Status of the realization and dissemination of the kilogram via silicon spheres

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***Abstract* - Silicon spheres are qualified standards for the realization and dissemination of the kilogram according to the new approach of the revised SI. Moderate costs, robustness, and practice oriented use are their unique features. The Physikalisch-Technische Bundesanstalt (PTB) is running two projects offering the advantages of silicon spheres to high level end users. The international project "Si-Trust" allows interested national metrology authorities to get familiar with the handling of 1-kg Si-spheres. The project "Si-kg" is establishing a technological and commercial infrastructure. A first silicon sphere made of ^{28}Si was sold to an Asian institute in 2017.**

***Index Terms* — Si-Trust, Si-kg, dissemination, unit kilogram, silicon sphere, metrology.**

I. INTRODUCTION

The PTB as the national metrology institute of Germany is traditionally and extensively involved in the realization and dissemination of the Planck based unit kilogram via silicon spheres [1]. As of the most probable revision of the SI in 2019 [2], the kilogram will be derived from the Planck constant h instead of using the International Kilogram Prototype (IPK) hosted by the Bureau International des Poids et Mesures (BIPM) [3] for the last 130 years. This will then enable end users to choose their referential kilogram in terms of precision, material and weight according to their very individual technical requirements and available budget.

The processes for manufacturing silicon spheres as well as the methods for characterizing their metrological properties and handling procedures on the highest level of measurement accuracy were made available by the PTB. Against this background, two projects have been initiated. The international project "Si-Trust" shall transfer all experience in handling silicon spheres to interested national metrology authorities. For this purpose, silicon spheres of 1 kg will be made temporarily available to the partners free of charge in order to gain their own experiences. The national project "Si-kg" will establish a technological and commercial infrastructure that allows silicon spheres to be manufactured and sold on a private basis.

II. CATEGORIES OF SILICON SPHERES

Silicon spheres can be classified into at least three different categories. The distinction is made according to the features such as material, geometry and surface quality.

The first category consists of spheres of highly enriched isotopic monocrystalline silicon ^{28}Si of 1 kg nominal weight with 99.998 % enrichment [4] used for the realization of the mass derived on the value of the Planck constant h according to equation 1.

$$N_\mathrm{A} = \frac{a^2 \cdot c}{2R_\infty h} A_\mathrm{r}^\mathrm{e} M_\mathrm{u} \qquad (1)$$

with

N_A : Avogadro constant
α : fine structure constant
c : speed of light in vacuum
R_∞: Rydberg constant
A_r^e : relative atomic mass of an electron
M_u: molar mass unit

Knowing the Avogadro constant, the relation with Planck's fundamental constant is then established using equation 2.

$$m = \frac{8\,V}{a_0^3} \frac{M_\mathrm{Si}}{N_\mathrm{A}} \qquad (2)$$

with

m : mass
V : volume of the silicon sphere
a_0 : lattice parameter of ^{28}Si

The raw material of the ^{28}Si spheres is purchased in Russia, the only supplier known to date. There, the high-purity silicon is enriched at the Electrochemical Plant in Zelenogorsk. Afterwards, polycrystalline silicon is deposited on slim rods at the Institute of the Chemistry of High Purity Substances of the Russian Academy of Sciences in Nishniy Novgorod. At the Institute for Crystal Growth (IKZ) in Berlin, a monocrystalline crystal is finally grown. Six kilograms of this material suffice to make two ^{28}Si spheres.

The second category comprises "quasi-primary" spheres $^{nat}Si_{qp}$ made of natural silicon which can be ordered by various suppliers form semiconductor industries. These spheres are at the same time high-quality monocrystalline and robust mass measurement standards with a nominal mass of 1 kg. In the future it will be possible, to retrace its mass to measurement standards of ^{28}Si [5]. Prior to a calibration, the volume of a $^{nat}Si_{qp}$ sphere must once be determined, for example by means of a sphere interferometer. Additionally, a density measurement based on the magnetic flotation principle will

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determine the density of the $^{nat}Si_{qp}$-sphere. It will simply be traced back to the density of a ^{28}Si-sphere according equation 3.

$$m_{qp} = (\rho_{28} + \Delta\rho)V_{qp} \quad (3)$$

where is

m_{qp}: searched mass of $^{nat}Si_{qp}$

ρ_{28}: density of ^{28}Si

$\Delta\rho$: difference between densities of $^{nat}Si_{qp}$ and ^{28}Si

V_{qp} : volume of the quasi primary silicon sphere

The magnetic flotation method requires a temperature stability of 0.1 mK, constant environmental conditions such as constant air pressure, and the use of ultrapure water (amongst others).

The third category - secondary silicon spheres $^{nat}Si_{sc}$ – are also made of natural monocrystalline silicon for industrial use. The mass will be calibrated by mass substitution methods.

The most important criterion for all spheres is the maximum mass deviation of 1 kg +/-10 mg, requiring frequent checks of the mass by means of a precision balance. The spheres of all categories can be offered with various specifications, cost and accuracy shown in table 1.

Table 1 Different categories of silicon spheres depending on material, geometry and surface quality

specification	^{28}Si	$^{nat}Si_{qp}$	$^{nat}Si_{sc}$
category	primary	"quasi-primary"	secondary
$u_{rel}(k=1)$ of mass	$2 \cdot 10^{-8}$	$3 \cdot 10^{-8}$	$3 \cdot 10^{-8}$
form error RONt	< 30 nm	< 20 nm	< 80 nm
average roughness Ra	< 0.3 nm	< 0.5 nm	< 1 nm
expected price	> 1 Mio. €	> 100 k €	> 10 k €
availability	limited, PTB	PTB/ industrial supplier	industrial supplier

All spheres have in common that they are extremely stable over time. Their monocrystalline structure makes it nearly impossible to be penetrated by other atoms. The silicon oxide also creates a very hard and protective surface layer. Suitable cleaning solutions and cleaning wipes ensure that all contaminants on the surface can be removed completely without damaging the silicon oxide layer. This is an essential criterion to ensure the reproducibility of measurements.

Obtaining a silicon sphere enables high level end users to disseminate of the mass. Currently, steel cylinders are used for this purpose. Calibration requires, that all significant systematic deviations of a measurement process must be determined and corrected in a traceable way to the SI. Main influences are the effective air density, which in turn depends on temperature, air pressure, humidity and gas composition, the standard's geometry, magnetic properties of the material and orientation of the mass standard during the measurement process. Most of these influences can be avoided if the measurements are carried out in vacuum. For this purpose, suitable mass comparators are available on the market. If, on the other hand, the calibration of a mass standard is carried out against a calibrated sphere in air, it must be corrected to environmental influences. Most significant systematic effects result from environmental conditions. Therefore, PTB runs the measurements under conditions listed in Table 2.

Table 2 Environmental conditions and specifications provided at PTB for calibrating Si-spheres at the highest level

measurand	specification
temperature	19 °*C* – 22 °C
$U(k=2)$ = 0.02 °C	
temperature drift	±0.05 °C/h
$U(k=2)$ = 0.02 °C	
temperature stability	±0.1 °C/24h
$U(k=2)$	
humidity	45% - 55%
humidity drift	±1%
air pressure	0.06 mbar
mass comparator	
electrical weighing range	1.5 g
resolution	0,1 g
linearity	≤ 2 µg
standard deviation	0.4 µg at 1 kg

III. DISTRIBUTION OF SILICON SPHERES DUE TO SI-TRUST COLLABORATION

A. Si-Trust collaboration

In June 2016 more than 42 countries participated in the workshop "Round & Ready" at PTB. The workshop showed the immense interest in mass standards made of silicon. In succession PTB established the Si-Trust collaboration. It enables interested international parties to lean silicon spheres for a limited period of time (approx. two years). The aim is to allow partners to become acquainted with the handling and cleaning of the silicon spheres.

For the Si-Trust collaboration both, $^{nat}Si_{qp}$ and $^{nat}Si_{sc}$ spheres are used. All silicon spheres to be distributed are at least mass calibrated as the apparatus for calibrating the $^{nat}Si_{qp}$ by density comparison with ^{28}Si is still under development. Besides, PTB offers additional available data referring to the sphere quality.

Figure 1 shows how ^{28}Si and $^{nat}Si_{qp}$ spheres are always marked in order to determine the crystal orientations [100], [110] and [111]. The markings are used as calibration points and for precise volume measurements.

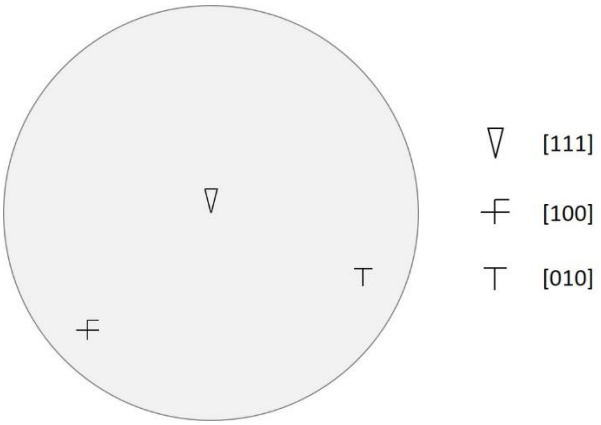

Fig. 1 Markings on a silicon sphere. The font size is approx. 2 mm

All markings are done with laser ablation and ensure minimum changes to the silicon surface.

A specific nomenclature allows to identify the classification of the spheres as well as the location of the ingot from which the material of the sphere was taken according to the scheme below.

Si	indicates the material used
28, QP, SC	indicates the sphere's category
kg	indicates the SI unit of mass
01	indicates the crystal ordered by PTB
a … e	indicates the position where the material of the sphere was taken from the ingot, starting with the sphere next to the ingot's tip (start of the ingot grows)

Example "Si28kg_01_b" indicates a sphere of highly enriched monocrystalline 28 isotope from silicon formed from ingot no 1. The sphere was located at the second sphere position from the ingot's tip.

Proper handling and storage of the spheres are essential for their long-term stability. Therefore, sophisticated low-cost procedures and materials have been identified avoiding stripes and scratches due to mechanical stress. Moreover, wipers and cleaning liquids have been identified preventing from any chemical interference or contamination with the sphere's silicon oxide surface. Below, please find a list of the individual components used for cleaning, storing and handling a silicon sphere of 1 kg as shown in Figure 2:

a) transport container allowing the silicon sphere to be fixed; the material of the plastic cylinder avoiding almost any outgassing of substances that could interfere with the silicon sphere's surface
b) robust transport case covered by an aluminum chassis filled with foam used for carrying the sphere with its transport container over long distances
c) bell jar for long term storage
d) rotary plate together with a flashlight and an air bellow used for visual inspection of the surface
e) tripod (sphere holder) used as cleaning aid; rods covered with peek tubes
f) nitrile gloves, for use in the cleaning of silicon sphere, 100 % nitrile, powder- and silicone-free
g) cleaning wipes for silicon spheres, knitted cloth, 40 x 40 cm, version: laser-cut, poured and washed
h) pads for silicon spheres, used as overlay (cover) in various sphere accessories, knitted cloth, D 60 mm, version: laser-cut, poured and washed
i) pads for silicon spheres, used as underlay with various sphere accessories, knitted cloth, D 100 mm, version: laser-cut, poured and washed
j) tongs for 1kg-silicon sphere, made of anodized special aluminum, spherical self-centering jaws, covered with a sterile microfiber cloth

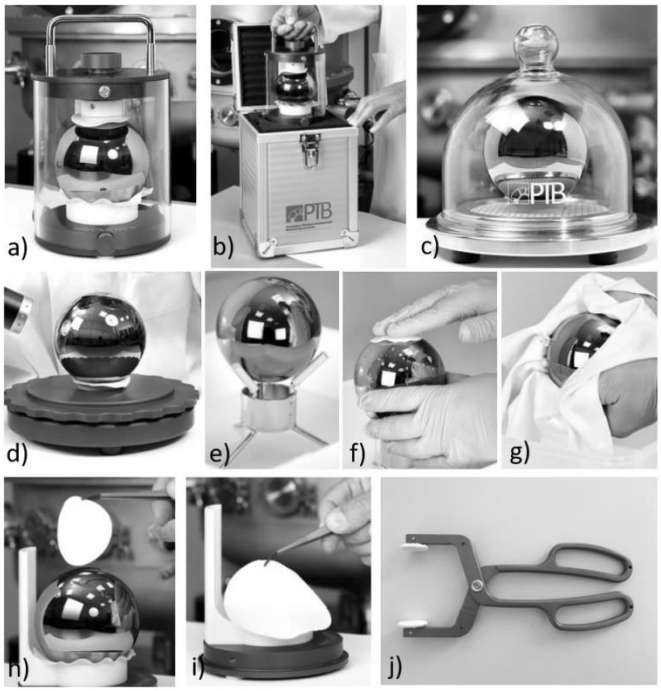

Fig. 2 Handling and cleaning tools for 1 kg silicon spheres

Silicon spheres require gentle cleaning liquids. Therefore, PTB recommends using only a specific pH neutral and salt-free cleaner used for precision optical components. The cleansing extract Deconex OP 163 is utilized for a 2 % solution with distilled water. This solution guarantees removing of adhering organic and inorganic residues on silicon sphere surface.

B. Si-Trust research investigations

Si-Trust increases data base on long term stability measurements of the silicon spheres. Basically, investigations depend on interest and equipment of the partner. The long-term study of mass monitoring in combination with PTB's reliable cleaning procedure are the most important investigations. Additional measurements in collaboration with PTB are welcomed and can be proposed by any partner. A list of additional possible research investigations is shown below:

- long-term study of the influence of repeated loading
- long-term study of drift effects (simple storage)
- training in mass calibration
- investigation of oxide layer growth
- investigation of long term stability by frequent cleaning
- investigation of stability against transportation, vibration and climatic changes
- elaboration of volume measurement techniques
- elaboration of roughness measurements
- investigation of Silicon-material

C. Status of Si-Trust collaboration

By now, eleven international partners from South and Central America, Europe, Africa and Asia already have received silicon spheres and have started their investigations. Until the end of 2018, about ten more partners (countries) will follow. The first feedback received from various partners is very positive.

Interested institutes are invited to contact PTB if they want to gain their own experience in handling Si-spheres. The experiences of the partners will be published after the project.

IV. Infrastructure for dissemination

A. Know-how transfer to industry

PTB is elaborating an infrastructure with two German companies in order to satisfy market demands for natural monocrystalline silicon spheres. Therefore, PTB transferred the manufacturing technology of natural monocrystalline silicon spheres to a manufacturing partner. The patented manufacturing process of the purpose-built machine provides contaminant-free spheres without subsurface damage of the crystalline structure, showing only minor shape errors, low roughness and a very uniform and stable oxide-layer. Figure 3 shows the polishing machine to manufacture silicon spheres.

Customers can purchase the required unit of the silicon sphere, certificates and accessories by PTBs sales partner.

The sales partner offers extensive accessories mentioned in Figure 2 such as transport cases, rotary plates, tongs and cleaning accessories. The service includes a technical training on the PTB cleaning procedure.

PTB provides calibration certificates of mass and volume/density upon customers request.

The comprehensive production process of ^{28}Si spheres will be handled by PTB only.

B. Manufacturing, characterization and calibration services for customers

PTB and industrial partners offer various services for silicon spheres. Technological services include manufacturing, marking and accessories along with different calibration services. A selection of services is listed in Table 3 below.

Table 3 Services provided by PTB and industrial partners for silicon spheres

services and calibration	^{28}Si	$^{nat}Si_{qp}$	$^{nat}Si_{sc}$
calibration			
mass	PTB	PTB	
(vacuum, < 20 µg)			
mass	PTB	PTB	industry
(air,15 µg)			
XPS/XRF	PTB	PTB	
density	PTB	PTB	industry
volume	PTB	PTB	
molar mass	PTB	PTB	
lattice parameter	PTB		
roundness			industry
ellipsometry	PTB	PTB	
roughness		PTB	
manufacturing	PTB	PTB/ industry	industry
marking	industry	industry	
accessories	industry	industry	industry

C. First status of sales

PTB already successfully sold the first ^{28}Si sphere to the Industrial Technology Research Institute (ITRI), Taiwan. In addition, PTB supports ITRI in building their own measuring device. It allows the characterization of the oxide layer and of unintentional contaminations on the surface by X-ray fluorescence spectroscopy (XRF) and X-ray photoelectron spectroscopy (XPS) techniques. As only mass deviations on the surface of the sphere are presumed, these measurements will show the long-term mass stability of the spheres in general.

Various other prospective customers are about to purchase secondary silicon spheres.

V. CONCLUSION AND OUTLOOK

PTB started the international Si-Trust collaboration with interested parties. Within the collaboration, partners get acquainted with the silicon spheres. In 2017 PTB already distributed silicon spheres to more than half a dozen partners in Africa, Asia, Europe, Central and South America. Various research topics are suggested complying with the partners' measurement equipment and interests.

What is more, PTB successfully transferred the manufacturing know-how of natural monocrystalline silicon spheres to industry. Customers are able to purchase secondary and "quasi-primary" silicon spheres by PTBs sales partner. The service includes training and extensive accessories.

^{28}Si spheres are distributed by PTB only. The first ^{28}Si sphere has already been sold.

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REFERENCES

[1] F. Haertig, H. Bettin, R. Schwartz "The new Kilogram Materialized by Silicon Isotopes", Conference Paper Conference on precision electromagnetic measurements (CPEM) Jul 10-15, 2016, ISBN 978-1-4673-9134-4.

[2] CIPM; Decisions of the 106th CIPM (October 2017) Decision CIPM/106-10

[3] The International System of Units (SI); Bureau International des Poids et Mésures, 8th edition 2006

[4] PTB; PTB Recipe for the New Kilogram; PTB news; 01/2015; www.ptb.de; access 07/2015.

[5] R. Wegge, H. Bettin, D. Knopf, F. Härtig „Dissemination of the kilogram via silicon spheres"; Euspen's 17 International Conference, Hannover 2017