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DESIGN OF SORPTION AND BUOYANCY ARTEFACTS MADE OF SILICON

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Abstract:
The design of sorption and buoyancy artefacts made of silicon will be shown. With these artefacts, also known as transfer standards, high-precision calibrations can be performed under atmospheric conditions. They are used to systematically determine and correct deviations in air density and deposits on the surface, such as water and hydrocarbons. This development has been of importance since the unit kilogram can be realized by monocrystalline spheres made of isotope enriched silicon in line with the new definition of the SI in 2019. The special constraints and the complete geometric design parameters for sorption and buoyancy artefacts will be presented.

Keywords: sorption artefact; buoyancy artefact; kilogram; revised SI

1. INTRODUCTION

Since the redefinition of the SI in 2019, silicon spheres came into focus in mass metrology. The best-known spheres have a nominal weight of one kilogram, and an uncertainty of 1.1×10^{-8} kg. They are made of highly enriched monocrystalline silicon of isotope 28 (^{28}Si) [1]. However, their use is very limited due to the rare availability of the material, its sophisticated manufacturing process and the very high price. The excellent behaviour of ^{28}Si spheres, such as mass stability and easy handling, makes it interesting to develop also spheres and transfer standards made of natural silicon (^{nat}Si) [2]. One disadvantage of silicon spheres is the important difference of density ρ between silicon 2 329 kg·m^{-3}, national mass standards made of platinum-iridium alloy 21 530 kg·m^{-3} or conventional mass standards made of steel 8 000 kg·m^{-3} [3]. In a first order these variations lead to distinct volume and surface areas when different standards are used during a calibration process. The disruptive environmental influences can be prevented by using mass comparators operating in vacuum.

An alternative method is the use of sorption and buoyancy artefacts [4]. Both types are also called transfer standards. They allow systematic effects resulting from environmental conditions to be easily corrected. However, their design and handling conditions must be determined carefully in order to provide an expected standard deviation for mass in the range of 2×10^{-8}. So far, only a few transfer standards made of natural silicon with nominal mass of 1 kg, that are comparable to silicon spheres, are manufactured and investigated [5].

2. OBJECTIVES OF NEW TRANSFER STANDARDS AND CONSTRAINTS

The main objective is the development of transfer standards that allow high accurate calibration of mass standards under environmental conditions without vacuum comparator. The technical application shall be explained, its optimized design parameters as well as the operation conditions for sorption and buoyancy artefacts made of natural monocrystalline silicon shall be determined.

For the construction of transfer standards, the following manufacturing and handling requirements must be fulfilled, sorted by priority:

- similar nominal mass as the reference
- similar material and surface quality as the reference, natural monocrystalline silicon without amorphous surfaces
- nominal surface ratios from sorption artefacts to reference sphere should ideally be designed as integers (this supports the clear assessment of the sorption effects), see Figure 1
- equal nominal surface area for all buoyancy and duplex artefacts
- considering geometric limitation of the measuring chambers within typical mass comparators, correlated parameters: total height and radius of the transfer standards
- practice-oriented assembly, taking into account the geometric mounting conditions

of the comparators, this requires a special design of the base of sorption, buoyancy and inlay artefacts
- easy demounting of the sorption and inlay artefacts for efficient cleaning
- statically determined storage by frictional locking of the sorption artefacts discs to be stacked
- high tilting stability of the sorption artefact discs

Particular focus is given to the development of what is referred to as a duplex transfer standard that embodies the functionality of both a sorption and a buoyancy artefact.

A further highlight will be another special transfer standard, the inlay buoyancy artefact. Due to an enclosed tungsten core, this standard has a large volume difference to other buoyancy bodies, which contributes directly to the determination of the air density.

3. DESIGN OF NEW TRANSFER STANDARDS

Mass changes of weights caused by deposits on their surfaces or by buoyancy effects can be described by at least two transfer standards. Figure 1 outlines systematically different variants of sorption and buoyancy artefacts. All transfer standards have the same nominal mass and closely similar surface properties as the reference standard, which is defined by a 1 kg silicon sphere.

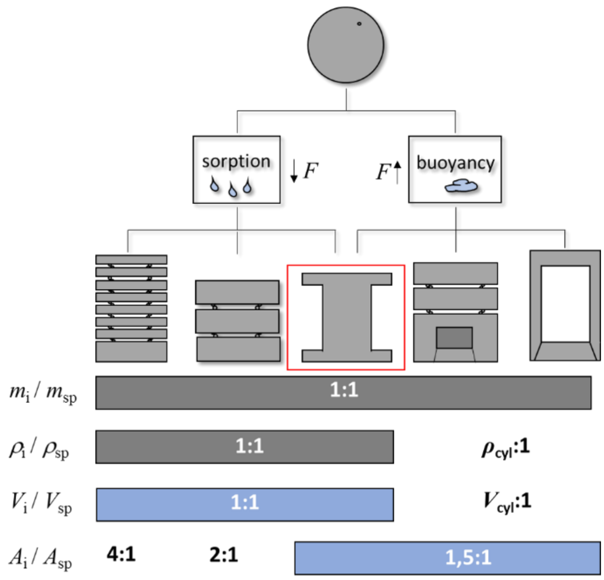

Figure 1: Schematic illustration of ratios of different sorption artefacts (left), buoyancy artefacts (right), duplex artefact (middle, red)

Sorption Artefacts

Depositions such as physically absorbed water or hydrocarbons can be determined by sorption artefacts. In Figure 1 these are the two transfer standards on the left. The geometric disc design increases the surface area while maintaining mass, density and volume. In this context, it is important to retain the volume so that a consistent buoyancy influences on the set of sorption artefacts is granted.

On the other hand, the nominal surface area ratios of the sorption artefacts are designed as possible integer multiples of the reference to permit rapid assessments. The systematic error of the mass due to deposits on the surface areas can be determined by comparing measurements in air and vacuum, and the knowledge of the well-known surface area of the sorption artefacts used. The surface difference was systematically designed and calculated for a set of sorption artefacts consisting of two or seven discs and a cylinder.

To simplify the loading of the comparators, the ground cylinder of the sorption artefact with seven discs was designed with a larger height than the discs on top of it.

Buoyancy Artefacts

Buoyancy effects caused by density differences between mass standards and air can be ascertained by buoyancy artefacts. In Figure 1 these are the two transfer standards on the right.

Key characteristics of these are the variations in volume and density while remaining the same mass and surface area. Since the surface area and surface properties of the transfer standards and the reference should be identical, the difference in density can only be created by forming a cavity or a denser core.

The hollow chamber can be vacuumed gas-tight or filled with a gas. In this case the buoyancy artefact is referred to as a hollow cylinder.

A new approach is to increase the buoyancy difference by using a transfer standard with a core made of a denser material than that of the reference. This inlay artefact has a smaller volume compared to other transfer standards. The air density used to calculate the buoyancy correction is determined from measurements of the mass differences between the buoyancy artefacts in air and in vacuum. It is obtained from the difference (air to vacuum) of the difference (of the masses).

Duplex Artefact

There is another exceptional transfer standard, which is referred to as duplex artefact and illustrated in Figure 1 in the centre. It may be used as both a sorption and a buoyancy artefact. Because of the geometry selected it is also known as dumbbell artefact.

The individual components of the transfer standards made of natural monocrystalline silicon are finished with a defined rotating chamfer to prevent chipping.

4. STATICALLY DISMOUNTABLE COUPLING

A key issue for handling transfer standards is the accurate and careful cleaning of the surfaces and interspaces. The construction of both, the sorption and the inlay artefacts as separable components ensures this overall cleaning in order to avoid unpredictable mass differences between the artefacts due to contamination. In this context, it was essential to determine the contact areas as best as possible and to keep the discs easy to be assembled and statically positioned. In addition, it was important to achieve a maximum tilting stability of the stack of discs.

Up to now, two construction principles are best known for sorption artefacts:

1. Artefacts with fixed shafts. Although this construction principle results in a stable connection, a serious risk applies that the shaft will be scratched during the assembly process. In consequence the surface area behaviour of the silicon will change and will become more sensitive to impurities that access into micro scratches. On top of this, the cleaning of the gaps is very time-consuming.
2. Construction in the form of disc stacks with discs placed on loose wires. However, putting the wires on the slippery silicon surface during the stacking process of the individual discs is very time-consuming. This technique also carries the risk that the stack may slip away or even collapse during handling and weighing process.

For the purpose of managing the risks stated above, a new and suitable construction has been realized with a combination of spherical distance pieces. Figure 2 shows the arrangement of the so-called coupling with spherical distance pieces. It shows the six green marked spheres on the top of the lower disc. The disc located above rests with its three red marked spheres on it. The resulting six-point contact is statically determined. The quasi-point-like area coverage will be minimal, so that it is negligible for further calculations.

In experiments with different arrangements of the spherical distance pieces, this model was identified to be the easiest to assemble. Likewise, the inclination stability with > 20° was also demonstrated experimentally. This tilt stability is more than sufficiently high to handle a stack of discs safely.

The spheres were manufactured from the same material as the remaining transfer standards and therefore have the same sorption properties. Their diameter of 4 mm was manufactured with a manufacturing tolerance of ±1 µm and a form deviation of λ/10 which are not relevant for further calculations [6].

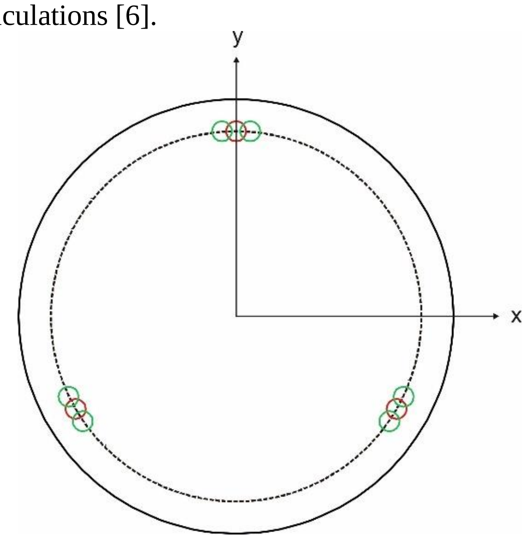

Figure 2: Top view of the location of the spherical distance pieces of a gap between two discs. Green marked spheres are fixed on the lower disc, red labelled spherical distance pieces are located on the upper disc.

As the radius of the coupling spheres decreases, the risk of plastic deformation or even chipping increases. To prove the stability, the limit value for the elastic deformation was evaluated. For this purpose, an analytical calculation [7] was carried out.

Table 1 lists the material properties of the material used in order to calculate the maximum stress of the contact points. Since the silicon supplier itself could not provide any information on further material properties, the values according to [8] were used as a reference.

The maximum load acting on a contact point of a sphere is assumed to be 0.333 kg. This static load can theoretically occur when a transfer standard is tilted. In this pessimistic view only three spheres are in point contact. This assumption can be regarded as an additional safety factor for following stability investigation.

Table 1: Analysis of contact mechanics for coupling

Parameter	**Value**
mass of contact point, in kg	0.333
acceleration of gravity, in $m \cdot s^{-2}$	9.81
radius of spherical distance piece, in m	0.002
elastic modulus, in $kg \cdot m^{-1} \cdot s^{-2}$	131×10^9
Poisson's ratio	0.221

The homogeneous and presumably isotropic raw material of the silicon used and the validity of Hooke's law fulfil the preconditions of the calculation for the Hertzian pressure [9].

The effective radius r resulting from the two identical individual radii r_{sph} of the coupling spheres is calculated according to equation (1).

$$r = \frac{1}{\left(\frac{1}{r_{\mathrm{sph}}} + \frac{1}{r_{\mathrm{sph}}}\right)} \quad (1)$$

Using this effective radius, the compressive stress can then be evaluated with the known mass of contact point m, Poisson's ratio v and Young's modulus E, according to equation (2).

$$\sigma = \frac{1}{\pi} \sqrt[3]{\frac{1.5 \cdot m \cdot g \cdot E^2}{r^2(1-v^2)^2}} \quad (2)$$

The calculation results in a compressive stress of 1.443×10^9 Pa. This is a factor of approximately 0.45 smaller than the maximum allowed compressive stress of 3.2×10^9 Pa which is given in literature [10]. Resulting from the observation above, the selected spherical spacers ensure sufficient stability and thus serve ideally as coupling components.

Equation (3) describes the expected deformation.

$$\omega_0 = \sqrt[3]{\frac{2.25 \cdot (1-v^2)^2 \cdot (m \cdot g)^2}{E^2 \cdot r}} \quad (3)$$

The technically also interesting value ω_0 for flattening is calculated to be 1.082×10^{-6} m. Compared to the sphere radius, this leads to a negligible deformation of less than 0.2 %.

5. MATHEMATICAL APPROACH

As previously pointed out in section 2, several constraints must be regarded for the determination of the geometric parameters of the transfer standards. Above all, it is particularly important to achieve a mass of one kilogram in the range of ± 100 mg, as the established mass comparators are configured most accurately for this measuring range. With all constraints being taken into account, the following correlated variables for all transfer standards: mass, volume, surface area ratios between the transfer standards, number of discs as well as diameter and height of the discs/cylinders must be determined. Due to the manufacturing process, the individual discs are finished with chamfers. Consequently, this leads to a further change in mass and surface area for the discs/cylinders, which must also be factored into the calculation. In the case of transfer standards consisting of mounted discs, the mass, volume and surface area corrections caused by the spherical distance pieces for the coupling must also be incorporated.

An exceptional case is the inlay artefact, as it is made of two different materials. In this application, the different densities are included in the complex calculations. Depending on the type of transfer standard a minimum of seven up to a maximum of ten correlated parameter must be determined. The interesting geometrical parameters for the transfer standards are determined by the use of a highly sophisticated multi fitting algorithm. Therefore, a Newton's multi parameter iteration method [7] in combination with a self-developed iteration method was used. The calculations were carried out in Mathematica [11]. The complex equations are not in focus of this paper.

6. RESULTS

Based on the requirements discussed in section 3, transfer standards of monocrystalline silicon with a nominal mass of 1 kg were designed. For the sorption artefacts, this resulted in two types, a sorption artefact stack with seven and a stack with two discs, each with one cylinder.

Following this, two variants were also calculated for the buoyancy artefacts. The hollow cylinder is evacuated in this configuration. The inlay artefact consists of two discs and a cylinder which embodies a core of tungsten. In addition, the parameters for a duplex artefact were also developed, which can be used both as a sorption and a buoyancy artefact.

The geometric parameters for the transfer standards are summarized in Table 2. The density of the silicon used was specified as 2 328.8 $\mathrm{kg \cdot m^{-3}}$ [12]. The calculations were based on a leg dimension of 0.5 mm and a bevel angle of 45° for all chamfers. The radius of the coupling spheres was defined as 2 mm. The chamber of the hollow cylinder was assumed to be evacuated. The inlay body was designed for a tungsten core with a density of 19 250 $\mathrm{kg \cdot m^{-3}}$ [13].

The most important results considering surface area and volume required for new designed sorption and buoyancy transfer standards made of silicon are presented in Table 3.

According to internal investigations made by PTB, the crystallographic orientation of the silicon bodies has no significant effect for the corrections.

Table 2: Geometric parameters of different transfer standards. Values are given in metres.

	sorption artefact n8	**sorption artefact n3**	**duplex artefact**	**inlay artefact**	**hollow artefact**
disc radius	0.042 3 to 0.043 4	0.043 4	0.045	0.034	-
disc height	0.008 to 0.015 5	0.024 2	0.025 5	0.030	-
radius cylinder	-	-	0.03	0.034	0.045
height cylinder	-	-	0.037	0.031	0.102
radius inlay core/ hollow chamber	-	-	-	0.016 9	0.030
height inlay core/ hollow chamber	-	-	-	0.015 2	0.077

Table 3: Example results for set of different transfer standards. Sorption artefacts with seven discs (n8) and two discs (n3).

Transfer standard	**Surface area A / m²**	**Volume V / m³**	**Density ρ / kg·m^{-3}**
sorption artefact n8	0.110 101	0.000 429 406	2 328.8
sorption artefact n3	0.055 050 3	0.000 429 406	2 328.8
duplex artefact	0.041 287 7	0.000 429 406	2 328.8
inlay artefact	0.041 287 7	0.000 330 603	3 024.78
hollow artefact	0.041 287 7	0.000 646 366	1 547.11

7. SUMMARY AND OUTLOOK

The design strategy and related parameters for sorption and buoyancy transfer standards are explained. Main focus is given on the geometrical design of the individual five artefacts. Mathematical multi parameter fit algorithms allow to determine the individual parameters considering the limiting conditions such as measurement volume, weight of the objects, object density, volume, surface area, couplings of the sorption artefacts and others.

In order to provide user friendly transfer standards, a dismountable, highly reproduceable coupling was developed that allows the disc stack of the sorption and inlay artefacts to be fixed with minimum risk of surface damage and sufficient inclination stability.

Next steps are the manufacturing of the transfer standards and the determination of the actual geometrical parameter in order to calculate the effective correction parameters including a solid measurement uncertainty budget. Finally, the results will be validated by real measurements taken on mass comparators in vacuum and in air.

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