EURAMET Key Comparison 1031

(EURAMET.M.D-K1.1)

Solid Density Comparison

Final Report

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Abstract

The results are presented of the key comparison EURAMET 1031 (EURAMET.M.D-K1.1) that covered the measurements of density and volume of silicon spheres of three different masses at 20 °C and 101325 Pa. The volume and density determinations of 15 national metrology institutes (NMIs) were checked and linked to the CCM.D-K1 key comparison. The measurements were carried out near 20 °C and at atmospheric pressure by the hydrostatic method in the time interval from 16 May 2008 to 18 Jan 2011.

The comparison was performed in two petals with three spheres in each petal. The travelling standards of petal 1 have a mass of 1001 g, 200 g and 35 g (Petal 2: 984 g, 239 g, 35 g). Whereas the reference values of the 1 kg travelling standards could be determined by the link to the CCM.D-K1 comparison, the density reference values for the smaller spheres were determined by density comparison to the 1 kg spheres using the pressure-of-flotation method.

One result was wrong due to a mistake in the mass determination. Additionally, four of the 57 volume (or density) values were discrepant with E_n values larger than 1.1, 1.2, 1.3 and 1.6.

Five NMIs achieved density uncertainties of about 1 ppm (1×10^{-6} in relative terms) or less for the 1 kg spheres. This satisfies the needs of all customers who wish to calibrate solid density standards for other laboratories.

Volume determinations of mass standards, air density artefacts or sorption artefacts should reach an uncertainty of about 1 mm^3 in order to reduce the effect on the mass uncertainty to about 1 µg. At least for silicon spheres this is reached by eight NMIs. Due to the higher density of stainless steel this may be different for weights and will be checked within the CCM.D-K3 comparison.

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

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1 Introduction

The aim of the EURAMET Project 1031 "Solid density comparison" is to compare the results of the volume and density determinations of solid samples of the participating laboratories and to evaluate the degrees of equivalence according to the Mutual Recognition Arrangement [1]. The samples are compared by hydrostatic weighing usually directly or indirectly to primary density standards, which are calibrated by mass and dimensional measurements. In this way, National Metrology Institutes (NMIs) disseminate the density unit to calibration laboratories, verification offices or other NMIs.

This comparison was agreed on the EURAMET meeting 2008 in Bucharest. It follows the CCM.D-K1 comparison, in which the 1 kg silicon sphere named “D1” was used as travelling standard. The final report of CCM.D-K1 was published in September 2006 [2, 3]. The link to CCM.D-K1 can be provided by the Centro Español de Metrología (CEM) of Spain, the Istituto Nazionale di Ricerca Metrologica (INRIM) of Italy, the Swiss Federal Office of Metrology (METAS), the National Metrology Institute of Japan (NMIJ), and the Physikalisch-Technische Bundesanstalt (PTB) of Germany.

The PTB is the Pilot Laboratory for the comparison. The Technical Protocol was set-up similar to that of the CCM.D-K1 comparison. The comparison is a regional key comparison according to the Mutual Recognition Arrangement [1]. It should support existing and new entries for the CMC tables in this sub-field.

Silicon spheres of about 1000 g, 220 g and 35 g were chosen as travelling standards. Each participating institute determined volume and density of the travelling standards at 20 °C and 101325 Pa. Two sets of three spheres were sent around in series in two petals. The petals are linked by PTB, CEM, METAS, and NMIJ. Additionally, the smaller spheres are compared to the 1 kg spheres by flotation measurements at PTB and partly at NMIJ. This allows to link the density of the smaller spheres to the results of the 1 kg spheres and to the result of the travelling standard D1 of CCM.D-K1.

2 Comparison

2.1 Participants

Sixteen laboratories took part in the comparison, 13 from EURAMET and three from outside Europe: NIS from Egypt, NMIJ from Japan, and VNIIM from Russia (see table 1).

Table 1: Participating laboratories, persons responsible and dates of measurement (first line: Petal 1, second line: Petal 2).

Laboratory (acronym)	Country code	Person responsible	Date of measurement (upper line: Petal 1)
Bundesamt für Eich- und Vermessungswesen (BEV), Austria	AT	Christian Buchner, Zoltan Zelenka	10 Feb. to 25 Feb. 2009
Centro Español de Metrología (CEM), Spain	ES	Nieves Medina	10 Nov. to 16 Dec. 2009 06 April to 12 May 2010
State Office for Metrology (DZM), Croatia	HR	Tijana Parlić-Risović, Mladen Bezjak	05 Feb. to 05 March 2010
Hellenic Institute of Metrology (EIM), Greece	GR	Chris Mitsas, A. Lefkopoulos	23 Dec. 2008 to 28 Jan. 2009
Central Office of Measures (GUM), Poland	PL	Elżbieta Lenard	19 Aug. to 26 Oct. 2009
National Institute of Metrology (INM), Romania	RO	George Florian Popa	12 Jan. to 19 Feb. 2010
Istituto Nazionale di Ricerca Metrologica (INRIM), Italy	IT	Andrea Malengo	08 Sept. to 08 Oct. 2008
Laboratoire National de Métrologie et d'Essais (LNE), France	FR	Tanguy Madec, Florian Beaudoux	04 Nov. to 22 Dec. 2008
Federal Office of Metrology (METAS), Switzerland	CH	Peter Fuchs, Kilian Marti, Christian Wüthrich	25 June to 03 Aug. 2009 25 Sept. to 22 Oct. 2008
Centre for Metrology and Accreditation (MIKES), Finland	FI	Heikki Kajastie	14 Jan. to 22 Jan. 2009
National Institute of Standard (NIS), Egypt	EG	Alaaeldin A. Eltawil	23 Sept. to 16 Dec. 2010
National Metrology Institute of Japan (NMIJ), Japan	JP	Ken-ichi Fujii, Naoki Kuramoto, Atsushi Waseda	12 May to 21 May 2009 17 Nov. 2010 to 18 Jan. 2011
National Physical Laboratory (NPL), United Kingdom	UK	Michael Perkin, Stuart Davidson	12 July to 04 Aug. 2008
Physikalisch-Technische Bundesanstalt (PTB), Germany	DE	Horst Bettin, Michael Borys, Martin Firlus	16 May to 25 June 2008 04 June to 04 Aug. 2008
Tubitak-Ulusal Metroloji Enstitüsü (UME), Turkey	TR	Ümit Y. Akçadağ	11 May to 25 June 2010
D. I. Mendeleyev Institute for Metrology (VNIIM), Russia	RU	Aleksey Domostroev	05 June to 26 June 2009

2.2 Solid samples

Silicon spheres of about 1000 g, 220 g and 35 g were chosen as travelling standards. Each participating institute determined volume and density at 20 °C and 101325 Pa of the travelling standards by hydrostatic weighing. The hydrostatic density determination includes a mass determination of the sample. Although the participants were asked to report also the mass values of the travelling standards, this comparison is not meant as a mass key comparison of the participating NMIs since volume and density determinations usually do not require mass measurements of the highest accuracy.

Due to the large number of participants, two sets of three spheres were sent around in series in two petals. The petals are linked by PTB, CEM, METAS, and NMIJ, who measured all six spheres. Additionally, the smaller spheres were compared to the 1 kg spheres by flotation measurements at PTB. NMIJ also performed some density comparisons by the flotation method (see section 4.2). The flotation measurements allow to link the density of the smaller spheres to the results of the 1 kg spheres and, thus, to the result of the travelling standard D1 of CCM.D-K1.

The set of petal 1 consists of the following travelling standards:

Silicon sphere PTB02, mass 1001 g, diameter 94 mm,
Silicon sphere BEV11, mass 200 g, diameter 55 mm,
Silicon sphere CZ2KB, mass 35 g, diameter 30 mm.

The set of petal 2 consists of the

Silicon sphere NPL01, mass 984 g, diameter 93 mm,
Silicon sphere Sik2, mass 239 g, diameter 58 mm,
Silicon sphere CZ2KA, mass 35 g, diameter 30 mm.

The sphere BEV11 was provided by BEV, and the sphere NPL01 was provided by NPL. All other spheres are from PTB.

Special care had to be taken to ensure that no electrostatic charges are on the spheres, in particular if the sphere has no electrical contact to the suspension or balance pan. Therefore, during weighing in air the relative humidity should be above 40%.
Values for the cubic thermal expansion and for the isothermal compressibility of crystalline silicon were listed in the Technical Protocol, see table 2.

Table 2: Nominal density, cubic thermal expansion coefficient and compressibility of silicon.

Quantity	Value	Standard uncertainty
Nominal density at 20 °C	2329 kg/m^3	
Volume thermal expansion coefficient at 20 °C	7.67 x 10^{-6} K^{-1}	3 x 10^{-8} K^{-1}
Isothermal compressibility at 20 °C	1.20 x 10^{-11} Pa^{-1}	1 x 10^{-13} Pa^{-1}

The spheres had to be measured near 20 °C and at atmospheric pressure. Volume and density had to be reported for 20 °C and 101325 Pa. For each sphere, at least ten weighing sequences had to be performed both in air and in liquid.
The results of the mass measurements are only reported as additional information.

2.3 Organisation of the comparison

The comparison started on March 31, 2008, by agreement on the Technical Protocol.

The participants measured the densities hydrostatically in the time interval from 16 May 2008 to 18 January 2011 (compare table 1) and forwarded their results to the Pilot Laboratory from October 2008 to March 2012.

In February 2012 the pilot laboratory informed the participants about anomalies in the volume and/or density values without giving any hint about amount or sign of the discrepancy. In total 12 anomalies in the values of 5 participants were detected. Anomalies in mass values – although existing – were not reported.

Additionally, the pilot laboratory checked the reports of the participants and asked in February and March 2013 some questions about details in the report that were not completely clear, e.g. method, traceability, calibration, and uncertainty calculation.

The last corrected measurement result was received in May 2013 and the last answer to the questions was received in September 2013.

In January 2013 NIS (Egypt) withdrew all their results due to technical problems. Therefore, no results or information about the measurements at NIS are reported in this report.

Transportation

For transportation, the travelling standards were housed in special transparent cases, see figure 1. The transportation cases were housed in a large aluminium container (see figure 2) that was locked by a combination lock. For the travelling between the participating laboratories, the aluminium container was protected by a cardboard box.

Figure 1: Transparent cases of the spheres

Figure 2: Aluminium container for transportation

Preparation of measurements

The participants were asked to clean the spheres before the measurements with water and pure ethanol (compare cleaning recommendations of CCM.D-K1). The pH value of the liquids should be checked, in particular, if water with a detergent is used. No liquid with a pH value above 7 should be used, as alkaline liquids may attack silicon. The whole cleaning procedure should be checked with another silicon sample, in order to avoid any damage of the travelling standards. The travelling standards should be checked at the beginning and at the end and any damage had to be reported to the Pilot Laboratory. Only small scratches without any significance for this comparison were detected and reported.

After cleaning, the travelling standard should acclimatise for at least 24 hours in the laboratory (under a suitable cover).

The spheres should be cleaned also after the hydrostatic weighing.

3 Apparatuses and Methods

Volume and density determination in this key comparison should be performed by the hydrostatic method. This method usually consists of a weighing comparison to mass standards in air and in a liquid.

The participants used a great variety of apparatuses; the quoted uncertainties of the density of the 1 kg spheres ranged from 0.00046 kg/m^3 to 0.019 kg/m^3 for a confidence level of 95%. The quoted expanded uncertainties of the 1 kg sphere volumes ranged from 0.078 mm^3 to 3.4 mm^3. The uncertainty had to calculated according to the “Guide to the Expression of Uncertainty in Measurement” [4].

3.1 Weighing in air

See table 3 for details about the equipment used for the weighing in air. All participants used commercially available single-pan flexure-hinge electronic balances. The air density was usually determined by pressure, temperature and humidity measurements using the CIPM formula of 2007 (CIPM-2007) [5]. INM used an approximate formula according OIML R111 [6]. NMIJ and NPL used also stainless-steel buoyancy artefacts. The NMIJ and the solid density working group of the PTB determined the mass of the 1 kg spheres by comparison to 1 kg silicon spheres whose mass was determined by using buoyancy artefacts.

METAS used Faraday cages in order to avoid effects by electrostatic charges on the silicon spheres.

Table 3. Details of balances and methods used for measuring the mass of the travelling standards. (CIPM formula see [5], SSW = calibrated stainless-steel weights)

NMI	Balance Maximum load, resolution, electronic range	Air density determination	Reference mass standard
BEV	1000 g, 1 µg, 20 g	CIPM formula	SSW
CEM	1001.5 g, 0.1 µg, 1.5 g 200 g, 10 µg, 200 g	CIPM formula	SSW
DZM	1000 g, 10 µg, 109 g 1011 g, 1 µg, 11 g 111 g, 1 µg, 11 g	CIPM formula	SSW
EIM	1111 g, 10 µg, 111 g	CIPM formula	SSW
GUM	1109 g, 10 µg, 109 g 220 g, 10 µg, 220 g	CIPM formula	SSW
INM	10050 g, 10 µg, 50 g 1 109 g, 10 µg, 109 g 211 g, 1 µg, 11 g	approximate formula acc. to OIML R111	SSW
INRIM	1109 g, 10 µg 109 g	CIPM formula	SSW
LNE	1001.5 g, 0.1 µg, 1.5 g	CIPM formula	SSW
METAS	1001.5 g, 0.1 µg, 1.5 g	CIPM formula	SSW
MIKES	20050 g, 100 µg, 50 g 1000.1 g, 1 µg, 0.15 g	CIPM formula	SSW
NMIJ	1011 g, 1 µg, 11 g	CIPM formula, Stainless steel buoyancy artefacts	Silicon sphere with a mass calibrated by using buoyancy artefacts, SSW
NPL	1001.5 g, 0.01 µg, 2.5 g 210 g, 10 µg, 210 g	Stainless steel buoyancy artefacts, CIPM formula	Calibrated PtIr weight or SSW (BEV11, CZ2KB)
PTB	1300 g, 1 µg, 11 g	CIPM formula	Silicon sphere with a mass calibrated by using buoyancy artefacts, SSW
PTB mass lab	1001.5 g, 0.1 µg, 1.5 g 1001.15 g, 0.1 µg, 0,15 g 111 g, 0.1 µg, 1 g / 0.1 g	Stainless steel buoyancy artefacts	SSW and PtIr
UME	1001.5 g, 0.1 µg, 1.5 g 230 g, 10 µg, 230 g	CIPM formula	SSW
VNIIM	2300 g, 100 µg, 2300 g 520 g, 100 µg, 520 g	CIPM formula	SSW

3.2 Hydrostatic measurements

Table 4 lists details about the equipment used for the hydrostatic weighing. All participants used commercially available single-pan flexure-hinge electronic balances. Not listed in table 4 are the details of the commercially available density comparison apparatus VC1005 made by Mettler-Toledo which was used by five laboratories (CEM, DZM, EIM, INM, UME). This apparatus uses a balance with a maximum load of 1011 g, a resolution of 10 µg, and an electronic balance range of about 109 g. The density standard and the samples are placed on a horizontal rotational circular pan with four places. This apparatus uses 3M Fluorinert Electronic Liquid FC40, an inert liquid of high density (about 1.88 g/cm^3). UME used for the small sphere a different apparatus, see table 4.

Table 4. Details of apparatuses and methods used for hydrostatic weighing of the travelling standards (except the commercially available VC1005).

NMI	Balance Maximum load, resolution, electronic range	Positions of the density standard and the travelling standard in the hydrostatic weighing apparatus	Working liquid
BEV	1200 g, 10 µg, 300 g	Travelling standard placed between two silicon density standards located in different heights.	n-tridecane (n-$C_{13}H_{28}$)
GUM	1109 g, 10 µg, 109 g 220 g, 10 µg, 220 g	Apparatus 1: Three-level vertical suspension. Apparatus 2: Only one sample at each time.	n-nonane (n-C_9H_{20})
INRIM	1109 g, 10 µg, 109 g	Travelling standard and a silicon density standard placed on a rotational circular pan with four places.	Water
LNE	1109 g, 10 µg, 109 g	Sample in water, no solid density standard.	Water
METAS	1109 g, 10 µg, 109 g	Travelling standard placed below a silicon density standard.	Water
MIKES	1109 g, 100 µg, 109 g	Travelling standard or silicon density standard placed on a two-position horizontal weight handler.	Water
NMIJ	1109 g, 10 µg, 109 g	Travelling standard placed between two silicon density standards located in different heights.	n-tridecane (n-$C_{13}H_{28}$)
NPL	1109 g, 10 µg, 109 g 205 g, 10 µg, 205 g	Four position horizontal weight handler. Only one sample at each time.	Water
PTB	1200 g, 1 µg, 11 g	Travelling standard placed between two silicon density standards located in different heights.	n-pentadecane (n-$C_{15}H_{32}$)
UME	405 g, 100 µg, 405 g (only for 35 g sphere)	Only one sample at each time.	Water
VNIIM	2300 g, 100 µg, 2300 g	Only one sample at each time.	Decane ($C_{10}H_{22}$)

In table 5 the density standards, their uncertainties and traceabilities are listed.

Table 5. Reference density standards used in this key comparison (some institutes used different density standards for travelling standards of different size).

NMI	Reference density standard (internal name)	Traceability of		Standard uncertainty of		
		Mass	Volume	Mass mg	Volume mm^3	Density kg/m^3
BEV	448 g silicon spheres (Si2, Si3)	PTB	PTB	0.075	0.25	0.0031
CEM	1000 g silicon sphere (DP4)	CEM	NMIJ	0.125	0.019	0.00031
DZM	980 g silicon spheres (1kg1, 1kg2) 238 g silicon spheres (Nr.1, Nr.2) 33 g silicon sphere (sphere 33g)	METAS PTB METAS	METAS PTB METAS	0.1 0.1 0.075	0.75 0.25 0.4	0.0042 0.0058 0.065
EIM	980 g silicon sphere (SILO 1) Stainless steel 100 g weight	PTB EIM	PTB DKD*	0.021 7.5	0.425 1.5	0.0024 1.1
GUM	997 g silicon sphere (SILO2) 153 g silicon prism (WASO 9.2)	PTB GUM	PTB PTB	0.15 0.077	0.155 0.07	0.00076 0.0010
INM	1000 g silicon sphere (INMSi1000g) 500 g glass weight (INMGs500g) 200 g glass weight (INMGs200g)	PTB INM INM	PTB INM INM	0.08 0.32 0.02	0.25 0.25 0.25	0.0014 0.0039 0.0088
INRIM	1001 g silicon sphere (AVO#2)	INRIM	PTB	0.043	0.033	0.00021
LNE	Water					0.0021
METAS	1000 g silicon sphere (RAW08)	METAS	IMGC**	0.16	0.07	0.00054
MIKES	744 g silicon sphere (Si85) 200 g silicon sphere (Si55) Water		METAS PTB	0.35 0.05	0.20 0.25	0.0018 0.0067 0.0020
NMIJ	1001 g silicon spheres (S4, S5)	NMIJ	NMIJ	0.026	0.058	0.00032
NPL	1006 g Zerodur sphere (S01) 248 g silicon disc (C5) Water	PTB NPL	PTB NPL	0.10 0.124	0.16 0.294	0.0010 0.0065 0.014
PTB	0.87 kg silicon spheres (Si1, Si2) 0.89 kg silicon spheres (Si3, Si4)	PTB PTB	PTB PTB	0.021 0.021	0.031 0.036	0.00019 0.00022
UME	1000 g silicon sphere (24329529) 500 g silicon sphere (24329530) Water	PTB PTB	PTB PTB	0.075 0.075	0.25 0.25	0.0014 0.0027 0.016
VNIIM	949 g Zerodur sphere (VNIIM1)	VNIIM	VNIIM	0.06	0.30	0.0019

*DKD now DAkkS, ** IMGC now INRIM

In the case of water as density standard the Tanaka formula was used [7].

Table 6 lists the quoted standard uncertainties of the main uncertainty contributions in the comparison for the 1 kg spheres, i. e. the uncertainties of the

density of the used density standard,

mass of the travelling standard,

meniscus mass difference for the measurements of water. (During the hydrostatic weighing with a sample, the meniscus mass may differ from the meniscus mass during weighing without sample, which is due to the elongation of the wire or a rise of the liquid surface level.)

Also listed in table 6 are the experimental standard deviations of the mean density and the expanded relative uncertainties (k = 2) of the results for the 1 kg travelling standards.

Table 6. Standard uncertainties of the main components and relative uncertainty of the 1 kg silicon sphere(s) (N/A: not applicable, negl.: neglected).

NMI	St. unc. of density of density standard in kg/m^3	St. unc. of mass of travelling standard in mg	Meniscus effect (for water) in mg	Standard deviation of mean density in 10^{-3} kg/m^3	Uncertainty (k = 2) of density of the 1 kg travelling standard in kg/m^3
BEV	0.0031	0.21	N/A	0.80	0.009
CEM	0.00031	0.78, 0.65	N/A	0.45, 0.61	0.0026, 0.0030
DZM	0.0042	1.1	N/A	0.26	0.0095
EIM	0.0024	0.18	N/A	0.27	0.005
GUM	0.00076	0.42	N/A	0.20	0.0052
INM	0.0014	0.12	N/A	0.19	0.0036
INRIM	0.00021	0.043	negl.	0.10	0.00046
LNE	0.0021	0.068	0.5	1.6	0.0098
METAS	0.0054	0.05, 0.09	0.28	1.0, 1.4	0.0046, 0.0046
MIKES	0.0018	0.38	0.10	0.80	0.016
NMIJ	0.00032	0.03, 0.07	N/A	0.01, 0.06	0.00071, 0.0017
NPL	0.0014	0.25	0.12	1.8	0.0056
PTB	0.00020	0.07	N/A	0.01	0.00059, 0.00061
UME	0.0014	0.076	N/A	0.40	0.0030
VNIIM	0.0019	0.20	N/A	9.2	0.019

At CEM the temperature measurement also contributed significantly to the total uncertainty. Similarly, at MIKES the temperature differences in the bath were important.
INRIM and NPL used platinised wires in order to avoid the meniscus effect in water.
UME did not use the VC1005 for the 35 g sphere, but a different apparatus with water as density standard. UME quoted a standard uncertainty due to the meniscus effect of 0.23 mg.
The tables 4 to 6 again show the large variety of apparatuses and uncertainties.

4 Results of check measurements

4.1 Stability of mass

The mass of the travelling standards was measured in the solid density working group of PTB at the beginning of the comparison (May to July 2008). During the comparison, in February and March 2009 the masses of Petal 1 spheres were checked, and in April 2009 the spheres of Petal 2. At the end of the comparison measurements the masses of all spheres were again checked (Dec. 2011 to Jan. 2012). All these mass measurements were performed in comparison to the masses of the silicon density standards which were calibrated by the PTB mass working group using air density artefacts.
Additionally, the PTB mass working group measured the mass of the spheres with very low uncertainty in January and February 2012 (Petal 1) and in July 2011 (Petal 2).
No significant mass change was detected, compare table 7.

Table 7: Results of the mass stability measurements of the travelling standards at PTB. In brackets: expanded uncertainty for $k = 2$.

a) Petal 1

Date	Mass of PTB02 in g	Date	Mass of BEV11 in g	Date	Mass of CZ2KB in g
22.05.2008	1000.652 289(70)	10.06.2008	200.127 178(40)	25.06.2008	34.662 131(25)
08.02.2009	1000.652 313(70)	05.02.2009	200.127 199(40)	06.02.2009	34.662 138(25)
19.12.2011	1000.652 294(70)	19.01.2012	200.127 155(40)	15.01.2012	34.662 138(25)
10.01.2012	1000.652 296(50)	09.02.2012	200.127 166(20)	09.02.2012	34.662 132(15)

b) Petal 2

Date	Mass of NPL01 in g	Date	Mass of Sik2 in g	Date	Mass of CZ2KA in g
01.07.2008	984.031 347(70)	05.06.2008	238.574 956(50)	19.06.2008	34.668 712(25)
21.04.2009	984.031 353(70)	31.03.2009	238.574 973(50)	28.03.2009	34.668 716(25)
28.07.2011	984.031 340(40)	28.07.2011	238.574 966(15)	28.07.2011	34.668 724(7)
14.12.2011	984.031 344(70)	18.01.2012	238.574 940(50)	28.01.2012	34.668 721(25)

4.2 Flotation measurements

The PTB performed density comparisons of the six travelling standards by the pressure-of-flotation method in the time interval from January 2008 to June 2008. Table 8 lists the results of the flotation measurements obtained at the PTB. The list contains redundant measurements performed to check the data set. The fourth column contains the fitted density differences taking into account the (statistical) uncertainty of the measurements. The fit changes the values by less than 0.000 10 kg/m^3 (0.04 ppm). The uncertainty in the fifth column was calculated by using new calibrations of the compressibility of the liquid mixture used in the flotation apparatus [8]. Since only an expanded uncertainty of 4% is internationally accepted in the CMC tables of PTB, in the following uncertainties are used that are calculated assuming an expanded uncertainty of 4% of the compressibility (last column of table 8).

Table 8: Results of the PTB flotation measurements (last column: uncertainty calculated for a 4% expanded uncertainty of the compressibility).

Sphere 1	Sphere 2	Density difference in kg/m^3	Fitted density difference in kg/m^3	Uncertainty (k = 2) in kg/m^3	CMC uncertainty (k = 2) in kg/m^3
PTB02	CZ2KB	0.004 588	0.004 570	0.000 396	0.000 435
NPL01	BEV11	-0.005 110	-0.005 056	0.000 210	0.000 290
BEV11	CZ2KB	0.020 892	0.020 973	0.000 331	0.000 893
CZ2KB	CZ2KA	-0.000 203	-0.000 233	0.000 196	0.000 196
Sik2	CZ2KA	0.011 767	0.011 827	0.000 340	0.000 578
PTB02	Sik2	-0.007 502	-0.007 493	0.000 140	0.000 328
NPL01	Sik2	0.003 862	0.003 855	0.000 140	0.000 207

The NMIJ compared the density of the travelling standards of Petal 2 (NPL01, Sik2, CZ2KA) with their primary density standard, the silicon sphere S4, in December 2010

(see table 9). Additionally, NMIJ compared the sphere PTB02 with the S4 sphere in September 2011. NMIJ determined the compressibility of their liquid mixture with an expanded uncertainty of 3.6% [9].
The NMIJ values agree with PTB values within the stated uncertainties (even without increasing the compressibility uncertainty of PTB).

Table 9: NMIJ flotation results of four travelling standards in comparison to the primary density standard S4 of NMIJ.

Sphere 1	Sphere 2	Density difference in kg/m^3	Uncertainty (k = 2) in kg/m^3
PTB02	S4	-0.004 9905	0.000 222
NPL01	S4	0.006 3270	0.000 260
Sik2	S4	0.002 4162	0.000 130
CZ2KA	S4	-0.009 6292	0.000 364

5 Reference values

5.1 CCM key comparison CCM.D-K1

The reference values of this regional key comparison are calculated using the results of the CCM key comparison CCM.D-K1, in which the 1 kg silicon sphere named “D1” was used as travelling standard. The link to CCM.D-K1 can be provided by CEM, INRIM, METAS, NMIJ, and PTB. The institutes CEM, METAS, NMIJ, and PTB measured the travelling standards of both petals. The smaller spheres were compared to the 1 kg spheres by flotation measurements at PTB and, partly, at NMIJ, see section 4.2. This allows to link the densities of the smaller spheres to the results of the 1 kg spheres and, thus, to the result of the 1 kg silicon travelling standard D1 of CCM.D-K1. The volume reference values of the smaller spheres can then be calculated from their density values using the mass values. The weighted mean of the mass is calculated taking into account the correlation between the two PTB values (up to about 30% for the 1 kg spheres) but excluding discrepant results (table 10).
Tables 11 and 12 list the degrees of equivalence of the volume and density measurements as determined in the CCM.D-K1 comparison. The uncertainty of the NMIJ in the CCM.D-K1 was far smaller than the uncertainties of all other participants, in particular for the linking labs, see tables 11 and 12. Thus, NMIJ determines mainly the key comparison reference value of CCM.D-K1 and of this key comparison.

The last two columns of tables 11 and 12 list the correlation coefficients between the current measurements and the measurements for CCM.D-K1. INRIM did not measure the travelling standard NPL01. The result for the sphere NPL01 by METAS is not used because it is obviously erroneous.

Table 10. Mass values of the travelling standards, calcuated from all measured masses including the results of the PTB mass lab but without discrepant results (last column), compare section 6.

Sphere	Mean mass value in g	Uncertainty (k = 2) in g	Excluded since discrepant
PTB02	1000.652 306	0.000 029	DZM
NPL01	984.031 341	0.000 035	EIM, METAS
BEV11	200.127 163	0.000 013	
Sik2	238.574 966	0.000 015	CEM, METAS, VNIIM
CZ2KB	34.662 137	0.000 007	CEM, MIKES, UME
CZ2KA	34.668 722	0.000 007	CEM

Table 11. Degrees of equivalence (D_{CCM}) of the volume and their uncertainties as determined in the CCM key comparison CCM.D-K1 [2, 3]. The last two columns list the correlation coefficients between the current measurements and the measurements for CCM.D-K1.

NMI	D_{CCM} in mm^3	Uncertainty (k = 2) in mm^3	Correlation coefficient for PTB02	Correlation coefficient for NPL01
NMIJ	0.038	0.057	0.9	0.3
PTB	0.031	0.665	0.1	0.1
INRIM	0.018	0.734	0.1	-
METAS	-0.843	0.841	0.7	-
CEM	-0.023	0.817	0.5	0.5

Table 12. Degrees of equivalence (D_{CCM}) of the density and their uncertainties as determined in the CCM key comparison CCM.D-K1 [2, 3]. The last two columns list the correlation coefficients between the current measurements and the measurements for CCM.D-K1.

NMI	D_{CCM} in kg/m³	Uncertainty (k = 2) in kg/m³	Correlation coefficient for PTB02	Correlation coefficient for NPL01
NMIJ	-0.00010	0.00024	0.9	0.4
PTB	-0.00014	0.00373	0.1	0.1
INRIM	-0.00020	0.00399	0.1	-
METAS	0.00459	0.00458	0.7	-
CEM	0.00037	0.00443	0.5	0.6

5.2 Reference values for the 1 kg spheres

From the volume or density results x_i of the link laboratories (see tables 17, 18, 26 and 27) for the 1 kg spheres and the Degrees of Equivalence $D_{\mathrm{CCM}i}$ of CCM.D-K1, the reference values $x_{\mathrm{R}i}$ and their expanded uncertainties $U_{\mathrm{R}i}$ are calculated by

$$x_{\mathrm{R}i} = x_i - D_{\mathrm{CCM}i} \quad \text{and} \tag{1}$$

$$U_{\mathrm{R}i} = \sqrt{(U^2(D_{\mathrm{CCM}i}) + U^2(x_i) - 8\,\mathrm{cov}(D_{\mathrm{CCM}i}, x_i))} \tag{2}$$

The covariance can be calculated with the correlation coefficient r_i by:

$$\mathrm{cov}(D_{\mathrm{CCM}i},x_i) = r_i\,U(D_{\mathrm{CCM}i})\,U(x_i) / 4. \tag{3}$$

Then, the reference values of volume and density can be calculated by the weighted mean of the $x_{\mathrm{R}i}$.

The tables 13 and 14 list the density and volume reference values of the 1 kg spheres as determined by the link to the CCM.D-K1. For the columns two and three all possible link laboratories were used to calculate the reference values. The volume and density values of the link laboratories CEM, INRIM, METAS, NMIJ and PTB for the sphere PTB02 are consistent with a Birge ratio below 1. The volume and density values of the link laboratories CEM, NMIJ and PTB for the sphere NPL01 are also consistent with a

Birge ratio below 1. The values of METAS for the sphere NPL01 are obviously erroneous and are therefore not used for the link.

On the right two columns in the tables 13 and 14 only the NMIJ values are used to calculate the reference values. This yields nearly the same result since the uncertainty of the Degree of Equivalence of NMIJ in the CCM.D-K1 comparison is far smaller than those of the other link laboratories. Therefore, in the following evaluations only the link by NMIJ is used. This simplifies greatly the calculation because no correlations between the linking laboratories must be taken into account.

Table 13. Density reference values of the 1 kg spheres as determined from the link to the CCM.D-K1. For the two right columns only the NMIJ values are used to calculate the reference values. The second lines are calculated using the flotation results (see section 5.3).

Travelling standard	Density reference value in kg/m^3	Uncertainty (k = 2) in kg/m^3	Density reference value in kg/m^3	Uncertainty (k = 2) in kg/m^3
PTB02	2329.082 66	0.000 49	2329.082 70 2329.082 63	0.000 51 0.000 49
NPL01	2329.093 19	0.001 37	2329.093 30 2329.093 98	0.001 62 0.000 50

Table 14. Volume reference values of the 1 kg spheres as determined from the link to the CCM.D-K1. For the two right columns only the NMIJ values are used to calculate the reference values. The second lines in the right columns are calculated using the flotation results and the mean mass values.

Travelling standard	Volume reference value in cm^3	Uncertainty (k = 2) in cm^3	Volume reference value in cm^3	Uncertainty (k = 2) in cm^3
PTB02	429.633 640	0.000 089	429.633 632 429.633 664	0.000 092 0.000 091
NPL01	422.495 459	0.000 272	422.495 442 422.495 334	0.000 328 0.000 092

The uncertainties of the reference values of the sphere PTB02 are nearly the same as the uncertainties of the reference values of the sphere D1 of the key comparison CCM.D-K1, which were determined as 0.000 135 cm^3 and 0.000 69 kg/m^3 (k = 2).

A more accurate density value of NPL01 is determined by using the PTB02 density value in combination with the flotation results of NMIJ and PTB for the density difference of the spheres, see second lines in table 13. This adjustment is performed together with the calculation of the density values of the smaller spheres, see section 5.3, and affects also slightly the density value of PTB02.

The final volume reference values in the second lines of table 14 are calculated from the density reference values and the mean mass values (tables 13 and 10).
The weighted mean value of the PTB02 mass (including the mass result of the PTB mass lab, but except the discrepant value of DZM, compare table 16 and figure 3) is: (1000.652 306 ± 0.000029) g. The weighted mean value of the NPL01 mass (including the mass result of the PTB mass lab, but except the discrepant EIM and METAS values) is: (984.031 341 ± 0.000 035) g (compare table 25 and figure 12). The uncertainty of the volume value is calculated from the uncertainties of density and mass neglecting possible correlations.

5.3 Reference values for the smaller spheres

The density reference values for the smaller samples (see table 15) are calculated from the reference values of the 1 kg spheres and the results of the pressure-of-flotation method (see section 4.2) by a least squares adjustment. This adjustment uses the hydrostatically determined values of the PTB02 and NPL01 spheres (first lines of the two right columns of table 13), the flotation density difference values of NMJ (table 9) and the fitted flotation density difference values of PTB (see table 8). The two redundant comparisons of PTB "BEV11-CZ2KB" and "Sik2-CZ2KA" are not used for this adjustment, since they are included for the fit of the density comparisons (see section 4.2). The flotation measurements are highly correlated (or anti-correlated), since the main uncertainty contribution stems from the compressibility value of the measuring liquid (see section 4.2). Due to the high precision of the flotation measurements, these correlations affect the final density values only by up to 0.000 05 kg/m^3 (or 0.02 ppm).

Table 15. Density and volume reference values of the smaller spheres as determined using the flotation measurements and – for the volume values – the mass measurements.

Sphere	Density reference value in kg/m^3	Uncertainty (k = 2) in kg/m^3	Volume reference value in cm^3	Uncertainty (k = 2) in cm^3
BEV11	2329.098 97	0.000 52	85.924 714	0.000 020
Sik2	2329.090 13	0.000 50	102.432 690	0.000 023
CZ2KB	2329.077 93	0.000 58	14.882 343	0.000 005
CZ2KA	2329.078 13	0.000 58	14.885 169	0.000 005

6 Results of participants and data analysis

In this section the results reported by the participants are given. The volume and density values are for a temperature of 20 °C and a pressure of 101325 Pa. Mass values are only used to calculate the volume reference values of the spheres from the density reference values.

The Degree of Equivalence D_i of the laboratory i with respect to the reference value x_{ref} with expanded uncertainty U_{ref} (see section 5) is calculated by

$$D_i = x_i - x_{\mathrm{ref}}, \tag{4}$$

with an expanded uncertainty

$$U(D_i) = \sqrt{U_i^2 + U_{\mathrm{ref}}^2}\ , \tag{5}$$

where x_i and $U(x_i)$ are the laboratory results and their expanded uncertainties, respectively.

The normalised error E_{n} of the laboratory i with respect to the reference value x_{ref} is calculated by

$$E_{\mathrm{n}} = \frac{x_i - x_{\mathrm{ref}}}{\sqrt{U_i^2 + U_{\mathrm{ref}}^2}} = \frac{D_i}{U(D_i)}. \tag{6}$$

The pilot laboratory informed the participants about anomalies in the volume and/or density values. Anomalies in mass values – although existing – were not reported.

Since no significant mass drift of the travelling standards could be observed and the influence of a possible drift (and its uncertainty) is negligible, no drift correction is made.

Sometimes participants calculated an uncertainty that is different to the uncertainty that is calculated by the Excel report sheet. In this case the uncertainty of the laboratory is used here.

6.1 Travelling standard PTB02 (Petal 1)

The density reference value (2329.082 63 ± 0.000 49) kg/m^3 for the travelling standard PTB02 was calculated by the link to the CCM.D-K1 comparison, slightly modified by the flotation comparisons, see section 5.2, table 13.
The weighted mean value (considering the correlation between the two PTB values of about 30%) of the PTB02 mass (1000.652 306 ± 0.000029) g is used to calculate the volume reference value (429.633 664 ± 0.000 091) cm^3 (see tables 10 and 14).
The reported mass, volume and density results for the silicon sphere PTB02 are listed in tables 16 to 18 and displayed in figures 3 to 5 in comparison to the mean or reference values. No severe discrepancy in the density or volume values is observed. The discrepancy of the DZM mass value has no consequence for their volume or density values.
The NMIJ determined the density of the PTB02 also by flotation comparison to one of their density standards. Result is: (2329.08238 ± 0.00068) kg/m^3.

Table 16: Reported mass results of the participants for the travelling standard PTB02. (PTB(m) denotes the mass lab of PTB.)

Institute	Mass in g	Uncertainty (95%) in g
CEM	1000.65238	0.00015
DZM	1000.65142	0.00063
GUM	1000.652558	0.000820
INRIM	1000.652269	0.000086
LNE	1000.65228	0.00014
METAS	1000.652385	0.000099
MIKES	1000.6520	0.0008
NMIJ	1000.652296	0.000056
NPL	1000.65233	0.00050
PTB	1000.652289	0.000070
PTB(m)	1000.652296	0.000050
UME	1000.65239	0.00015

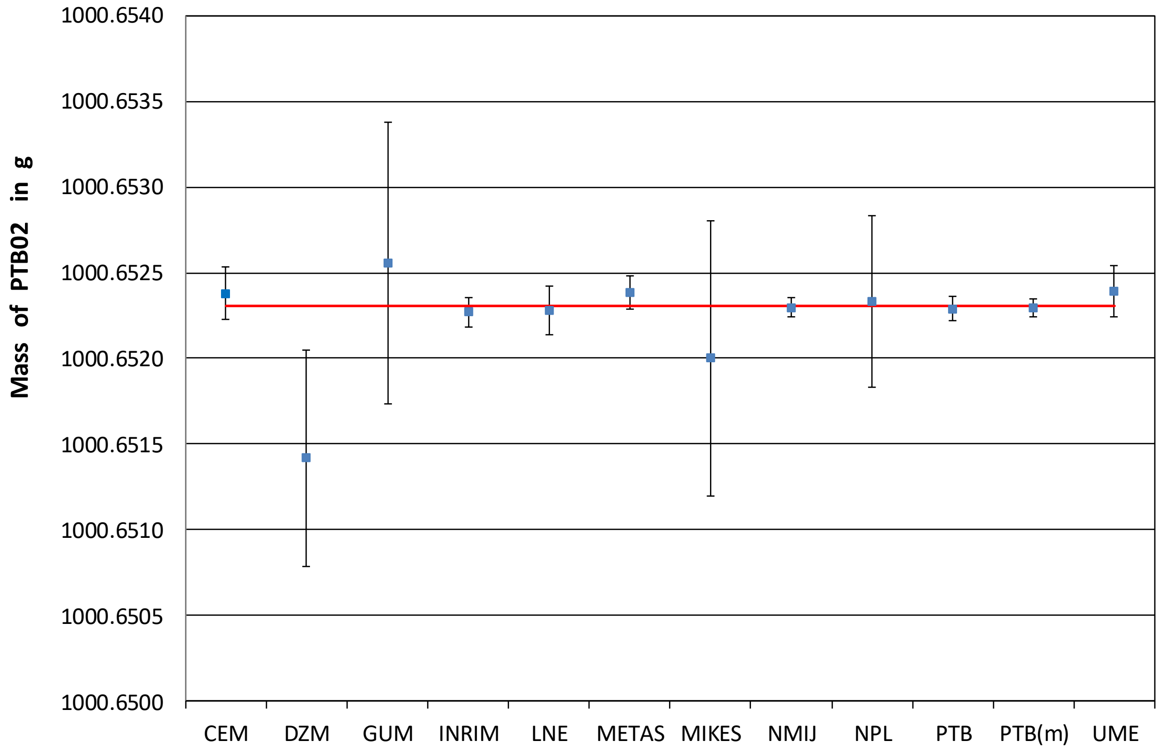

Figure 3: Reported mass results of the participants for the travelling standard PTB02 and the mean value (red line). The uncertainties are for a confidence level of 95%.

Table 17: Reported volume results of the participants for the travelling standard PTB02 with the resulting Degrees of Equivalence *D* and the normalized errors E_n.

Institute	Volume at 20 °C in cm^3	Uncertainty (95%) in cm^3	D in cm^3	$U(D)$ in cm^3	E_n
CEM	429.63378	0.00048	0.00012	0.00049	0.24
DZM	429.6333	0.0016	-0.00036	0.00160	-0.23
GUM	429.63275	0.00128	-0.00091	0.00128	-0.71
INRIM	429.633688	0.000078	0.00002	0.00012	0.20
LNE	429.6348	0.0018	0.00114	0.00180	0.63
METAS	429.63304	0.00077	-0.00062	0.00078	-0.80
MIKES	429.6324	0.0029	-0.00126	0.00290	-0.44
NMIJ	429.63367	0.00014	0.00001	0.00017	0.04
NPL	429.6338	0.0010	0.00014	0.00100	0.14
PTB	429.633652	0.000110	-0.00001	0.00014	-0.08
UME	429.63377	0.00057	0.00011	0.00058	0.18

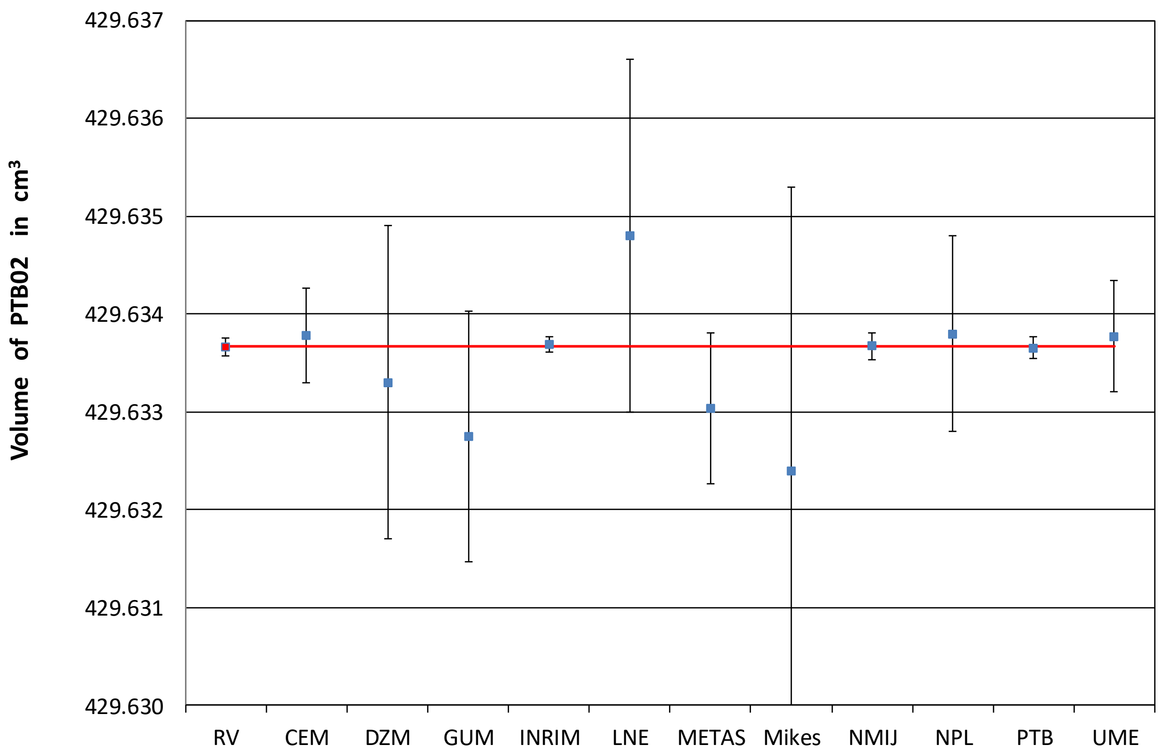

Figure 4: Reported volume results of the participants for the travelling standard PTB02 and the reference value (RV). The uncertainties are for a confidence level of 95%.

Table 18: Reported density results of the participants for the travelling standard PTB02 with the resulting Degrees of Equivalence *D* and the normalized errors E_n.

Institute	Density at 20 °C in kg/m³	Uncertainty (95%) in kg/m³	*D* in kg/m³	*U*(*D*) in kg/m³	E_n
CEM	2329.0822	0.0026	-0.00043	0.00265	-0.16
DZM	2329.0825	0.0087	-0.00013	0.00871	-0.01
GUM	2329.08819	0.00523	0.00556	0.00525	1.06
INRIM	2329.08242	0.00046	-0.00021	0.00067	-0.31
LNE	2329.0764	0.0097	-0.00623	0.00971	-0.64
METAS	2329.0860	0.0046	0.00337	0.00463	0.73
MIKES	2329.089	0.016	0.00637	0.01601	0.40
NMIJ	2329.08260	0.00071	-0.00003	0.00086	-0.03
NPL	2329.0818	0.0056	-0.00083	0.00562	-0.15
PTB	2329.08266	0.00059	0.00003	0.00077	0.04
UME	2329.082	0.003	-0.00063	0.00304	-0.21

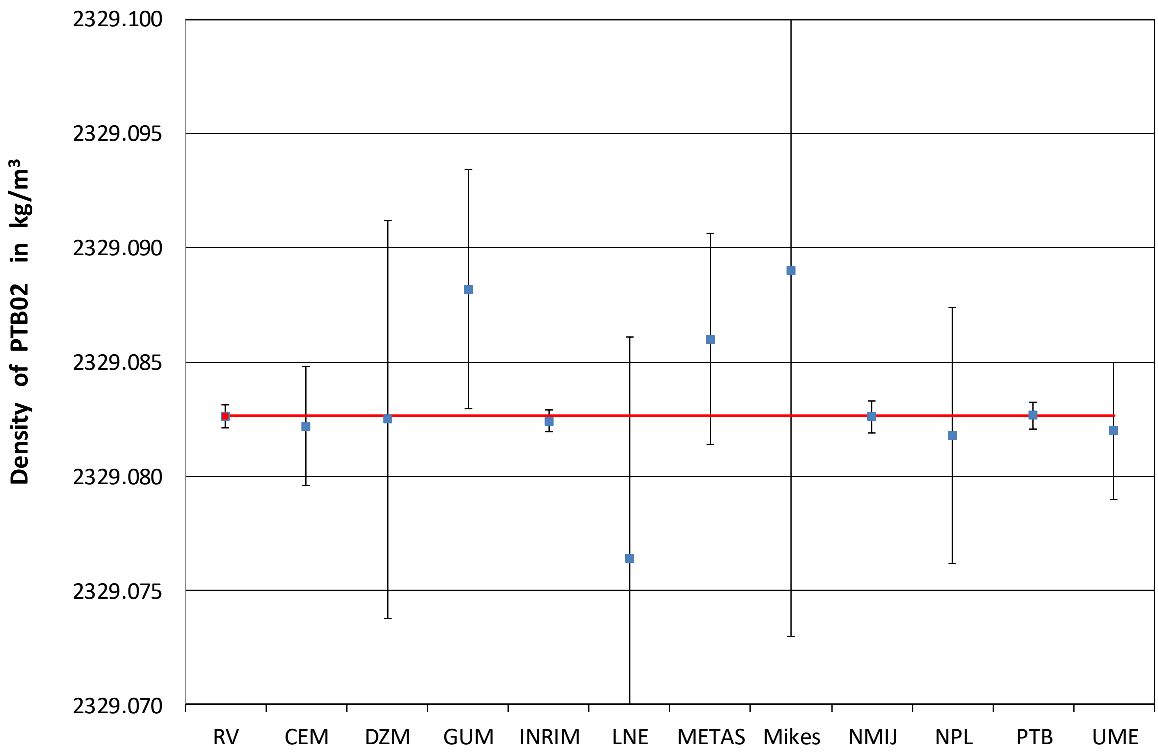

Figure 5: Reported density results of the participants for the travelling standard PTB02 and the reference value (RV). The uncertainties are for a confidence level of 95%.

6.2 Travelling standard BEV11 (Petal 1)

The reference density value (2329.098 97 ± 0.000 52) kg/m^3 for the travelling standard BEV11 was determined by the flotation measurements in comparison to the 1 kg travelling standards PTB02 and NPL01, see section 5.3, table 15.
No discrepancy in the mass determinations is observed. The weighted mean value (taking into account the correlation between the two PTB values of about 10%) of the BEV11 mass (200.127 163 ± 0.000 013) g is used to calculate the volume reference value (85.924 714 ± 0.000 020) cm^3.

The reported mass, volume and density results for the silicon sphere BEV11 are listed in tables 19 to 21 and displayed in figures 6 to 8 in comparison to the mean or reference values. Only the LNE volume and density values show a severe discrepancy. (This anomaly had been reported to the LNE.)

Table 19: Reported mass results of the participants for the travelling standard BEV11. (PTB(m) denotes the mass lab of PTB.)

Institute	Mass in g	Uncertainty (95%) in g
CEM	200.127174	0.000039
DZM	200.12716	0.00004
GUM	200.127214	0.000172
INRIM	200.127150	0.000048
LNE	200.127142	0.000031
METAS	200.127178	0.000061
MIKES	200.12712	0.00014
NMIJ	200.12714	0.00029
NPL	200.12717	0.00010
PTB	200.127178	0.000040
PTB(m)	200.127166	0.000020
UME	200.12722	0.00013

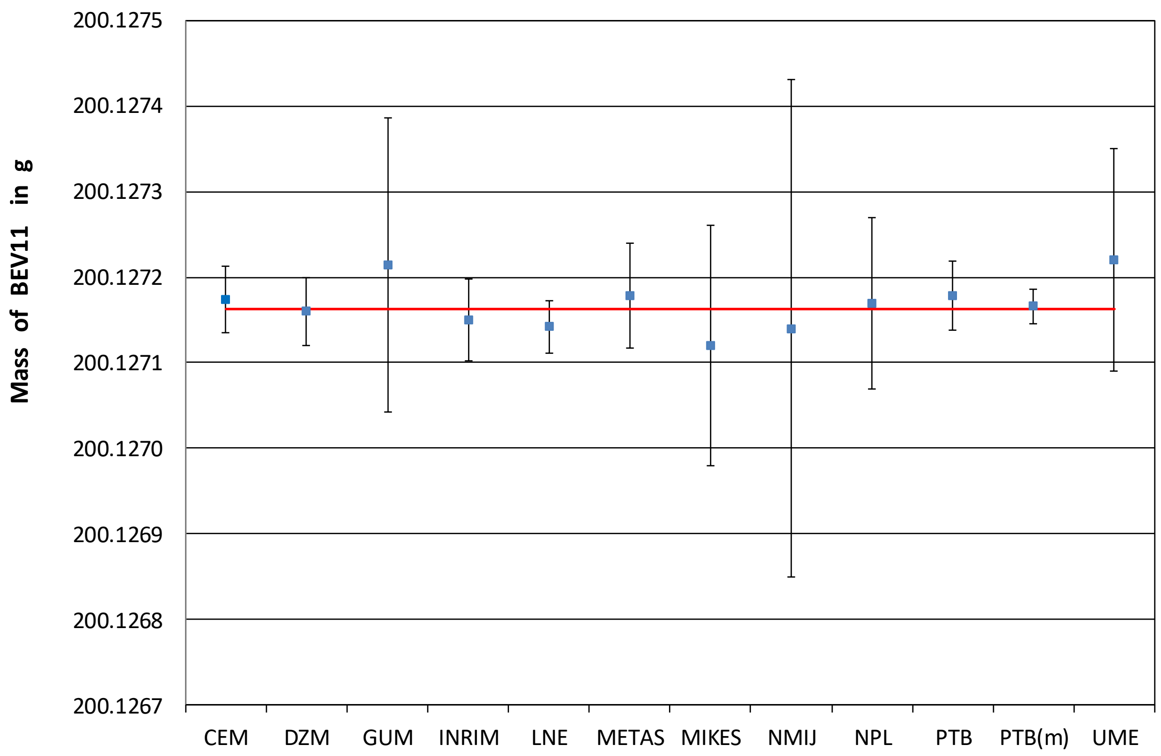

Figure 6: Reported mass results of the participants for the travelling standard BEV11 and the mean value. The uncertainties are for a confidence level of 95%.

Table 20: Reported volume results of the participants for the travelling standard BEV11 with the resulting Degrees of Equivalence *D* and the normalized errors E_n.

Institute	Volume at 20 °C in cm³	Uncertainty (95%) in cm³	*D* in cm³	*U*(*D*) in cm³	E_n
CEM	85.9250	0.0058	0.00029	0.00580	0.05
DZM	85.9248	0.0005	0.00009	0.00061	0.14
GUM	85.925127	0.000612	0.00041	0.00061	0.68
INRIM	85.924774	0.000090	0.00006	0.00009	0.65
LNE	85.92660	0.00114	0.00189	0.00114	1.65
METAS	85.92422	0.00080	-0.00049	0.00080	-0.62
MIKES	85.9246	0.0010	-0.00011	0.00100	-0.11
NMIJ	85.92470	0.00049	-0.00001	0.00049	-0.03
NPL	85.92481	0.00080	0.00010	0.00080	0.12
PTB	85.924779	0.000097	0.00007	0.00010	0.66
UME	85.92601	0.00114	0.00130	0.00114	1.14

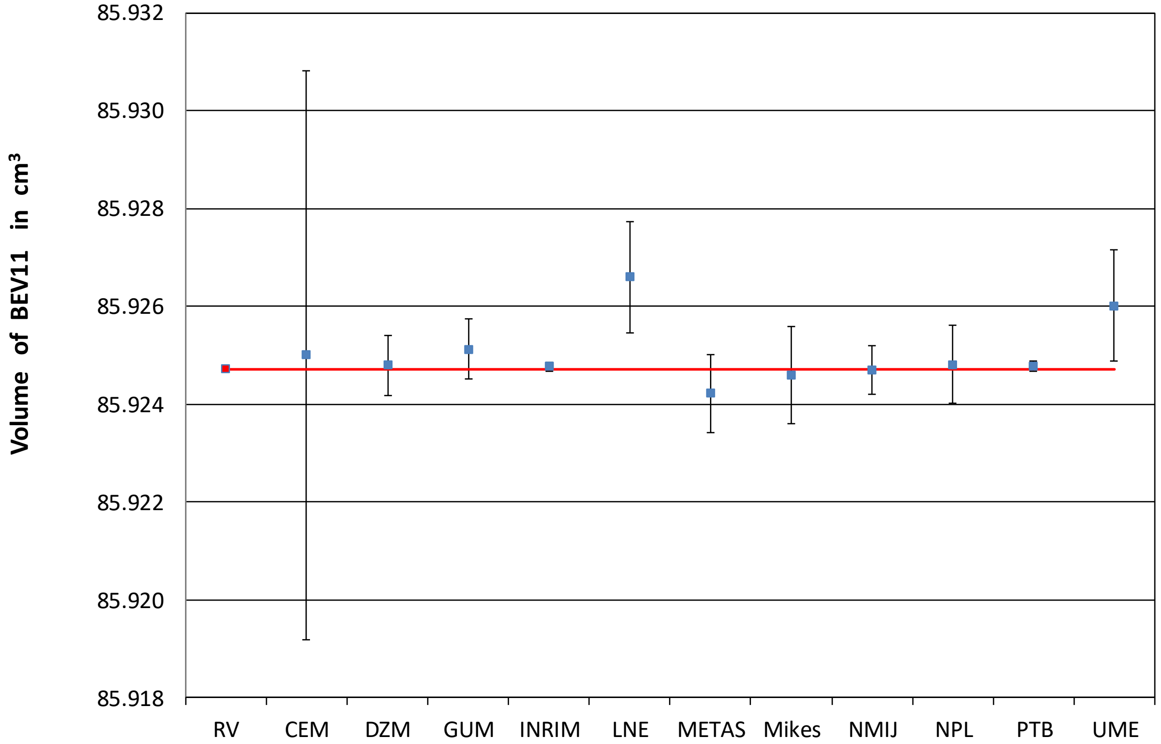

Figure 7: Reported volume results of the participants for the travelling standard BEV11 and the reference value (RV). The uncertainties are for a confidence level of 95%.

Table 21: Reported density results of the participants for the travelling standard BEV11 with the resulting Degrees of Equivalence *D* and the normalized errors E_n.

Institute	Density at 20 °C in kg/m³	Uncertainty (95%) in kg/m³	*D* in kg/m³	*U*(*D*) in kg/m³	E_n
CEM	2329.09	0.13	-0.0090	0.1300	-0.07
DZM	2329.0957	0.0146	-0.0033	0.0146	-0.22
GUM	2329.0884	0.0159	-0.0106	0.0159	-0.66
INRIM	2329.0972	0.0026	-0.0018	0.0027	-0.67
LNE	2329.048	0.031	-0.0510	0.0310	-1.64
METAS	2329.1125	0.0183	0.0135	0.0183	0.74
MIKES	2329.102	0.027	0.0030	0.0270	0.11
NMIJ	2329.099	0.011	0.0000	0.0110	0.00
NPL	2329.096	0.022	-0.0030	0.0220	-0.13
PTB	2329.0974	0.0024	-0.0016	0.0025	-0.64
UME	2329.065	0.031	-0.0340	0.0310	-1.10

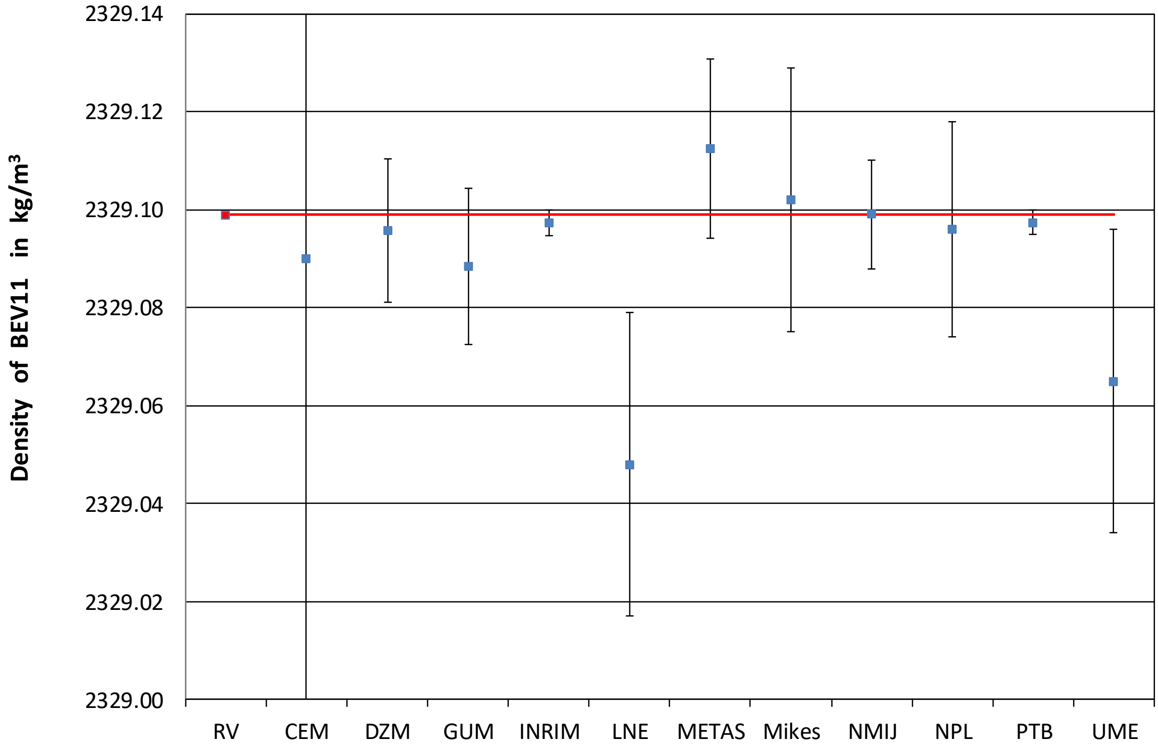

Figure 8: Reported density results of the participants for the travelling standard BEV11 and the reference value (RV). The uncertainties are for a confidence level of 95%.

6.3 Travelling standard CZ2KB (Petal 1)

The density reference value (2329.077 93 ± 0.000 58) kg/m^3 for the travelling standard CZ2KB was determined by the flotation measurements in comparison to the 1 kg travelling standards PTB02 and NPL01, see section 5.3, table 15.
The mass values of CEM, MIKES and UME for the travelling standard CZ2KB are discrepant but this has no severe consequences for the volume or density values. The weighted mean value (taking into account the correlation between the two PTB values of about 20%) of the mass (34.662 137 ± 0.000 007) g is used to calculate the volume reference value (14.882 343 ± 0.000 005) cm^3.
The reported mass, volume and density results for the silicon sphere CZ2KB are listed in tables 22 to 24 and are displayed in figures 9 to 11 in comparison to the mean or reference values. Only the LNE volume and density values shows a discrepancy. (This anomaly had been reported to the LNE.)

Table 22: Reported mass results of the participants for silicon sphere CZ2KB.
(PTB(m) denotes the mass lab of PTB.)

Institute	Mass in g	Uncertainty (95%) in g
CEM	34.662085	0.000032
DZM	34.66215	0.00002
GUM	34.662126	0.000091
INRIM	34.662146	0.000026
LNE	34.662136	0.000011
METAS	34.662127	0.000025
MIKES	34.66189	0.00010
NMIJ	34.66214	0.00012
NPL	34.66214	0.00004
PTB	34.662131	0.000025
PTB(m)	34.662132	0.000015
UME	34.66219	0.00004

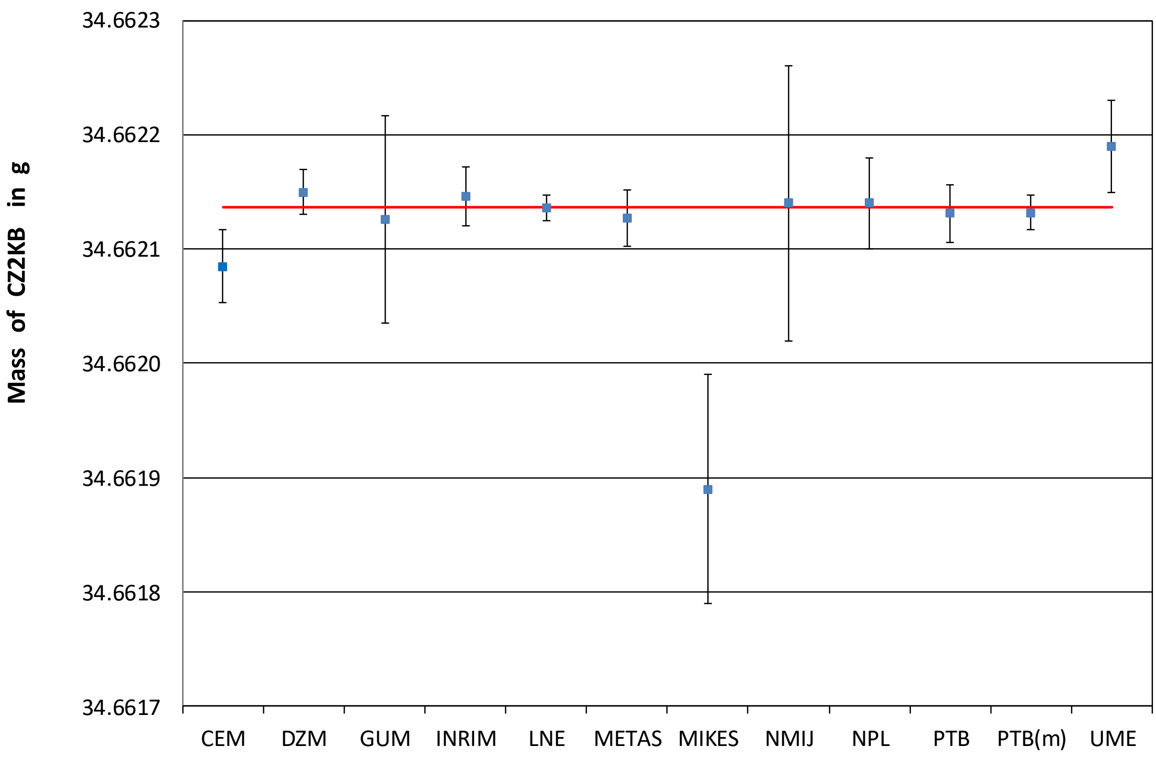

Figure 9: Reported mass results of the participants for the travelling standard CZ2KB and the mean value (red line). The uncertainties are for a confidence level of 95%.

Table 23: Reported volume results of the participants for the travelling standard CZ2KB with the resulting Degrees of Equivalence *D* and the normalized errors E_n.

Institute	Volume at 20 °C in cm^3	Uncertainty (95%) in cm^3	*D* in cm^3	*U*(*D*) in cm^3	E_n
CEM	14.8844	0.0058	0.00206	0.00580	0.35
DZM	14.8827	0.0008	0.00036	0.00080	0.45
GUM	14.882372	0.000595	0.00003	0.00060	0.05
INRIM	14.882380	0.000090	0.00004	0.00009	0.41
LNE	14.8838	0.0011	0.00146	0.00110	1.32
METAS	14.88198	0.00080	-0.00036	0.00080	-0.45
MIKES	14.8821	0.0008	-0.00024	0.00080	-0.30
NMIJ	14.88233	0.00038	-0.00001	0.00038	-0.03
NPL	14.88255	0.00050	0.00021	0.00050	0.41
PTB	14.882254	0.000096	-0.00009	0.00010	-0.93
UME	14.88285	0.00076	0.00051	0.00076	0.67

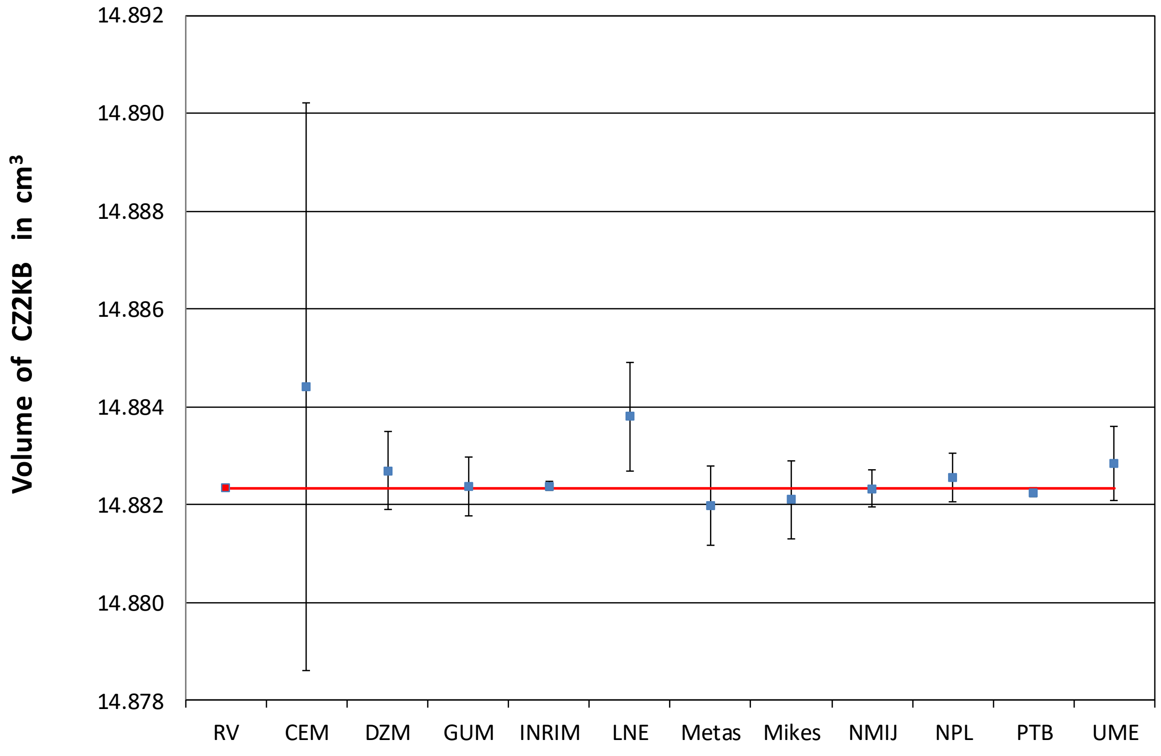

Figure 10: Reported volume results of the participants for the travelling standard CZ2KB and the reference value (RV). Uncertainties are for a confidence level of 95%.

Table 24: Reported density results of the participants for the travelling standard CZ2KB with the resulting Degrees of Equivalence *D* and the normalized errors E_n.

Institute	Density at 20 °C in kg/m³	Uncertainty (95%) in kg/m³	D in kg/m³	$U(D)$ in kg/m³	E_n
CEM	2328.75	0.90	-0.328	0.900	-0.36
DZM	2329.021	0.126	-0.057	0.126	-0.45
GUM	2329.0725	0.0921	-0.005	0.092	-0.06
INRIM	2329.073	0.015	-0.005	0.015	-0.33
LNE	2328.85	0.17	-0.228	0.170	-1.34
METAS	2329.134	0.125	0.056	0.125	0.45
MIKES	2329.10	0.13	0.022	0.130	0.17
NMIJ	2329.080	0.057	0.002	0.057	0.04
NPL	2329.046	0.072	-0.032	0.072	-0.44
PTB	2329.0915	0.0150	0.014	0.015	0.90
UME	2329.002	0.118	-0.076	0.118	-0.64

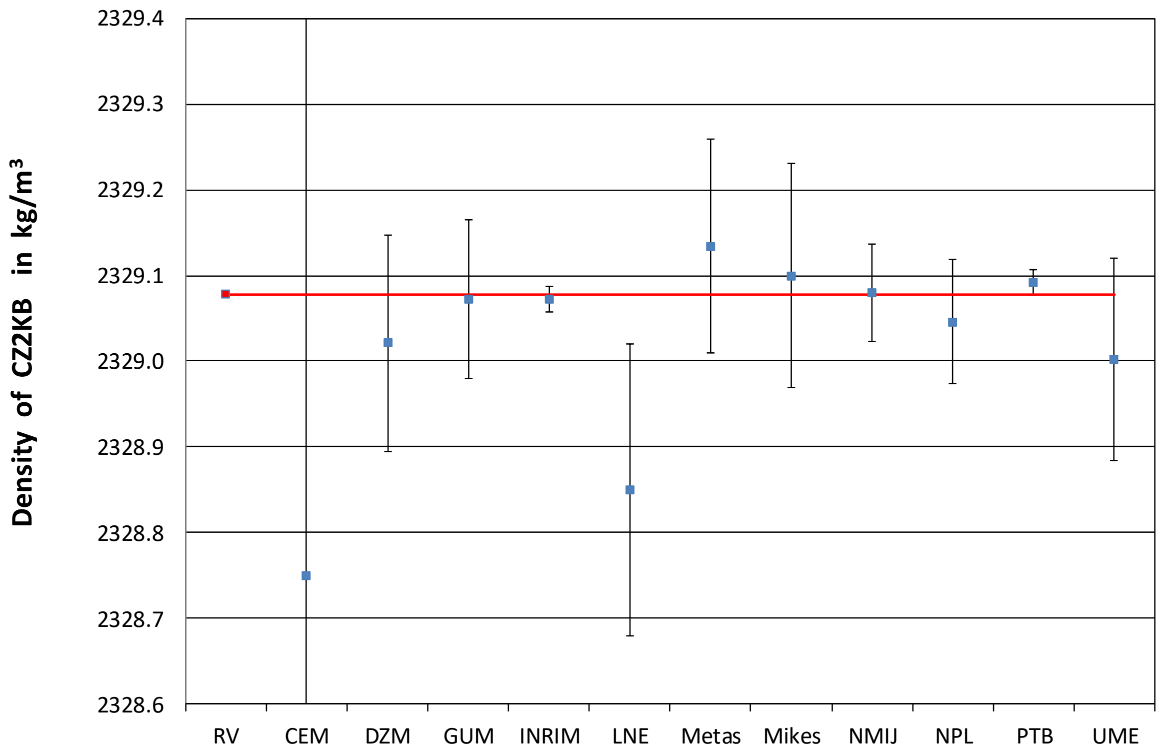

Figure 11: Reported density results of the participants for the travelling standard CZ2KB and the reference value (RV). The uncertainties are for a confidence level of 95%.

6.4 Travelling standard NPL01 (Petal 2)

The density reference value (2329.093 98 ± 0.000 50) kg/m^3 for the travelling standard NPL01 was calculated by the link to the CCM.D-K1 comparison and the flotation measurements, see section 5.2, table 13.

The weighted mean value (taking into account the correlation between the two PTB values of about 30 %) of the NPL01 mass (984.031 341 ± 0.000 035) g is used to calculate the volume reference value (422.495 334 ± 0.000 092) cm^3 (see tables 10 and 14).

The reported mass, volume and density results for the silicon sphere NPL01 are listed in tables 25 to 27 and are displayed in figures 12 to 14 in comparison to the mean or reference values. Only the METAS values are discrepant. (This had been reported to the METAS.) These discrepancies are the consequence of the erroneous mass value. The mass discrepancy of EIM has no consequence for the volume or density values.

The NMIJ determined the density of the NPL01 also by flotation comparison to one of their density standards. Result is: (2329.093 70 ± 0.000 70) kg/m^3.

Table 25: Reported mass results of the participants for the travelling standard NPL01. (PTB(m) denotes the mass lab of PTB.)

Institute	Mass in g	Uncertainty (95%) in g
BEV	984.03117	0.00042
CEM	984.03134	0.00013
EIM	984.0325	0.0004
INM	984.03134	0.00023
METAS	984.043147	0.000177
NMIJ	984.03135	0.00014
PTB	984.031347	0.000070
PTB(m)	984.031340	0.000040
VNIIM	984.03147	0.00040

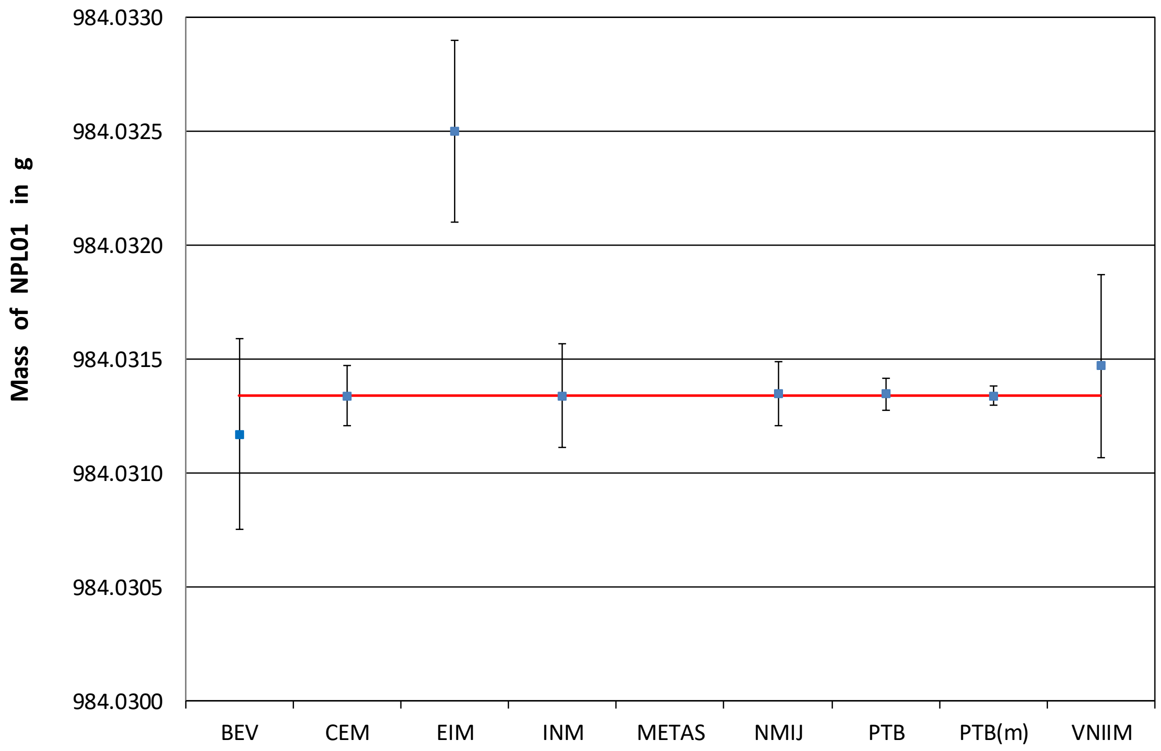

Figure 12: Reported mass results of the participants for the travelling standard NPL01 and the mean value (red line). The uncertainties are for a confidence level of 95%. The value of METAS is outside the scale.

Table 26: Reported volume results of the participants for the travelling standard NPL01. The volume value of METAS is discrepant due to an erroneous mass value.

Institute	Volume at 20 °C in cm³	Uncertainty (95%) in cm³	*D* in cm³	*U*(*D*) in cm³	E_n
BEV	422.4951	0.0016	-0.00023	0.00160	-0.15
CEM	422.49552	0.00050	0.00019	0.00051	0.37
EIM	422.4961	0.0009	0.00077	0.00090	0.85
INM	422.49526	0.00053	-0.00007	0.00054	-0.14
METAS	422.50668	0.00084	0.01135	0.00085	13.43
NMIJ	422.49548	0.00034	0.00015	0.00035	0.41
PTB	422.495487	0.000120	0.00015	0.00015	1.01
VNIIM	422.4980	0.0034	0.00267	0.00340	0.78

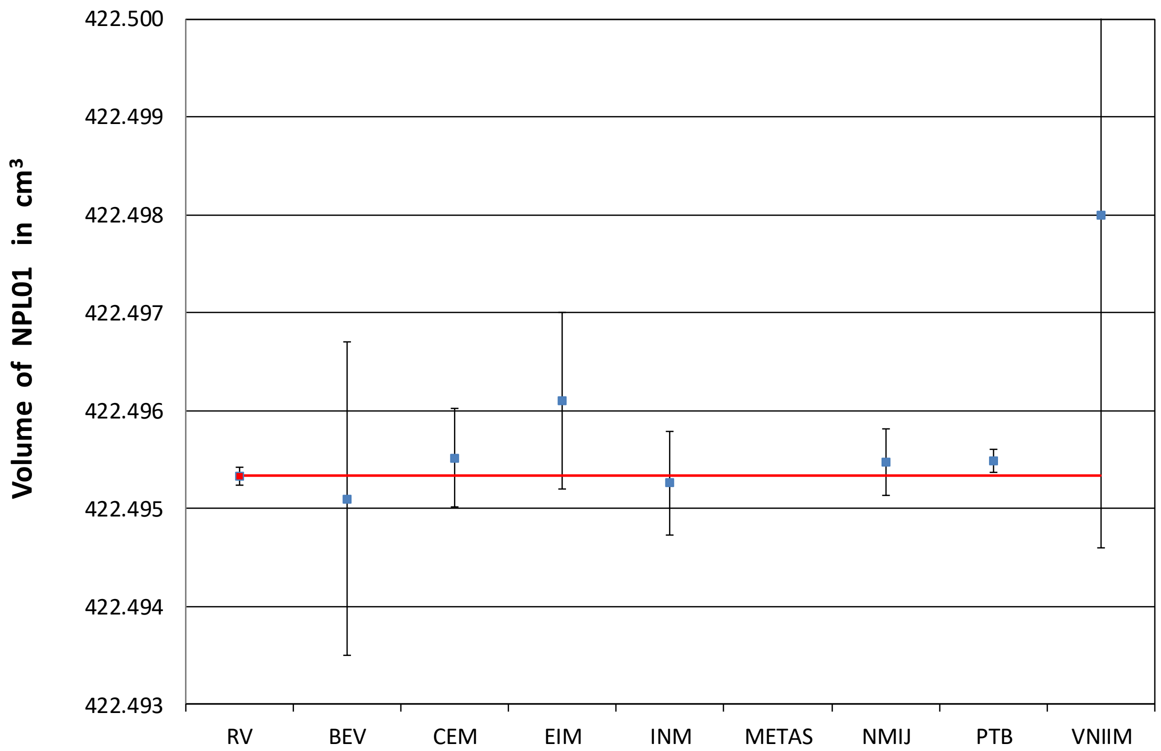

Figure 13: Reported volume results of the participants for the travelling standard NPL01 and the reference value (RV). The uncertainties are for a confidence level of 95%. The value of METAS is outside the scale.

Table 27: Reported density results of the participants for the travelling standard NPL01. The density value of METAS is discrepant due to an erroneous mass value.

Institute	Density at 20 °C in kg/m^3	Uncertainty (95%) in kg/m^3	D in kg/m^3	$U(D)$ in kg/m^3	E_n
BEV	2329.0948	0.0086	0.0008	0.0086	0.10
CEM	2329.0929	0.0030	-0.0011	0.0030	-0.36
EIM	2329.092	0.005	-0.0020	0.0050	-0.39
INM	2329.0944	0.0036	0.0004	0.0036	0.12
METAS	2329.0590	0.0046	-0.0350	0.0046	-7.56
NMIJ	2329.0932	0.0017	-0.0008	0.0018	-0.44
PTB	2329.09315	0.00061	-0.0008	0.0008	-1.05
VNIIM	2329.080	0.019	-0.0140	0.0190	-0.74

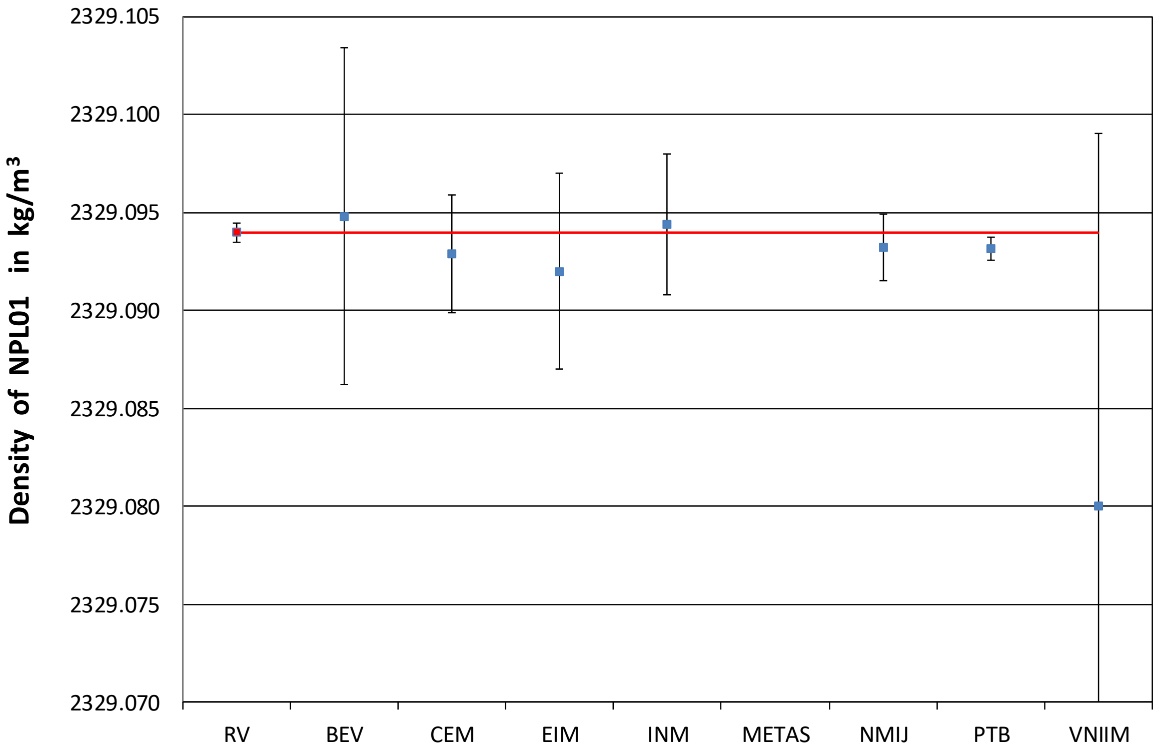

Figure 14: Reported density results of the participants for the travelling standard NPL01 and the reference value (RV). The uncertainties are for a confidence level of 95%. The value of METAS is outside the scale.

6.5 Travelling standard Sik2 (Petal 2)

The density reference value (2329.090 13 ± 0.000 50) kg/m^3 for the travelling standard Sik2 was determined by the flotation measurements in comparison to the 1 kg travelling standards PTB02 and NPL01, see section 5.3, table 15.
The mass values of CEM, METAS, and VNIIM are discrepant but this has no consequences for their volume or density values. The weighted mean value (taking into account the correlation between the two PTB values of about 15%) of the mass (238.574 966 ± 0.000 015) g is used to calculate the volume reference value from the density reference value: (102.432 690 ± 0.000 023) cm^3.
The reported mass, volume and density results for the silicon sphere Sik2 are listed in tables 28 to 30 and are displayed in figures 15 to 17 in comparison to the mean or reference values. Only the INM volume and density values show a small discrepancy. (This small anomaly could not be detected before the calculation of the reference value and had thus not been reported to the INM.)

Table 28: Reported mass results of the participants for the travelling standard Sik2. (PTB(m) denotes the mass lab of PTB.)

Institute	Mass in g	Uncertainty (95%) in g
BEV	238.57496	0.00010
CEM	238.574834	0.000037
EIM	238.57490	0.00012
INM	238.575018	0.000078
METAS	238.575157	0.000124
NMIJ	238.57487	0.00035
PTB	238.574956	0.000050
PTB	238.574966	0.000015
VNIIM	238.57511	0.00010

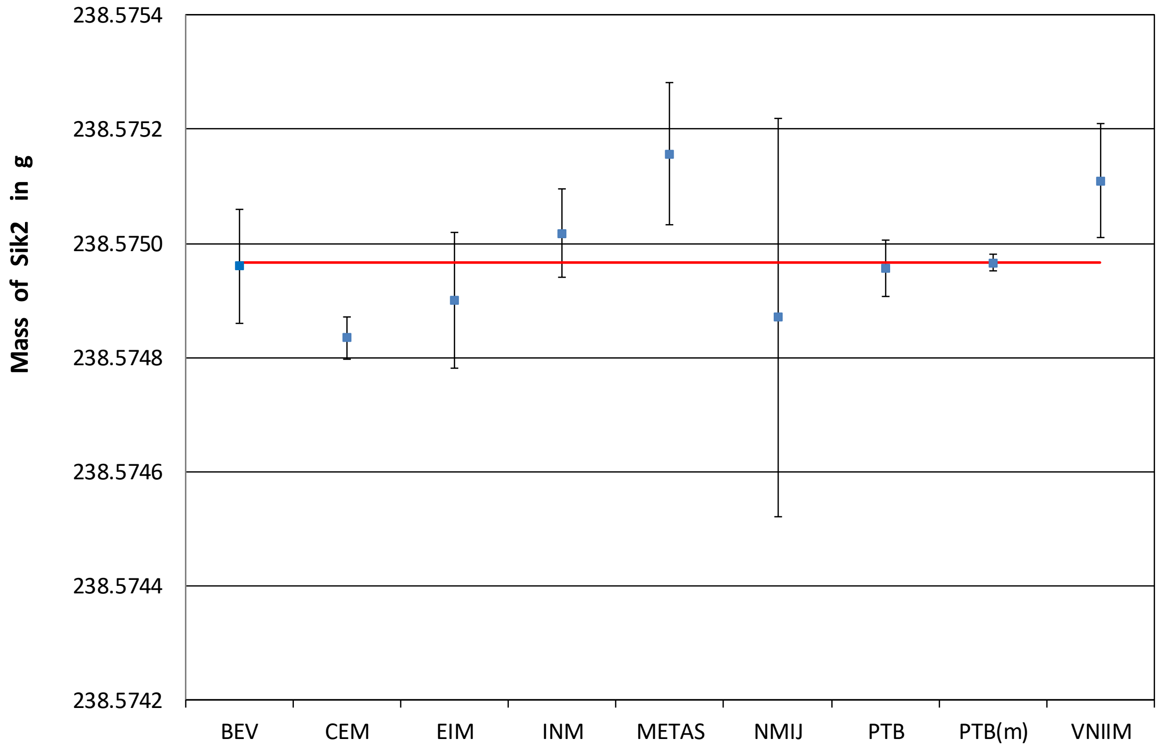

Figure 15: Reported mass results of the participants for the travelling standard Sik2 and the mean value (red line). The uncertainties are for a confidence level of 95%.

Table 29: Reported volume results of the participants for the travelling standard Sik2 with the resulting Degree of Equivalence *D* and the normalized error E_n.

Institute	Volume at 20 °C in cm^3	Uncertainty (95%) in cm^3	*D* in cm^3	*U*(*D*) in cm^3	E_n
BEV	102.43294	0.00046	0.00025	0.00046	0.54
CEM	102.4333	0.0046	0.00061	0.00460	0.13
EIM	102.434	0.004	0.00131	0.00400	0.33
INM	102.43351	0.00066	0.00082	0.00066	1.24
METAS	102.43229	0.00076	-0.00040	0.00076	-0.53
NMIJ	102.43276	0.00056	0.00007	0.00056	0.12
PTB	102.432722	0.000100	0.00003	0.00010	0.31
VNIIM	102.4315	0.0020	-0.00119	0.00200	-0.59

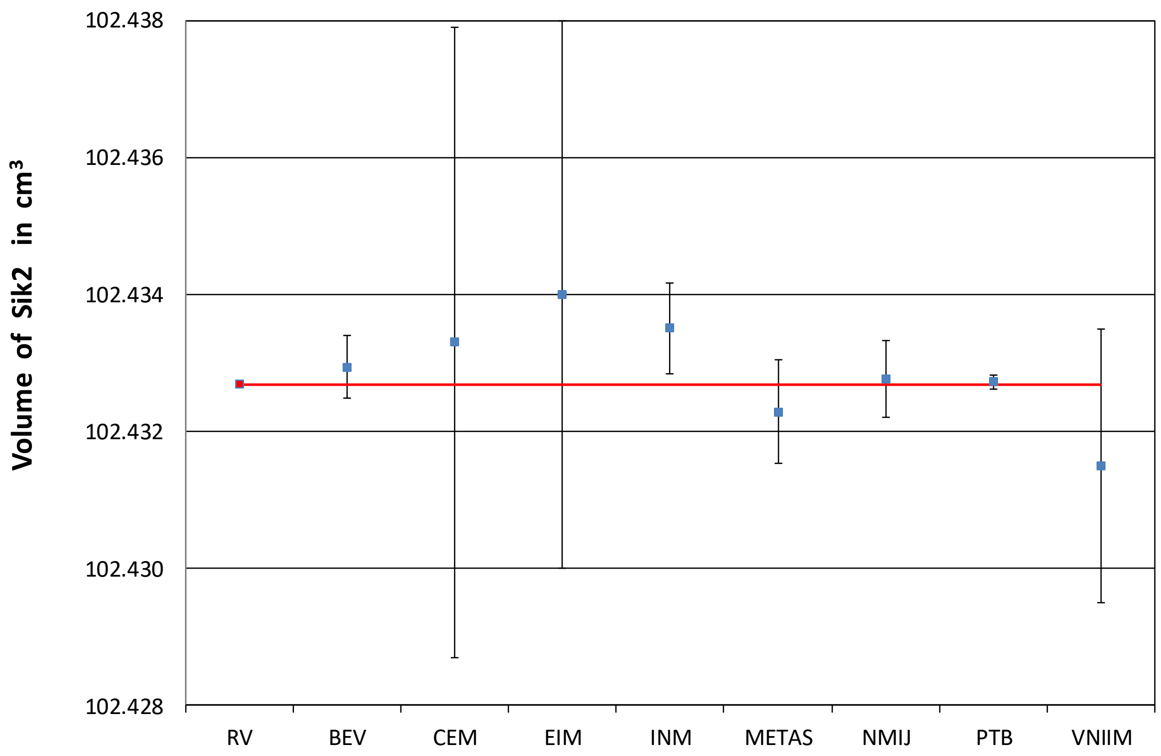

Figure 16: Reported volume results of the participants for the travelling standard Sik2 and the reference value (RV). The uncertainties are for a confidence level of 95%.

Table 30: Reported density results of the participants for the travelling standard Sik2 with the resulting Degree of Equivalence *D* and the normalized error E_n.

Institute	Density at 20 °C in kg/m^3	Uncertainty (95%) in kg/m^3	*D* in kg/m^3	*U*(*D*) in kg/m^3	E_n
BEV	2329.0844	0.0120	-0.0057	0.0120	-0.48
CEM	2329.08	0.10	-0.0101	0.1000	-0.10
EIM	2329.05	0.08	-0.0401	0.0800	-0.50
INM	2329.072	0.014	-0.0181	0.0140	-1.29
METAS	2329.099	0.018	0.0089	0.0180	0.49
NMIJ	2329.088	0.010	-0.0021	0.0100	-0.21
PTB	2329.0893	0.0021	-0.0008	0.0022	-0.38
VNIIM	2329.119	0.051	0.0289	0.0510	0.57

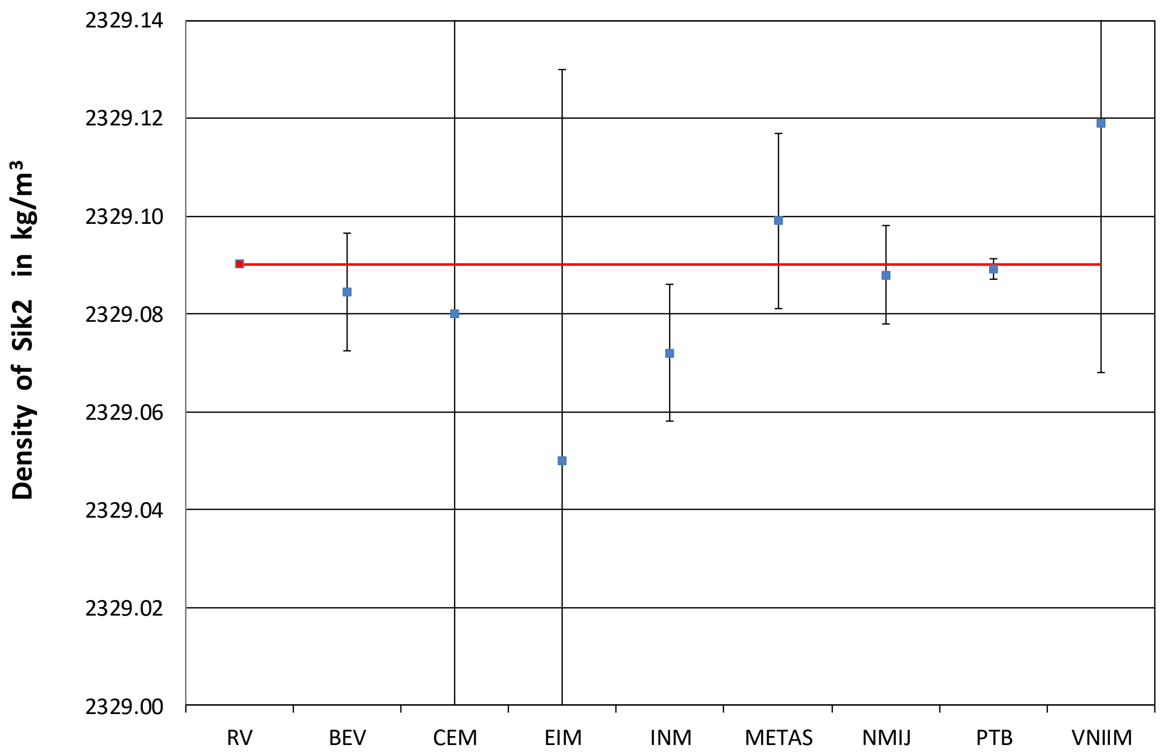

Figure 17: Reported density results of the participants for the travelling standard Sik2 and the reference value (RV). The uncertainties are for a confidence level of 95%.

6.6 Travelling standard CZ2KA (Petal 2)

The reference density value (2329.078 13 ± 0.000 58) kg/m^3 for the travelling standard CZ2KA was determined by the flotation measurements in comparison to the 1 kg travelling standards PTB02 and NPL01, see table 15 in section 5.3.

The mass value of CEM is discrepant but this has no consequence for the volume and density values. The weighted mean value (taking into account the correlation between the two PTB values is about 20%) of the mass (34.668 722 ± 0.000 007) g is used to calculate the volume reference value (14.885 169 ± 0.000 005) cm^3.

The reported mass, volume and density results for the silicon sphere CZ2KA are listed in tables 31 to 33 and are displayed in figures 18 to 20 in comparison to the mean or reference values.

Table 31: Reported mass results of the participants for the travelling standard CZ2KA. (PTB(m) denotes the mass lab of PTB.)

Institute	Mass in g	Uncertainty (95%) in g
BEV	34.668702	0.000020
CEM	34.668633	0.000039
EIM	34.66873	0.00005
INM	34.668733	0.000022
METAS	34.668669	0.000200
NMIJ	34.66867	0.00024
PTB	34.668712	0.000025
PTB(m)	34.668724	0.000007
VNIIM	34.66877	0.00031

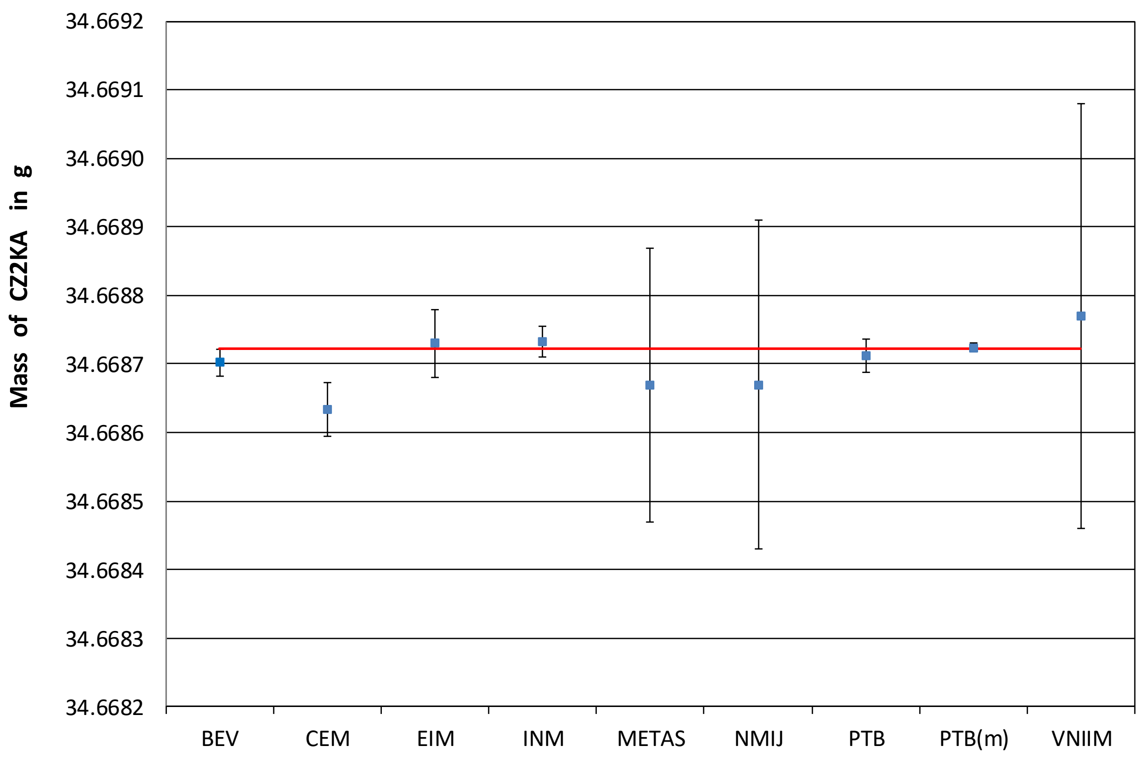

Figure 18: Reported mass results of the participants for the travelling standard CZ2KA and the mean value (red line). The uncertainties are for a confidence level of 95%.

Table 32: Reported volume results of the participants for the travelling standard CZ2KA with the resulting Degree of Equivalence *D* and the normalized error E_n.

Institute	Volume at 20 °C in cm^3	Uncertainty (95%) in cm^3	*D* in cm^3	*U*(*D*) in cm^3	E_n
BEV	14.88535	0.00022	0.00018	0.00022	0.82
CEM	14.8861	0.0058	0.00093	0.00580	0.16
EIM	14.887	0.003	0.00183	0.00300	0.61
INM	14.88527	0.00064	0.00010	0.00064	0.16
METAS	14.88495	0.00075	-0.00022	0.00075	-0.29
NMIJ	14.88525	0.00050	0.00008	0.00050	0.16
PTB	14.885055	0.000110	-0.00011	0.00011	-1.04
VNIIM	14.8847	0.0008	-0.00047	0.00080	-0.59

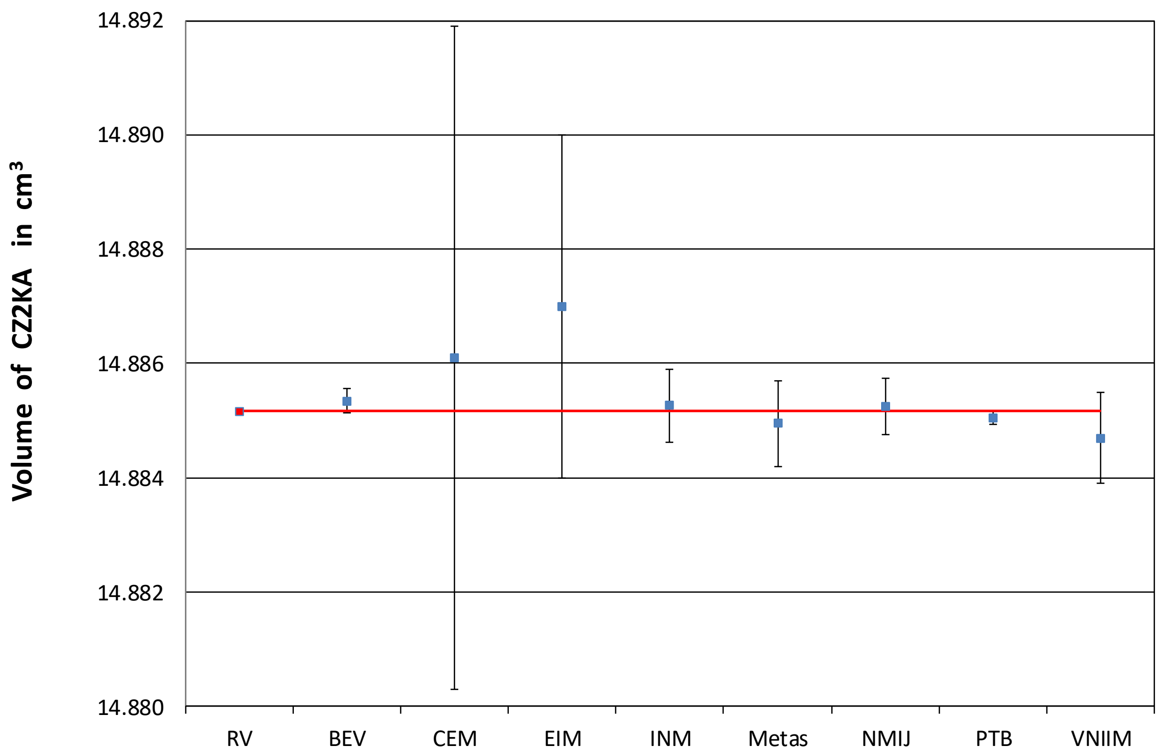

Figure 19: Reported volume results of the participants for the travelling standard CZ2KA and the reference value (RV). The uncertainties are for a confidence level of 95%.

Table 33: Reported density results of the participants for the travelling standard CZ2KA with the resulting Degree of Equivalence *D* and the normalized error E_n.

Institute	Density at 20 °C in kg/m³	Uncertainty (95%) in kg/m³	*D* in kg/m³	*U*(*D*) in kg/m³	E_n
BEV	2329.0482	0.036	-0.030	0.036	-0.83
CEM	2328.93	0.90	-0.148	0.900	-0.16
EIM	2328.8	0.5	-0.278	0.500	-0.56
INM	2329.06	0.10	-0.018	0.100	-0.18
METAS	2329.110	0.120	0.032	0.120	0.27
NMIJ	2329.063	0.069	-0.015	0.069	-0.22
PTB	2329.0953	0.0170	0.017	0.017	1.01
VNIIM	2329.151	0.095	0.073	0.095	0.77

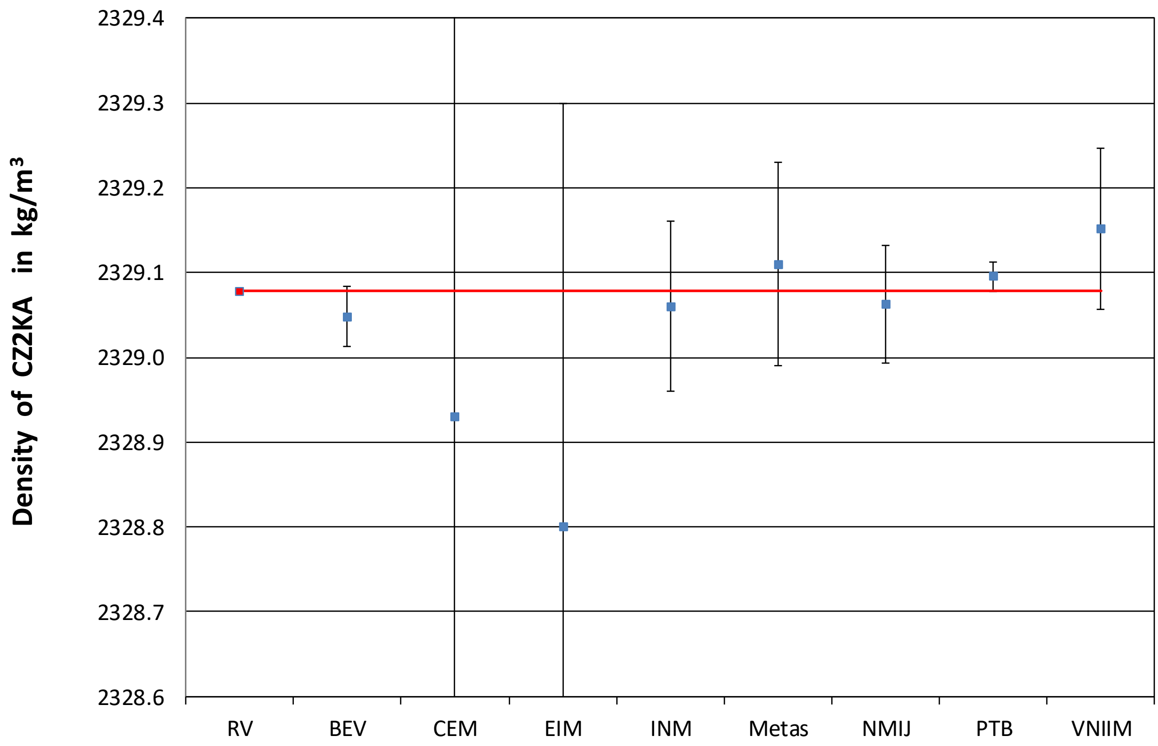

Figure 20: Reported density results of the participants for the travelling standard CZ2KA and the reference value (RV). The uncertainties are for a confidence level of 95%.

7 Conclusion

In this regional key comparison, the volume and density determinations of silicon spheres by 15 national metrology institutes (NMIs) were checked and linked to the CCM.D-K1 comparison. The measurements were carried out near 20 °C and at atmospheric pressure by the hydrostatic method.

The spheres had masses of about 35 g, 220 g and 1 kg. Whereas the reference values of the 1 kg travelling standards could be determined by the link to the CCM.D-K1 comparison, the reference values for the smaller spheres were determined by density comparisons to the 1 kg spheres using the pressure-of-flotation method.

One result was wrong due to a mistake in the mass determination. Additionally, four of the 57 volume (or density) values were discrepant with normalized error (E_n) values larger than 1.1, 1.2, 1.3, and 1.6.

Five NMIs achieved density uncertainties of about 1 ppm (1×10^{-6} in relative terms) or less for the 1 kg spheres. This satisfies the needs of all customers who wish to calibrate solid density standards for other laboratories.

Volume determinations of mass standards, air density artefacts or sorption artefacts should reach an uncertainty of about 1 mm^3 in order to reduce the effect on the mass uncertainty to about 1 µg. At least for silicon spheres this is reached by eight NMIs. Due to the higher density of stainless steel this may be different for weights and will be checked within the CCM.D-K3 comparison.

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. The participants checked if their results if they are consistent with their existing CMC entries. Four participants defined corrective actions.

8 References

[1] "Mutual recognition of national measurement standards and of calibration and measurement certificates issued by national metrology institutes," BIPM, Paris, 14 October 1999

[2] K. Fujii, H. Bettin, A. Peuto, K.-H. Chang, P. Richard, C. Jacques, C. Matilla Vicente, L. O. Becerra: “Final report on CIPM key comparison CCM.D-K1: density measurements of a silicon sphere,“ *Metrologia*, 2006, vol. 43, Technical Supplement 07007

[3] K. Fujii: “CIPM key comparison of density measurements of a silicon sphere,” 2006, pp. 1-26, *KCDB of BIPM*

[4] "Guide to the Expression of Uncertainty in Measurement," International Organization for Standardization (ISO), 1995.
JCGM 100:2008 - Evaluation of measurement data — Guide to the expression of uncertainty in measurement
http://www.bipm.org/utils/common/documents/jcgm/JCGM_100_2008_E.pdf

[5] A. Picard, R.S. Davis, M. Gläser, K. Fujii: "Revised formula for the density of moist air (CIPM-2007)," *Metrologia*, 2008, vol. 45, pp.149-155.

[6] Organisation Internationale de Métrologie Légale (Organization of Legal Metrology) International Recommendation OIML R 111-1 Edition 2004 (E)

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

[8] H. Bettin, H. Toth: "Solid density determination by the pressure-of-flotation method," *Meas. Sci. Technol.,* 2006, vol. 17, pp. 2567–2573

[9] A Waseda, K Fujii: "High precision density comparison measurement of silicon crystals by the pressure of flotation method," *Meas. Sci. Technol*., 2001, vol. 12, pp. 2039–2045

9 Acknowledgements

CEM

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PTB

The highly professional work of Hans Toth and Martin Vogtmann, who performed at PTB the hydrostatic and mass measurements and of Michael Hämpke, who performed the mass determination in the PTB mass lab, is gratefully acknowledged.

10 Comments

INM

Regarding the small discrepancy of the INM values in tables 29 and 30, I estimate this is originated in an underestimated uncertainty for the volume of the “transfer standard 500 g glass weight”.

I mention that in recent years the thermostatic control of the laboratory was greatly improved, achieving a better temperature stability in the bath of the volume comparator VC1005.