown in table 3. The uncertainty of this source was significantly underestimated in the volume measurement in 2007 [8]. After the volume measurement in 2007, the uncertainty of the diffraction effect was increased by a rigorous evaluation of the diffraction effect. Therefore, the uncertainty in 2007 is compatible with that in this work.

As to the mass measurement, the masses of the two spheres in air were measured with a standard uncertainty of 16 µg in 2007. The largest uncertainty source was the mass of the national prototype of the kilogram of Japan. After this mass measurement, two 1 kg platinum–iridium standard weights of NMIJ were calibrated in the Extraordinary Calibrations conducted by the Bureau International des Poids et Measures (BIPM) [36, 37]. On the basis of the calibration results of the two weights, the standard uncertainty of the mass of the national prototype of Japan was re-evaluated and significantly reduced to 3.4 µg [35]. As a result of this improvement, the standard uncertainty of the sphere mass measurement was improved to 11 µg for NMIJ-S4 and 12 µg for NMIJ-S5 in this work. The masses of the spheres used to determine the

| Uncertainty source                      | Uncertainty       | Uncertainty in the relative density difference/10⁻⁶ |
|-----------------------------------------|-------------------|--------------------------------------------------|
| Flotation pressure                      | 0.04 kPa          | 0.0066                                           |
| Effective isothermal compressibility    | 0.009 kPa⁻¹        | 0.0038                                           |
| Residual temperature inhomogeneity in the vessel | 0.017 mK          | 0.017                                            |
| Manometer                               | 0.003 kPa         | 0.0014                                           |
| Center of gravitation                   | 0.17 mm           | 0.017                                            |
| Surface effect                          | 0                 | 0                                                |
| Combined standard uncertainty           |                   | 0.025                                            |

In Table 7, the uncertainty budget of the density difference measurement between NMIJ-S4 and NMIJ-S5 by the pressure-of-floatation method is presented.
densities in 2003 and 2007 are not corrected by the effect of the Extraordinary Calibrations. However, the effect is very small and does not significantly change the positions of the density data shown in figure 1.

The masses of the silicon spheres in this study were measured before the redefinition of the kilogram implemented on 20 May 2019 and the mass measurements were traceable to the International Prototype of the Kilogram as described in section 4. The densities of the spheres were therefore determined by setting the uncertainty of the mass of the International Prototype of the Kilogram to be zero. However, after the redefinition the uncertainty of the International Prototype of the Kilogram was set to be 10 μg [40]. This slightly increases the uncertainties of the densities of the spheres by only about 5%.

The densities of various solids and liquids are calibrated at NMIJ based on the two silicon spheres for the dissemination of density standards [25, 41, 42]. Accurate density measurements traceable to the SI are very important in many fields. The reduction in the uncertainty of the density of the two spheres in this study will therefore contribute to reducing the uncertainty of such density measurements.

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