EFFECT OF COVARIANCES IN A DENSITY MEASUREMENT OF SILICON SAMPLES BY HYDROSTATIC WEIGHING

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Abstract: A density standard realized by 1 kg silicon spheres has been used for measuring the density of solid samples by hydrostatic weighing. Details are given for the structure of the measurement system, procedure for the solid density measurement, and uncertainty evaluation. The density of a 1 kg silicon sample has been measured with a relative combined standard uncertainty of 1.2 parts in 10^7. When the effect of covariances in input quantities is taken into account, the relative combined uncertainty in measuring the density difference between the silicon spheres and the silicon sample may be reduced to 3.6 parts in 10^8. Uncertainty sources in the hydrostatic weighing and the effect of covariance in the input quantities are discussed.

Keywords: density standard, silicon crystal, hydrostatic weighing, correlation, covariance.

1. INTRODUCTION

Hydrostatic weighing is one of reliable methods for measuring the density of gases, liquids, and solids. Water is the most common material used for a density standard. Since the density of water is dependent on its isotopic compositions, Standard Mean Ocean Water (SMOW) is usually chosen for specifying isotopic compositions of water. The relative expanded uncertainty ($k = 2$) for the density of water having the same isotopic compositions with those of SMOW is estimated to be 8-9 parts in 10^7 [1].

Through a research for the determination of the Avogadro constant, N_A, by the X-Ray Crystal Density (XRCD) method, the density of a 1-kg silicon sphere has been determined with a relative standard uncertainty of 7 parts in 10^8 [2], being much less than that of water. Such a silicon sphere is therefore useful for measuring the density of solid samples by hydrostatic weighing.

In the hydrostatic weighing system described here [3, 4], two 1-kg silicon spheres are used as a density standard. A 1 kg silicon sample is placed between the two standards. When the mass of the sample is measured relative to one of the silicon spheres, their masses are correlated. Since the diameters of the two silicon spheres were measured by optical interferometry, their volumes are also correlated. In this study the effect of the correlations has been taken into

account for accurately evaluating the uncertainty in the density measurement by hydrostatic weighing.

2. HYDROSTATIC WEIGHING SYSTEM

Figure 1 shows a hydrostatic weighing system developed in this study. Two silicon spheres, S4 and S5, are used as the solid density standards. Their volumes have already been calibrated by optical interferometry [5-8]. Tridecane (*n*-$C_{13}H_{28}$, $\rho \cong 756$ kg/m^3 at 20 °C) is used as a working liquid, in which the two silicon spheres and the solid sample under study are weighed alternately with an electronic balance using a weight exchange mechanism. The reason for using the two silicon spheres is to cancel the effect of vertical density gradient in the liquid, which may by introduced by the temperature gradient and the gravity [9]. The two silicon spheres and the solid sample are independently
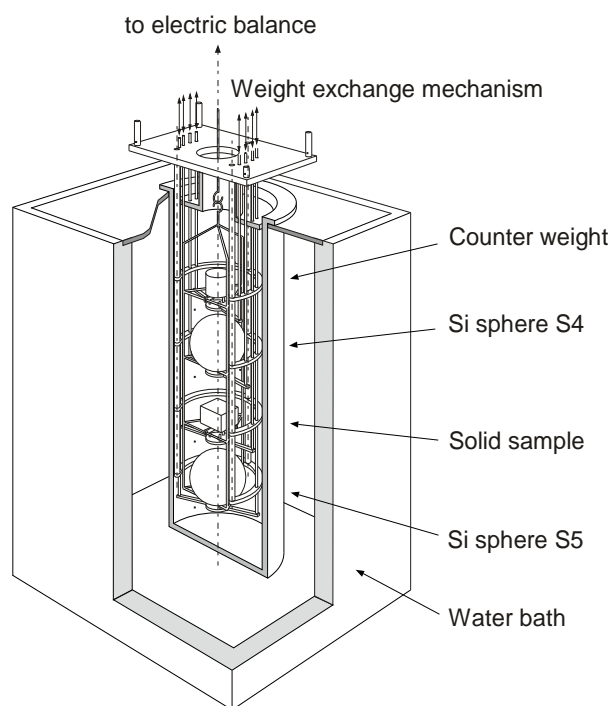

Fig. 1 Hydrostatic weighing system for measuring the density of solid samples with respect to the single-crystal silicon spheres [3, 4].
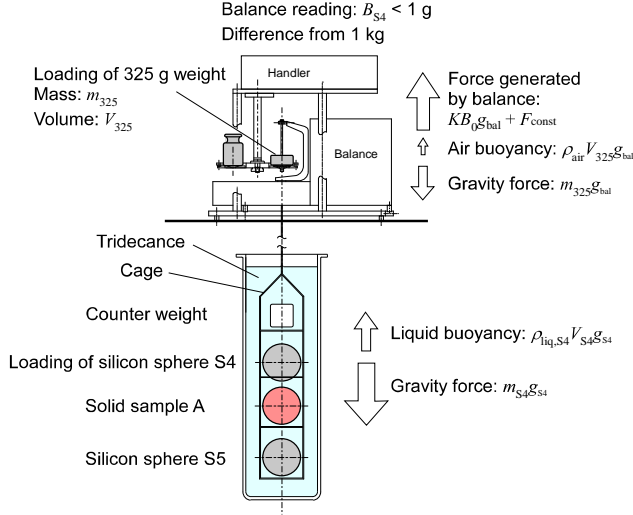
Fig. 2 Forces acting in the system when the 325 g stainless steel weight in air and the silicon sphere S4 in the liquid are loaded on the electronic balance.
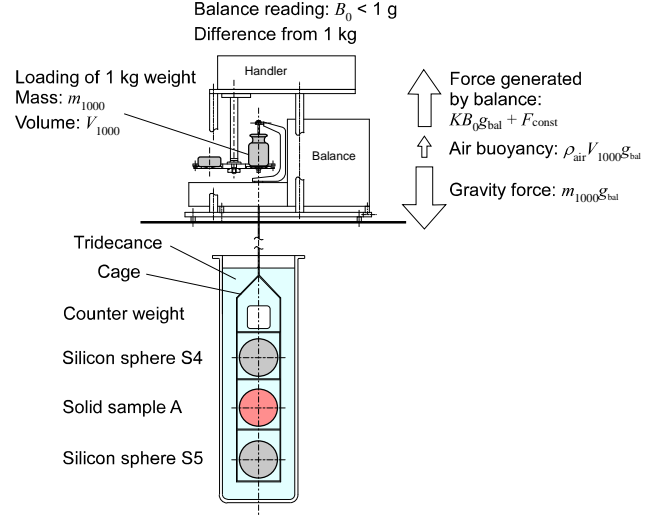

Fig. 3 Forces acting in the system when the 1 kg stainless steel weight in air is loaded on the electronic balance. Nothing is loaded in the cage.

placed on and removed from the cage by the weight exchange mechanism. As long as the level of the liquid is kept constant during the weight exchange, the buoyancy force acting on the cage can be canceled.

2.1. Procedure for the density measurement

When S4 is weighed in the liquid, as shown in figure 2, its apparent mass in the liquid is about 675 g because of the buoyancy force acting on the sphere. In order to operate the balance near 1 kg, a stainless steel weight with a mass of 325 g is placed on the balance pan with the automatic handler. At this state, the balance reading, B_{S4}, being a difference from 1 kg, is recorded. The sphere and the weight are then removed from the balance, and a 1 kg stainless steel weight is placed on the balance pan with the automatic handler, as shown in figure 3. At this state, the balance reading, B_0, being a difference from 1 kg, is recorded. The relation of the forces acting in this system are therefore summarized to be

$$m_{S4}\,g_{S4} - \rho_{liq,S4}(t)V_{S4}(t)g_{S4} + m_{324}\,g_{bal}$$
$$- \rho_{air}(t_{air})V_{325}(t_{air})g_{bal} - KB_{S4}\,g_{bal}$$
$$= m_{1000}\,g_{bal} - \rho_{air}(t_{air})V_{1000}(t_{air})\,g_{bal} - KB_0\,g_{bal} \qquad (1)$$

where m_{S4}, m_{325}, and m_{1000} are the masses of the sphere S4, 325 g weight, and 1 kg weight, respectively, $\rho_{liq,S4}(t)$ and $\rho_{air}(t_{air})$ the density of the liquid near the silicon sphere S4 at temperature t and density of air at temperature t_{air}, respectively, $V_{S4}(t)$ the volume of S4 in the liquid at temperature t, $V_{325}(t_{air})$ and $V_{1000}(t_{air})$ the volumes of the 325 g and 1 kg weights at temperature t_{air}, respectively, g_{S4} and g_{bal} the local accelerations due to gravity at the levels of silicon sphere S4 and the balance, respectively, and K the balance sensitivity. Since the vertical distance between the balance and the sphere S4 is about 1 m, the gravity gradient coefficient, $C_{S4} = g_{bal}/g_{S4}$, is estimated to be 0.999 9997.

In equation (1), the balance sensitivity K, which is the relationship between the force and the balance reading, may be determined by loading and unloading a calibrated weight on the balance pan with the automatic handler. From equation (1), the liquid density near S4 is determined as

$$\rho_{liq,S4}(t) = \{m_{S4} + C_{S4}(m_{325} - m_{1000}) + KC_{S4}(B_0 - B_{S4})$$
$$+ C_{S4}\rho_{air}(t_{air})[V_{1000}(20°C) - V_{325}(20°C)]$$
$$\times[1 + \beta_{SS}(t_{air} - 20°C)]\}\{V_{S4}(20°C)$$
$$\times[1 + 3\alpha_{Si}(t - 20°C)]\}^{-1} \qquad (2)$$

where α_{Si} is the linear thermal expansion coefficient of silicon crystals, and β_{SS} the bulk thermal expansion coefficient of the stainless steel weight.

When S5 is weighed in the liquid, the liquid density near S5 is similarly given by

$$\rho_{liq,S5}(t) = \{m_{S5} + C_{S5}(m_{325} - m_{1000}) + KC_{S5}(B_0 - B_{S4})$$
$$+ C_{S5}\rho_{air}(t_{air})[V_{1000}(20°C) - V_{325}(20°C)]$$
$$\times[1 + \beta_{SS}(t_{air} - 20°C)]\}\{V_{S5}(20°C)$$
$$\times[1 + 3\alpha_{Si}(t - 20°C)]\}^{-1} \qquad (3)$$

where m_{S5} is the mass of the silicon sphere S5, B_{S5} the balance reading when S5 is weighed in the liquid, $V_{S5}(t)$ the volume of S5 in the liquid at temperature t, and $C_{S5} = g_{bal}/g_{S5}$ with g_{S5} being the acceleration due to gravity at the level of S5. From equations (2) and (3), the liquid density near a solid sample A is determined, assuming that any vertical density gradient in the liquid is linear, with

$$\rho_{liq,A}(t) = [\rho_{liq,S4}(t) + \rho_{liq,S5}(t)]/2 \qquad (4)$$

When a 1-kg silicon sample A under study is weighed in the liquid, its volume at a temperature t is given by

$$V_A(t) = \{m_A + C_A(m_{325} - m_{1000}) + KC_A(B_0 - B_A)$$
$$+ C_A\rho_{air}(t_{air})[V_{1000}(20°C) - V_{325}(20°C)] \qquad (5)$$
$$\times[1 + \beta_{SS}(t_{air} - 20°C)]\}/\rho_{liq,A}(t)$$

where m_A is the mass of the sample A, B_A the balance reading when the sample A is weighed in the liquid, and $C_A = g_{bal}/g_A$ with g_A being the acceleration due to gravity at the level of sample A. The density of the sample A at temperature t is therefore given by

$$\rho_A(t) = m_A/V_A(t). \qquad (6)$$

The density of the sample A under study is thus measured with respect to those of the silicon spheres. When the apparent mass of the solid sample in the liquid is different from 675 g, a different weight is placed on the balance so that the balance is always operated near 1 kg.

The procedure for a single density measurement of a solid sample therefore concists of the following steps:

Step 1 Measurements of the air temperature, pressure, and humidity for determining the air density ρ_{air}. Measurement of the liquid temperature t.

Step 2 Calibration of the balance sensitivity K by loading and unloading a calibrated weight on the balance.

Step 3 Loading a 1 kg weight on the balance with loading nothing in the cage, and recording balance reading B_0. This reading is used as a zero point in the hydrostatic weighing.

Step 4 Unloading the 1 kg weight and loading 325 g weight on the balance. Loading the silicon sphere S4, and recording the balance reading B_{S4} for determining the liquid density $\rho_{liq,S4}$ near S4.

Step 5 Unloading S4 and loading S5 in the cage. Recording the balance reading B_{S4} for determining the liquid density $\rho_{liq,S5}$ near S5.

Step 6a For measuring the density of a 1 kg silicon crystal, unloading S5 and loading the sample A in the cage. Recording the balance reading B_A for determining the sample density ρ_A at temperatute t.
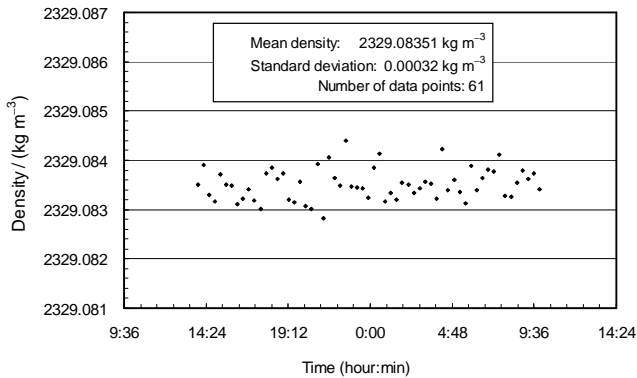

Fig. 4 An example of density measurements of a 1 kg silicon crystal by hydrostatic weighing. Values are at 20.000 °C and 101.325 kPa.

Step 6b When the apparent mass of the sample A in the liquid is different from 675 g, unloading the 325 g weight and loading a different weight on the balance so that the balance is operated near 1 kg. Unloading S5 and loading the sample A in the cage. Recording the balance reading B_A for determining the sample density ρ_A at temperatute t.

For completing these steps 1 to 6, it usually takes 20 minutes. This system is presently used at the NMIJ for calibrating the density of silicon crystals and solid samples, such as stainless steel weights, glasses, metals, and polymers.

An example of density measurements of a 1 kg silicon crystal is shown in figure 4. A total of 61 density measurements were conducted in this example. Each data point was deduced from the procedure with steps 1 to 6. As can be seen from the figure, a very stable result was obtained for a total of about 20 hours. The density of the sample was thus measured with a relative standard deviation of 1.8×10^{-7}.

2.2. Uncertainty in the hydrostatic weighing

When equations (2) to (6) used for deducing the density of a solid sample, ρ_A, are expressed as a function with N input quantities

$$\rho_A = f(x_1, x_2, x_3, \cdots, x_i, \cdots, x_N) \qquad (7)$$

the combined variance of ρ_A is generally given by

$$u_c^2(\rho_A) = \sum_{i=1}^{N}\left(\frac{\partial f}{\partial x_i}\right)^2 u^2(x_i) + 2\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\frac{\partial f}{\partial x_i}\frac{\partial f}{\partial x_j}u(x_i, x_j) \quad (8)$$

where $u_c(\rho_A)$ is the combined standard uncertainty of ρ_A, $u(x_i)$ the standard uncertainty of the imput quantity x_i, and $u(x_i, x_j)$ the covariance between the two imput quantities x_i and x_j. In equation (8), the first and second terms therefore correspond to the variance and covariance components, respectively [10].

In general, the variances for all imput quantities may be evaluated for estimating u_c, but it is rather difficult to evaluate all covariances between pairs of so many input quantities. In this work, the effect of dominat covariances are therefore evaluated: one is the covariance between the masses of the two silicon spheres, m_{S4} and m_{S5}, and the other is the covariance between their volumes, V_{S4} and V_{S5}. In the example of density measurement shown in figure 4, the mass of the 1 kg silicon sample was measured with respect to that of S4. This means that the mass of sample A, m_A, is strongly correlated to m_{S4} and m_{S5}. Following correlation coefficients were therefore taken into account for estimating the combined standard uncertainty in the density measurement:

$$r(m_{S4}, m_{S5}) = u(m_{S4}, m_{S5})/[u(m_{S4})u(m_{S5})] \qquad (9)$$
$$r(V_{S4}, V_{S5}) = u(V_{S4}, V_{S5})/[u(V_{S4})u(V_{S5})] \qquad (10)$$
$$r(m_{S4}, m_A) = u(m_{S4}, m_A)/[u(m_{S4})u(m_A)] \qquad (11)$$
$$r(m_{S5}, m_A) = u(m_{S5}, m_A)/[u(m_{S5})u(m_A)] \qquad (12)$$

These correlation coefficients are all positive in this case.

In stead of analytical evaluation given in equation (8), the combined standard uncertainty may be deduced from numerical evaluation [10]. When a change in ρ_A due to a change in an input quantity x_i is expressed as

$$Z_i = [f(x_1,\ldots, x_i + u(x_i),\ldots, x_N)$$
$$- f(x_1,\ldots, x_i - u(x_i),\ldots, x_N)]/2 \qquad (13)$$

the combined standard uncertainty in ρ_A is numerically obtained as

$$u_c^2(\rho_A) = \sum_{i=1}^{N} Z_i^2 + 2\sum_{i=1}^{N-1} \sum_{j=i+1}^{N} Z_i Z_j r(x_i, x_j) \qquad (14)$$

From equation (14), the combined standard uncertainty was estimated in this study.

One of difficulties in evaluating the uncertainty in the hydrostatic weighing described here is how to estimate the effect of non-linear density gradient in the liquid. As can be seen in equation (4), the density of the liquid near the solid sample, $\rho_{liq,A}$, may not be determined accurately if the vertical temperature gradient in the liquid has a relatively large non-linearity. In order to evaluate the effect, the differences in the measured solid densities determined from the hydrostatic weighing and from the pressure-of-flotation method [11, 12] were compared. Results of the measurements for five samples have shown that the relative difference in the densities determined by the two independent methods was as small as 3.0×10^{-8} with a standard deviation of 3.3×10^{-8}. Since the result from the pressure-of-flotation method is considered to be almost free from the non-linear gradient in the liquid density, this difference is considered to be the magnitude of possible non-linear effect in the hydrostatic weighing.

Table 1 lists influence quantities in the hydrostatic weighing of the 1 kg silicon crystal. Major influence factors are attributed to the volume uncertainties, $u(V_{S4})$ and $u(V_{S5})$, and also to their covariance, $u(V_{S4}, V_{S5})$. It should be noted that the effects of covariances $u(m_{S4}, m_A)$ and $u(m_{S5}, m_A)$ on $u_c(\rho_A)$ are negative because the sensitivity coefficient $\partial f/\partial m_A$ is negative and those for $\partial f/\partial m_{S4}$ and $\partial f/\partial m_{S5}$ are positive. The covariance between the masses of silicon sphere and the solid sample therefore contributes to reduce the combined standard uncertainty in ρ_A, but the contribution is trivial in this case because the major uncertainty comes from the uncertainty in the volumes of S4 and S5. In this example, the density of the 1 kg silicon sample, ρ_A, was thus determined with a relative combined standard uncertainty of 1.2×10^{-7}.

Table 2 shows an uncertainty evaluation for the same solid sample. In this case, the combined standard uncertainty of the density difference, $\Delta\rho = \rho_A - (\rho_{S4} + \rho_{S5})/2$, is evaluated. Evaluation of such a density difference is especially useful for determining the Avogadro constant, where the densities of many silicon samples are measured with respect to those of reference silicon spheres [2, 13]. As can be seen in the table, the uncertainty in the volumes, $u(V_{S4})$ and $u(V_{S5})$, does not contribute to the uncertainty in $\Delta\rho$. Consequently, the density difference $\Delta\rho$ was determined with a relative combined standard uncertainty of 3.6×10^{-8}. If the covariances between the masses m_{S4}, m_{S5}, and m_A are not taken into account, the relative combined standard uncertainty increases to 5.4×10^{-8}, showing importance of evaluating covariances in input quantities. If the effect of non-linear gradient in the liquid density is

Table 1 Uncertainty evaluation for the density measurement of a 1-kg silicon crystal under the presence of covariances. Correlation coefficients: $r(m_{S4}, m_{S5}) = 0.974$, $r(m_A, m_{S4}) = 0.964$, $r(m_A, m_{S5}) = 0.939$, and $r(V_{S4}, V_{S5}) = 0.433$.

Uncertainty source	$u(x_i)$	$Z_i^2/(kg/m^3)^2$ or $2Z_iZ_jr(x_i, x_j)/(kg/m^3)^2$
Mass		
m_{S4}	16.0 μg	0.33×10^{-8}
m_{S5}	16.0 μg	0.33×10^{-8}
Covariance between m_{S4} and m_{S5}		0.64×10^{-8}
m_{1000}	28.0 μg	0.00×10^{-8}
m_{325}	51.0 μg	0.00×10^{-8}
m_A	16.4 μg	0.63×10^{-8}
Covariance between m_A and m_{S4}		-0.88×10^{-8}
Covariance between m_A and m_{S5}		-0.85×10^{-8}
Volume		
V_{S4}	0.000 052 cm³	1.99×10^{-8}
V_{S5}	0.000 064 cm³	3.01×10^{-8}
Covariance between V_{S4} and V_{S5}		2.12×10^{-8}
V_{1000}	0.020 cm³	0.00×10^{-8}
V_{325}	0.025 cm³	0.00×10^{-8}
Non-linear liquid density gradient		0.49×10^{-8}
Standard deviation of the mean		0.17×10^{-8}
$u_c(\rho_A)$		0.000 28 kg/m³

Table 2 Uncertainty evaluation for the density difference, $\Delta\rho = \rho_A - (\rho_{S4} + \rho_{S5})/2$, under the presence of covariances. Correlation coefficients: $r(m_{S4}, m_{S5}) = 0.974$, $r(m_A, m_{S4}) = 0.964$, $r(m_A, m_{S5}) = 0.939$, and $r(V_{S4}, V_{S5}) = 0.433$.

Uncertainty source	$u(x_i)$	$Z_i^2/(kg/m^3)^2$ or $2Z_iZ_jr(x_i, x_j)/(kg/m^3)^2$
Mass		
m_{S4}	16.0 μg	0.15×10^{-8}
m_{S5}	16.0 μg	0.15×10^{-8}
Covariance between m_{S4} and m_{S5}		0.29×10^{-8}
m_{1000}	28.0 μg	0.00×10^{-8}
m_{325}	51.0 μg	0.00×10^{-8}
m_A	16.4 μg	0.63×10^{-8}
Covariance between m_A and m_{S4}		-0.59×10^{-8}
Covariance between m_A and m_{S5}		-0.58×10^{-8}
Volume		
V_{S4}	0.000 052 cm³	0.00×10^{-8}
V_{S5}	0.000 064 cm³	0.00×10^{-8}
Covariance between V_{S4} and V_{S5}		0.00×10^{-8}
V_{1000}	0.020 cm³	0.00×10^{-8}
V_{325}	0.025 cm³	0.00×10^{-8}
Non-linear liquid density gradient		0.49×10^{-8}
Standard deviation of the mean		0.17×10^{-8}
$u_c(\Delta\rho)$		0.000 084 kg/m³

Table 3 Uncertainty evaluation for the density measurement of a 1 kg stainless steel. Correlation coefficients: $r(m_{S4}, m_{S5}) = 0.974$, $r(m_A, m_{S4}) = 0.000$, $r(m_A, m_{S5}) = 0.000$, and $r(V_{S4}, V_{S5}) = 0.433$.

Uncertainty source	$u(x_i)$	$Z_i^2/(\text{kg/m}^3)^2$ or $2Z_iZ_jr(x_i, x_j)/(\text{kg/m}^3)^2$
Mass		
m_{S4}	16.0 μg	3.78×10^{-8}
m_{S5}	16.0 μg	3.78×10^{-8}
Covariance between m_{S4} and m_{S5}		7.37×10^{-8}
m_{1000}	28.0 μg	2.66×10^{-6}
m_{325}	51.0 μg	1.54×10^{-6}
m_{100}	8.0 μg	4.36×10^{-7}
m_A	15.0 μg	1.25×10^{-6}
Covariance between m_A and m_{S4}		0.00×10^{-8}
Covariance between m_A and m_{S5}		0.00×10^{-8}
Volume		
V_{S4}	0.000 052 cm³	2.29×10^{-7}
V_{S5}	0.000 064 cm³	3.46×10^{-7}
Covariance between V_{S4} and V_{S5}		2.44×10^{-7}
V_{1000}	0.020 cm³	1.89×10^{-6}
V_{325}	0.025 cm³	5.15×10^{-7}
V_{100}	0.0038 cm³	1.34×10^{-7}
Liquid temperature	0.003 °C	7.83×10^{-7}
Air temperature	0.05 °C	0.37×10^{-9}
Air density	0.0012 kg/m³	7.34×10^{-5}
Bulk thermal expansion		
Silicon crystal	3.0×10^{-8} K⁻¹	0.00×10^{-9}
Stainless steel weight	3.0×10^{-6} K⁻¹	0.00×10^{-9}
Solid sample A	3.0×10^{-6} K⁻¹	2.36×10^{-8}
Balance sensitivity K	1.8×10^{-6}	4.69×10^{-7}
Gravity gradient C	2.0×10^{-8}	7.62×10^{-7}
Non-linear liquid density gradient		5.62×10^{-8}
Standard deviation of the mean		7.64×10^{-7}
$u_c(\rho_A)$	0.0093 kg/m³	

Table 4 Examples of density measurements for different solid materials. Values are at 20.000 °C and 101.325 kPa.

Material	m_A/g	$\rho_A/(\text{kg/m}^3)$	V_A/cm³	$u_c(V_A)$/cm³
Silicon crystal	1000	2329.08351	429.581 071	0.000 052
Silicon crystal	500	2329.1504	214.556 11	0.000 16
Silicon crystal	200	2329.0899	86.620 14	0.000 17
Silicon crystal	62	2329.0766	26.706 16	0.000 18
Stainless steel	1000	7965.9660	125.534 07	0.000 15
Stainless steel	500	7991.6104	62.487 57	0.000 15
Stainless steel	200	7994.9408	25.015 82	0.000 14
Stainless steel	100	7995.2595	12.507 41	0.000 14
Stainless steel	50	7995.1272	6.253 81	0.000 18
Gold	100	19279.573	5.249 80	0.000 14
Fused quartz	190	2199.7074	85.973 75	0.000 18
Polystyrene	1.43	1048.1416	1.364 82	0.000 21

removed, the relative combined standard uncertainty in the measurement of $\Delta\rho$ further reduces to 2.0×10^{-8}.

Table 3 lists influence quantities in the density measurement of a 1 kg stainless steel. Since the apparent mass of this sample in the liquid was about 900 g, a 100 g weight with a mass m_{100} and a volume V_{100} was placed on the balance during the hydrostatic weighing of the sample. As can be seen in this table, the number of influence quantities is much more than that for density measurements of 1 kg silicon crystals because different weights were used in the hydrostatic weighing: 325 g weight for the two silicon spheres and 100 g weight for the solid sample. In this case, the largest uncertainty source lies in the uncertainty in the air density measurement. The density of the 1 kg stainless steel weight, ρ_A, was thus determined with a relative combined standard uncertainty of 1.2×10^{-6}. Precise measurements of the volumes of stainless steel weights are especially important for calibrating the volumes of air-density artifacts [14]. They have nearly the same masses, but different volumes. By weighing them in air, the density of air is directly measured from their apparent masses in air, providing much better uncertainty than that obtained from air pressure, temperature, and humidity measurements [15].

Table 4 lists examples of density measurements for different materials. Solid samples with different masses and densities have been measured by the hydrostatic weighing system described in section 3.1. The uncertainty in the density measurement depends on the mass and density of each sample, but the uncertainty in the volume is almost the same for any solid samples except for 1 kg silicon crystals. As can be seen from equation (5), hydrostatic weighing determines the volume of the sample from mass measurement in air and from apparent mass measurement in liquid. Since the uncertainty in the mass of a combination of weights is almost the same for any measurement described here, the combined standard uncertainty in the volume determination of the solid sample is almost equal to or less than 0.0002 cm³ = 0.2 mm³. This means that when the volume of the solid sample is larger, better uncertainty is obtained.

3. DISCUSSIONS

In this work, examples of density measurements for silicon crystals, metals, glasses, and polymers have been presented. Best uncertainties were obtained for 1 kg silicon crystals because their mass, volume, and thermal expansion coefficient are nearly the same with those of silicon spheres used as a solid density standard. Uncertainty evaluations for 1 kg silicon crystals have therefore shown that $u_{c,r}(\rho) = 1.2 \times 10^{-7}$ and $u_{c,r}(\Delta\rho) = 3.6 \times 10^{-8}$. For other materials, the uncertainty depends on their mass and density, but the combined standard uncertainty in their volume determination, $u_c(V)$, is approximately equal to or less than 0.2 mm³.

Such a capability in the density measurement is presently used at the NMIJ for the determination of the Avogadro constant, N_A, by the x-ray crystal density (XRCD), where both the hydrostatic weighing method and the pressure-of-flotation method are used for measuring density differences between silicon crystals.

In the field of material science, density measurements for solid samples with small volumes, such as 1 cm³ or less, are often needed. Further reduction of uncertainty in the volume determination is therefore being considered at the NMIJ for measuring the density of small samples. As can be seen in figure 7, one of the serious uncertainty sources lies in a scatter in the density measurement. The most serious cause of this scatter is attributed to the instability in the effect of meniscus at the suspension rod. One of

possible ways to reduce the scatter is to implement a magnetic coupling used in magnetic suspension densimeters [16-20]. The magnetic suspension densimeter is a device developed to measure the density of fluids. When the coil suspended from the balance is kept in air and the permanent magnet is kept in the liquid, the buoyancy forces acting on solid materials in the liquid may be measured without the effect of meniscus. Such a principle will be useful for measuring the volume and density of new materials.

REFERENCES

[1] M. Tanaka, G. Girard, R. Davis, A. Peuto, and N. Bignell, "Recommended table for the density of water between 0 °C and 40 °C based on recent experimental results," *Metrologia*, Vol. 38, pp. 301-309, 2001.

[2] K. Fujii, A. Waseda, N. Kuramoto, S. Mizushima, P. Becker, H. Bettin, A. Nicolaus, U. Kuetgens, S. Valkiers, P. Taylor, P. De Bièvre, G. Mana, E. Massa, R. Matyi, E. G. Kessler, Jr., and M. Hanke, "Present State of the Avogadro Constant Determination from Silicon Crystals with Natural Isotopic Compositions," *IEEE Trans. Instrum. Meas.*, Vol. 54, No. 2, pp. 854-859, April 2005.

[3] K. Fujii, A. Waseda, and N. Kuramoto, "Development of a silicon density standard and precision density measurements of solid materials by hydrostatic weighing," *Meas. Sci. Technol.*, Vol. 12, pp. 2031-2038, 2001.

[4] K. Fujii, "Present state of the solid and liquid density standards," *Metrologia*, Vol. 41, pp. S1-S15, 2004.

[5] K. Fujii, M. Tanaka, Y. Nezu, K. Nakayama, R. Masui, and G. Zosi, "Interferometric measurements of the diameters of a single-crystal silicon sphere," *Rev. Sci. Instrum.*, Vol. 63, pp. 5320-5325, 1992.

[6] K. Fujii, M. Tanaka, Y. Nezu, A. Leistner, and W. Giardini, "Absolute measurement of the density of silicon crystals in vacuo for a determination of the Avogadro constant," *IEEE Trans. Instrum. Meas.*, Vol. 44, No. 2, pp. 542-545, 1995

[7] K. Fujii, M. Tanaka, Y. Nezu, K. Nakayama, H. Fujimoto, P. De Bièvre, and S. Valkiers, "Determination of the Avogadro constant by accurate measurement of the molar volume of a silicon crystal," *Metrologia*, Vol. 36, pp. 455-464, 1999.

[8] N. Kuramoto and K. Fujii, "Volume determination of a silicon sphere using a improved interferometer with optical frequency tuning," *IEEE Trans. Instrum. Meas.*, Vol. 54, pp. 868-871, 2005.

[9] F. Spieweck, A. Kozdon, H. Wagenbreth, H. Toth, and D. Hoburg, "A computer-controlled solid-density measuring apparatus," *PTB-Mitteilungen*, Vol. 100, pp. 169-173, 1990.

[10] *Guide to the Expression of Uncertainty in Measurement* (Genève: International Organization for Standardization), 1995.

[11] A. Waseda and K. Fujii, "High precision density comparison measurement of silicon crystals by the pressure of flotation method," *Meas. Sci. Technol.*, Vol. 12, pp. 2039-2045, 2001.

[12] A. Waseda and K. Fujii, "Density comparison measurements of silicon crystals by a pressure-of-flotation method at NMIJ," *Metrologia*, Vol. 41, pp. S62-S67, 2004.

[13] K. Fujii, A. Waseda, N. Kuramoto, S. Mizushima, S. Valkiers, P. Taylor, and P. De Bièvre, "Evaluation of molar volume of silicon crystals for a determination of the Avogadro constant," *IEEE Trans. Instrum. Meas.*, Vol. 52, pp. 646-651, 2003.

[14] Y. Kobayashi, Y. Nezu, K. Uchikawa, S. Ikeda, and H. Yano, "Prototype kilogram balance II of NRLM," *Bulletin of NRLM*, Vol. 35, pp. 143-158, 1986.

[15] M. Gläser, R. Schwartz, and M. Mecke, "Experimental determination of air density using a 1-kg mass comparator in vacuum," *Metrologia*, Vol. 28 pp. 45-50, 1991.

[16] W. M. Haynes, M. J. Hiza, and N. V. Frederick, "Magnetic suspension densimeter for measurements of fluids of cryogenic interest," *Rev. Sci. Instrum.*, Vol. 47, pp. 1237-1250, 1976.

[17] N. Bignell, "A magnetic float densimeter for the measurement of changes in water density on aeration," *J Phys E: Sci Instrum*, Vol. 15, pp. 378-381, 1982.

[18] R. Masui, W. M. Haynes, R. F. Chang, H. A. Davis, and J. M. H. Levelt Sengers, "Densimetry in compressed fluids by combining hydrostatic weighing and magnetic levitation," *Rev. Sci. Instrum.*, Vol. 55, pp. 1132-1142, 1984.

[19] W. Wagner and R. Kleinrahm, "Densimeters for very accurate density measurements of fluids over large ranges of temperature, pressure, and density," *Metrologia*, Vol. 41, pp. S24-S39, 2004.

[20] N. Kuramoto, K. Fujii, and A. Waseda, "Accurate density measurements of reference liquids by a magnetic suspension balance," *Metrologia*, Vol. 41 pp. S84-S94, 2004.