CCM.D-K1.2023

Final Report

"Density Measurements of a silicon sphere (1 kg) by hydrostatic weighing"

Final Report

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Abstract

This report presents the results of the key comparison CCM.D-K1.2023 of solid density measurements by hydrostatic weighing, which was carried out through May 2022 to June 2024. As transfer standard act a 1 kg sphere made of natural silicon, which is compared directly or indirectly to primary density standards calibrated by mass and dimensional measurements.

Ten laboratories participated in this key comparison of five regional metrology organizations (RMO): three of European association metrology institutes (EURAMET), three of Asia pacific metrology programme (APMP), two of inter-American metrology system (SIM), one of intra-Africa metrology system (AFRIMET) and one of Gulf association for metrology (GULFMET). This CIPM key comparison, was coordinated by the Physikalisch-Technische Bundesanstalt (PTB, DE) as the pilot laboratory, and Centro Nacional de Metrología (CENAM) and Istituto Nazionale di Ricerca Metrologica (INRIM) as co-pilot laboratories.

The Key Comparison Reference Values (KCRVs) have been obtained for the volume and density values related to the transfer standard by the results of participants, whereby the method of least squares χ^2 is estimated. The KCRVs and the corresponding uncertainties were calculated by the weighted mean in case of consistent results. Only two laboratories differed and were excluded from the analysis (E_n-value greater than 1).

For each participant, the degree of equivalence (DoE) was determined with respect to the corresponding KCRV and between the other laboratories.

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1. Introduction

The present comparison is designated as CCM Key Comparison and is based on the comparison CCM.D-K1 from 2001 [1]. The CCM designated PTB as the pilot laboratory for this comparison, while CENAM and INRIM acted as co-pilot laboratories.

The primary objective of the present comparison, designated CCM.D-K1.2023, is to evaluate the results of density and volume determinations of a 1 kg sphere made of natural silicon from the participating laboratories. This is undertaken to assess the degree of equivalence in accordance with the mutual recognition agreement [2]. The transfer standard is compared directly or indirectly with primary density standards calibrated by mass and dimensional measurements. In this way national metrology institutes (NMIs) typically transfer the density unit to calibration laboratories, verification offices, or other NMIs. The utilization of silicon spheres has become a well-established practice for the purpose of facilitating the comparability of density and volume determinations of solids. This is primarily attributable to the high-density stability of the material and the ease with which it can be cleaned.

As part of this key comparison, the volume and density of each participating institute are determined. A silicon sphere is utilized as a transfer standard at the reference conditions of 20 °C and 101 325 Pa in relation to the solid density standards of each NMI. This process is carried out by hydrostatic weighing. It is customary for the hydrostatic density determination to be accompanied by a mass determination of the transfer standard. While the participants are requested to ascertain the mass values of the transfer standard, this is not a component of the comparison.

The comparison measurements were conducted between May 2022 and May 2024, while PTB, as the pilot laboratory, performed three measurements during the entire time window, at the beginning, during and at the end of the circulation, in order to monitor the stability of the transfer standard.

Each participant was given approximately five weeks to receive the transfer standard, perform the measurements and send the transfer standard to the next participant. However, the schedule encountered delays due to challenges pertaining to transport and customs. INRIM was unable to participate in the comparative measurements due to technical problems at the density laboratory, but provided support as a co-pilot laboratory.

2. Participants and schedule

Ten laboratories took part in this key comparison of five regional metrology organizations (RMO): three of European association metrology institutes (EURAMET), three of Asia pacific metrology programme (APMP), two of inter-American metrology system (SIM), one of intra-Africa metrology system (AFRIMET) and one of Gulf association for metrology (GULFMET).
Despite the presence of metrological problems, INRIM attempted to carry out the required measurements. However, this attempt was not successful, and did not send the results.
To monitor the stability of the mass, volume, and density of the transfer standard, these parameters were measured three times at PTB during the whole period; at the beginning, at the meanwhile, and the end of the circulation.
The measurements were performed from May 2022 to June 2024. The unforeseen difficulties related to transport and customs changes delayed the original schedule for the comparison. The time delay occurred due to customs problems. Table 2.1 lists all participated laboratories and the circulation scheme.

Table 2.1. List of the participating NMIs and the circulation scheme of the transfer standard.

Measuring date		**Date of report**	**NMI/Country**	**RMO**
18th May 2022	03rd June 2022		PTB/DE	EURAMET
09th June 2022	16th June 2022	5th September 2022	METAS/CH	EURAMET
19th July 2022	28th July 2022	4th October 2022	NRC/CA	SIM
13th September 2022	22nd September 2022	9th November 2022	NIM/CN	APMP
22nd October 2022	20th November 2022	25th March 2023	CENAM/MX	SIM
12th January 2023	08th February 2023	5th April 2023	PTB/DE	EURAMET
2nd April 2023	09th April 2023	29th May 2023	NMIJ/JP	APMP
11th June 2023	15th August 2023	14th December 2023	NIS/EG	AFRIMET
12th September 2023	27th October 2023	17th January 2024	NMIA/AU	APMP
29th November 2023	06th December 2023	22nd February 2024	UME/TR	EURAMET
27th December 2023	28th February 2024	23th May 2024	SASO-NMCC/SA	GULFMET
15th March 2024	07th May 2024	18th June 2024	PTB/DE	EURAMET
29th March 2024	22nd May 2024	-	INRIM/IT	EURAMET

3. Transfer standard

For the comparison the PTB provide the transfer standard: a sphere made of natural silicon with a nominal mass of 1 kg, named as SiSCkg05a. This sphere was fabricated by Leibniz-Institut für Kristallzüchtung, IKZ and J. Hauser GmbH & Co. KG, and unknown for all participating laboratories in this comparison.

Physical properties of the transfer standard are given in Table 3.1, together with their uncertainties. The cubic expansion and isothermal compressibility were used as given and common parameters in this key comparison.

Table 3.1. Physical properties of the transfer standard, SiSCkg05a, a sphere made of a single crystal grown natural silicon with a nominal mass of 1 kg.

Nominal density at 20 °C and 101.325 kPa	2 329 kg/m³
Volume thermal expansion at 20 °C and 101.325 kPa	7.67(3) x 10^{-6} K^{-1}
Isothermal compressibility at 20 °C and 101.325 kPa	1.001(15) x 10^{-11} Pa^{-1}

Uncertainties are standard uncertainties (k = 1).

4. Stability of transfer standard

The stability of the transfer standard, SiSCkg05a, was evaluated by the pilot laboratory through a comparison of the measurement values (mass, volume, and density) at three distinct time points: prior to the commencement of the comparison, during the middle phase, and at the final stage. The results are presented in Figure 4.1 and Table 4.1. The three measurements conducted at PTB over a period of two years.

A slight drift in the mass value was observed, within the measurement uncertainty, which could not be confirmed in the volume or density measurements. The maximum relative deviation between the initial and final measurements was less than $5.8 \cdot 10^{-8}$, which can be considered negligible and is coherent with the typical uncertainty of reproducibility. Respectively, the effect of the possible drift was neglected in this key comparison.

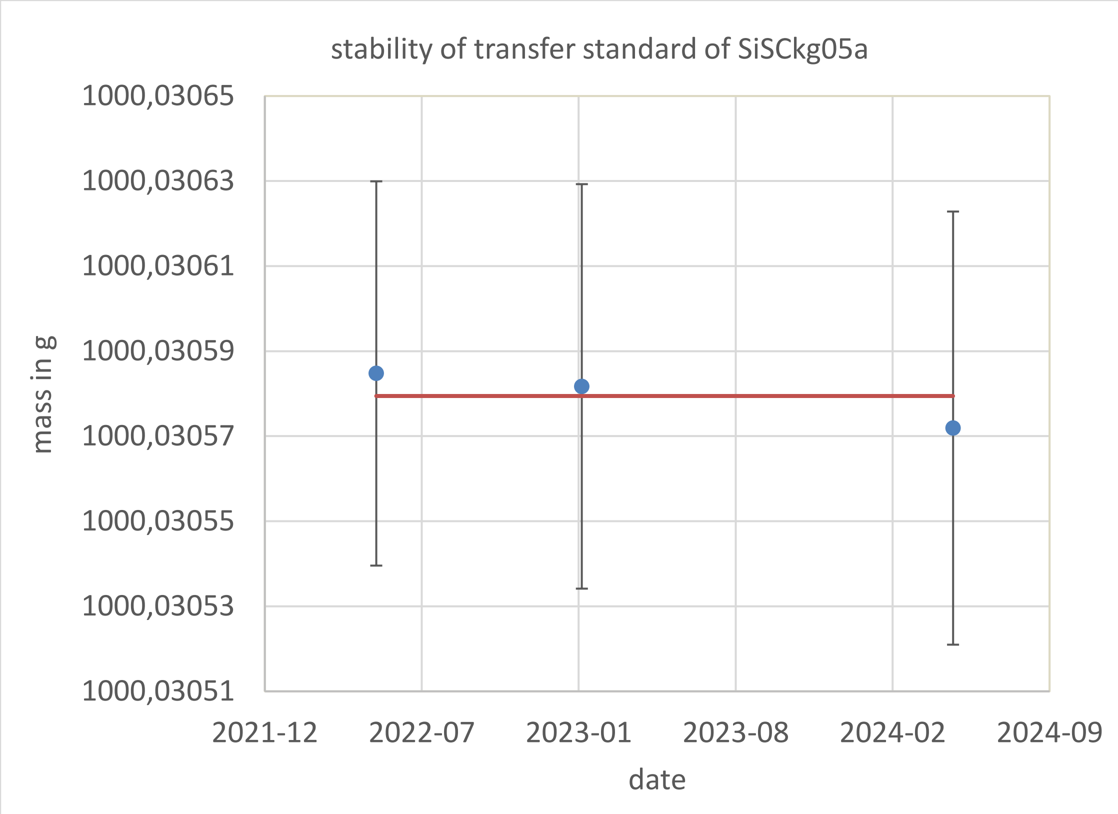

Figure 4.1. Results of mass stability of the transfer standard measured at PTB. The bars express the expanded uncertainties U_{95}.

Table 4.1. Measurements performed by PTB, at the start, middle and end of circulation.

	Value			*U*	*Δ*	*Δ/value*
	May 2022	January 2023	May 2024			
mass in g	1 000.030 585	1 000.030 582	1 000.030 572	0.000 048	0.000 013	1.3×10^{-8}
volume in cm^3	429.366 65	429.366 70	429.366 68	0.000 13	-0.000 02	-5.8×10^{-8}
density in kg/m^3	2 329.083 02	2 329.082 79	2 329.082 89	0.000 65	0.000 13	5.8×10^{-8}

5. Density standards of participating NMIs

Table 5.1 lists the density standards used by the participating NMIs. Except for CENAM and NRC, all participating NMIs utilized monocrystalline silicon spheres as solid density standards. At CENAM, Zerodur spheres were used as reference density standards, while at NRC water was utilized as a reference density.

Some mass and volume values of the solid density standards are traceable to other NMIs, which, in addition to mass determination, have the capability of measuring the volume by optical interferometry. The density of water used by NRC as density standard was determined from the table recommended by the CIPM [4]. According to the table, the density of distilled tap water used in the hydrostatic weighing at NRC was determined by correcting for the effects of isotopic abundance and gases dissolved in the water.

Table 5.1. Reference volume standards used in this key comparison.

NMI	**Reference volume standard**	**Traceability**		**Expanded uncertainty (*k* = 2)**	
		Mass	**Volume**	**Mass/g**	**Volume/cm³**
PTB	Two 1 kg spheres made of natural silicon, Si10 and Si12	PTB	PTB	0.000 035	0.000 044
METAS	1 kg sphere made of natural silicon, RAW08	METAS	INRIM/ NMIJ	0.000 132	0.000 09
NRC	Water *)	-	-	-	-
NIM	1 kg sphere made of natural silicon	NIM	NIM	0.000 074	0.000 078
CENAM	Two 1 kg spheres made of Zerodur, Z-01 and Z-02	PTB	PTB	0.000 200	0.000 60
NMIJ	1 kg silicon spheres made of natural silicon, S4 and S5	NMIJ	NMIJ	0.000 034	0.000 046
NIS	1 kg silicon spheres made of natural silicon	NIS	NIS	0.000 450	0.000 068
NMIA	1 kg silicon sphere made of natural silicon, AVO#3	NMIA	NPL	0.000 464	0.001 900
UME	1 kg silicon sphere and 500 mg silicon sphere made of natural silicon	PTB	PTB	0.000 100 0.000 150	0.000 80 0.000 50
SASO-NMCC	1 kg silicon sphere made of natural silicon	PTB	PTB	0.000 150	0.000 80

*) The density of water determined from the CIPM recommended formula [3] was used as a reference standard of the NRC.

6. Procedure and method for measurement

As part of the mass measurements and hydrostatic weighing, it is usually necessary to determine the density of the air; this is also the case in the present comparison. The air density was determined in the participating NMIs from measurements of air temperature, air pressure and air humidity. The CIPM formula [4] was utilized as a common equation to calculate the air density in this key comparison.

Furthermore, the technical protocol of this key comparison provides detailed descriptions of the measurement procedure and the handling of the transfer standard. It includes the handling and cleaning of the transfer standard, the minimum number of measurements required, and the method of uncertainty analysis. At least ten weighing sequences had to be performed in air and in liquid to determine the volume, density, and mass of the transfer standard. The uncertainties pertaining to the mass, volume and density of the transfer standard are to be specified with a confidence level of 95 % and by analyzing the effective degrees of freedom, denoted by ν_{eff} [5].

6.1 Mass measurement

Table 6.1 provides an overview of the method used for mass measurement of each individual NMI. All participants measured the mass of transfer standard SiSCkg05a in air. The methodology for determining the density of air and the reference mass standard utilized for this measurement are also listed in this table. The reference mass standard differs of silicon sphere and stainless-steel weights.

Table 6.1. Method used for measuring the mass of the transfer standard.

NMI	**Balance** **Maximum load, resolution**	**Method used for determining the density of air**	**Reference mass standard**
PTB	Mass comparator AT1006, Mettler-Toledo, modified by PTB with an automatic weight change mechanism Maximum load: 1 320 g Resolution: 1 µg Electronic balance range: 11 g	CIPM formula	Calibrated silicon sphere
METAS	Automatic mass comparator M_one, Mettler-Toledo with an automatic weight exchange mechanism.	CIPM formula	Calibrated stainless-steel weights

	Maximum load: 1 001.5 g Resolution: 0.1 µg Electronic balance range: 1.5 g		
NRC	Automatic mass comparator M_one, Mettler-Toledo with an automatic weight exchange mechanism. Maximum load: 1 001.5 g Resolution: 0.1 µg Electronic balance range: 1.5 g	CIPM formula, CO_2 content measured	Calibrated stainless-steel weights and silicon sphere
NMI	Mass comparator AX1005, Mettler-Toledo, with modified hanging pan Maximum load: 1 109 g Resolution: 10 µg Electronic balance range: 109 g	CIPM formula	Calibrated stainless-steel weights
CENAM	Automatic mass comparator M_one, Mettler-Toledo with an automatic weight exchange mechanism. Maximum load: 1 001.5 g Resolution: 0.1 µg Electronic balance range: 1.5 g	CIPM formula	Calibrated stainless-steel weights
NMIJ	Mass comparator AT-1006, Mettler-Toledo Maximum load: 1 011 g Resolution: 1 µg Electronic balance range: 11 g	CIPM formula	Calibrated silicon sphere
NIS	Mass comparator CC10000U-L, Sartorius Maximum load: 10 000 g Resolution: 0.01 mg	CIPM formula	Calibrated silicon sphere
NMIA	Top loading balance, Sartorius Maximum load: 10 050 g Resolution: 0.1 mg Electronic balance range: 60 g	CIPM formula	Calibrated stainless-steel weights
UME	Automatic mass comparator M_one, Mettler-Toledo with an automatic weight exchange mechanism. Maximum load: 1 001.5 g Resolution: 0.1 µg Electronic balance range: 1.5 g	CIPM formula	Calibrated silicon sphere
SASO-NMCC	Automatic mass comparator M_one, Mettler-Toledo with an automatic weight exchange mechanism. Maximum load: 1 001.5 g Resolution: 0.1 µg Electronic balance range: 1.5 g	CIPM formula	Calibrated silicon sphere

6.2 Hydrostatic weighing

Table 6.2 provides a summary of the method used for hydrostatic weighing at each NMI. While the PTB, METAS, NIM, CENAM, NMIJ, and NMIA employ hydrostatic weighing equipment comprising a mass comparator, the NRC, NIS, UME, and SASO utilize a volume comparator.

Table 6.2. Method used for measuring the volume of the transfer standard.

NMI	**Balance** **Maximum load, resolution, electronic balance**	**Positions of density standard and transfer standard in the hydrostatic weighing apparatus**	**Working liquid**
PTB	Mass comparator AX1006 Mettler-Toledo with automatic handler Maximum load: 1 111 g Resolution: 1 µg Electronic balance range: 11 g	Transfer standard placed between two silicon density standards located in a different height. They are placed in a cage.	Pentadecane ($n\text{-}C_{15}H_{32}$)
METAS	Mass comparator AT1005, Mettler-Toledo, with automatic handler system Maximum load: 1 109 g Resolution: 10 µg Electronic balance range: 109 g	Transfer standard placed above a silicon density standard. They are placed in a cage.	Pure water
NRC	Volume comparator VC1005X, Mettler-Toledo automatic handler system Maximum load: 1 109 g Resolution: 10 µg Electronic balance range: 109 g	Transfer standard placed on a rotational circular pan with four places.	Pure Water
NIM	Mass comparator AX1005, Mettler-Toledo with automatic handler Maximum load: 1 109 g Resolution: 10 µg Electronic balance range: 109 g	Transfer standard placed between two silicon density standards located in a different height. They are placed in a cage.	Tridecane ($n\text{-}C_{13}H_{28}$)
CENAM	Mass comparator AX1005, Mettler-Toledo, with an automatic mass handler system Maximum load: 1 109 g Resolution: 10 µg Electronic balance range: 109 g	The transfer standard and density standard are placed alternately on a support.	Pentadecane ($n\text{-} C_{15}H_{32}$)
NMIJ	Mass comparator AT1005, Mettler-Toledo Maximum load: 1 190 g Resolution: 10 µg Electronic balance range: 190 mg	Transfer standard placed between two silicon density standards located in a	Tridecane ($n\text{-}C_{13}H_{28}$)

		different height. They are placed in a cage.	
NIS	Volume comparator VC1005, Mettler-Toledo with automatic handler Maximum load: 1 055 g Resolution: 10 µg Electronic balance range: 10 µg	Transfer standard placed on a rotational circular pan.	FC-40
NMIA	Top loading balance, Mettler-Toledo Maximum load: 2 300 g Resolution: 0.1 mg	Transfer standard placed below a silicon density standard. They are placed in a cage.	Deionised distilled water
UME	Volume comparator VC1005, Mettler-Toledo automatic handler system Maximum load: 1 055 g Resolution: 10 µg Electronic balance range: 109 g	Transfer standard placed on a rotational circular pan.	FC-40
SASO-NMCC	Volume comparator VC1005X, Mettler-Toledo automatic handler system Maximum load: 1 000 g Resolution: 10 µg	Transfer standard placed on a rotational circular pan.	FC-40

7. Result and data analysis

In this comparison, a series of measurements were conducted to determine mass, volume and density by each participating laboratory. Different measuring instruments and measuring liquids were used. The detailed measurement data are listed in Tables 5.1 and 6.2.

Each participated laboratory calculated the average value of the mass, volume and density at 20 °C and 101 325 Pa and the standard uncertainty u_c. The measurement results of mass, volume, and density measurements submitted by each participating NMI, including all associated uncertainties, are shown in Tables 7.1 to 7.3 (the error bars given in term of the expanded uncertainty U_{95}).

The uncertainties of measurements were calculated as given in the technical report, as well as the effective degrees of freedom ν_{eff} of the combined standard uncertainty u_c, the t-factor $t_{95}(\nu_{eff})$ taken from the t-distribution for a 95 % confidence level and the expanded uncertainty for the corrections as as $U_{95} = t_{95}(\nu_{eff}) \cdot u_c$. In the case of PTB, the mean value from the three repeated measurements was used for the following evaluation (see section 4).

As is evident from the figures 7.1 to 7.3, the mass, volume and density values given for the NMIs were found to be in the most cases in agreement within the expanded uncertainties. However, for volume and density values NRC and NIS deviate from this, see section 8. Furthermore, the most significant comparative reference values are demonstrated in Figures 7.1 to 7.3, with the calculation method elucidated in the subsequent chapter.

Table 7.1. Results of mass measurements of the transfer standard.

NMI	m	u_c	$t_{95}(\nu_{eff})$	U_{95}
	g			
PTB	1 000.030 579	0.000 024	1.982	0.000 048
METAS	1 000.030 595	0.000 066	1.984	0.000 132
NRC	1 000.030 580	0.000 033	1.976	0.000 065
NIM	1 000.030 553	0.000 065	1.989	0.000 129
CENAM	1 000.030 520	0.000 037	1.972	0.000 072
NMIJ	1 000.030 591	0.000 033	1.997	0.000 066
NIS	1 000.031 220	0.000 325	1.984	0.000 645
NMIA	1 000.031 081	0.000 260	1.973	0.000 514
UME	1 000.030 500	0.000 050	1.984	0.000 099
SASO-NMCC	1 000.030 535	0.000 257	1.984	0.000 509

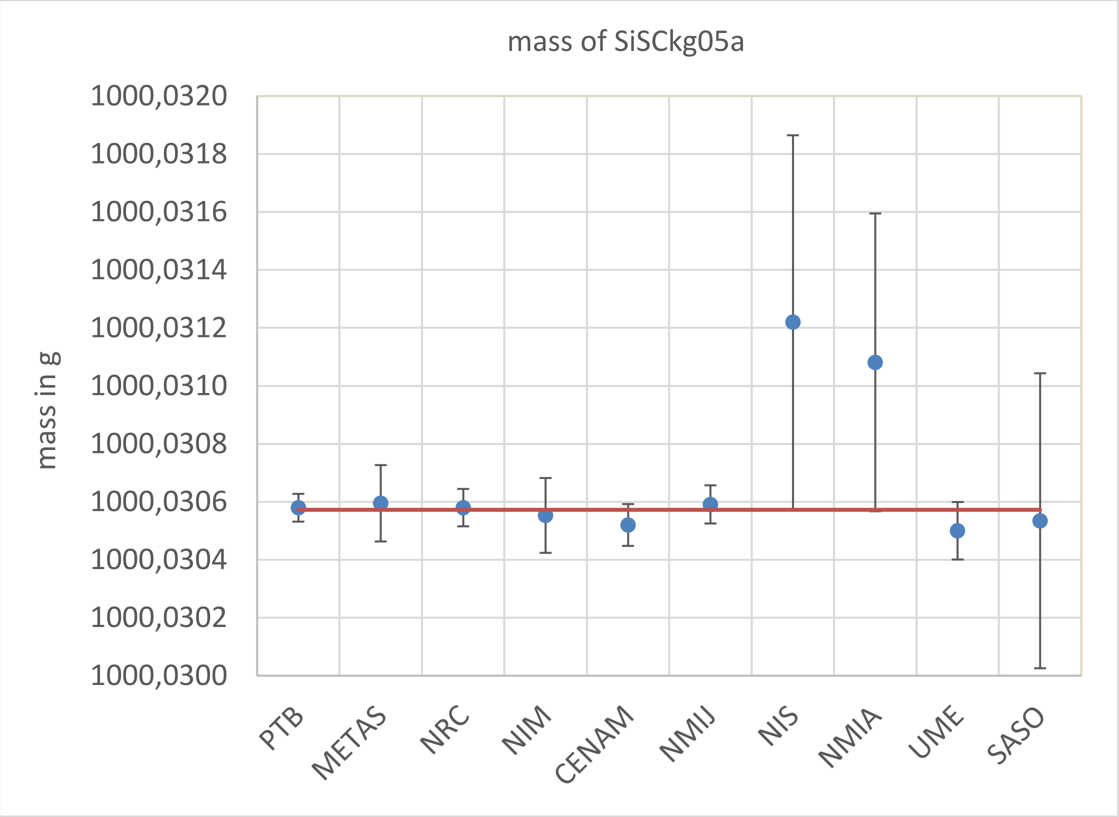

Figure 7.1. Results of mass measurements of the transfer standard. The bars express the expanded uncertainties U_{95}.

Table 7.2. Results of volume measurements of the transfer standard.

NMI	***V***	***u***	***t_{95}***	***U_{95}***
	cm^3			
PTB	429.366 677	0.000 066	1.963	0.000 129
METAS	429.365 848	0.001 864	1.972	0.003 676
NRC	429.368 505	0.000 348	1.971	0.000 686
NIM	429.366 472	0.000 136	1.983	0.000 270
CENAM	429.366 060	0.000 750	1.977	0.001 483
NMIJ	429.366 711	0.000 072	1.967	0.000 142
NIS	429.364 162	0.001 030	1.986	0.002 045
NMIA	429.367 324	0.001 048	1.993	0.002 088
UME	429.366 800	0.000 400	1.984	0.000 794
SASO-NMCC	429.365 412	0.000 904	2.120	0.001 917

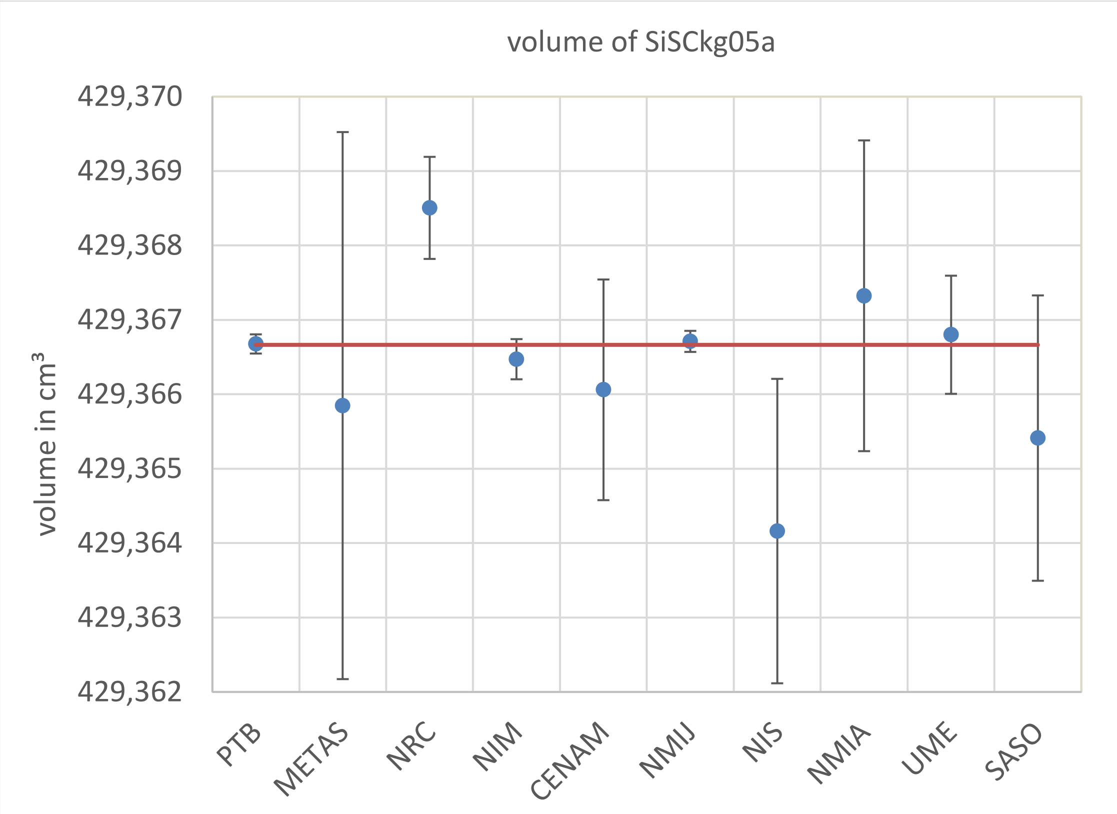

Figure 7.2. Results of volume measurements of the transfer standard. The bars express the expanded uncertainties U_{95}.

Table 7.3. Results of density measurements of the transfer standard.

NMI	***ρ***	***u***	t_{95}	U_{95}
	kg/m³			
PTB	2 329.082 9	0.000 3	1.963	0.000 7
METAS	2 329.087 4	0.010 2	1.972	0.020 2
NRC	2 329.073 0	0.001 9	1.971	0.003 7
NIM	2 329.084 0	0.000 8	1.983	0.001 5
CENAM	2 329.086 1	0.004 1	1.976	0.008 1
NMIJ	2 329.082 7	0.000 4	1.965	0.000 7
NIS	2 329.098 0	0.005 0	1.962	0.009 9
NMIA	2 329.080 5	0.005 6	1.996	0.011 1
UME	2 329.082 0	0.002 0	1.984	0.004 0
SASO-NMCC	2 329.089 6	0.004 9	1.982	0.009 7

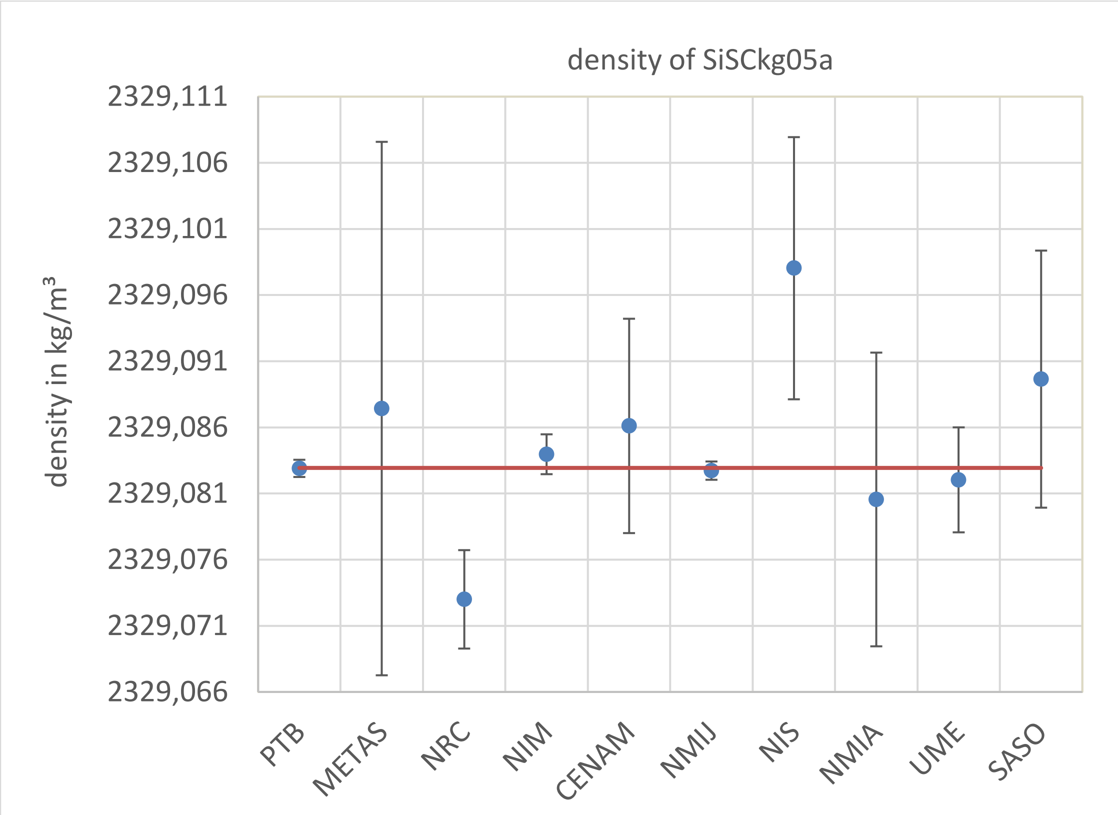

Figure 7.3. Results of density measurements of the transfer standard. The bars express the expanded uncertainties U_{95}.

8. Results of Comparison

In this key comparison, the mass of the transfer standard was measured independently at each NMI. However, a correlation exists due to the consensus value for the kilogram [7]. Therefore, the common uncertainty term due to the consensus value of 20 µg (k = 1) must be considered. Regarding volume and density data, the correlation contribution of the consensus value was considered negligible.

However, the volumes of the solid density standards at CENAM, UME and SASO-NMCC were determined by PTB, as stated in Table 4.1. This indicates that the volume and density data reported by these NMIs are correlated by the common uncertainty of the volume standards of PTB. In contrast to PTB and CENAM, UME and SASO utilize two volume standards that are included within the uncertainty budget, with a contribution for both mass and volume. Therefore, the covariance $u(y_i, y_j)$ between PTB y_i and the other NMIs y_j is determined to be 0.050 mm³. In accordance with the standard uncertainty of the respective NMIs (see table 7.2), the degree of correlation can be determined as outlined in [6]

$$r(y_i, y_j) = \frac{u(y_i, y_j)}{u(y_i)u(y_j)} \ . \qquad (1)$$

In all cases, the correlation $r(y_i, y_j)$ was found to be very low with values of 0.051 for CENAM, 0.094 for UME and 0.042 for SASO-NMCC ($r(y_i, y_j) \leq 1$). Consequently, correlation between volume and density can be disregarded, in a manner analogous to the correlation due to consensus value of mass.

To determine the key comparison reference value KCRV for the mass, volume and density of the transfer standard, the method of least squares χ^2 is estimated, whereby the matrix notation is best used.

The reported data of mass, volume and density are generally represented in the form of a column matrix $\boldsymbol{y}$ with N elements, where N describes the number of reported data. The column matrix $\boldsymbol{y}$ is associated with the laboratory measurements, and $\boldsymbol{\beta}$ with the reference value *KCRV,* to be estimated by a matrix formula defined as follows $\boldsymbol{y} \cong \boldsymbol{\beta X}$, where $\boldsymbol{X}$ is a unit column matrix with N elements. The correlations of the uncertainties are analyzed by taking into account the N x N covariance matrix Σ [8] associated to $\boldsymbol{y}$. The diagonal elements represent the squares of the standard uncertainty and the off-diagonal elements the squared common uncertainty of the consensus value of the kilogram. Σ for mass, volume and density are given in Appendix Table 12.1 to 12.3.

This means that the best estimate for the weighted mean of the reference value KCRV is given by

$$KCRV = \hat{\boldsymbol{y}} = (\boldsymbol{X}^{\mathrm{T}}\boldsymbol{\Sigma}^{-1}\boldsymbol{X})^{-1}\boldsymbol{X}^{\mathrm{T}}\boldsymbol{\Sigma}^{-1}\boldsymbol{y}. \qquad (2)$$

And the variance of KRCV

$$u^2(KCRV) = (\boldsymbol{X}^{\mathrm{T}}\boldsymbol{\Sigma}^{-1}\boldsymbol{X})^{-1}, \qquad (3)$$

where $\boldsymbol{X}^{\mathrm{T}}$ are transpose of matrix $\boldsymbol{X}$, and $\boldsymbol{\Sigma}^{-1}$ the inverse of matrix $\boldsymbol{\Sigma}$, respectively.

To evaluate the statistical consistency of the reported data, the integrated probability $P\{\chi^2(\nu) > \chi^2_{\mathrm{obs}}\}$ was utilised as the recommended method to ascertain the reference value for the key comparison. In this context *v* denotes the degrees of freedom with $\nu = N - 1$. If the integrated probability $P\{\chi^2(\nu) > \chi^2_{\mathrm{obs}}\}$ has a value greater than 0.05, the reported data are considered consistent. The observed value for χ^2_{obs} [8] using the covariances is given by

$$\chi^2_{\mathrm{obs}} = (\boldsymbol{y} - \hat{\boldsymbol{y}})^{\mathrm{T}}\boldsymbol{\Sigma}^{-1}(\boldsymbol{y} - \hat{\boldsymbol{y}}) \qquad (4)$$

As can be seen 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 (2), see Table 8.1. For the reference values of volume and density, the data from NRC and NIS were excluded as their normalized error $E_n = {|D_{\mathrm{i}}|}/{U(D_{\mathrm{i}})} > 1$, see section 9 and Table 9.1.

Table 8.1. Reference values for the mass, volume and density of the transfer standard, SiSCkg05a.

Quantity	Reference value *KCRV*	Standard uncertainty u*(KCRV)*	χ^2_{obs}	v	P[χ²(v) > χ²obs]
mass	1000.030 572 g	0.000 022 g	14.35	9	0.11
volume	429.366 664 cm³	0.000 045 cm³	5.73	7	0.57
density	2329.082 94 kg/m³	0.000 23 kg/m³	5.25	7	0.63

9. Degrees of Equivalence

The degree of equivalence of national measurement standards is defined as the degree to which those standards are consistent with the *KCRV* and, by extension, with other national standards. The degree of equivalence is expressed quantitatively by a deviation from *KCRV* and an expanded uncertainty in that deviation, evaluated at a 95% level of confidence. Therefore, the degrees of equivalence D_i of each laboratory with respect to KCRV and the degrees of equivalence D_ij between two laboratories have been calculated.

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

The degree of equivalence D_i of the laboratory *i* = 1, .., N with respect to the key comparison reference value KCRV for mass, volume and density is calculated as follows

$$D_\mathrm{i} = y_\mathrm{i} - KCRV \qquad (5)$$

and the expanded uncertainty $U(D_\mathrm{i})$ is as follows for all NMIs involved in the determination of the KCRV:

$$U(D_\mathrm{i}) = 2\,u(D_\mathrm{i}) = 2\sqrt{u^2(y_\mathrm{i}) - u^2(KCRV)}. \qquad (6)$$

For those NMIs that are not involved in the determination of the KCRV because their values have a normalised error $E_n > 1$, the expanded uncertainty is calculated as follows

$$U(D_\mathrm{i}) = 2\,u(D_\mathrm{i}) = 2\sqrt{u^2(y_\mathrm{i}) + u^2(KCRV)} \qquad (7)$$

The differences from the KCRV for mass, volume and density demonstrate a high degree of congruence in the capabilities, except for the NRC and NIS.

The degree of equivalence D_i and the expanded values are given in Table 9.1, and for volume and density the graph of equivalence are shown in Figure 9.1 and 9.2.

Table 9.1. For the mass, volume and density the En-values, degree of equivalence di and expanded uncertainties $U(D_i)$ of each laboratory with respect to the reference value are given.

NMI	***mass***			***volume***			***density***		
	E_n	D_i	$U(D_i)$	E_n	D_i	$U(D_i)$	E_n	D_i	$U(D_i)$
		µg			mm^3			10^{-3} kg/m³	
PTB	0.37	7	19	0.13	0.01	0.10	0.07	-0.04	0.48
METAS	0.18	22	125	0.22	-0.82	3.73	0.22	4.49	20.44
NRC	0.16	8	48	2.62	1.84	0.70	2.61	-9.94	3.80
NIM	0.16	-19	122	0.75	-0.19	0.26	0.71	1.03	1.45
CENAM	0.90	-52	58	0.40	-0.60	1.50	0.39	3.17	8.19
NMIJ	0.38	19	49	0.42	0.05	0.11	0.39	-0.21	0.54
NIS	1.00	648	648	1.21	-2.50	2.06	1.49	15.10	10.11
NMIA	0.98	509	519	0.31	0.66	2.09	0.21	-2.39	11.11
UME	0.81	-72	90	0.17	0.14	0.79	0.23	-0.90	3.97
SASO-NMCC	0.07	-38	511	0.69	-1.25	1.81	0.69	6.71	9.79

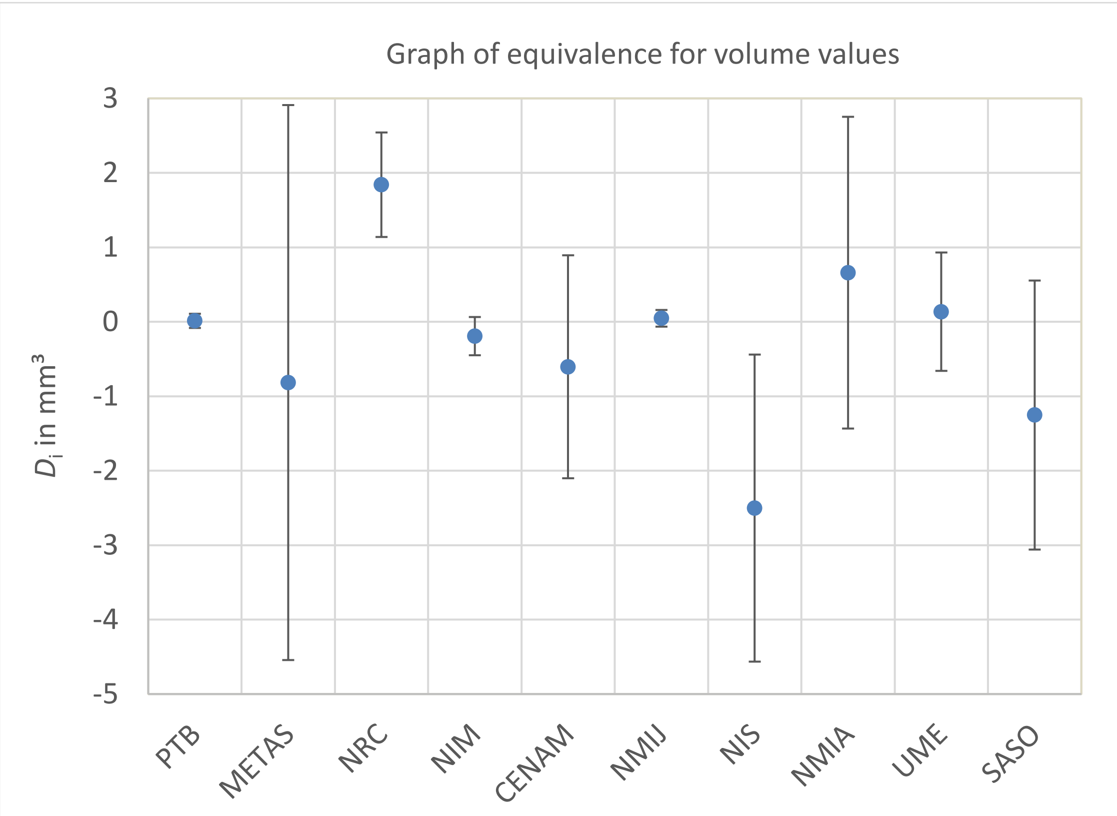

Figure 9.1. Degrees of equivalence for volume values of each laboratory with respect to the reference value.

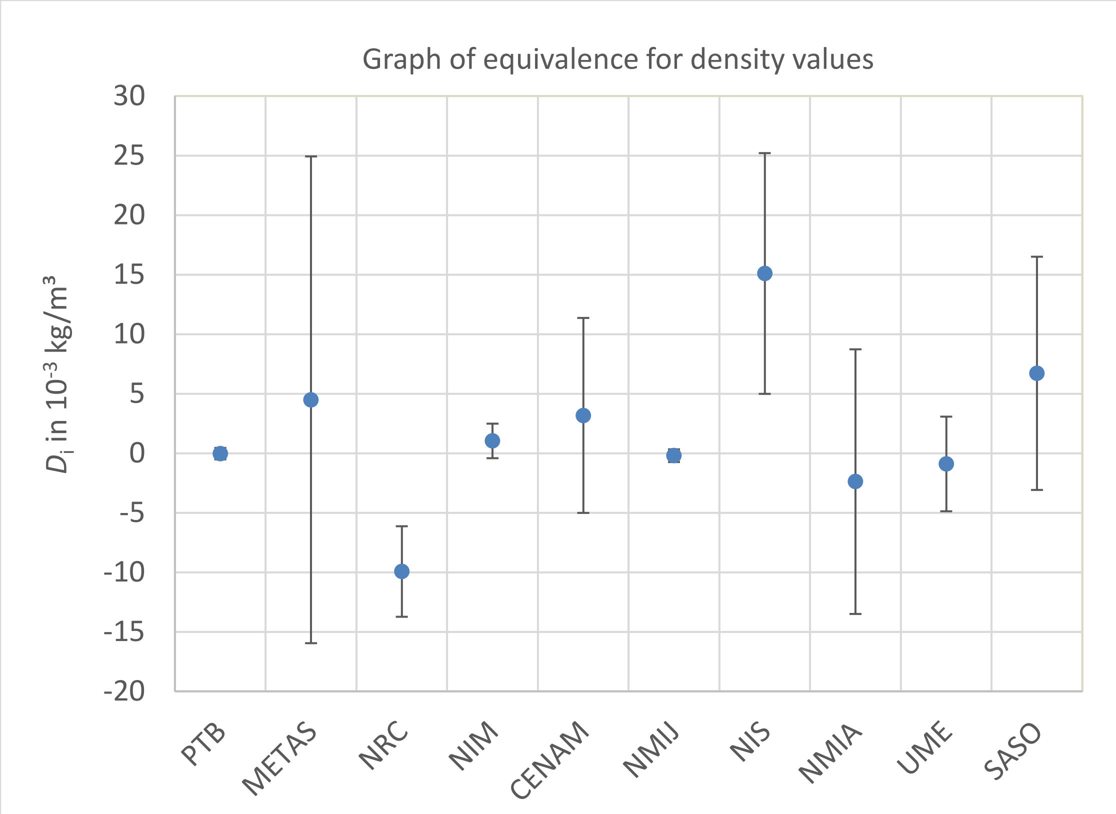

Figure 9.2. Degrees of equivalence for density values of each laboratory with respect to the reference value.

9.2 Degrees of equivalence between two laboratories

The degree of equivalence D_{ij} between two laboratories denoted by *i* and *j* is evaluated by calculating the difference for each pair of two laboratories as follows

$$D_{\mathrm{ij}} = y_{\mathrm{i}} - y_{\mathrm{j}}. \qquad (8)$$

The volume and density measurements described in section 8 can be considered negligible in this comparison, no covariance needs to be considered, and the expanded uncertainty is calculated as follows:

$$U\left(D_{\mathrm{ij}}\right) = 2\,u\left(D_{\mathrm{ij}}\right) = 2\sqrt{u^2(y_{\mathrm{i}}) + u^2\left(y_{\mathrm{j}}\right)}. \qquad (9)$$

Results of this evaluation are given in Tables 12.4 and 12.5 in Appendix.

10. Conclusions

In this key comparison, the volume and density determinations of a 1 kg silicon spheres by ten NMIs were evaluated. The measurements were reported at 20 °C and 101 325 Pa in relation to the solid density standards of each NMI by the hydrostatic method, whereby hydrostatic weighing systems with a mass comparator were used as well as volume comparators. The transfer standard was compared directly or indirectly to primary density standards calibrated by mass and dimensional measurements. The measurements of this comparison were conducted during May 2022 and May 2024.

The key comparison reference values for volume and density data of the 1 kg transfer standard were determined by the weighted mean value of all NMIs, excluding the data from NRC and NIS. Consequently, the degrees of equivalence of all participants (apart from NRC and NIS) were smaller than expanded uncertainties with respect to the reference value.

Five NMIs achieved volume and density uncertainties of approximately 1 ppm (1×10^{-6} relative) or less for the transfer standard. The smallest relative uncertainties for density were found to be as low as 0.14 ppm. This finding indicates that the proposed approach fulfils the requirements of all customers who wish to calibrate solid density standards for other laboratories.

The results of the comparison can be used to submit new or improved entries in the calibration measurement capabilities (CMC) table in the BIPM key comparison database.

11. References

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12. Appendix

Table 12.1. Covariance matrix Σ of the uncertainty of mass data. Diagonal elements equal to squares of standard uncertainty, and off-diagonal elements equal to squared common uncertainty of consensus value.

	PTB	METAS	NRC	NIM	CENAM	NMIJ	NIS	NMIA	UME	SASO
	x 10^{-10} g^2									
PTB	5.85	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
METAS	4.00	44.11	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
NRC	4.00	4.00	10.67	4.00	4.00	4.00	4.00	4.00	4.00	4.00
NIM	4.00	4.00	4.00	42.14	4.00	4.00	4.00	4.00	4.00	4.00
CENAM	4.00	4.00	4.00	4.00	13.38	4.00	4.00	4.00	4.00	4.00
NMIJ	4.00	4.00	4.00	4.00	4.00	10.89	4.00	4.00	4.00	4.00
NIS	4.00	4.00	4.00	4.00	4.00	4.00	1056.25	4.00	4.00	4.00
NMIA	4.00	4.00	4.00	4.00	4.00	4.00	4.00	678.08	4.00	4.00
UME	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	25.00	4.00
SASO	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	658.04

Table 12.2. Covariance matrix Σ of the uncertainty of volume data with diagonal elements equal to squares of standard uncertainty, off-diagonal elements are zero.

	PTB	METAS	NIM	CENAM	NMIJ	NMIA	UME	SASO
	x 10^{-9} $(cm^3)^2$							
PTB	4.32	0.00	0.00	0.00	0.00	0.00	0.00	0.00
METAS	0.00	3474.50	0.00	0.00	0.00	0.00	0.00	0.00
NIM	0.00	0.00	18.53	0.00	0.00	0.00	0.00	0.00
CENAM	0.00	0.00	0.00	562.50	0.00	0.00	0.00	0.00
NMIJ	0.00	0.00	0.00	0.00	5.18	0.00	0.00	0.00
NMIA	0.00	0.00	0.00	0.00	0.00	1097.63	0.00	0.00
UME	0.00	0.00	0.00	0.00	0.00	0.00	160.00	0.00
SASO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	817.95

Table 12.3. Covariance matrix Σ of the uncertainty of density data with diagonal elements equal to squares of standard uncertainty, off-diagonal elements are zero.

	PTB	**METAS**	**NIM**	**CENAM**	**NMIJ**	**NMIA**	**UME**	**SASO**
	x 10^{-7} (kg/m³)^2							
PTB	1.10	0.00	0.00	0.00	0.00	0.00	0.00	0.00
METAS	0.00	1045.26	0.00	0.00	0.00	0.00	0.00	0.00
NIM	0.00	0.00	5.78	0.00	0.00	0.00	0.00	0.00
CENAM	0.00	0.00	0.00	168.10	0.00	0.00	0.00	0.00
NMIJ	0.00	0.00	0.00	0.00	1.24	0.00	0.00	0.00
NMIA	0.00	0.00	0.00	0.00	0.00	309.32	0.00	0.00
UME	0.00	0.00	0.00	0.00	0.00	0.00	40.00	0.00
SASO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	240.35

Table 12.4. Degrees of equivalence D_{ij} and expanded uncertainties U(D_{ij}) between laboratories for volume measurements.

	PTB		**METAS**		**NRC**		**NIM**		**CENAM**		**NMIJ**		**NIS**		**NMIA**		**UME**		**SASO**	
	D_{ij}	$U(D_{ij})$	D_{ij}	$U(D_{ij})$	D_{ij}	$U(D_{ij})$	D_{ij}	$U(D_{ij})$	D_{ij}	$U(D_{ij})$	D_{ij}	$U(D_{ij})$	D_{ij}	$U(D_{ij})$	D_{ij}	$U(D_{ij})$	D_{ij}	$U(D_{ij})$	D_{ij}	$U(D_{ij})$
	mm^3																			
PTB			0.83	7.36	-1.83	0.71	0.21	0.30	0.62	1.51	-0.03	0.19	2.51	2.06	-0.65	2.10	-0.12	0.81	1.27	1.81
METAS	-0.83	3.73			-2.66	3.79	-0.62	3.74	-0.21	4.02	-0.86	3.73	1.69	4.26	-1.48	4.28	-0.95	3.81	0.44	4.14
NRC	1.83	3.79	2.66	7.48			2.03	2.03	2.45	1.65	1.79	0.71	4.34	2.17	1.18	2.21	1.71	1.06	3.09	1.94
NIM	-0.21	0.75	0.62	7.37	-2.03	0.75			0.41	1.52	-0.24	0.31	2.31	2.08	-0.85	2.11	-0.33	0.85	1.06	1.83
CENAM	-0.62	1.52	0.21	7.93	-2.45	1.65	-0.41	1.52			-0.65	1.51	1.90	2.55	-1.26	2.58	-0.74	1.70	0.65	2.35
NMIJ	0.03	1.51	0.86	7.36	-1.79	0.71	0.24	0.31	0.65	1.51			2.55	2.07	-0.61	2.10	-0.09	0.81	1.30	1.81
NIS	-2.51	2.07	-1.69	8.41	-4.34	2.17	-2.31	2.08	-1.90	2.55	-2.55	2.07			-3.16	2.94	-2.64	2.21	-1.25	2.74
NMIA	0.65	2.94	1.48	8.45	-1.18	2.21	0.85	2.11	1.26	2.58	0.61	2.10	3.16	2.94			0.52	2.24	1.91	2.77
UME	0.12	2.24	0.95	7.52	-1.71	1.06	0.33	0.85	0.74	1.70	0.09	0.81	2.64	2.21	-0.52	2.24			1.39	1.98
SASO	-1.27	1.98	-0.44	8.29	-3.09	1.94	-1.06	1.83	-0.65	2.35	-1.30	1.81	1.25	2.74	-1.91	2.77	-1.39	1.98		

Table 12.5. Degrees of equivalence D_{ij} and expanded uncertainties $U(D_{ij})$ between laboratories for density measurements.

	PTB		**METAS**		**NRC**		**NIM**		**CENAM**		**NMIJ**		**NIS**		**NMIA**		**UME**		**SASO**	
	D_{ij}	$U(D_{ij})$	D_{ij}	$U(D_{ij})$	D_{ij}	$U(D_{ij})$	D_{ij}	$U(D_{ij})$	D_{ij}	$U(D_{ij})$	D_{ij}	$U(D_{ij})$	D_{ij}	$U(D_{ij})$	D_{ij}	$U(D_{ij})$	D_{ij}	$U(D_{ij})$	D_{ij}	$U(D_{ij})$
	10^{-3} kg/mm³																			
PTB			-4.5	40.3	9.9	3.8	-1.1	1.7	-3.2	8.2	0.2	1.0	-15.1	10.1	2.4	11.1	0.9	4.1	-6.7	9.8
METAS	4.5	20.5			14.4	20.8	3.5	20.5	1.3	22.0	4.7	20.5	-10.6	22.8	6.9	23.3	5.4	20.8	-2.2	22.7
NRC	-9.9	20.8	-14.4	41.0			-11.0	4.1	-13.1	9.0	-9.7	3.8	-25.0	10.8	-7.5	11.7	-9.0	5.5	-16.6	10.5
NIM	1.1	4.1	-3.5	40.4	11.0	4.1			-2.1	8.3	1.2	1.7	-14.1	10.2	3.4	11.2	1.9	4.3	-5.7	9.9
CENAM	3.2	8.3	-1.3	43.5	13.1	9.0	2.1	8.3			3.4	8.2	-11.9	13.0	5.6	13.8	4.1	9.1	-3.5	12.8
NMIJ	-0.2	8.1	-4.7	40.3	9.7	3.8	-1.2	1.7	-3.4	8.2			-15.3	10.1	2.2	11.1	0.7	4.1	-6.9	9.8
NIS	15.1	10.1	10.6	44.9	25.0	10.8	14.1	10.2	11.9	13.0	15.3	10.1			17.5	15.0	16.0	10.9	8.4	14.1
NMIA	-2.4	15.0	-6.9	46.0	7.5	11.7	-3.4	11.2	-5.6	13.8	-2.2	11.1	-17.5	15.0			-1.5	11.8	-9.1	14.8
UME	-0.9	11.8	-5.4	41.1	9.0	5.5	-1.9	4.3	-4.1	9.1	-0.7	4.1	-16.0	10.9	1.5	11.8			-7.6	10.6
SASO	6.7	10.6	2.2	44.8	16.6	10.5	5.7	9.9	3.5	12.8	6.9	9.8	-8.4	14.1	9.1	14.8	7.6	10.6		