CCM.D-K1: Final Report

CIPM key comparison of density measurements of a silicon sphere

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Claude Jacques⁶, Carmen Matilla Vicente⁷, and Luis Omar Becerra⁸

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 $2.9 \times 10^{-7}$. 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/m³, 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, NMII, 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:

- National Metrology Institute of Japan (NMIJ), Japan, APMP
  Kenichi Fujii
- Physikalisch–Technische Bundesanstalt (PTB), Germany, EUROMET
  Horst Bettin
- Istituto di Metrologia “G. Colonnetti” (IMGC), Italy, EUROMET
  Anna Peuto
- Korea Research Institute of Standards and Science (KRISS), Korea, APMP
  Kyung-Ho Chang
- Swiss Federal Office of Metrology and Accreditation (METAS), Switzerland, EUROMET
  Philippe Richard
- National Research Council Canada (NRC), Canada, SIM
  Claude Jacques
- Centro Español de Metrología (CEM), Spain, EUROMET
  Carmen Matilla Vicente
- National Center of Metrology (CENAM), Mexico, SIM
  Luis Omar Becerra

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.

<table>
<thead>
<tr>
<th>NMI</th>
<th>Reference density standard</th>
<th>Traceability</th>
<th>Standard uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Mass</td>
<td>Volume</td>
</tr>
<tr>
<td>NMIJ</td>
<td>1 kg silicon spheres, S4 and S5</td>
<td>NMIJ</td>
<td>NMIJ</td>
</tr>
<tr>
<td>PTB</td>
<td>870 g silicon spheres, Si1 and Si2</td>
<td>PTB</td>
<td>PTB</td>
</tr>
<tr>
<td>IMGC</td>
<td>1 kg silicon sphere, Si3</td>
<td>IMGC</td>
<td>IMGC</td>
</tr>
<tr>
<td>KRISS</td>
<td>1 kg silicon sphere, Si</td>
<td>KRISS</td>
<td>NMIJ</td>
</tr>
<tr>
<td>METAS</td>
<td>1 kg silicon sphere, RAW08</td>
<td>METAS</td>
<td>IMGC</td>
</tr>
<tr>
<td>NRC</td>
<td>Water *)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CEM</td>
<td>1 kg silicon sphere, S1</td>
<td>CEM</td>
<td>IMGC</td>
</tr>
<tr>
<td>CENAM</td>
<td>1 kg zerodur spheres, Z-01 and Z-02</td>
<td>CENAM</td>
<td>PTB</td>
</tr>
</tbody>
</table>

*) 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/m³ 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

<table>
<thead>
<tr>
<th>Physical properties</th>
<th>Parameter</th>
<th>Standard uncertainty</th>
<th>Degrees of freedom</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
<td>Silicon single crystal</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Diameter (nominal) at 20 °C and 101.325 kPa</td>
<td>93.6 mm</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Mass (nominal)</td>
<td>1000.5 g</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Volume (nominal) at 20 °C and 101.325 kPa</td>
<td>429.6 cm³</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Bulk thermal expansion coefficient at 20 °C and 101.325 kPa</td>
<td>$7.67 \times 10^{-6}$ K$^{-1}$</td>
<td>$0.03 \times 10^{-6}$ K$^{-1}$</td>
<td>50</td>
</tr>
<tr>
<td>Isothermal compressibility at 20 °C and 101.325 kPa</td>
<td>$1.02 \times 10^{-11}$ Pa$^{-1}$</td>
<td>$0.01 \times 10^{-11}$ Pa$^{-1}$</td>
<td>50</td>
</tr>
</tbody>
</table>

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.

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

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 \( \nu_{\text{eff}} \) [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.

<table>
<thead>
<tr>
<th>NMI</th>
<th>Balance</th>
<th>Method used for determining the density of air</th>
<th>Reference mass standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMJJ</td>
<td>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</td>
<td>CIPM formula</td>
<td>Silicon sphere with a mass calibrated by using air-density artefacts</td>
</tr>
<tr>
<td>PTB</td>
<td>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</td>
<td>CIPM formula and air-density artefacts *)</td>
<td>Calibrated stainless steel weights</td>
</tr>
<tr>
<td>IMGC</td>
<td>Commercially available single-pan knife-edge balance with an automatic weight exchange mechanism. Maximum load: 1 kg Resolution: 1 μg</td>
<td>CIPM formula</td>
<td>Calibrated stainless steel weights</td>
</tr>
<tr>
<td>KRISS</td>
<td>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</td>
<td>CIPM formula</td>
<td>Calibrated stainless steel weights</td>
</tr>
<tr>
<td>METAS</td>
<td>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</td>
<td>CIPM formula</td>
<td>Calibrated stainless steel weights</td>
</tr>
<tr>
<td>NRC</td>
<td>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</td>
<td>CIPM formula</td>
<td>Calibrated stainless steel weights</td>
</tr>
<tr>
<td>CEM</td>
<td>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</td>
<td>CIPM formula</td>
<td>Calibrated stainless steel weights</td>
</tr>
<tr>
<td>CENAM</td>
<td>Commercially available single-pan flexure-hinge electronic balance with a modified pan. Maximum load: 1109 g Resolution: 10 μg Electronic balance range: 109 g</td>
<td>CIPM formula</td>
<td>Calibrated stainless steel weights</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>NMI</th>
<th>Balance</th>
<th>Positions of the density standard and the travelling standard in the hydrostatic weighing apparatus</th>
<th>Working liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMIJ</td>
<td>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</td>
<td>Travelling standard placed between two silicon density standards located in a different height. They are placed in a cage.</td>
<td>Tridecane ((n-C_{13}H_{28}))</td>
</tr>
<tr>
<td>PTB</td>
<td>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</td>
<td>Travelling standard placed between two silicon density standards located in a different height. They are placed in a cage.</td>
<td>Pentadecane ((n-C_{15}H_{32}))</td>
</tr>
<tr>
<td>IMGC</td>
<td>See Table 4</td>
<td>Travelling standard and a silicon density standard placed on a rotational circular pan with six places.</td>
<td>Water</td>
</tr>
<tr>
<td>KRISS</td>
<td>See Table 4</td>
<td>Travelling standard placed below a silicon density standard. They are placed in a cage.</td>
<td>Tridecane ((n-C_{13}H_{28}))</td>
</tr>
<tr>
<td>METAS</td>
<td>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</td>
<td>Travelling standard placed above a silicon density standard. They are placed in a cage.</td>
<td>Water</td>
</tr>
<tr>
<td>NRC</td>
<td>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</td>
<td>Travelling standard placed on a rotational circular pan with four places.</td>
<td>Water</td>
</tr>
<tr>
<td>CEM</td>
<td>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</td>
<td>Travelling standard and a silicon density standard placed on a rotational circular pan with four places.</td>
<td>Water and Fluorinert Electronic Liquid FC40 *1</td>
</tr>
<tr>
<td>CENAM</td>
<td>See Table 4</td>
<td>Travelling standard placed between two zerodur density standards located in a different height. They are placed in a cage.</td>
<td>Pentadecane ((n-C_{15}H_{32}))</td>
</tr>
</tbody>
</table>

*1 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 $\nu_{\text{eff}}$ 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.

<table>
<thead>
<tr>
<th>Data label</th>
<th>m/g</th>
<th>$u_g$</th>
<th>$\nu_{\text{eff}}$</th>
<th>$U_{95}$/g</th>
<th>$V$/cm$^3$</th>
<th>$u/V$</th>
<th>$\nu_{\text{eff}}$</th>
<th>$U_{95}$/cm$^3$</th>
<th>$\rho/(kg/m^3)$</th>
<th>$u/(kg/m^3)$</th>
<th>$\nu_{\text{eff}}$</th>
<th>$U_{95}/(kg/m^3)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMIJ-1</td>
<td>1000.530 188 0.000 031</td>
<td>72.9</td>
<td>0.000 061</td>
<td>429.581 071</td>
<td>0.000 074</td>
<td>121.3</td>
<td>0.000 146</td>
<td>2329.083 51</td>
<td>0.000 37</td>
<td>100.0</td>
<td>0.000 73</td>
<td></td>
</tr>
<tr>
<td>PTB</td>
<td>1000.530 161 0.000 055</td>
<td>1050.5</td>
<td>0.000 109</td>
<td>429.581 064</td>
<td>0.000 344</td>
<td>206.7</td>
<td>0.000 678</td>
<td>2329.083 48</td>
<td>0.001 92</td>
<td>185.8</td>
<td>0.003 79</td>
<td></td>
</tr>
<tr>
<td>IMGC</td>
<td>1000.530 102 0.000 048</td>
<td>62.8</td>
<td>0.000 096</td>
<td>429.581 051</td>
<td>0.000 375</td>
<td>87.7</td>
<td>0.000 746</td>
<td>2329.083 41</td>
<td>0.002 04</td>
<td>88.3</td>
<td>0.004 05</td>
<td></td>
</tr>
<tr>
<td>KRISS</td>
<td>1000.530 122 0.000 047</td>
<td>124.5</td>
<td>0.000 093</td>
<td>429.580 853</td>
<td>0.000 121</td>
<td>319.0</td>
<td>0.000 237</td>
<td>2329.084 54</td>
<td>0.000 66</td>
<td>336.4</td>
<td>0.001 31</td>
<td></td>
</tr>
<tr>
<td>NMIJ-2</td>
<td>1000.530 182 0.000 031</td>
<td>72.9</td>
<td>0.000 061</td>
<td>429.581 101</td>
<td>0.000 074</td>
<td>121.3</td>
<td>0.000 146</td>
<td>2329.083 33</td>
<td>0.000 37</td>
<td>100.0</td>
<td>0.000 73</td>
<td></td>
</tr>
<tr>
<td>METAS</td>
<td>1000.530 154 0.000 091</td>
<td>114.2</td>
<td>0.000 181</td>
<td>429.580 190</td>
<td>0.000 432</td>
<td>203.6</td>
<td>0.000 852</td>
<td>2329.088 21</td>
<td>0.002 35</td>
<td>206.8</td>
<td>0.004 63</td>
<td></td>
</tr>
<tr>
<td>NMIJ-3</td>
<td>1000.530 208 0.000 031</td>
<td>72.9</td>
<td>0.000 061</td>
<td>429.581 125</td>
<td>0.000 074</td>
<td>121.3</td>
<td>0.000 146</td>
<td>2329.083 26</td>
<td>0.000 37</td>
<td>100.0</td>
<td>0.000 73</td>
<td></td>
</tr>
<tr>
<td>NRC</td>
<td>1000.530 063 0.000 090</td>
<td>83.8</td>
<td>0.000 178</td>
<td>429.581 684</td>
<td>0.000 554</td>
<td>17.6</td>
<td>0.001 169</td>
<td>2329.079 84</td>
<td>0.003 01</td>
<td>17.8</td>
<td>0.006 35</td>
<td></td>
</tr>
<tr>
<td>CEM</td>
<td>1000.530 253 0.000 049</td>
<td>112.5</td>
<td>0.000 097</td>
<td>429.581 010</td>
<td>0.000 386</td>
<td>14.9</td>
<td>0.000 828</td>
<td>2329.083 99</td>
<td>0.002 09</td>
<td>14.8</td>
<td>0.004 48</td>
<td></td>
</tr>
<tr>
<td>CENAM</td>
<td>1000.530 050 0.000 226</td>
<td>53.6</td>
<td>0.000 454</td>
<td>429.581 960</td>
<td>0.000 662</td>
<td>154.1</td>
<td>0.001 308</td>
<td>2329.078 40</td>
<td>0.003 86</td>
<td>161.1</td>
<td>0.007 22</td>
<td></td>
</tr>
<tr>
<td>NMIJ-4</td>
<td>1000.530 222 0.000 031</td>
<td>72.9</td>
<td>0.000 061</td>
<td>429.581 119</td>
<td>0.000 074</td>
<td>121.3</td>
<td>0.000 146</td>
<td>2329.083 33</td>
<td>0.000 37</td>
<td>100.0</td>
<td>0.000 73</td>
<td></td>
</tr>
</tbody>
</table>

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 \(\chi^2\) [13].

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

\[
x_{ref} = g A^t V^{-1} X
\]

where \(g = (A^t V^{-1} A)^{-1}\), \(V\) is the covariance matrix of the reported data \(X\), and \(A^t\) and \(A^{-1}\)
are transpose and inverse of the matrix $A$, respectively. The variance of $x_{\text{ref}}$ is given by [13]

$$u^2(x_{\text{ref}}) = \text{cov}(x_{\text{ref}}) = (gA^tV^{-1})V(gA^tV^{-1})^t = g$$  \hspace{1cm} (2)

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

$$\chi^2_{\text{obs}} = (X - AX_{\text{ref}})V^{-1}(X - AX_{\text{ref}})$$  \hspace{1cm} (3)

where $(X - AX_{\text{ref}})$ 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., $P[\chi^2(\nu) > \chi^2_{\text{obs}}] > 0.05$. 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 $V$ 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 $P[\chi^2(\nu) > \chi^2_{\text{obs}}]$ was 0.330, satisfying the condition $P[\chi^2(\nu) > \chi^2_{\text{obs}}] > 0.05$. The reference value for the mass of D1 is given in Table A1 in Appendix 1. It was determined with $U = 2u(m_{\text{ref}}) = 37 \mu g$.

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.
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, $\Delta V_A/V_A$, results in a relative change in the measured volume of the solid sample, $\Delta V_B/V_B$, and they are related as [2]

$$
\left( \frac{\partial V_B}{\partial V_A} \right) u(V_A)/V_B = u(V_A)/V_A
$$

(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 \( 2.60 \times 10^{-9} \) \((\text{cm}^3)^2\) 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

\[
\left( \frac{\partial V_C}{\partial V_B} \right) u(V_B) / V_C = u(V_B) / V_B
\]

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 \( 3.74 \times 10^{-9} \) \((\text{cm}^3)^2\) may be attributed for the data reported by NMIJ and KRISS, \( 8.05 \times 10^{-8} \) \((\text{cm}^3)^2\) for the data reported by PTB and CENAM, and \( 9.74 \times 10^{-8} \) \((\text{cm}^3)^2\) 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 \( V \) for the volume data, which was deduced in this way. When the reference value was calculated from equation (1), the integrated probability \( P[\chi^2(\nu) > \chi^2_{\text{obs}}] \) was 0.121, satisfying the condition \( P[\chi^2(\nu) > \chi^2_{\text{obs}}] > 0.05 \). The reference value for the volume of D1 is given in Table A1 in Appendix 1. It was determined with \( U = 2u(V_{\text{ref}}) = 0.000 \ 135 \ \text{cm}^3 \), resulting in a relative expanded uncertainty of \( 3.1 \times 10^{-7} \)
Table 7. Covariance matrix of the volume data. Unit: $(\text{cm}^3)^2$. 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.

<table>
<thead>
<tr>
<th></th>
<th>NMIJ</th>
<th>PTB</th>
<th>IMGC</th>
<th>KRISS</th>
<th>METAS</th>
<th>NRC</th>
<th>CEM</th>
<th>CENAM</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMIJ</td>
<td>5.34 × 10^{-9}</td>
<td>0</td>
<td>0</td>
<td>3.74 × 10^{-9}</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>PTB</td>
<td>0</td>
<td>1.15 × 10^{-7}</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>8.05 × 10^{-8}</td>
</tr>
<tr>
<td>IMGC</td>
<td>0</td>
<td>0</td>
<td>1.39 × 10^{-7}</td>
<td>0</td>
<td>2.60 × 10^{-9}</td>
<td>0</td>
<td>9.74 × 10^{-8}</td>
<td>0</td>
</tr>
<tr>
<td>KRISS</td>
<td>0.43</td>
<td>0</td>
<td>0</td>
<td>1.41 × 10^{-8}</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>METAS</td>
<td>0</td>
<td>0</td>
<td>0.02</td>
<td>0</td>
<td>1.81 × 10^{-7}</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>NRC</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>3.42 × 10^{-7}</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CEM</td>
<td>0</td>
<td>0</td>
<td>0.63</td>
<td>0</td>
<td>0</td>
<td>1.71 × 10^{-7}</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CENAM</td>
<td>0</td>
<td>0.36</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>4.28 × 10^{-7}</td>
</tr>
</tbody>
</table>

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](image-url)
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, \(\text{cov}(V)\), was already evaluated in section 7.4, the covariance in the density, \(\text{cov}(\rho)\), may be expressed by

\[
\text{cov}(\rho) = \text{cov}(V) \frac{\rho^2}{V^2}
\] (6)

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

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.

<table>
<thead>
<tr>
<th></th>
<th>NMIJ</th>
<th>PTB</th>
<th>IMGC</th>
<th>KRISS</th>
<th>METAS</th>
<th>NRC</th>
<th>CEM</th>
<th>CENAM</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMIJ</td>
<td>(1.32 \times 10^{-7})</td>
<td>0</td>
<td>0</td>
<td>1.10 \times 10^{-7}</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>PTB</td>
<td>0</td>
<td>(3.59 \times 10^{-6})</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2.36 \times 10^{-6}</td>
</tr>
<tr>
<td>IMGC</td>
<td>0</td>
<td>0</td>
<td>(4.09 \times 10^{-6})</td>
<td>0</td>
<td>7.66 \times 10^{-8}</td>
<td>0</td>
<td>2.86 \times 10^{-6}</td>
<td>0</td>
</tr>
<tr>
<td>KRISS</td>
<td>0.46</td>
<td>0</td>
<td>0</td>
<td>(4.26 \times 10^{-7})</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>METAS</td>
<td>0</td>
<td>0</td>
<td>0.02</td>
<td>0</td>
<td>(5.36 \times 10^{-6})</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>NRC</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>(1.01 \times 10^{-5})</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CEM</td>
<td>0</td>
<td>0</td>
<td>0.63</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>(5.02 \times 10^{-6})</td>
<td>0</td>
</tr>
<tr>
<td>CENAM</td>
<td>0</td>
<td>0.35</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>(1.30 \times 10^{-5})</td>
</tr>
</tbody>
</table>

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 $x_{\text{ref}}$ and its variance $u^2(x_{\text{ref}})$ are deduced from equations (1) and (2), respectively, the variance of the difference $d_i = x_i - x_{\text{ref}}$ is simply given by

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

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, \( d_i = x_i - x_{\text{ref}} \), 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]

\[
U^2(d_{ij}) = U^2(x_i) + U^2(x_j) - 2u(x_i, x_j)
\]

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

\[
U_{ij} = 2u(d_{ij}) = 2\sqrt{U^2(x_i) + U^2(x_j) - 2u(x_i, x_j)}
\]

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 $1 \times 10^{-6}$. The PTB then measured the density of the IMGC reference standard, Si3, by the pressure-of-flotation method, and found a relative discrepancy of $0.81 \times 10^{-6}$ 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 $0.86 \times 10^{-6}$. 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.

References


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>
<thead>
<tr>
<th>Quantity</th>
<th>Reference value ( x_{\text{ref}} )</th>
<th>Expanded uncertainty ( U = 2u(x_{\text{ref}}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass</td>
<td>1000.530 164 g</td>
<td>0.000 037 g</td>
</tr>
<tr>
<td>Volume</td>
<td>429.581 033 cm(^3)</td>
<td>0.000 135 cm(^3)</td>
</tr>
<tr>
<td>Density</td>
<td>2329.083 62 kg/m(^3)</td>
<td>0.000 69 kg/m(^3)</td>
</tr>
</tbody>
</table>

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, \( d_i = x_i - x_{\text{ref}} \), under the presence of covariances, following matrices are defined as given in section 7.2:

\[
X = \begin{bmatrix} x_1 \\ x_2 \\ x_3 \\ \vdots \\ x_N \end{bmatrix}
\]

\[
A = \begin{bmatrix} 1 \\ 1 \\ \vdots \\ 1 \end{bmatrix}
\]
where \( X \) and \( \mathcal{A} \) are the column matrices with \( N \) elements. The covariance matrix for the reported data \( X \) are generally expressed as

\[
\text{cov}(X) = V = \begin{bmatrix}
    u^2(x_1) & u(x_1,x_2) & u(x_1,x_3) & \cdots & u(x_1,x_N) \\
    u(x_2,x_1) & u^2(x_2) & u(x_2,x_3) & \cdots & u(x_2,x_N) \\
    u(x_3,x_1) & u(x_3,x_2) & u^2(x_3) & \cdots & u(x_3,x_N) \\
    \vdots & \vdots & \vdots & \ddots & \vdots \\
    u(x_N,x_1) & u(x_N,x_2) & u(x_N,x_3) & \cdots & u^2(x_N)
\end{bmatrix}
\]

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]:

\[
x_{\text{ref}} = g \mathcal{A}^\dagger V^{-1} X
\]

\[
u^2(x_{\text{ref}}) = \text{cov}(x_{\text{ref}}) = \left(g \mathcal{A}^\dagger V^{-1}\right)^T \left(g \mathcal{A}^\dagger V^{-1}\right) = g
\]

where \( g = \left(\mathcal{A}^\dagger V^{-1} \mathcal{A}\right)^{-1} \). In equation (A4), the statistical weights for the reported data \( X \) are given by

\[
W = g \mathcal{A}^\dagger V^{-1} = [w_1 \ w_2 \ w_3 \ \cdots \ w_N]
\]

where the row matrix \( W \) is the weight matrix with \( N \) elements, and these elements satisfy the following condition:

\[
\sum_{i=1}^{N} w_i = 1
\]

\[
WX = x_{\text{ref}}
\]

From equation (A6), the following relations are obtained:
\[ WV = gA^t = \begin{bmatrix} g & g & \cdots & g \end{bmatrix} \]  

(A9)

\[ VW^t = V^tW^t = (WV)^t = \begin{bmatrix} g \\ g \\ \vdots \end{bmatrix} \]  

(A10)

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

\[
D = \begin{bmatrix}
  d_1 \\
  d_2 \\
  d_3 \\
  \vdots \\
  d_N \\
\end{bmatrix} = \begin{bmatrix}
  x_1 - x_{\text{ref}} \\
  x_2 - x_{\text{ref}} \\
  x_3 - x_{\text{ref}} \\
  \vdots \\
  x_N - x_{\text{ref}} \\
\end{bmatrix} = \begin{bmatrix}
  x_1 \\
  x_2 \\
  x_3 \\
  \vdots \\
  x_N \\
\end{bmatrix} - \begin{bmatrix}
  x_{\text{ref}} \\
  x_{\text{ref}} \\
  x_{\text{ref}} \\
  \vdots \\
  x_{\text{ref}} \\
\end{bmatrix} = X - \begin{bmatrix}
  x_{\text{ref}} \\
  x_{\text{ref}} \\
  x_{\text{ref}} \\
  \vdots \\
  x_{\text{ref}} \\
\end{bmatrix} = X - E \cdot X
\]

(A11)

where \( E \) is the unit matrix with \( N \) rows and \( N \) columns, being expressed as

\[
E = \begin{bmatrix}
  1 & 0 & 0 & \cdots & 0 \\
  0 & 1 & 0 & \cdots & 0 \\
  0 & 0 & 1 & \cdots & 0 \\
  \vdots & \vdots & \vdots & \ddots & \vdots \\
  0 & 0 & 0 & \cdots & 1 \\
\end{bmatrix}
\]

(A12)

Considering the relationship between equations (A4) and (A5) for deducing a covariance matrix [13], the covariance matrix for \( D \) is immediately deduced from equation (A11) as
\[
\text{cov}(D) = E - \cdot \text{cov}(X) \cdot E - \cdot \\
= E - \cdot V(E - [W^1 \ W^1 \ \cdots \ \ W^1]) \\
= V - V[W^1 \ W^1 \ \cdots \ \ W^1] - \cdot V + \cdot V[W^1 \ W^1 \ \cdots \ \ W^1] \\
= V \begin{bmatrix} g & \cdots & g \\
. & \cdots & . \\
. & \cdots & . \\
g & \cdots & g \\
\end{bmatrix} - \begin{bmatrix} g & \cdots & g \\
. & \cdots & . \\
. & \cdots & . \\
g & \cdots & g \\
\end{bmatrix} + \begin{bmatrix} g \sum_{i=1}^{N} w_i & \cdots & g \sum_{i=1}^{N} w_i \\
. & \cdots & . \\
. & \cdots & . \\
g \sum_{i=1}^{N} w_i & \cdots & g \sum_{i=1}^{N} w_i \\
\end{bmatrix} \\
= V - 2 \begin{bmatrix} g & \cdots & g \\
. & \cdots & . \\
. & \cdots & . \\
g & \cdots & g \\
\end{bmatrix} + \begin{bmatrix} g \sum_{i=1}^{N} w_i & \cdots & g \sum_{i=1}^{N} w_i \\
. & \cdots & . \\
. & \cdots & . \\
g \sum_{i=1}^{N} w_i & \cdots & g \sum_{i=1}^{N} w_i \\
\end{bmatrix} \\
= V \begin{bmatrix} g & \cdots & g \\
. & \cdots & . \\
. & \cdots & . \\
g & \cdots & g \\
\end{bmatrix} \\
= V - \begin{bmatrix} u^2(x_{\text{ref}}) & \cdots & u^2(x_{\text{ref}}) \\
. & \cdots & . \\
. & \cdots & . \\
u^2(x_{\text{ref}}) & \cdots & u^2(x_{\text{ref}}) \\
\end{bmatrix} \\
= V - \begin{bmatrix} u^2(x_{\text{ref}}) \\
. & \cdots & . \\
. & \cdots & . \\
u^2(x_{\text{ref}}) & \cdots & u^2(x_{\text{ref}}) \\
\end{bmatrix}
\]
The diagonal elements of equation (A13) therefore satisfy the following equation for the variance of the difference from the reference value:

\[ u^2(d_i) = u^2(x_i) - u^2(x_{\text{ref}}) \]  \hspace{1cm} (A14)

The uncertainty of the difference from the reference value is thus obtained from equation (A14) in a simple way even if the reported data \( x_1, x_2, x_3, \ldots, x_i, \ldots, x_N \) 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, \( d_i = x_i - x_{\text{ref}} \), and the expanded uncertainty of this difference, \( U_i = 2u(d_i) = 2\sqrt{u^2(x_i) - u^2(x_{\text{ref}})} \), for the mass, volume, and density, respectively. They were deduced 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.

<table>
<thead>
<tr>
<th>Lab i</th>
<th>Lab j</th>
<th>Mass (μg)</th>
<th>NMIJ</th>
<th>PTB</th>
<th>IMGC</th>
<th>KRISS</th>
<th>METAS</th>
<th>NRC</th>
<th>CEM</th>
<th>CENAM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>/μg</td>
<td>/μg</td>
<td>/μg</td>
<td>/μg</td>
<td>/μg</td>
<td>/μg</td>
<td>/μg</td>
<td>/μg</td>
<td>/μg</td>
</tr>
<tr>
<td>NMIJ</td>
<td>24</td>
<td>49</td>
<td>27</td>
<td>125</td>
<td>86</td>
<td>114</td>
<td>66</td>
<td>111</td>
<td>34</td>
<td>191</td>
</tr>
<tr>
<td>PTB</td>
<td>-3</td>
<td>102</td>
<td>-27</td>
<td>125</td>
<td>59</td>
<td>145</td>
<td>39</td>
<td>143</td>
<td>7</td>
<td>211</td>
</tr>
<tr>
<td>IMGC</td>
<td>-62</td>
<td>89</td>
<td>-86</td>
<td>114</td>
<td>-59</td>
<td>145</td>
<td>-20</td>
<td>134</td>
<td>-52</td>
<td>205</td>
</tr>
<tr>
<td>KRISS</td>
<td>-42</td>
<td>86</td>
<td>-66</td>
<td>111</td>
<td>-39</td>
<td>143</td>
<td>20</td>
<td>134</td>
<td>-32</td>
<td>204</td>
</tr>
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<td>METAS</td>
<td>-10</td>
<td>178</td>
<td>-34</td>
<td>191</td>
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<td>211</td>
<td>52</td>
<td>205</td>
<td>32</td>
<td>204</td>
</tr>
<tr>
<td>NRC</td>
<td>-101</td>
<td>174</td>
<td>-125</td>
<td>188</td>
<td>-98</td>
<td>200</td>
<td>-39</td>
<td>202</td>
<td>-59</td>
<td>201</td>
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<tr>
<td>CEM</td>
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<td>90</td>
<td>65</td>
<td>115</td>
<td>92</td>
<td>146</td>
<td>151</td>
<td>136</td>
<td>131</td>
<td>134</td>
</tr>
<tr>
<td>CENAM</td>
<td>-114</td>
<td>453</td>
<td>-138</td>
<td>458</td>
<td>-111</td>
<td>467</td>
<td>-52</td>
<td>464</td>
<td>-72</td>
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### Table A3. Degrees of equivalence for the volume measurement.

<table>
<thead>
<tr>
<th>Lab i</th>
<th>Lab j</th>
<th>Volume (mm³)</th>
<th>NMIJ</th>
<th>PTB</th>
<th>IMGC</th>
<th>KRISS</th>
<th>METAS</th>
<th>NRC</th>
<th>CEM</th>
<th>CENAM</th>
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<tr>
<td></td>
<td></td>
<td>/mm³</td>
<td>/mm³</td>
<td>/mm³</td>
<td>/mm³</td>
<td>/mm³</td>
<td>/mm³</td>
<td>/mm³</td>
<td>/mm³</td>
<td>/mm³</td>
</tr>
<tr>
<td>NMIJ</td>
<td>0.038</td>
<td>0.057</td>
<td>0.007</td>
<td>0.694</td>
<td>0.020</td>
<td>0.760</td>
<td>0.218</td>
<td>0.219</td>
<td>0.881</td>
<td>0.864</td>
</tr>
<tr>
<td>PTB</td>
<td>0.031</td>
<td>0.665</td>
<td>-0.007</td>
<td>0.694</td>
<td>0.013</td>
<td>1.008</td>
<td>0.211</td>
<td>0.718</td>
<td>0.874</td>
<td>1.089</td>
</tr>
<tr>
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<td>0.018</td>
<td>0.794</td>
<td>-0.020</td>
<td>0.760</td>
<td>-0.013</td>
<td>1.000</td>
<td>0.198</td>
<td>0.783</td>
<td>0.861</td>
<td>1.123</td>
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<tr>
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<td>-0.180</td>
<td>0.196</td>
<td>-0.218</td>
<td>0.219</td>
<td>-0.211</td>
<td>0.718</td>
<td>-0.198</td>
<td>0.783</td>
<td>0.663</td>
<td>0.841</td>
</tr>
<tr>
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<td>0.841</td>
<td>-0.881</td>
<td>0.864</td>
<td>-0.874</td>
<td>1.089</td>
<td>-0.861</td>
<td>1.123</td>
<td>-0.663</td>
<td>0.884</td>
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<td>0.623</td>
<td>1.178</td>
<td>0.630</td>
<td>1.352</td>
<td>0.643</td>
<td>1.397</td>
<td>0.841</td>
<td>1.193</td>
</tr>
<tr>
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<td>-0.232</td>
<td>0.817</td>
<td>-0.061</td>
<td>0.841</td>
<td>-0.054</td>
<td>1.070</td>
<td>-0.041</td>
<td>0.680</td>
<td>0.157</td>
<td>0.861</td>
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<tr>
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<td>0.927</td>
<td>1.301</td>
<td>0.889</td>
<td>1.316</td>
<td>0.896</td>
<td>1.236</td>
<td>0.909</td>
<td>1.506</td>
<td>1.107</td>
<td>1.325</td>
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</table>

### Table A4. Degrees of equivalence for the density measurement.

<table>
<thead>
<tr>
<th>Lab i</th>
<th>Lab j</th>
<th>Density (10^-3 kg/m³)</th>
<th>NMIJ</th>
<th>PTB</th>
<th>IMGC</th>
<th>KRISS</th>
<th>METAS</th>
<th>NRC</th>
<th>CEM</th>
<th>CENAM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>/ (10^-3 kg/m³)</td>
<td>/ (10^-3 kg/m³)</td>
<td>/ (10^-3 kg/m³)</td>
<td>/ (10^-3 kg/m³)</td>
<td>/ (10^-3 kg/m³)</td>
<td>/ (10^-3 kg/m³)</td>
<td>/ (10^-3 kg/m³)</td>
<td>/ (10^-3 kg/m³)</td>
<td>/ (10^-3 kg/m³)</td>
</tr>
<tr>
<td>NMIJ</td>
<td>-0.10</td>
<td>0.24</td>
<td>0.03</td>
<td>3.86</td>
<td>0.10</td>
<td>4.11</td>
<td>-1.03</td>
<td>1.16</td>
<td>-4.70</td>
<td>4.69</td>
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<tr>
<td>PTB</td>
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<td>3.73</td>
<td>-0.03</td>
<td>3.86</td>
<td>-0.02</td>
<td>5.54</td>
<td>-1.06</td>
<td>4.01</td>
<td>-4.73</td>
<td>5.98</td>
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<tr>
<td>IMGC</td>
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<td>3.99</td>
<td>-0.10</td>
<td>4.11</td>
<td>-0.07</td>
<td>5.54</td>
<td>-1.12</td>
<td>4.25</td>
<td>-4.80</td>
<td>6.10</td>
</tr>
<tr>
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<td>0.92</td>
<td>1.11</td>
<td>1.03</td>
<td>1.16</td>
<td>1.06</td>
<td>4.01</td>
<td>1.12</td>
<td>4.25</td>
<td>-3.67</td>
<td>4.81</td>
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<tr>
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<td>4.59</td>
<td>4.58</td>
<td>4.70</td>
<td>4.69</td>
<td>4.73</td>
<td>5.98</td>
<td>4.80</td>
<td>6.10</td>
<td>3.67</td>
<td>4.81</td>
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<td>-3.64</td>
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<td>-3.58</td>
<td>7.53</td>
<td>-4.70</td>
<td>6.49</td>
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<td>4.43</td>
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<td>5.87</td>
<td>0.50</td>
<td>5.87</td>
<td>0.58</td>
<td>3.68</td>
<td>-0.55</td>
<td>4.67</td>
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<tr>
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<td>7.19</td>
<td>-5.11</td>
<td>7.26</td>
<td>-5.08</td>
<td>6.90</td>
<td>-5.01</td>
<td>8.28</td>
<td>-6.14</td>
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