CCM.D-K1.2023

Technical Protocol for the CCM Key Comparison

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

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The following document and its construction are oriented on the latest CCM Key Comparison, designated as CCM.D-K1, "*CIPM key comparison of density measurements of a silicon sphere*" [1].

1. Outline

The key comparison, CCM.D-K1.2023, conducted by the CCM Density Working Group, aims to compare the results of the density and volume determinations of a 1 kg sphere of natural silicon from participating laboratories and to evaluate the degrees of equivalence according to the mutual recognition arrangement [2]. The transfer standard will be compared directly or indirectly to primary density standards, which are calibrated by mass and dimensional measurements. In this way, National Metrology Institutes (NMIs) usually disseminate the density unit to calibration laboratories, verification offices or other NMIs. For the comparability of density and volume determinations of solids, the use of silicon spheres has become established due to a high stability of density of the material and by the easiness of cleaning.
In this key comparison each participating institute determines the density and volume of a silicon spheres as transfer standard at 20 °C and 101 325 Pa with respect to solid density standards of each NMI by hydrostatic weighing. The hydrostatic density determination usually

includes a mass determination of the transfer standard. Although the participants are asked to report the mass values of the transfer standard, this the comparison does not include a mass comparison of the participating NMIs.

The CCM agreed the PTB as the pilot laboratory for this comparison, and CENAM and INRIM as co-pilot laboratories. The technical protocol was set-up similar to the CCM.D-K1 comparison of 2001 [1].

2. Purpose of this document

The purpose of this document is to provide the participating laboratories with instructions on handling the transfer standard (silicon spheres) and to report on the measurement results, the measuring procedure, and the apparatuses.

It is important that all the instructions given in this document are followed. This will ensure that all the measurement data are obtained under comparable conditions and are presented in the same format. Any deviation from the instructions has to be reported to the pilot laboratory. It will also enable the data analysis to be carried out efficiently, thus simplifying the task of the pilot institutes.

3. Transfer standard and transportation

For the comparison the pilot laboratory provides the transfer standard: A sphere of natural silicon with a nominal mass of 1 kg, named as SiSCkg05a.

The transfer standard is placed in an appropriate container (transport container and aluminum carrying case), provided by the pilot laboratory. The packaging system is shown in the Figure 1 and its handling is explained in detail in chapter 4.1, other methods are not allowed. For the travelling between the participating laboratories, the aluminum carrying case is protected by a cardboard box fixed on a pallet, see Figure 1. The total weight of the whole package including the silicon sphere is 8.5 kg in total, with the size of 60 cm x 41 cm x 58 cm. The package will be provided with a warning, shock watches and a documentation of the contents. If the shock watch has damage or the displays are red, the shock watch should be replaced. New shock watches are included in the packaging.

After arrival of the package, the laboratory has to inform the pilot laboratory without delay giving details of the arrival date, the state of the package and its contents (Appendix D). The participating institute has to check the transfer standard for any damage, and report this.

Figure 1 a - d. For transportation, the silicon sphere will be shipped in a cardboard box on a pallet (a), additionally enclosed are auxiliary tools (b). For this purpose, the silicon sphere is placed in an aluminum carrying case (c) and in a transport container (d).

The mass determination of the sphere should be performed as soon as possible after receipt, and the determined mass should be reported to the pilot laboratory. For the approximate measurement of the mass, the nominal value of the density is used, i.e., 2329 kg/m³. This confirmation is necessary to determine a possible defect as soon as possible.

Each participating laboratory has got five weeks to measure the transfer standard and send it to the next laboratory (or back to the pilot laboratory), according to the circulation scheme (Appendix C). Transportation of the transfer standard to the next laboratory are the responsibility of the respective institute, including costs. Customs duties and taxes must be

paid in each case for the own country. An ATA Carnet cannot be provided as it is not accepted in some countries. Please declare the silicon sphere with the cost of the goods valued at 10000 Euro to the customs. Note: In some countries it is possible to declare a temporary import to a third country. You can give the following reasons for this: international comparison, no commercial purpose, for a period of 5 weeks.

The receiving laboratory and the pilot laboratory have to be informed about the date of dispatch, giving details of the transportation (Appendix E). If possible, give the freight No. that allows tracking the package during travelling.

The transfer standard is accompanied by customs documents, which are attached to the rest of the shipping documents and note of contents, so that the handling agent can perform customs clearance.

4. Handling of the transfer standard – 1 kg sphere of natural silicon

4.1 Handling

The silicon sphere (transfer standard) is kept in a transport container, which is stored in an aluminum carrying case as shown in Figure 1 c – d.

The silicon sphere is fixed in the transport container between a Teflon bearing and a stamp. This stamp, which is connected to the upper screw of the transport container, has an integrated spring that can keep the sphere fixed with a maximum force of 1 kg. A guide plate is attached

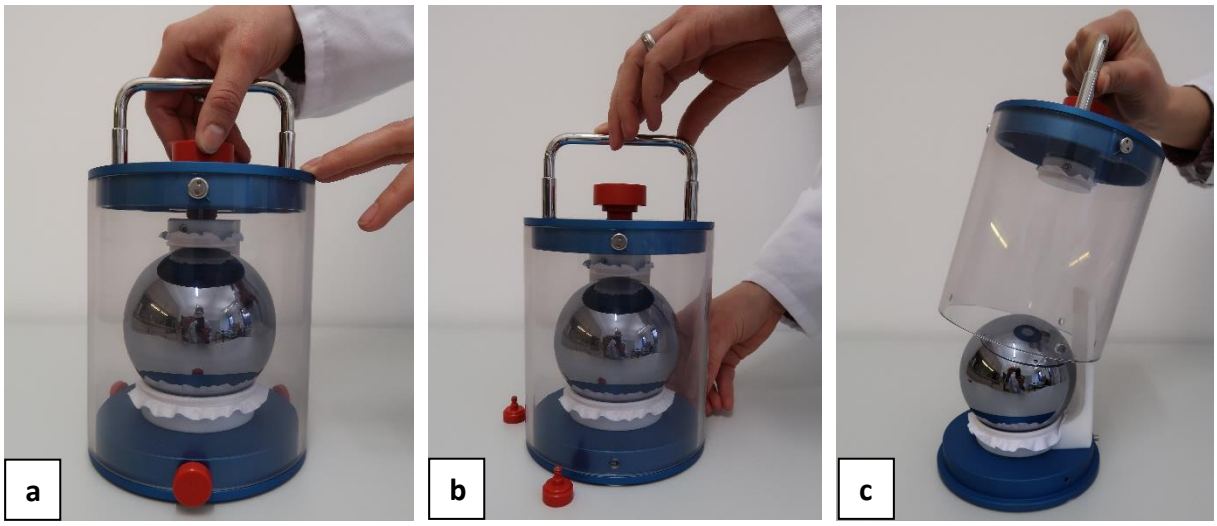

Figure 2 a - c. Open the transport container by loosening the upper screw (a), unscrewing the three screws on the bottom of the transport container (b) and moving the cover of the container along the guide plate (c).

to the Teflon bearing, along which the cover of the transport container is to be guided when the container is removed or put on. The Teflon bearing and stamp are additionally equipped with a microfiber pad.

To remove or placing the silicon sphere in the transport container, the cover has to be disassembled, see Figure 2. Loosen the upper screw completely by rotating the red screw.

(For closing, the spring force must be applied to the sphere by rotating the screw hand-tight until its stop.) Then, the three screws on the bottom at the transport container has to be loosed. Now the cover can be lift carefully by moving it along the guide plate without contact to the silicon sphere. Afterwards remove the fixed microfiber pads and throw it away, because it is not sure if the pads are clean or dirty.

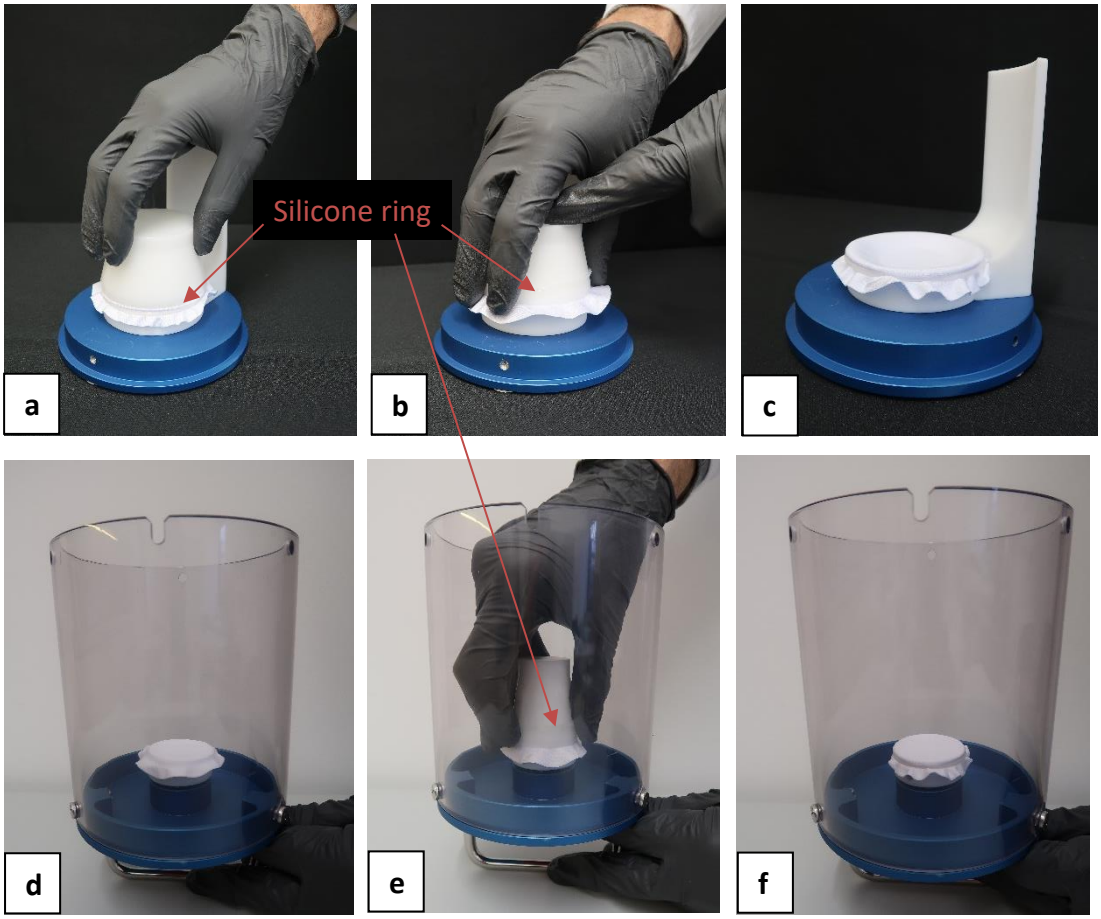

Figure 3 a - f. Microfiber pads are fixed to the Teflon bearing and stamp with silicone rings using the auxiliary tools. The silicone rings are turned over the auxiliary tools until it is fitted at the Teflon bearing or stamp and the microfiber pad are fixed. The large microfiber pad is fixed at the Teflon bearing at the bottom (a – c), the smaller one on the Teflon stamp at the top (d – f) of the transport container.

Now you can handle with the silicon sphere, use always clean gloves and clean microfiber pads. When the transfer standard is not in this case nor on the weighing systems, the transfer standard shall be stored under a suitable cover.

When the transfer standard should be sent to the next institute, the silicon sphere hast to be kept in the same way in the transport container, always using new microfiber pads on the Teflon bearing and stamp. The two microfiber pads can be replaced using the provided auxiliary tools (Figure 3), new microfiber pads carry along.

The microfiber pads are fixed to the Teflon bearing and stamp with silicone rings, the larger microfiber pad at the bottom and the smaller one at the top of the transport container. The silicone ring can be fitted to secure the microfiber pad using the tools supplied by Häfner Gewichte GmbH [3], see Figure 3 a - f.

Afterwards, the silicon sphere can be placed on the microfiber pad and the transport container can be closed. Confirm that the top screw is released, cover, and turn the cover to close, fasten the lower screw and then finally fasten the top screw to hold the silicon sphere. Do not turn the screws too tightly, the top screw has got a fixed end.

4.2 Cleaning procedure

The silicon sphere should be cleaned with pure ethanol (≥ 99.8 %) and water before the measurements, always wearing gloves. Do not use any liquid with a pH value above 7, as alkaline liquids attack silicon. Check the pH value of your liquids when using water with detergent.

Make sure that the cleaning procedures used are suitable for silicon spheres. Check the transfer standard after cleaning. If you find any damage, please report it to the pilot laboratory immediately. The cleaning procedure can influence the behavior of measurements. Therefore, please document your cleaning procedure in the Report Forms.

4.3 Acclimatization

After cleaning, the transfer standard should acclimatize to the weighing conditions in the laboratory (under a suitable cover) for at least 24 hours before mass measurements can be performed.

4.4 Electrostatic charges

Although the surface of the silicon sphere is covered by oxide layers, it still has a good electrical conductivity to discharge. Special care must be taken to ensure that no electrostatic charging of the spheres, especially if the sphere has no electrical contact to suspension or balance pan. If the silicon sphere is placed on the weighing pan without any electrical contact, special care must be taken to avoid electrostatic charges that may disturb mass measurement in air. During weighing in air, the relative humidity should be above 40 %. Please inform the pilot institute of any other measures taken to reduce the possible effects of electrostatic charges. The same care must be taken with hydrostatic weighing.

5. Measurement procedure

The participating laboratories have to make at least all measurements that are necessary to support their CMC entries. The silicon sphere has to be measured at 20 °C and at atmospheric pressure. Volume and density have to be reported for 20 °C and 101 325 Pa. At least ten weighing sequences have to be performed both in air and in liquid to determine the volume, density, and mass of the transfer standard and to evaluate the experimental standard deviation.

Before measuring, check your apparatuses with another sample to make sure that the transfer standards are not damaged by the measurement procedure. Each damage must be reported to pilot laboratory without delay.

Approximate values of the cubic expansion and isothermal compressibility of the silicon sphere is given in table 1, together with their uncertainties. Use these values as given parameters in this key comparison.

Table 1. Physical constants of the sphere of single crystal grown natural silicon.

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

Uncertainties are standard uncertainties (k = 1).

The transfer standard should be sent to the next laboratory (or back to the pilot laboratory) as soon as possible after the measurements have been completed, according to the circulation scheme (Appendix C). Please keep in mind that it is mandatory to follow the schedule. The receiving laboratory and the pilot laboratory hast to be informed (Appendix E).

The mean, minimum and maximum values of the parameters contributing to the evaluation of air density are to be recorded, i.e., pressure, temperature, relative humidity (or dew point), and CO_2 content (whether measured or assumed). The measurements shall be carried out under laboratory ambient conditions at a temperature close to 20 °C. For the calculation of air density, the CIPM 2007 formula is to be used [4]. Mean, minimum and maximum values of the air density are to be reported. If artefacts are used to determine the air density gravimetrically, report also the difference to the air density determined by the CIPM formula.

The measurement results for volume, density, and mass will be sent as soon as possible to the pilot laboratory using the Report Forms (Appendix F).

6. Reports

Each participating institute has to report the measurement results at 20 °C and 101 325 Pa using the Report Forms 1 to 3 (MS Excel and MS Word documents). The measuring results and information of used equipment and standards have to be filled in, in different Excel sheets, one for the weighing in air and one for the hydrostatic weighing. A description of the measurements procedure and calculation for weighing in air and for the hydrostatic weighing has to be given in the MS Word document (Appendix F).

The completed report forms must send to the pilot laboratory as soon as possible and at the latest six weeks after the measurements are completed. When the pilot laboratory has received all data, they will be sent to the co-pilot laboratory for the comparison evaluation.

6.1 Report Form 1

It concerns information about the information about measuring dates, used instrumentations and standards differed for weighing in air (*Report Form 1a*) and hydrostatic weighing (*Report Form 1b*). Please add any additional information to your measurements.

For the balance/s used to determine the weighing value in air/liquid, the following information is to be given:

a) Manufacturer and type of balance.

b) Maximum capacity, electronic range, and resolution.

c) Standard deviation, maximum nonlinearity, out-of-center error.

d) Adjustment or calibration: method, uncertainty, and frequency.

For the instruments used for the measurement of air pressure, temperature, humidity, and CO_2 content, the following information is to be given:

e) Manufacturer and type.

f) Resolution.

g) Frequency of measurement.

h) Calibration uncertainty, date, and traceability.

i) Siting of sensor.

For the mass/density standards and set of weights used to calibrate or adjust the balance or to substitute the apparent weights of the density standard and transfer standard, the following information is to be given. Please give the information for the weighing in air (a) and in liquid separately (b).

j) Identification and material.

k) Shape, dimensions, and manufacturer

l) Mass and volume values at their reference temperature and their uncertainties.

m) Date of last calibration, method of determination, and traceability of values.

For the instruments used for measurements of the liquid temperature in the case of hydrostatic weighing (b), the following information's is to be given:

n) Manufacturer and type of sensors.

o) Manufacturer and type of resistance bridge and standard resistor (if applicable).

p) Resolution of temperature measurement.

q) Calibration uncertainty, date, and traceability.

For the reference liquid, the following information is to be given:

r) Manufacturer.

s) Product Name.

t) Molecular formula and assay.

6.2 Report Form 2

For both measurements, weighing in air (*Report Form 2a*) and hydrostatic weighing (*Report Form 2b*), general information and results of measurements is to be given.

a) Date of arrival and departure of the transfer standard.

b) Condition of package and transfer standard.

c) Company responsible for transportation.

d) Date of measurement (start and end).

e) Name of used standards (and nominal mass).

f) Material and diameter of used wire, in the case of hydrostatic weighing.

g) Mean balance indication with transfer and mass/density standard.

h) Mean temperature of air/ liquid at transfer standard.

i) Ambient condition during the mass measurement.

j) Mass, volume, and density of the transfer standard with the experimental standard deviation and uncertainty budget for each value. For volume and density, the values are given at 20 °C and 101 325 Pa.

k) If artefacts are used for the air density determination: difference to CIPM-formula.

For the uncertainty of measurement results for mass, volume, and density, the following information is to be given in Report Form 2a and b.

The uncertainties of mass, volume and density have to be given as expanded uncertainty U_{95} for a confidence level of 95 %. The uncertainty evaluation should include a list of all influence quantities, values, their degree of freedom ν_{eff} and their combined standard uncertainty u_c, as well as the t-factor $t_{95}(\nu_{eff})$ taken from the t-distribution for a 95 % level of confidence. This is obtained by combining the individual standard uncertainties resulting from Type A and Type B evaluations according to ISO "*Guide to the Expression of Uncertainty in Measurement*" [5].

The expanded uncertainty of mass, volume and density is calculated with the Excel sheet from the above given data with $U_{95} = t_{95}(\nu_{eff})\, u_c$.

l) Uncertainty budget for mass, volume, and density determination of the transfer standard, a list of main components should be given. Please add any additional component occurring in your measurements.

m) Uncertainty of measurement results for mass, volume, and density.

6.3 Report Form 3

A description of the measurement's procedure and calculation for weighing in air and for hydrostatic weighing have to be given in Report Form 3, the MS Word document. Please add any additional information to your measurements.

For the details of weighing in air, the following information is to be given in *Report Form 3a*. Give a summary of the apparatus with figures or photos and include information about the thermostat and its temperature control, the air parameter measurement and the transfer standard and weight exchange.) Give a summary of the following procedures:

a) Handling of samples including cleaning.

b) Detection and removing of electrostatic charges.

c) Adjustment or calibration of the balance.

d) Measurement procedure and weighing sequence.

Give the mathematical model equations for calculating the mass of the transfer standard. Describe how the standard uncertainties of the individual influence quantities in the uncertainty of the mass were estimated. Please give references to publications about your apparatus.

For the details of hydrostatic weighing, the following information is to be given in *Report Form 3b*. Give a summary of the hydrostatic weighing apparatus with figures or photos and include information about:

e) Thermostat: manufacturer, type, volume, cooling system, temperature regulator.

f) Preparation of wire.

g) Liquid used for the hydrostatic weighing.

h) Use of transfer standards, density standards and weights.

Give a summary of the following procedures:

i) Preparation of apparatus.

j) Measurement and results of temperature differences in the hydrostatic liquid.

k) Adjustment or calibration of the balance.

l) Measurement procedure and weighing sequence.

m) Cleaning of the transfer standard the measurements.

Give the mathematical model equations for calculating the density of the transfer standard at the target temperature and pressure. Describe how the standard uncertainties of the individual influence quantities in the uncertainty of the solid volume and density were estimated. Please give references to publications about your apparatus.

7. Evaluation of results

In this key comparison, the quantities volume and density for a density transfer standard, a 1 kg sphere made of natural silicon, are compared. After completion of the measurements by all participating institutes, the pilot and co-pilot laboratories will provide the comparison reference values that will be used to determine the degree of equivalence for the rest of the participants. The pilot and co-pilot laboratories will perform the comparison evaluation and report together. If any serious deviations, correlations, or any other scientific difficulties are found in calculation of the reference value, some different statistical method will be discussed by the pilot and co-pilot laboratories.

The stability of the transfer standard will be checked, and the drift will be determined with the initial, mid, and final measurements of the measuring scheme by the pilot laboratory (Appendix C). During the comparison measurements, the pilot will ask all participants about the achieved mass value to verify that everything is in order.

8. Reference

[1] K. Fujii, H. Bettin, A. Peuto, K.-Ho Chang, Ph. Richard, C. Jacques, C. M. Vicente and L. O. Becerra: “Final report on CIPM key comparison CCM.D-K1: density measurements of a silicon sphere”, Metrologia (2006) **43**, 07007 - 07007.

[2] “Mutual recognition of national measurement standards and of calibration and measurement certificates issued by national metrology institutes.”, Accred Qual Assur (2000) **5**, 69–73.

[3] Parts of the equipment were donated by Häfner Gewichte GmbH, https://www.haefner.de/en/haefner/home.html.

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

[5] "Guide to the Expression of Uncertainty in Measurement," International Organization for Standardization (ISO) (1995).

Appendices

A. Participants

NMI	Country	Contact Person	E-mail	Address
PTB	Germany	Daniela EPPERS	daniela.eppers@ptb.de	Physikalisch-Technische Bundesanstalt WG 1.13 "Solid State Density" Bundesallee 100 38116 Braunschweig Germany
CENAM	México	Luis Omar BECERRA	lbecerra@cenam.mx	Centro Nacional de Metrología Km. 4.5 Carretera a los Cués El Marqués, Querétaro México C.P. 76246
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UME	Turkey	Beste KORUTLU	beste.korutlu@tubitak.gov.tr	TÜBİTAK UME Gebze Yerleşkesi 41470, Turkey
NMIJ	Japan	Naoki KURAMOTO, Atsushi WASEDA	n.kuramoto@aist.go.jp, waseda.atsushi@aist.go.jp	National Metrology Institute of Japan (NMIJ) 1-1-1 Umezono, Tsukuba, Ibaraki 305-8563 Japan

NMI	Country	Contact Person	E-mail	Address
SASO-NMCC	Saudi Arabia	Rayan A. ALYOUSEFI	r.yousefi@saso.gov.sa	Saudi Standards, National Measurement and Calibration Center SASO – NMCC, Building No. 4, Imam Saud Bin Abdulaziz Bin Mohammed Rd, P.O. Box 3437, 11471, Riyadh, Kingdom of Saudi Arabia
NIS	Egypt	Mohammed Hamdy MOHAMMED, Alaaeldin A. ELTAWIL	mohamed.hamdy@nis.sci.eg, alaa.eltawil@nis.sci.eg	National Institute of Standards, Mass, density and pressures laboratory, Tersa St., El Haram -El Giza P.O. 136 Giza, Code: 12211, Egypt

B. Timetable for the comparison

May 2022	Start of measurements (pilot laboratory)
May 2022 until July 2023	Measurements by all participants and Reports from all participants
November 2023	Draft A of the comparison
December 2023	Draft B of the comparison: end of comparison

C. Circulation scheme for the comparison

Each participating laboratory has got five weeks for measuring the transfer standard and transfer it to the next laboratory.

Date		NMI/Country	RMO
18th May 2022	15th June 2022	PTB/DE	EURAMET
15th June 2022	20th July 2022	METAS/CH	EURAMET
20th July 2022	24th August 2022	NRC/CA	SIM
24th August 2022	28th September 2022	NIM/CN	APMP
28th September 2022	2nd November 2022	UME/TR	EURAMET
2nd November 2022	07th December 2022	CENAM/MX	SIM
07th December 2022	04th January 2023	PTB/DE	EURAMET
04th January 2023	08th February 2023	NMIJ/JP	APMP

Date		**NMI/Country**	**RMO**
08th February 2023	15th March 2023	NIS/EG	AFRIMET
15th March 2023	19th April 2023	SASO-NMCC/SA	GULFMET
19th April 2023	24th May 2023	NMIA/AU	APMP
24th May 2023	31st May 2023	PTB/DE*	EURAMET
31st May 2023	05th July 2023	INRIM/IT	EURAMET
05th July 2023	26th July 2023	PTB/DE	EURAMET

*Only for transport.

D. Receipt of the transfer standard

To monitor the progress of the comparison, it is required, upon receipt of the package, to kindly send an e-mail to:

pilot laboratory: Daniela Eppers, e-mail: daniela.eppers@ptb.de

Object: CCM.D-K1.2023

This e-mail should contain the information about the status of the silicon sphere, the shock watch and it is package.

E. End of measurements and shipping

To monitor the progress of the comparison, it is required, upon completion of the measures, before shipment, to kindly send an e-mail to:

pilot laboratory: Daniela Eppers, e-mail: daniela.eppers@ptb.de

and the contact person of the next laboratory.

Object: CCM.D-K1.2023

This e-mail should contain the following information:

- the achieved mass value to verify that everything is ok
- date of the end of measurements
- shipping date and tracking number.

F. Results

Calibration results should be sent within six weeks after the end of the measurements. It is required to kindly send an e-mail to:

pilot laboratory: Daniela Eppers, e-mail: daniela.eppers@ptb.de

Object: CCM.D-K1.2023

This e-mail should contain the following information:

- Calibration results (Excel Report Form)
- A summary of the procedure used and a description of the apparatus