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DISSEMINATION OF THE NEW KILOGRAM VIA SILICON SPHERES

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Abstract – The Physikalisch-Technische Bundesanstalt (PTB) is currently elaborating a concept for the maintenance and dissemination of the SI unit kilogram on the basis of silicon spheres. For this purpose, handling procedures and work instructions are elaborated. These contain, for example, the cleaning procedures of the spheres, the safe transport and storage as well as procedures for the monitoring of the growth of oxide on the sphere surface. Realisation of the redefined kilogram by means of ^{28}Si spheres and $^{nat}Si_{qp}$ spheres as primary respectively "quasi primary" mass measurement standards and disseminated with industrially manufactured $^{nat}Si_{sc}$ spheres as secondary mass measurement standards. The described procedures are to be developed in cooperation with European National Metrology Institutes (NMIs) and Destignated Institutes (DIs).

Keywords: kilogram, Avogadro constant, silicon mass measurement standard

1. INTRODUCTION

In the future SI, the kilogram, is realized and disseminated by means of three different types of silicon spheres with a nominal mass of 1 kg: the primary realization ^{28}Si, the "quasi-primary" realization $^{nat}Si_{qp}$, and the secondary measurement standard $^{nat}Si_{sc}$ (Figure 1). The reasons for this reside mainly on four points a) the kind of mass determination, b) the different availability of the silicon material they are made of, c) the surface qualities of the spheres depending on the manufacturing processes and d) the resulting different purchase prices. All spheres are characterized by their shape: contrary to the known material measures of PtIr or steel, spheres are not cylindrical and they have a larger surface due to their lower density. What first looks like a disadvantage turns out to be compensated by the fact that the spheres are much easier to clean if required – and thus to handle.

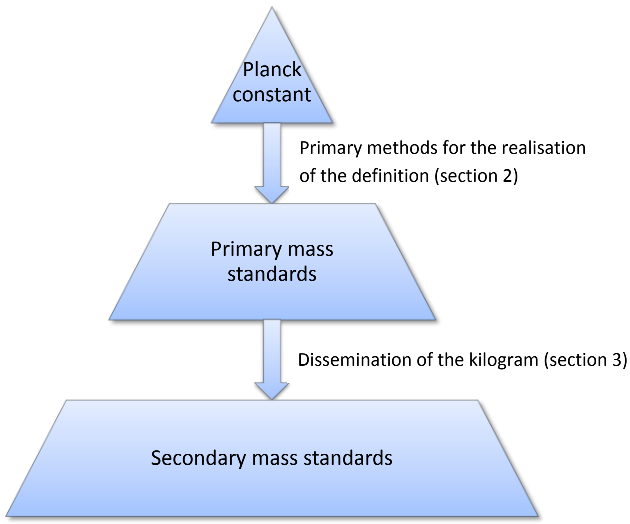

Fig. 1. Illustration of the traceability pyramid from the definition of the kilogram to primary and secondary mass measurement standards. The unit of the Planck constant being kg m^2 s^{-1}, the units second and metre are needed to derive a primary mass measurement standard from the Planck constant [1].

2. PRIMARY REALIZATION

The primary realization of the 1 kg mass as a measurement standard will, in future, be made of a high-purity monocrystalline silicon isotope ^{28}Si with 99.998 % enrichment [2]. For mass realization, this is, thus, the most important of the three silicon spheres. Over the next two years, its mass is to be realized with a relative standard measurement uncertainty of 1.0×10^{-8} - 1.5×10^{-8}. It is currently being reliably determined with a relative standard measurement uncertainty of 2×10^{-8} [3]. Thus, the conditions relating to the redefinition of the international system of units (SI), which is planned to be implemented at the General Conference for Weights and Measures in 2018

[4], are already met. Contrary to the existing definition, the SI mass will then no longer be linked up with the international prototype of the kilogram (IKP) [5], but defined via Planck's fundamental constant h [6]. For silicon 28 this leads to equations 1 and 2.

$$N_A = \frac{a^2 \cdot c}{2 R_\infty h} A_r^e M_{Si} \quad (1)$$

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_{Si}: molar mass of ^{28}Si

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

$$m = \frac{8\,V}{a_0^3} \frac{M_{Si}}{N_A} \quad (2)$$

with

m : mass

V : volume of the silicon sphere

a_0 : lattice parameter of ^{28}Si

The raw material is purchased in Russia, the only supplier known to date. There, the high-purity silicon is enriched at the Electrochemical Plant in Zelenogorsk. This requires the operation of hundreds of centrifuges for months. Then, 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.

A multi-level manufacturing procedure is used to produce the silicon spheres. Hereby, important edge conditions must be complied with; these are listed below in order of priority. The most important criterion is the maximum admissible deviation of the mass of +/-10 mg. It is the pre-condition for a low measurement uncertainty deviation of the subsequent weighing in the mass comparators. Volume measurement, as the basis of the determination of Avogadro's constant, requires a form error RONt of less than 30 nm and an average roughness value Ra of less than 0.3 nm. Furthermore, contamination with impurity atoms due to the lapping paste must be prevented. The favoured material for this purpose is pitch with an appropriate grain size. During the processing, the monocrystalline lattice structure at the surface of the sphere is damaged. This generates an amorphous boundary layer in which silicon oxide forms.

The smallest form errors of today's spheres lie around 35 nm for ^{28}Si (PTB reference: Avo28-S5c) and around 16 nm for $^{nat}Si_{sc}$ (PTB reference: Si-PTB-12-05). They exhibit a surface roughness of 0.2 nm. The deviation from the IPK of the AVO28-S8 was approximately -300 mg. In comparison, the PTB's national 1 kg mass measurement standard No. 70 differs to the IPK about -239 µg.

Due to the limited purchase opportunities, there are only two ^{28}Si spheres manufactured today; they are in the possession of the international Avogadro coordination (IAC). PTB is currently manufacturing its own two spheres which are expected to be completed by the end of 2015. Manufacturing another eight ^{28}Si spheres has been scheduled by PTB.

3. QUASI-PRIMARY REALIZATION

In addition to the realisation of the future kilogram by means of ^{28}Si spheres, PTB is currently developing a fully new approach for the realization of mass via a density comparison. This new approach uses monocrystalline spheres $^{nat}Si_{qp}$ made of natural silicon. In the following this is called quasi-primary realization. The main motivations for this development, compared to silicon 28, are the practically unlimited availability of natural silicon, and the purchase and manufacturing costs of approx. 100 k€ – which is at least 10 times less than for the ^{28}Si spheres. For a 1 kg silicon sphere, a relative measurement uncertainty of 3×10^{-8} is aimed for. This normally suffices to disseminate the unit of mass with sufficient accuracy to industry within the calibration pyramid of a country.

The manufacturing quality (i.e. the surface deviations and maximum admissible mass deviations) corresponds to that of a ^{28}Si sphere, as described in the section above.

Prior to a calibration, the volume of a $^{nat}Si_{qp}$ sphere must be determined once, for example, by means of a sphere interferometer. Additionally, a density measurement based on the magnetic flotation principle [6] will determine the density of the $^{nat}Si_{qp}$-sphere. It will be simply 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 primaty silicon sphere

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

4. SECONDARY MASS MEASUREMENT STANDARD

The secondary mass measurement standard $^{nat}Si_{sc}$, which is made of silicon, is a high-quality monocrystalline and robust mass measurement standard with a nominal mass of 1 kg. It will, in future, be possible to compare its mass to primary mass measurement standard of silicon 28 with a relative standard measurement uncertainty between 30 µg and 80 µg in vacuum as well as in air. To guarantee the envisaged measurement uncertainties in the case of a comparator measurement, various conditions have to be taken into account for the manufacturing. The most important criterion is a maximum mass deviation of 1 kg +/-10 mg. This requires frequent checks of the mass with a precision balance (reproducibility <= 1 mg, linearity <= 3 mg, air density determination of < 1%) during the manufacturing process. Further requirements are: a form error RONt < 80 nm and an average roughness value Ra < 1 nm. These specifications have meanwhile been attained by industrial enterprises.

The main characteristics of the different spheres are presented in table 1

Table 1. Different realizations of the 1 kg silicon sphere mass measurement standard

type	mass measurement standard	u_{rel} (k=1) of mass	form deviation RONt in nm	average roughness Ra in nm	expected price in Mio €
^{28}Si	primary	$2\ 10^{-8}$	< 30	< 0.2	> 1
$^{nat}Si_{qp}$	quasi primary	$3\ 10^{-8}$	< 20	< 0.2	~ 0.1
$^{nat}Si_{sc}$	secondary	$3\ 10^{-8}$	< 80	< 1	~ 0.01

5. CLEANING

Wet cleaning is the preferred procedure in front of a weighing process. The described procedure removes dust particles, and human organic compounds on the silicon surface without any measurable change of mass. Of course careful handling is required. In front of the cleaning process the sphere is placed on a mechanical tripod covered by teflon supports at the contacting areas. Afterwards the sphere will be washed. The liquid used is a compound of distilled water fulfilling the specification described in DIN 43530-1 table 4 [8] enriched by 2 % Deconex [9] lotion. During the washing process the executor shall carry unused gloves of Nitril comprising corrugated fingercaps. This is recommended as it supports the save handling of the wet and slippery sphere. The liquid should have a temperature of approximately 40 °C in order to unroll its best cleaning effects. During the washing procedure the particles will be carefully removed by using smooth microfiber wipers. By overturning the silicon sphere on the tripod the remaining hemisphere will be cleaned in an adjacent process. Afterward the remaining liquid will be removed by natured ethanol. The ethanol itself volatilize free of residues on the silicon surface. For the final procedures the executor shall change to new and cleaned gloves of Nitril. A final check allows the inspection of the sphere by sprinkling water vapor on its surface. This allows an easy and reliable detection of uncleaned parts. In case particles are still visible, the washing procedure has to be repeated. The cleaned silicon sphere will be dried in order to remove a last drop at its bottom. Therefore, it is recommended to use precision clean room wipers fulfilling the specification such as kit wiper 160 g/m^2 and 750 stitches/cm^2 [10].

6. TRANSPORT

As any physical body, mass measurement standards are subject to mechanical, chemical and electrostatic interactions with their environment. This is of particular importance, since this may cause the mass of the measurement standards to change significantly. Abrasive wear, for example, leads to weight reduction. Hereby, the highest source of risk is the moment when the sphere is put into holding equipment. These are present in all storage and transport containers as well as inside comparators. Material growth also has important impacts. This mainly means the formation of a silicon oxide layer. Contrary to all influence quantities, this cannot be prevented, since it occurs due to the interaction between the silicon surface and air. But also cleaning or simply holding silicon spheres with tongs or gloves may cause changes in weight as dust, dandruff, hairs or fibers from the cleaning cloths as well as biological substances which float in the air after someone has coughed or blown their nose may stick to the surface of the sphere.

For transportation over short distances and under clean conditions an executor will either use new gloves of Nitril or adjusting tongs. Tongs are used in areas that are difficult to access. The metallic jaws are hereby covered with leather. Lint-free microfibre cloths are placed between the leather surfaces and the silicon. When pressed onto the sphere, the leather adapts to the contact areas of the spheres without damaging their surface. Usually, the executor decides on his own preference whether he prefers gloves or adjusting tongs.

For longer distances where spheres have to be moved between measuring laboratories and over corridors the spheres have to be protected mainly against dust and any mechanical stress. Therefore, the PTB developed special transport containers (Figure 2).

Fig. 2. Transport container for silicon spheres. The material used avoids significant interference with the silicon.

These are high sophisticated objects as significant interference between the materials used has to be avoided. The cylindrical container is manufactured by two aluminum discs, one at the bottom and one at the top of the container. A 105 mm diameter pipe made of transparent polycarbonate is connecting in between the two aluminum discs. The electrostatic properties of the pipe attract conventional particles at its inner surface. This minimizes the contamination of the spheres. The sphere itself is mounted on a teflon ring at the bottom disk and a teflon stamp at the top disk. However, smooth wipers with clean room specifications are clamped between the contacting areas in order to avoid a direct contact between the teflon material and the silicon surface. A plastic screw containing a spring at the top disc allows fixing the sphere with a maximum force of 20 N. This absorbs small hits during the transportation or when putting the container on a table.

An additional shell made of polystyrene that coats the inner space of an aluminum suitcase is used to protect the transport container on longer distances. The suitcase additional protects the sphere from bigger hits, fast changes of climate conditions, and of course from mechanical damages. The size allows to carry the suitcases inside the overhead compartment of airplanes. All materials used must avoid significant degassing which could lead to a chemical interaction with the silicon surface.

7. LONG-TERM STABILITY

An essential reason for the realization and dissemination of the unit of mass via monocrystalline silicon bodies is the property according to which all significant influence quantities can be determined quantitatively. This is a significant advantage compared to the conventional high-quality material measures made of PtIr or of steel. In the case of these materials, neither can a statement on the quantitative composition of the atoms be made, nor can the effective pore depth at the surfaces and inside the mostly cylindrical bodies be determined due to their material properties. Thus, chemical changes or the out-gassing of impurity atoms cannot be detected with the required accuracy.

The mass of the silicon spheres changes over time. If these changes are due to mechanical destruction of the surfaces (such as scratches), then the primary and quasi-primary realization requires the volume and the surface layers to be redetermined. Such damage can, however, be easily prevented by handling the spheres with care. In contrast, the growth of an oxide layer and contamination of the surface layers cannot be prevented. They are quantitatively determined by an apparatus on a regular basis. This apparatus consists of a monochromatic X-ray source, a fluorescence detector (XRF) and an electron spectrometer (XPS). Irradiating the surface with Al K-alpha photons of an energy of 1486.7 eV allows transition metals as well as lighter elements such as oxygen and carbon to be excited. The irradiation provokes X-ray fluorescence radiation. The mass deposition of the existing elements is determined quantitatively by means of a radiometrically characterized detector. A high-resolution photoelectron detector allows the determination of the silicon oxide layer's stoichiometry.

8. FUTRURE ACTIVITIES

Within the scope of the dissemination of the future SI unit kilogram based on silicon spheres, several developments are planned over the next few years. The activities will, among other things, be focussed on setting up a density comparison apparatus by means of magnetic floatation. The quasi-primary realization of mass will be performed via $^{nat}Si_{qp}$ spheres. Furthermore, alternative cleaning methods (such as, e.g., dry cleaning or ultrasonic cleaning) for silicon spheres will be investigated. Mass comparators, weighing instruments of the classes E0 and E1 as well as weighing robots will, in addition, be upgraded for the use of silicon spheres. These developments are to take place in association with worldwide located metrology institutes, university institutes and with partners from industry. To this end, a research project within the scope of the European research initiative EMPIR [11] is planned. In June 2016, PTB will be hosting a workshop [12] to which all metrology institutes as well as designated institutes are invited in order to learn a simple way of handling silicon spheres.

9. CONCLUSIONS

Due to their material and surface properties and with it the easy handling, silicon spheres are well suited not only for the realization, but also for the maintenance and dissemination of the SI unit the kilogram. Three spheres of monocrystalline silicon have been presented. The most significant one is the future primary realization by means of ^{28}Si spheres with smallest measurement uncertainties. It is made of silicon highly enriched of isotope 28 and is characterized by the number of its atoms. Besides the primary realization, there will, in future, be the quasi-primary realization $^{nat}Si_{qp}$. It is made of natural silicon. The molar mass of the material is determined via a density comparison measurement and a volume determination. Due to their well suited material and surface properties, spheres made of natural silicon $^{nat}Si_{sc}$ are suited especially as high-precision secondary mass measurement standards. These three silicon spheres differ in the availability and in the composition of their respective materials, in the requirements placed on their surface properties and, thus, in their purchase prices.

The handling, cleaning, storage and transport procedures for silicon presented here show that the interactions in the daily handling of the silicon spheres and, thus, the dimensional accuracy are, compared to alternative mass measurement standards, easy to deal with. This applies to measurements in vacuum as well as in air. Due to its monocrystalline structure, significant changes are only possible at the surface and in the atom layers close to the surface. A special part of the activities therefore deals with methods for the characterization and long-term observation of silicon surfaces. Finally, guidance will be outlined as to how a worldwide collaboration of metrology institutes and companies will develop the dissemination of the SI unit the kilogram based on silicon spheres.

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