CCM.D-K1: Final Report

CIPM key comparison of density measurements of a silicon sphere

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Abstract

This report describes the results on a CIPM key comparison of solid density measurements, which was carried out through July 2001 to May 2003. This CIPM key comparison, designated as CCM.D-K1, was coordinated by the National Metrology Institute of Japan (NMIJ, Japan), Swiss Federal Office of Metrology and Accreditation (METAS, Switzerland), and National Research Council Canada (NRC, Canada). These three National Metrology Institutes (NMIs) formed a pilot group to determine the technical protocol for this key comparison. A total of eight NMIs, namely NMIJ, Physikalisch-Technische Bundesanstalt (PTB, Germany), Istituto di Metrologia "G. Colonnetti" (IMGC, Italy), Korea Research Institute of Standards and Science (KRISS, Korea), METAS, NRC, Centro Espanol de Metrologia (CEM, Spain), and National Center of Metrology (CENAM, Mexico), participated in this key comparison. A 1 kg single-crystal silicon sphere, prepared by NMIJ, was circulated to each of the NMIs as a travelling standard. Each NMI determined the mass, volume and density of the travelling standard with respect to the mass standard and solid density standard of each NMI by mass measurement and hydrostatic weighing. The reference value of the density was determined with a relative expanded uncertainty of 2.9×10^{-7}. When the degrees of equivalence was evaluated by differences from the reference value, the differences for the mass, volume, and density were almost equal to or less than expanded uncertainties of the differences, showing a good equivalence of the capabilities for the solid density measurement at the participating NMIs.

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1. Introduction

The unit of density, kg/m^3, consists of the two SI base units. The traceability to the definition of the kilogram is realised by the standard technique used for mass comparisons. Most of the difficulties in realising the unit of density are attributed to the conversion of the length standard to the volume standard. Different technologies have therefore been implemented to determine the volume of a solid object with a small uncertainty. Recent techniques for determining the volume of the solid object use a sphere because its volume is determined only from diameters and it is much less susceptible to be damaged than objects of any other shapes. Silicon single-crystal is chosen as the material of the solid density standard because of its high-stability in the density. Independent silicon density standards have already been established at some of the National Metrology Institutes (NMIs), and these density standards have already been disseminated to other NMIs.

Considering these situations, the Working Group on Density (WG-Density) of the Consultative Committee for Mass and Related Quantities (CCM) held a meeting on May 11th, 1999 at the BIPM, and decided to organise a CIPM key comparison to evaluate the degrees of equivalence of the solid density standards at NMIs. After the meeting, the method for comparing the density standards was discussed by representatives from NMIJ (Japan), METAS (Switzerland), and NRC (Canada). These three NMIs formed a pilot group to determine the technical protocol for the CIPM key comparison designated as CCM.D-K1. On January 8th, 2000, a questionnaire was distributed to NMIs to know their facilities and measurement capabilities. Based on the information received from the NMIs, the pilot group determined the technical protocol, and nominated seven participating NMIs: NMIJ, PTB (Germany), IMGC (Italy), KRISS (Korea), METAS, NRC and NIST (USA).

As a travelling standard, a 1 kg single-crystal silicon sphere, identified as D1, was prepared at NMIJ, and this travelling standard was circulated to each of the participating NMIs in series. The mass, volume and density of the travelling standard were determined with respect to the mass standard and solid density standard of each NMI by mass measurement and hydrostatic weighing.

After starting this key comparison in July 2001, the WG-Density meeting held on May 21st, 2002 at the BIPM, decided to include two more participating NMIs: CEM (Spain) and CENAM (Mexico). During the circulation of the travelling standard, NIST decided not to participate in this key comparison because the hydrostatic weighing apparatus of NIST may not be operational till the scheduled date of participation. Finally, NMIJ, PTB, IMGC, KRISS, METAS, NRC, CEM, and CENAM participated in this key comparison, and all measurements were completed in May 2003.

2. List of participating NMIs

The pilot group of this key comparison decided that at least two NMIs shall participate from each of the Regional Metrology Organizations (RMOs) to link the results of key comparisons conducted in RMOs to that of this CIPM key comparison. Considering the total period of time needed to circulate the travelling standard in series, the number of participating NMIs from each RMO were therefore chosen to be two from APMP, four from EUROMET, and two from SIM, as shown below:

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3. Density standards of participating NMIs

Table 1 lists the density standards used at the participating NMIs. The solid density standards used at NMIJ, PTB, IMGC, KRISS, METAS, and CEM were the single-crystal silicon sphere(s) [1-7], while at CENAM, zerodur spheres were used. Some of their volumes are traceable to other NMIs that have the capability for measuring the volume by optical interferometry [1, 4, 5]. As an exceptional case, the density of water was used as a density standard of NRC, where the density of water was determined from the table recommended by the CIPM [8]. According to the table, the density of distilled tap water used in the hydrostatic weighing at NRC was determined by correcting the effect of isotopic abundance and dissolved gases in water.

Table 1. Reference density standards used in this key comparison.

NMI	Reference density standard	Traceability		Standard uncertainty	
		Mass	Volume	Mass/g	Volume/cm^3
NMIJ	1 kg silicon spheres, S4 and S5	NMIJ	NMIJ	0.000 030	0.000 052 0.000 064
PTB	870 g silicon spheres, Si1 and Si2	PTB	PTB	0.000 050	0.000 25
IMGC	1 kg silicon sphere, Si3	IMGC	IMGC	0.000 048	0.000 061
KRISS	1 kg silicon sphere, Si	KRISS	NMIJ	0.000 095	0.000 087
METAS	1 kg silicon sphere, RAW08	METAS	IMGC	0.000 14	0.000 10
NRC	Water *)	—	—	—	—
CEM	1 kg silicon sphere, S1	CEM	IMGC	0.000 050	0.000 38
CENAM	1 kg zerodur spheres, Z-01 and Z-02	CENAM	PTB	0.000 13	0.000 40

*) The density of water determined from the CIPM recommended formula [8] was used as a reference standard of the NRC. The isotopic compositions of the water were measured at the NRC. Assuming that the water was saturated with dissolved air, a value of 998.2012(11) kg/m^3 was found for the density of water at 20 °C and 101.325 kPa, where the value in the parentheses expresses the standard uncertainty.

4. Travelling standard

A 1 kg single-crystal silicon sphere, identified as D1, was prepared at NMIJ. This sphere was fabricated by an optical company in Japan and used as a travelling standard for this key comparison. Physical properties of the travelling standard are given in Table 2. The bulk thermal expansion coefficient and the isothermal compressibility listed in this table were used as given and common parameters in this key comparison.

Table 2. Physical properties of the travelling standard D1

Physical properties	Parameter	Standard uncertainty	Degrees of freedom
Material	Silicon single crystal	—	—
Diameter (nominal) at 20 °C and 101.325 kPa	93.6 mm	—	—
Mass (nominal)	1000.5 g	—	—
Volume (nominal) at 20 °C and 101.325 kPa	429.6 cm^3	—	—
Bulk thermal expansion coefficient at 20 °C and 101.325 kPa	7.67×10^{-6} K^{-1}	0.03×10^{-6} K^{-1}	50
Isothermal compressibility at 20 °C and 101.325 kPa	1.02×10^{-11} Pa^{-1}	0.01×10^{-11} Pa^{-1}	50

5. Circulation scheme

The travelling standard, D1, was circulated to the participating NMIs in series with a circulation schedule shown in Table 3. The first measurement started at NMIJ in July 2001 and the final measurement at NMIJ was completed in May 2003. In February 2002, it was sent to NRC, but the measurement was not performed because of a failure of the hydrostatic weighing apparatus at NRC. After returning the travelling standard to NMIJ in May 2002, it was sent to NRC again in August 2002. To monitor the stability of the mass, volume, and density of the travelling standard, these parameters were measured four times at NMIJ during the whole period. These data were labelled as NMIJ-1, NMIJ-2, NMIJ-3, and NMIJ-4, as shown in Table 3.

Table 3. Circulation scheme of the travelling standard.

Participating NMI	Data label	Date of arrival (year/month/day)	Date of departure (year/month/day)	Comment
NMIJ	NMIJ-1	—	2001/08/09	—
PTB	PTB	2001/08/16	2001/09/13	—
IMGC	IMGC	2001/09/14	2001/10/25	—
KRISS	KRISS	2001/11/05	2001/12/03	—
NMIJ	NMIJ-2	2001/12/12	2001/01/11	—
METAS	METAS	2002/01/22	2002/02/14	—
NRC	—	2002/02/28	2002/05/10	Not measured
NMIJ	NMIJ-3	2002/05/28	2002/07/19	—
NRC	NRC	2002/08/02	2002/08/30	—
CEM	CEM	2002/09/06	2002/10/07	—
CENAM	CENAM	2002/10/07	2002/11/12	—
NMIJ	NMIJ-4	2002/11/18	—	—

6. Procedure and method for measurement

Mass measurements and hydrostatic weighing generally need to determine the density of air. Air-density artefacts composed of stainless steel weights with nearly the same masses and surface areas but different volumes may be used for a direct determination of the density of air [9, 10]. When such an artefact was not available or not used, the density of air was determined from measurements of air temperature, pressure, and humidity. For this purpose, the CIPM formula [11] was used as a common equation in this key comparison for calculating the density of air.

The technical protocol of this key comparison determines the details on handling and cleaning the travelling standard, minimum number of measurements, and the method for uncertainty analysis. The uncertainties of the mass, volume, and density of the travelling standard were reported at the 95 % level of confidence and by evaluating the effective degrees of freedom ν_{eff} [12].

6.1 Mass measurement

Table 4 summarizes the method used for mass measurement at each NMI. All the participants measured the mass of D1 in air. The method used for determining the density of air, and the reference mass standard used for this measurement are given in this table.

Table 4. Method used for measuring the mass of the travelling standard.

NMI	Balance	Method used for determining the density of air	Reference mass standard
NMIJ	Commercially available single-pan flexure-hinge electronic balance with an automatic weight exchange mechanism. Maximum load: 1011 g Resolution: 1 μg Electronic balance range: 11 g	CIPM formula	Silicon sphere with a mass calibrated by using air-density artefacts
PTB	Hydrostatic principle single-pan balance made in PTB with an automatic weight exchange mechanism. Maximum load: 1030 g Resolution: 0.1 μg Electronic balance range: 100 mg	CIPM formula and air-density artefacts *)	Calibrated stainless steel weights
IMGC	Commercially available single-pan knife-edge balance with an automatic weight exchange mechanism. Maximum load: 1 kg Resolution: 1 μg	CIPM formula	Calibrated stainless steel weights
KRISS	Commercially available single-pan flexure-hinge electronic balance with an automatic weight exchange mechanism. Maximum load: 1109 g Resolution: 10 μg Electronic balance range: 109 g	CIPM formula	Calibrated stainless steel weights
METAS	Commercially available single-pan flexure-hinge electronic balance with an automatic weight exchange mechanism. Maximum load: 1001.5 g Resolution: 0.1 μg Electronic balance range: 1.5 g	CIPM formula	Calibrated stainless steel weights
NRC	Commercially available single-pan flexure-hinge electronic balance with an automatic weight exchange mechanism. Maximum load: 10 011 g Resolution: 10 μg Electronic balance range: 11 g	CIPM formula	Calibrated stainless steel weights
CEM	Commercially available single-pan flexure-hinge electronic balance with an automatic weight exchange mechanism. Maximum load: 10 011 g Resolution: 10 μg Electronic balance range: 11 g	CIPM formula	Calibrated stainless steel weights
CENAM	Commercially available single-pan flexure-hinge electronic balance with a modified pan. Maximum load: 1109 g Resolution: 10 μg Electronic balance range: 109 g	CIPM formula	Calibrated stainless steel weights

*) For calculating the buoyancy correction, the air density was evaluated from the two methods, and the mean value was taken for the final value with the uncertainty of air-density measurements using the CIPM formula.

6.2 Hydrostatic weighing

Table 5 summarizes the method used for hydrostatic weighing at each NMI. At IMGC, KRISS and CENAM, the same balance was used both for mass measurement and for hydrostatic weighing.

Table 5. Method used for hydrostatic weighing of the travelling standard.

NMI	Balance	Positions of the density standard and the travelling standard in the hydrostatic weighing apparatus	Working liquid
NMIJ	Commercially available single-pan flexure-hinge electronic balance with an automatic weight exchange mechanism. Maximum load: 1109 g Resolution: 10 μg Electronic balance range: 109 g	Travelling standard placed between two silicon density standards located in a different height. They are placed in a cage.	Tridecane (n-$C_{13}H_{28}$)
PTB	Commercially available single-pan knife-edge electronic balance with an automatic weight exchange mechanism. Maximum load: 1100 g Resolution: 1 μg Electronic balance range: 150 mg	Travelling standard placed between two silicon density standards located in a different height. They are placed in a cage.	Pentadecane (n-$C_{15}H_{32}$)
IMGC	See Table 4	Travelling standard and a silicon density standard placed on a rotational circular pan with six places.	Water
KRISS	See Table 4	Travelling standard placed below a silicon density standard. They are placed in a cage.	Tridecane (n-$C_{13}H_{28}$)
METAS	Commercially available single-pan flexure-hinge electronic balance with an automatic weight exchange mechanism. Maximum load: 1109 g Resolution: 10 μg Electronic balance range: 109 g	Travelling standard placed above a silicon density standard. They are placed in a cage.	Water
NRC	Commercially available single-pan flexure-hinge electronic balance with an automatic weight exchange mechanism. Maximum load: 1109 g Resolution: 10 μg Electronic balance range: 109 g	Travelling standard placed on a rotational circular pan with four places.	Water
CEM	Commercially available single-pan flexure-hinge electronic balance with an automatic weight exchange mechanism. Maximum load: 1109 g Resolution: 10 μg Electronic balance range: 109 g	Travelling standard and a silicon density standard placed on a rotational circular pan with four places.	Water and Fluorinert Electronic Liquid FC40 *)
CENAM	See Table 4	Travelling standard placed between two zerodur density standards located in a different height. They are placed in a cage.	Pentadecane (n-$C_{15}H_{32}$)

*) In order to compare the results, hydrostatic weighing was performed with both liquids: water and Fluorinert Electronic Liquid FC40. The final value was deduced from the result with water.

7. Result and data analysis

Table 6 lists the results of measurements by the participating NMIs. The expanded uncertainty U_{95} was determined from the standard uncertainty u and the effective degrees of freedom ν_{eff} reported by the participating NMIs. Since the measurements at NMIJ were repeated four times, the first data (NMIJ-1) were used as the data from NMIJ to calculate the reference values. The four sets of measurements at NMIJ were used to evaluate the stability of the travelling standard.

Table 6. Results of measurements.

Data label	Value at 20.000 °C and 101.325 kPa											
	Mass				Volume				Density			
	m/g	u/g	ν_{eff}	U_{95}/g	V/cm^3	u/cm^3	ν_{eff}	U_{95}/cm^3	ρ/(kg/m^3)	u/(kg/m^3)	ν_{eff}	U_{95}/(kg/m^3)
NMIJ-1	1000.530 188	0.000 031	72.9	0.000 061	429.581 071	0.000 074	121.3	0.000 146	2329.083 51	0.000 37	100.0	0.000 73
PTB	1000.530 161	0.000 055	1050.5	0.000 109	429.581 064	0.000 344	206.7	0.000 678	2329.083 48	0.001 92	185.8	0.003 79
IMGC	1000.530 102	0.000 048	62.8	0.000 096	429.581 051	0.000 375	87.7	0.000 746	2329.083 41	0.002 04	88.3	0.004 05
KRISS	1000.530 122	0.000 047	124.5	0.000 093	429.580 853	0.000 121	319.0	0.000 237	2329.084 54	0.000 66	336.4	0.001 31
NMIJ-2	1000.530 182	0.000 031	72.9	0.000 061	429.581 101	0.000 074	121.3	0.000 146	2329.083 33	0.000 37	100.0	0.000 73
METAS	1000.530 154	0.000 091	114.2	0.000 181	429.580 190	0.000 432	203.6	0.000 852	2329.088 21	0.002 35	206.8	0.004 63
NMIJ-3	1000.530 208	0.000 031	72.9	0.000 061	429.581 125	0.000 074	121.3	0.000 146	2329.083 26	0.000 37	100.0	0.000 73
NRC	1000.530 063	0.000 090	83.8	0.000 178	429.581 694	0.000 554	17.6	0.001 169	2329.079 84	0.003 01	17.8	0.006 35
CEM	1000.530 253	0.000 049	112.5	0.000 097	429.581 010	0.000 386	14.9	0.000 828	2329.083 99	0.002 09	14.8	0.004 48
CENAM	1000.530 050	0.000 226	53.6	0.000 454	429.581 960	0.000 662	154.1	0.001 308	2329.078 40	0.003 66	161.1	0.007 22
NMIJ-4	1000.530 222	0.000 031	72.9	0.000 061	429.581 119	0.000 074	121.3	0.000 146	2329.083 33	0.000 37	100.0	0.000 73

Figures 1 to 3 show the results of mass, volume, and density measurements at the participating NMIs, respectively. The bars in the figures express the expanded uncertainties U_{95} at the 95 % level of confidence. As shown in the figures, the reported mass values agreed within the expanded uncertainties, while for the reported volume values, relatively a larger scatter was observed. This propagated to the results for density.

Considering the difference in the degrees of freedom for the data reported by the participants, the standard uncertainty, u, is determined as $u = U_{95}/2$ in the following sections, where U_{95} is given in Table 6.

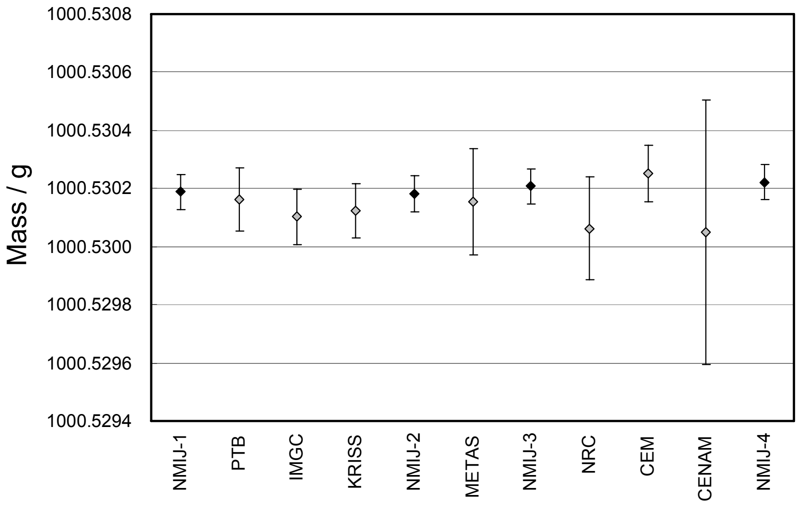

Figure 1. Results for mass measurements. The bars express the expanded uncertainties U_{95}.

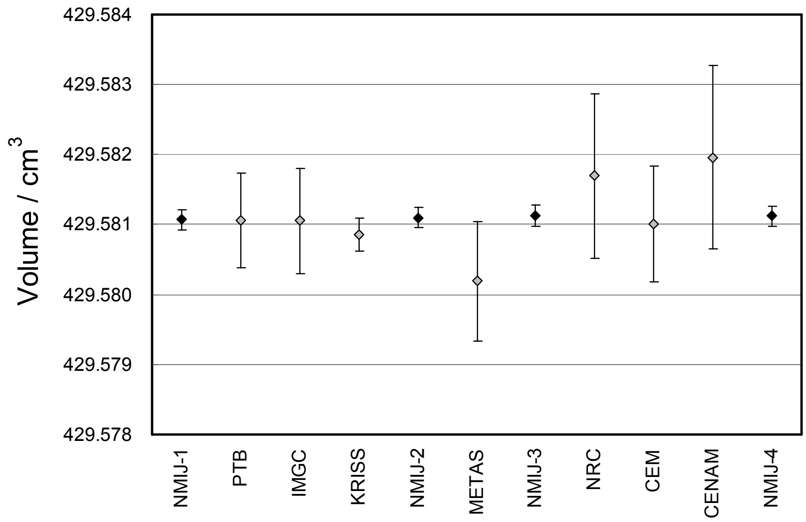

Figure 2. Results for volume measurements. The bars express the expanded uncertainties U_{95}.

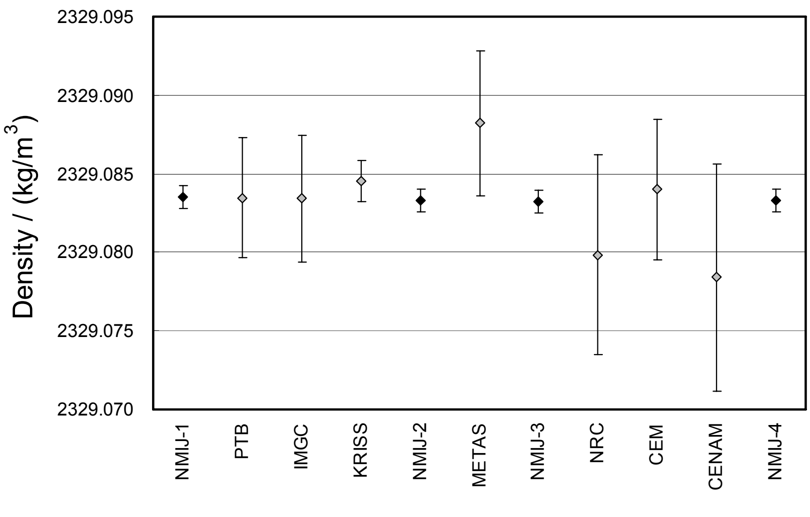

Figure 3. Results for density calibrations. The bars express the expanded uncertainties U_{95}.

7.1 Stability of the travelling standard

The stability of the travelling standard D1 was evaluated with the four measurements conducted at NMIJ for a period of 22 months through July 2001 to May 2003. When a possible drift during this period is assumed to be linear, it is estimated as follows:

mass: +38 μg with a standard deviation of 13 μg,

volume: +0.000 051 cm^3 with a standard deviation of 0.000 015 cm^3,

density: –0.000 19 kg/m^3 with a standard deviation of 0.000 11 kg/m^3,

where the standard deviations of the drifts were determined from least-square fitting of a straight line to the four measurements at NMIJ as a function of time. Since the expanded uncertainties of the measurements at NMIJ for the mass, volume, and density were 61 μg, 0.000 146 cm^3, and 0.000 73 kg/m^3, respectively, the effect of the possible drift was neglected in this key comparison.

7.2 Method of least-squares

In this key comparison, the mass of the travelling standard was measured independently at each NMI so that there is no correlation between the mass data reported by the participating NMIs. However, the volumes of the solid density standards at KRISS, METAS, CEM, and CENAM were determined by other NMIs, as shown in Table 1. This means that the volume and density data reported by some of the participating NMIs are correlated with each other. In order to take into account the effect of the correlation, the reference values for the mass, volume, and density of the travelling standard were estimated by the method of χ^2 [13].

In general, the reported data, namely the mass, volume, and density, are expressed as a column matrix $\boldsymbol{X}$ with N elements, i. e., x_1, x_2, x_3, $\cdots$, x_N, where N is the number of the reported data. The column matrix $\boldsymbol{X}$ is related to the reference value x_{ref}, that is to be estimated, by a matrix formula $\boldsymbol{X} \cong \boldsymbol{A} x_{\text{ref}}$, where $\boldsymbol{A}$ is a unit column matrix with N elements. The best estimate for the weighted mean of the reference value x_{ref} is given by

$$x_{\text{ref}} = g \boldsymbol{A}^{\text{t}} \boldsymbol{V}^{-1} \boldsymbol{X} \qquad (1)$$

where $g = \left(\boldsymbol{A}^{\text{t}} \boldsymbol{V}^{-1} \boldsymbol{A} \right)^{-1}$, $\boldsymbol{V}$ is the covariance matrix of the reported data $\boldsymbol{X}$, and $\boldsymbol{A}^{\text{t}}$ and $\boldsymbol{A}^{-1}$

are transpose and inverse of the matrix $\boldsymbol{A}$, respectively. The variance of x_{ref} is given by [13]

$$u^2(x_{\mathrm{ref}}) = \mathrm{cov}(x_{\mathrm{ref}}) = \left(g\boldsymbol{A}^{\mathrm{t}}\boldsymbol{V}^{-1}\right)\boldsymbol{V}\left(g\boldsymbol{A}^{\mathrm{t}}\boldsymbol{V}^{-1}\right)^{\mathrm{t}} = g \quad (2)$$

In order to evaluate the statistical consistency of the reported data, the integrated probability $P[\chi^2(\nu) > \chi^2_{\mathrm{obs}}]$ was deduced as a recommended procedure for evaluating the key comparison reference value [14], where ν is the degrees of freedom. In the present case, $\nu = N - 1$. When the integrated probability $P[\chi^2(\nu) > \chi^2_{\mathrm{obs}}]$ is greater than 0.05, the reported data are regarded as consistent. If the covariances of the reported data are known, the observed value for χ^2 is given by [13]

$$\chi^2_{\mathrm{obs}} = \left(\boldsymbol{X} - \boldsymbol{A}x_{\mathrm{ref}}\right)^{\mathrm{t}}\boldsymbol{V}^{-1}\left(\boldsymbol{X} - \boldsymbol{A}x_{\mathrm{ref}}\right) \quad (3)$$

where $\left(\boldsymbol{X} - \boldsymbol{A}x_{\mathrm{ref}}\right)$ is the residual matrix.

As can be seen in the following sections, the reported data for the mass, volume and density were all consistent in this key comparison, i. e., $P[\chi^2(\nu) > \chi^2_{\mathrm{obs}}] > 0.05$. Their reference values were therefore determined from the weighted means by using equation (1).

7.3 Mass

The mass measurements of the participating NMIs were performed independently using the mass standard of each NMI. This means that there is no correlation between the reported data. The covariance matrix $\boldsymbol{V}$ for the mass data is therefore expressed in a simple way; except the diagonal elements, others are all zero.

When the reference value was calculated from equation (1), the integrated probability $P[\chi^2(\nu) > \chi^2_{\mathrm{obs}}]$ was 0.330, satisfying the condition $P[\chi^2(\nu) > \chi^2_{\mathrm{obs}}] > 0.05$. The reference value for the mass of D1 is given in **Table A1** in **Appendix 1**. It was determined with $U = 2u(m_{\mathrm{ref}}) = 37$ μg.

Figure 4 shows relative differences of the reported data from the reference value. The bars express the expanded uncertainties. All reported values agree with the reference value within the expanded uncertainties.

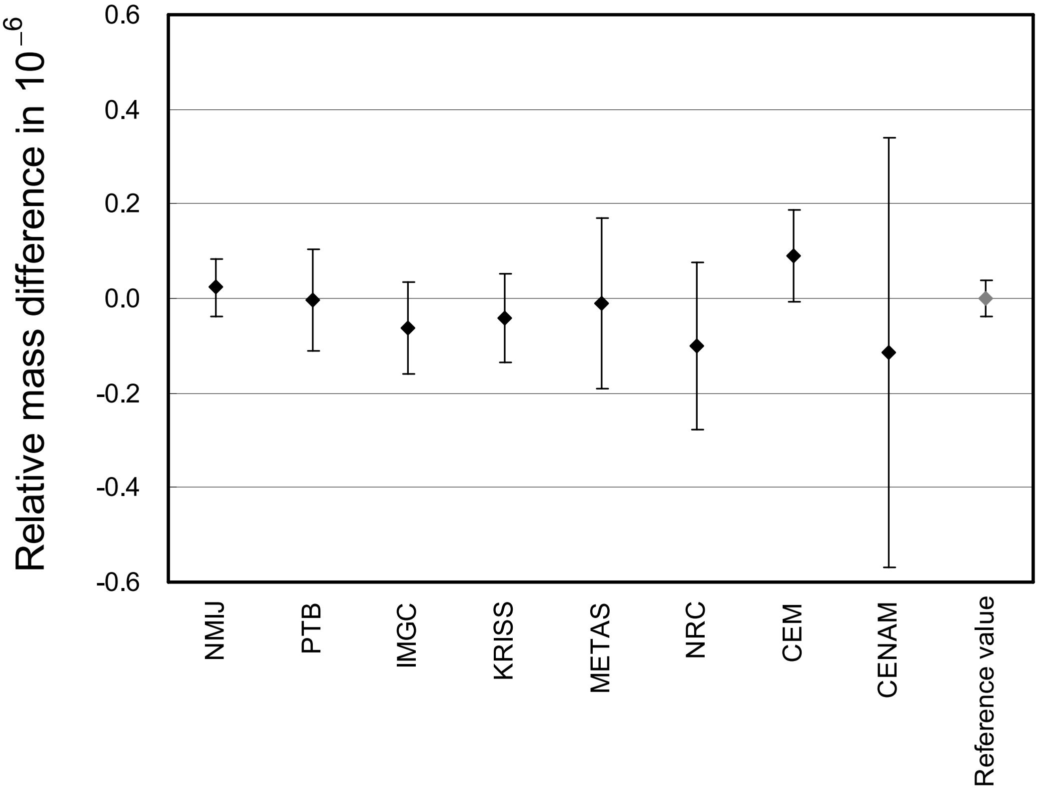

Figure 4. Comparison of the relative mass differences from the reference value. The bars express the expanded uncertainties.

7.4 Volume

The volume of the travelling standard was measured by the participating NMIs using a solid density standard of each NMI. As shown in Table 1, some of the volumes of the solid density standards were calibrated at other NMIs by hydrostatic weighing or dimensional measurement. This means that there is a correlation between the volume values reported by some of the participating NMIs.

In order to evaluate the effect of the correlation, a mathematical model was considered to understand the propagation of the uncertainty in the hydrostatic weighing. When the density of a solid sample B under study is measured by hydrostatic weighing using a solid density standard A, a relative change in the volume of the density standard, $\Delta V_{\mathrm{A}}/V_{\mathrm{A}}$, results in a relative change in the measured volume of the solid sample, $\Delta V_{\mathrm{B}}/V_{\mathrm{B}}$, and they are related as [2]

$$\left(\frac{\partial V_{\mathrm{B}}}{\partial V_{\mathrm{A}}}\right) u(V_{\mathrm{A}})/V_{\mathrm{B}} = u(V_{\mathrm{A}})/V_{\mathrm{A}} \tag{4}$$

where $u(V_A)$ is the standard uncertainty of V_A. Equation (4) means that the relative uncertainty in V_B due to the uncertainty of V_A is equal to $u(V_A)/V_A$. This applies to the data reported by IMGC and METAS. Their volume standards were calibrated at IMGC by optical interferometry and roundness evaluation. Assuming that the dimensional measurement at IMGC performed for the IMGC and METAS density standards are strongly correlated with a correlation coefficient of 0.7, a covariance of 2.60×10^{-9} $(cm^3)^2$ may be attributed for the data reported by IMGC and METAS.

When the calibrated solid sample B is used as a solid density standard to measure the density of another sample C by hydrostatic weighing, the relative uncertainty in V_C due to the uncertainty in V_B is similarly given by

$$\left(\frac{\partial V_C}{\partial V_B}\right) u(V_B)/V_C = u(V_B)/V_B \tag{5}$$

This applies to the data reported by NMIJ, PTB, IMGC, KRISS, CEM, and CENAM. The density standard of KRISS was calibrated at NMIJ by hydrostatic weighing, that of CENAM by PTB, and that of CEM by IMGC. Assuming that the results of the hydrostatic weighing conducted at the same institute are strongly correlated with a correlation coefficient of 0.7, a covariance of 3.74×10^{-9} $(cm^3)^2$ may be attributed for the data reported by NMIJ and KRISS, 8.05×10^{-8} $(cm^3)^2$ for the data reported by PTB and CENAM, and 9.74×10^{-8} $(cm^3)^2$ for the data reported by IMGC and CEM. Though the assumption used for estimating the covariance may not be the most accurate method, this would contribute to deduce the reference value and its uncertainty under the presence of covariances, and to evaluate the uncertainty without being too optimistic.

Table 7 shows the covariance matrix $\boldsymbol{V}$ for the volume data, which was deduced in this way. When the reference value was calculated from equation (1), the integrated probability $P[\chi^2(\nu) > \chi^2_{obs}]$ was 0.121, satisfying the condition $P[\chi^2(\nu) > \chi^2_{obs}] > 0.05$. The reference value for the volume of D1 is given in **Table A1** in **Appendix 1**. It was determined with $U = 2u(V_{ref}) = 0.000\ 135\ cm^3$, resulting in a relative expanded uncertainty of 3.1×10^{-7}.

Table 7. Covariance matrix of the volume data. Unit: $(\mathrm{cm}^3)^2$. Diagonal components express the variances. They are shown in bolder face. Covariances are shown above the diagonal components. Correlation coefficients are shown below the diagonal components.

	NMIJ	PTB	IMGC	KRISS	METAS	NRC	CEM	CENAM
NMIJ	**5.34×10^{-9}**	0	0	3.74×10^{-9}	0	0	0	0
PTB	0	**1.15×10^{-7}**	0	0	0	0	0	8.05×10^{-8}
IMGC	0	0	**1.39×10^{-7}**	0	2.60×10^{-9}	0	9.74×10^{-8}	0
KRISS	0.43	0	0	**1.41×10^{-8}**	0	0	0	0
METAS	0	0	0.02	0	**1.81×10^{-7}**	0	0	0
NRC	0	0	0	0	0	**3.42×10^{-7}**	0	0
CEM	0	0	0.63	0	0	0	**1.71×10^{-7}**	0
CENAM	0	0.36	0	0	0	0	0	**4.28×10^{-7}**

Figure 5 shows the relative difference of the reported data from the reference value. The bars express the expanded uncertainties. All reported values agree with the reference value within the expanded uncertainties.

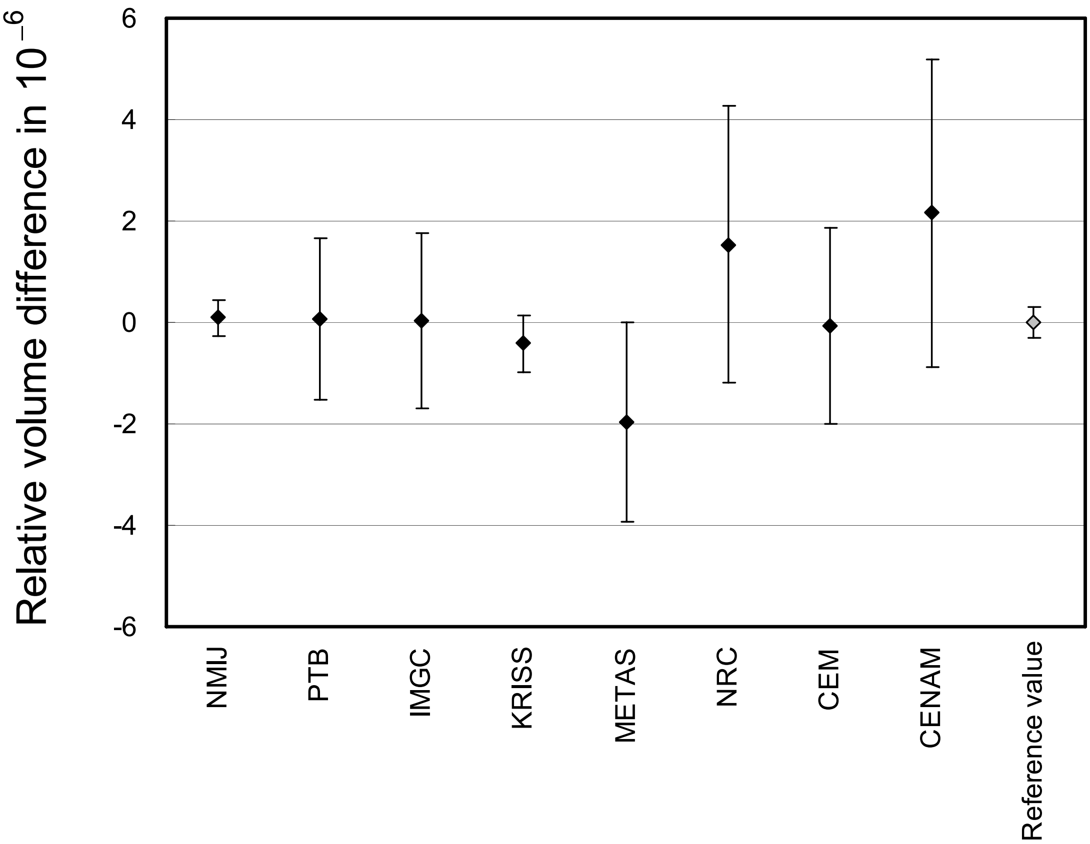

Figure 5. Comparison of the relative volume differences from the reference value. The bars express the expanded uncertainties.

7.5 Density

As explained in section 7.4, some of the volume data reported by the participating NMIs were correlated with each other, resulting in a similar correlation in the density data. Since the covariance in the volume, $\mathrm{cov}(V)$, was already evaluated in section 7.4, the covariance in the density, $\mathrm{cov}(\rho)$, may be expressed by

$$\mathrm{cov}(\rho) = \mathrm{cov}(V)\, \rho^2/V^2 \tag{6}$$

Table 8 shows the covariance matrix $\boldsymbol{V}$ for the density data. When the reference value was calculated from equation (1), the integrated probability $P[\chi^2(\nu) > \chi^2_{\mathrm{obs}}]$ was 0.144, satisfying the condition $P[\chi^2(\nu) > \chi^2_{\mathrm{obs}}] > 0.05$. The reference value for the density of D1 is given in **Table A1** in **Appendix 1**. It was determined with $U = 2u(\rho_{\mathrm{ref}})$ = 0.000 69 kg/m^3, resulting in a relative expanded uncertainty of 2.9×10^{-7}.

Table 8. Covariance matrix of the density data. Unit: (kg/m^3)^2. Diagonal components express the variances. They are shown in bolder face. Covariances are shown above the diagonal components. Correlation coefficients are shown below the diagonal components.

	NMIJ	PTB	IMGC	KRISS	METAS	NRC	CEM	CENAM
NMIJ	**1.32×10^{-7}**	0	0	1.10×10^{-7}	0	0	0	0
PTB	0	**3.59×10^{-6}**	0	0	0	0	0	2.36×10^{-6}
IMGC	0	0	**4.09×10^{-6}**	0	7.66×10^{-8}	0	2.86×10^{-6}	0
KRISS	0.46	0	0	**4.26×10^{-7}**	0	0	0	0
METAS	0	0	0.02	0	**5.36×10^{-6}**	0	0	0
NRC	0	0	0	0	0	**1.01×10^{-5}**	0	0
CEM	0	0	0.63	0	0	0	**5.02×10^{-6}**	0
CENAM	0	0.35	0	0	0	0	0	**1.30×10^{-5}**

Figure 6 shows relative differences of the reported data from the reference value. The bars express the expanded uncertainties. All reported values almost agree with the reference value within the expanded uncertainties.

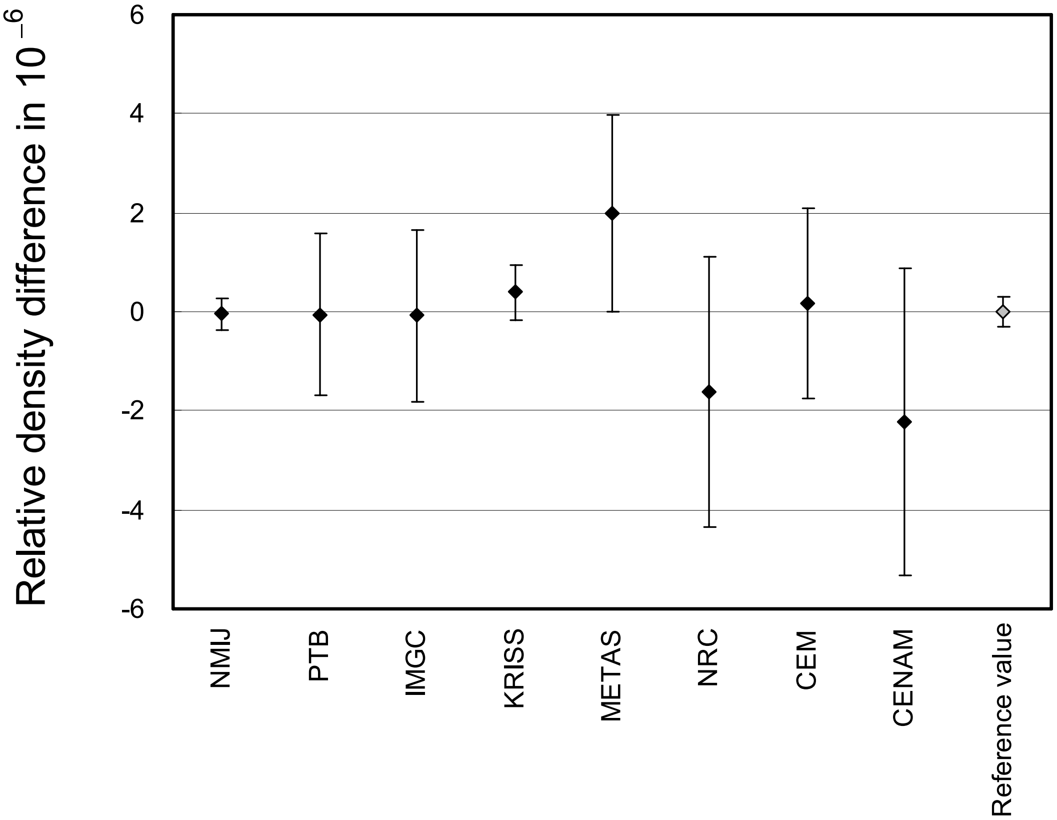

Figure 6. Comparison of the relative density differences from the reference value. The bars express the expanded uncertainties.

8. Degrees of equivalence

8.1 Degrees of equivalence of each laboratory with respect to the reference value

Under the presence of covariances, the reference value may not be obtained from the procedure given by Cox [14] because it applies only when the data reported by the participants are independent. However, if the reference value x_{ref} and its variance $u^2(x_{\mathrm{ref}})$ are deduced from equations (1) and (2), respectively, the variance of the difference $d_i = x_i - x_{\mathrm{ref}}$ is simply given by

$$u^2(d_i) = u^2(x_i) - u^2(x_{\mathrm{ref}}) \tag{7}$$

The mathematical proof for equation (7) is given in **Appendix 2**. This means that even if the data reported by the participants are correlated, the uncertainty of the difference from the key comparison reference value may be obtained as simple as the procedure proposed by Cox [14].

The difference from the reference value, $d_i = x_i - x_{ref}$, and the expanded uncertainty of the difference, $U_i = 2u(d_i)$, are given in **Table A2** to **A4** in **Appendix 3**. The differences from the reference values for the mass, volume, and density were almost equal to or less than the expanded uncertainties for the differences, showing a good equivalence of capabilities for the solid density measurements at the participants.

8.2 Degrees of equivalence between two laboratories

In order to evaluate the degrees of equivalence between two laboratories denoted by i and j, the difference $d_{ij} = x_i - x_j$ was calculated for each pair of two laboratories. When the covariance between x_i and x_j is denoted by $u(x_i, x_j)$, the variance of this difference d_{ij} is given by [12]

$$u^2(d_{ij}) = u^2(x_i) + u^2(x_j) - 2\,u(x_i, x_j) \tag{8}$$

Under the presence of covariance, the expanded uncertainty of the difference is then given by the following equation:

$$U_{ij} = 2u(d_{ij}) = 2\sqrt{u^2(x_i) + u^2(x_j) - 2u(x_i, x_j)} \tag{9}$$

The covariances for the volume and density are given in Tables 7 and 8, respectively. Results of this evaluation are given in **Tables A2 to A4** in **Appendix 3**.

9. Note to this key comparison

As discussed in section 8.1, the results of all participants were almost consistent within the expanded uncertainties when they were compared with the reference values. This means that the results of the IMGC in this CIPM key comparison, measured in 2001, agreed with those of the other participating institutes within the reported expanded uncertainty. This agreement is, however, not compatible with the results of subsequent intercomparisons of density measurements and reference standards conducted in 2002 between the institutes participating in the CCM Working Group on the Avogadro Constant (WGAC): IMGC, PTB, NMIJ and NMIA. The results of the NMIJ and PTB were in good agreement whereas the IMGC's were significantly different. A first large discrepancy was found between the IMGC and PTB measurements of the density of silicon spheres, the IMGC value being relatively lower by more than 1×10^{-6}. The PTB then measured the density of the IMGC reference standard, Si3, by the pressure-of-flotation method, and found a relative discrepancy of 0.81×10^{-6} with respect to the PTB reference standards.

To investigate the cause of this inconsistency, the IMGC prepared a new balance in 2003 and repeated some of the comparisons between solid standards, obtaining significantly different results. In particular, the travelling standard D1, used in CCM.D-K1, was sent to the IMGC again in 2004, and its volume was measured with the new balance, resulting in a volume relatively larger than measured in 2001 by 0.86×10^{-6}. On the basis of the new measurements the IMGC concluded that the incompatibility of the old results was caused by a reproducible systematic error of the old balance, due to an inadequate correction for the increased non-linearity. The uncertainties of the IMGC's measurements reported here were then corrected by increasing the uncertainty of the sensitivity of the balance. The reliability of the IMGC reference standard,Si3, is still under question.

The uncertainties of the CEM measurements reported here were also increased because the reference density standard of the CEM, 1 kg silicon sphere S1, was traceable to the IMGC reference standard through hydrostatic weighing at the IMGC. Due to the increase in the uncertainty of hydrostatic weighing at the IMGC, the data reported by the CEM have been reviewed and corrected.

This situation found in this CIPM key comparison shall be taken into account in conducting further key comparisons and intercomparisons in the future.

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Appendices

Appendix 1

Reference value

Reference values and expanded uncertainties for the mass, volume, and density obtained in this key comparison are shown in Table A1. They were calculated by the method of least-squares given in section 7.2.

Table A1. Reference values for the mass, volume and density of the travelling standard D1.

Quantity	Reference value x_{ref}	Expanded uncertainty $U = 2u(x_{\mathrm{ref}})$
Mass	1000.530 164 g	0.000 037 g
Volume	429.581 033 cm^3	0.000 135 cm^3
Density	2329.083 62 kg/m^3	0.000 69 kg/m^3

Appendix 2

Uncertainty of the difference from the reference value under the presence of covariance

In order to determine the uncertainty, $u(d_i)$, of the difference from the reference value, $d_i = x_i - x_{\mathrm{ref}}$, under the presence of covariances, following matrices are defined as given in section 7.2:

$$\boldsymbol{X} = \begin{bmatrix} x_1 \\ x_2 \\ x_3 \\ x_i \\ x_N \end{bmatrix} \tag{A1}$$

$$\boldsymbol{A} = \begin{bmatrix} 1 \\ 1 \\ \cdot \\ \cdot \\ 1 \end{bmatrix} \tag{A2}$$

where $\boldsymbol{X}$ and $\boldsymbol{A}$ are the column matrices with N elements. The covariance matrix for the reported data $\boldsymbol{X}$ are generally expressed as

$$\mathrm{cov}(\boldsymbol{X}) = \boldsymbol{V} = \begin{bmatrix} u^2(x_1) & u(x_1, x_2) & u(x_1, x_3) & u(x_1, x_j) & u(x_1, x_N) \\ u(x_2, x_1) & u^2(x_2) & u(x_2, x_3) & u(x_2, x_j) & u(x_2, x_N) \\ u(x_3, x_1) & u(x_3, x_2) & u^2(x_3) & u(x_3, x_j) & u(x_3, x_N) \\ u(x_i, x_1) & u(x_i, x_2) & u(x_i, x_3) & u^2(x_i) & u(x_i, x_N) \\ u(x_N, x_1) & u(x_N, x_2) & u(x_N, x_3) & u(x_N, x_j) & u^2(x_N) \end{bmatrix} \tag{A3}$$

where $u^2(x_i)$ is the variance of x_i, and $u(x_i, x_j) = u(x_j, x_i)$ is the covariance between x_i and x_j. The reference value and its variance are simply given as follows [13]:

$$x_{\mathrm{ref}} = g\boldsymbol{A}^{\mathrm{t}}\boldsymbol{V}^{-1}\boldsymbol{X} \tag{A4}$$

$$u^2(x_{\mathrm{ref}}) = \mathrm{cov}(x_{\mathrm{ref}}) = (g\boldsymbol{A}^{\mathrm{t}}\boldsymbol{V}^{-1})\boldsymbol{V}(g\boldsymbol{A}^{\mathrm{t}}\boldsymbol{V}^{-1})^{\mathrm{t}} = g \tag{A5}$$

where $g = (\boldsymbol{A}^{\mathrm{t}}\boldsymbol{V}^{-1}\boldsymbol{A})^{-1}$. In equation (A4), the statistical weights for the reported data $\boldsymbol{X}$ are given by

$$\boldsymbol{W} = g\boldsymbol{A}^{\mathrm{t}}\boldsymbol{V}^{-1} = [w_1 \quad w_2 \quad w_3 \quad w_i \quad w_N] \tag{A6}$$

where the row matrix $\boldsymbol{W}$ is the weight matrix with N elements, and these elements satisfy the following condition:

$$\sum_{i=1}^{N} w_i = 1 \tag{A7}$$

$$\boldsymbol{W}\boldsymbol{X} = x_{\mathrm{ref}} \tag{A8}$$

From equation (A6), the following relations are obtained:

$$\boldsymbol{WV} = g\boldsymbol{A}^{\mathrm{t}} = \begin{bmatrix} g & g & \cdot & \cdot & g \end{bmatrix} \tag{A9}$$

$$\boldsymbol{VW}^{\mathrm{t}} = \boldsymbol{V}^{\mathrm{t}}\boldsymbol{W}^{\mathrm{t}} = (\boldsymbol{WV})^{\mathrm{t}} = \begin{bmatrix} g \\ g \\ \cdot \\ \cdot \\ g \end{bmatrix} \tag{A10}$$

The differences from the reference value, $d_i = x_i - x_{\mathrm{ref}}$, are then expressed by the following matrix formula:

$$\begin{aligned}\boldsymbol{D} &= \begin{bmatrix} d_1 \\ d_2 \\ d_3 \\ d_i \\ d_N \end{bmatrix} = \begin{bmatrix} x_1 - x_{\mathrm{ref}} \\ x_2 - x_{\mathrm{ref}} \\ x_3 - x_{\mathrm{ref}} \\ x_i - x_{\mathrm{ref}} \\ x_N - x_{\mathrm{ref}} \end{bmatrix} = \begin{bmatrix} x_1 \\ x_2 \\ x_3 \\ x_i \\ x_N \end{bmatrix} - \begin{bmatrix} x_{\mathrm{ref}} \\ x_{\mathrm{ref}} \\ \cdot \\ \cdot \\ x_{\mathrm{ref}} \end{bmatrix} = \begin{bmatrix} x_1 \\ x_2 \\ x_3 \\ x_i \\ x_N \end{bmatrix} - \begin{bmatrix} \boldsymbol{WX} \\ \boldsymbol{WX} \\ \cdot \\ \cdot \\ \boldsymbol{WX} \end{bmatrix} = \boldsymbol{X} - \begin{bmatrix} \boldsymbol{W} \\ \boldsymbol{W} \\ \cdot \\ \cdot \\ \boldsymbol{W} \end{bmatrix}\boldsymbol{X} \\ &= \left(\boldsymbol{E} - \begin{bmatrix} \boldsymbol{W} \\ \boldsymbol{W} \\ \cdot \\ \cdot \\ \boldsymbol{W} \end{bmatrix} \right)\boldsymbol{X}\end{aligned} \tag{A11}$$

where $\boldsymbol{E}$ is the unit matrix with N rows and N columns, being expressed as

$$\boldsymbol{E} = \begin{bmatrix} 1 & 0 & 0 & \cdot & 0 \\ 0 & 1 & 0 & \cdot & 0 \\ 0 & 0 & 1 & \cdot & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ 0 & 0 & 0 & \cdot & 1 \end{bmatrix} \tag{A12}$$

Considering the relationship between equations (A4) and (A5) for deducing a covariance matrix [13], the covariance matrix for $\boldsymbol{D}$ is immediately deduced from equation (A11) as

$$
\begin{aligned}
\operatorname{cov}(\boldsymbol{D}) &= \left(\boldsymbol{E}-\begin{bmatrix}\boldsymbol{W}\\ \boldsymbol{W}\\ \cdot\\ \cdot\\ \boldsymbol{W}\end{bmatrix}\right)\operatorname{cov}(\boldsymbol{X})\left(\boldsymbol{E}-\begin{bmatrix}\boldsymbol{W}\\ \boldsymbol{W}\\ \cdot\\ \cdot\\ \boldsymbol{W}\end{bmatrix}\right)^{\mathrm{t}} \\
&= \left(\boldsymbol{E}-\begin{bmatrix}\boldsymbol{W}\\ \boldsymbol{W}\\ \cdot\\ \cdot\\ \boldsymbol{W}\end{bmatrix}\right)\boldsymbol{V}\left(\boldsymbol{E}-\begin{bmatrix}\boldsymbol{W}^{\mathrm{t}} & \boldsymbol{W}^{\mathrm{t}} & \cdot & \cdot & \boldsymbol{W}^{\mathrm{t}}\end{bmatrix}\right) \\
&= \boldsymbol{V}-\boldsymbol{V}\begin{bmatrix}\boldsymbol{W}^{\mathrm{t}} & \boldsymbol{W}^{\mathrm{t}} & \cdot & \cdot & \boldsymbol{W}^{\mathrm{t}}\end{bmatrix}-\begin{bmatrix}\boldsymbol{W}\\ \boldsymbol{W}\\ \cdot\\ \cdot\\ \boldsymbol{W}\end{bmatrix}\boldsymbol{V}+\begin{bmatrix}\boldsymbol{W}\\ \boldsymbol{W}\\ \cdot\\ \cdot\\ \boldsymbol{W}\end{bmatrix}\boldsymbol{V}\begin{bmatrix}\boldsymbol{W}^{\mathrm{t}} & \boldsymbol{W}^{\mathrm{t}} & \cdot & \cdot & \boldsymbol{W}^{\mathrm{t}}\end{bmatrix} \\
&= \boldsymbol{V}-\begin{bmatrix}g & \cdot & \cdot & \cdot & g\\ \cdot & \cdot & \cdot & \cdot & \cdot\\ \cdot & \cdot & \cdot & \cdot & \cdot\\ \cdot & \cdot & \cdot & \cdot & \cdot\\ g & \cdot & \cdot & \cdot & g\end{bmatrix}-\begin{bmatrix}g & \cdot & \cdot & \cdot & g\\ \cdot & \cdot & \cdot & \cdot & \cdot\\ \cdot & \cdot & \cdot & \cdot & \cdot\\ \cdot & \cdot & \cdot & \cdot & \cdot\\ g & \cdot & \cdot & \cdot & g\end{bmatrix}+\begin{bmatrix}\boldsymbol{W}\\ \boldsymbol{W}\\ \cdot\\ \cdot\\ \boldsymbol{W}\end{bmatrix}\begin{bmatrix}g & \cdot & \cdot & \cdot & g\\ \cdot & \cdot & \cdot & \cdot & \cdot\\ \cdot & \cdot & \cdot & \cdot & \cdot\\ \cdot & \cdot & \cdot & \cdot & \cdot\\ g & \cdot & \cdot & \cdot & g\end{bmatrix} \\
&= \boldsymbol{V}-2\begin{bmatrix}g & \cdot & \cdot & \cdot & g\\ \cdot & \cdot & \cdot & \cdot & \cdot\\ \cdot & \cdot & \cdot & \cdot & \cdot\\ \cdot & \cdot & \cdot & \cdot & \cdot\\ g & \cdot & \cdot & \cdot & g\end{bmatrix}+\begin{bmatrix}g\sum_{i=1}^{N}w_i & \cdot & \cdot & \cdot & g\sum_{i=1}^{N}w_i\\ \cdot & \cdot & \cdot & \cdot & \cdot\\ \cdot & \cdot & \cdot & \cdot & \cdot\\ \cdot & \cdot & \cdot & \cdot & \cdot\\ g\sum_{i=1}^{N}w_i & \cdot & \cdot & \cdot & g\sum_{i=1}^{N}w_i\end{bmatrix} \\
&= \boldsymbol{V}-\begin{bmatrix}g & \cdot & \cdot & \cdot & g\\ \cdot & \cdot & \cdot & \cdot & \cdot\\ \cdot & \cdot & \cdot & \cdot & \cdot\\ \cdot & \cdot & \cdot & \cdot & \cdot\\ g & \cdot & \cdot & \cdot & g\end{bmatrix} \\
&= \boldsymbol{V}-\begin{bmatrix}u^2(x_{\mathrm{ref}}) & \cdot & \cdot & \cdot & u^2(x_{\mathrm{ref}})\\ \cdot & \cdot & \cdot & \cdot & \cdot\\ \cdot & \cdot & \cdot & \cdot & \cdot\\ \cdot & \cdot & \cdot & \cdot & \cdot\\ u^2(x_{\mathrm{ref}}) & \cdot & \cdot & \cdot & u^2(x_{\mathrm{ref}})\end{bmatrix}
\end{aligned}
\tag{A13}
$$

The diagonal elements of equation (A13) therefore satisfy the following equation for the variance of the difference from the reference value:

$$u^2(d_i) = u^2(x_i) - u^2(x_{\mathrm{ref}}) \qquad \text{(A14)}$$

The uncertainty of the difference from the reference value is thus obtained from equation (A14) in a simple way even if the reporteded data $x_1, x_2, x_3, \cdots, x_i, \cdots, x_N$ are correlated. This is an important consequence in evaluating the reported data under the presence of covariances.

Appendix 3

Degrees of equivalence of each laboratory with respect to the reference value

Tables A2 to A4 list the difference from the reference value, $d_i = x_i - x_{\mathrm{ref}}$, and the expanded uncertainty of this difference, $U_i = 2u(d_i) = 2\sqrt{u^2(x_i) - u^2(x_{\mathrm{ref}})}$, for the mass, volume and density, respectively. They were dedeuced from equation (7). The differences were almost equal to or less than the expanded uncertainties, showing a good equivalence of the capabilities for the solid density measurements at the participating NMIs.

Degrees of equivalence between two laboratories

Tables A2 to A4 list the difference, $d_{ij} = x_i - x_j$, and the expanded uncertainty of this difference, $U_{ij} = 2u(d_{ij}) = 2\sqrt{u^2(x_i) + u^2(x_j) - 2u(x_i, x_j)}$, for the mass, volume and density, respectively. They were deduced from equations (8) and (9).

Table A2. Degrees of equivalence for the mass measurement.

Mass — Lab j ⟹

Lab i ⇓	d_i / µg	U_i	NMIJ d_{ij} / µg	NMIJ U_{ij}	PTB d_{ij} / µg	PTB U_{ij}	IMGC d_{ij} / µg	IMGC U_{ij}	KRISS d_{ij} / µg	KRISS U_{ij}	METAS d_{ij} / µg	METAS U_{ij}	NRC d_{ij} / µg	NRC U_{ij}	CEM d_{ij} / µg	CEM U_{ij}	CENAM d_{ij} / µg	CENAM U_{ij}
NMIJ	**24**	49			**27**	125	**86**	114	**66**	111	**34**	191	**125**	188	**-65**	115	**138**	458
PTB	**-3**	102	**-27**	125			**59**	145	**39**	143	**7**	211	**98**	209	**-92**	146	**111**	467
IMGC	**-62**	89	**-86**	114	**-59**	145			**-20**	134	**-52**	205	**39**	202	**-151**	136	**52**	464
KRISS	**-42**	86	**-66**	111	**-39**	143	**20**	134			**-32**	204	**59**	201	**-131**	134	**72**	464
METAS	**-10**	178	**-34**	191	**-7**	211	**52**	205	**32**	204			**91**	254	**-99**	206	**104**	489
NRC	**-101**	174	**-125**	188	**-98**	209	**-39**	202	**-59**	201	**-91**	254			**-190**	203	**13**	488
CEM	**89**	90	**65**	115	**92**	146	**151**	136	**131**	134	**99**	206	**190**	203			**203**	464
CENAM	**-114**	453	**-138**	458	**-111**	467	**-52**	464	**-72**	464	**-104**	489	**-13**	488	**-203**	464		

Table A3. Degrees of equivalence for the volume measurement.

Volume — Lab j ⟹

Lab i ⇓	d_i / mm^3	U_i	NMIJ d_{ij} / mm^3	NMIJ U_{ij}	PTB d_{ij} / mm^3	PTB U_{ij}	IMGC d_{ij} / mm^3	IMGC U_{ij}	KRISS d_{ij} / mm^3	KRISS U_{ij}	METAS d_{ij} / mm^3	METAS U_{ij}	NRC d_{ij} / mm^3	NRC U_{ij}	CEM d_{ij} / mm^3	CEM U_{ij}	CENAM d_{ij} / mm^3	CENAM U_{ij}
NMIJ	**0.038**	0.057			**0.007**	0.694	**0.020**	0.760	**0.218**	0.219	**0.881**	0.864	**-0.623**	1.178	**0.061**	0.841	**-0.889**	1.316
PTB	**0.031**	0.665	**-0.007**	0.694			**0.013**	1.008	**0.211**	0.718	**0.874**	1.089	**-0.630**	1.352	**0.054**	1.070	**-0.896**	1.236
IMGC	**0.018**	0.734	**-0.020**	0.760	**-0.013**	1.008			**0.198**	0.783	**0.861**	1.123	**-0.643**	1.387	**0.041**	0.680	**-0.909**	1.506
KRISS	**-0.180**	0.196	**-0.218**	0.219	**-0.211**	0.718	**-0.198**	0.783			**0.663**	0.884	**-0.841**	1.193	**-0.157**	0.861	**-1.107**	1.329
METAS	**-0.843**	0.841	**-0.881**	0.864	**-0.874**	1.089	**-0.861**	1.123	**-0.663**	0.884			**-1.504**	1.446	**-0.820**	1.188	**-1.770**	1.561
NRC	**0.661**	1.161	**0.623**	1.178	**0.630**	1.352	**0.643**	1.387	**0.841**	1.193	**1.504**	1.446			**0.684**	1.433	**-0.266**	1.754
CEM	**-0.023**	0.817	**-0.061**	0.841	**-0.054**	1.070	**-0.041**	0.680	**0.157**	0.861	**0.820**	1.188	**-0.684**	1.433			**-0.950**	1.548
CENAM	**0.927**	1.301	**0.889**	1.316	**0.896**	1.236	**0.909**	1.506	**1.107**	1.329	**1.770**	1.561	**0.266**	1.754	**0.950**	1.548		

Table A4. Degrees of equivalence for the density measurement.

Density — Lab j ⟹

Lab i ⇓	d_i / (10^{-3} kg/m^3)	U_i	NMIJ d_{ij} / (10^{-3} kg/m^3)	NMIJ U_{ij}	PTB d_{ij} / (10^{-3} kg/m^3)	PTB U_{ij}	IMGC d_{ij} / (10^{-3} kg/m^3)	IMGC U_{ij}	KRISS d_{ij} / (10^{-3} kg/m^3)	KRISS U_{ij}	METAS d_{ij} / (10^{-3} kg/m^3)	METAS U_{ij}	NRC d_{ij} / (10^{-3} kg/m^3)	NRC U_{ij}	CEM d_{ij} / (10^{-3} kg/m^3)	CEM U_{ij}	CENAM d_{ij} / (10^{-3} kg/m^3)	CENAM U_{ij}
NMIJ	**-0.10**	0.24			**0.03**	3.86	**0.10**	4.11	**-1.03**	1.16	**-4.70**	4.69	**3.67**	6.40	**-0.48**	4.54	**5.11**	7.26
PTB	**-0.14**	3.73	**-0.03**	3.86			**0.07**	5.54	**-1.06**	4.01	**-4.73**	5.98	**3.64**	7.40	**-0.51**	5.87	**5.08**	6.90
IMGC	**-0.20**	3.99	**-0.10**	4.11	**-0.07**	5.54			**-1.12**	4.25	**-4.80**	6.10	**3.58**	7.53	**-0.58**	3.68	**5.01**	8.28
KRISS	**0.92**	1.11	**1.03**	1.16	**1.06**	4.01	**1.12**	4.25			**-3.67**	4.81	**4.70**	6.49	**0.55**	4.67	**6.14**	7.34
METAS	**4.59**	4.58	**4.70**	4.69	**4.73**	5.98	**4.80**	6.10	**3.67**	4.81			**8.37**	7.86	**4.22**	6.45	**9.81**	8.58
NRC	**-3.78**	6.32	**-3.67**	6.40	**-3.64**	7.40	**-3.58**	7.53	**-4.70**	6.49	**-8.37**	7.86			**-4.15**	7.78	**1.44**	9.62
CEM	**0.37**	4.43	**0.48**	4.54	**0.51**	5.87	**0.58**	3.68	**-0.55**	4.67	**-4.22**	6.45	**4.15**	7.78			**5.59**	8.50
CENAM	**-5.22**	7.19	**-5.11**	7.26	**-5.08**	6.90	**-5.01**	8.28	**-6.14**	7.34	**-9.81**	8.58	**-1.44**	9.62	**-5.59**	8.50		