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EVALUATION OF ADSORPTION EFFECT BY USING SILICON SPHERE AND SILICON SURFACE ARTEFACTS

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Abstract: KRISS mass laboratory is studying the adsorption effect of the weight and silicon (Si) surface by using the precise mass comparator which can be used in vacuum and developing the ellipsometric system. For its preliminary study, the mass of Si sphere which is using for the density standard at KRISS density laboratory is measured in air before and after vacuum. Si surface artifacts (SAs) are fabricated and measured dimension and roughness. Preliminary experiments are carried out in vacuum and in air.

In this paper, we report on a preliminary study conducted at the KRISS in which we examined the adsorption mass measurement of 1 kg Si sphere, SA cylinder (SA-C) and SA disks (SA-D).

Keywords: adsorption mass, Avogadro constant, Si sphere

1. INTRODUCTION

Recently lots of National Metrology Institute (NMIs) are investigating for re-definition of kilogram, for example, Watt balance, Avogadro constant, and ion accumulation etc., according to CIPM resolution. These experiments are carried out in vacuum state, thus the evaluation of adsorption effect on the surface of mass standards is required. Specially adsorption effect on Si surface is one of the important factors in Avogadro constant project[1-3]. The principle of gravimetric method for the adsorption mass is represented by the following equation (1);

$$\mu' = \frac{\Delta m_{air} - \Delta m_{vac}}{\Delta S} \qquad (1)$$

Where μ' is the adsorption mass change per area, Δm_{air} and Δm_{vac} are mass difference of two artefacts in air and in vacuum respectively and ΔS is surface area difference of two artifacts[4]. As a part of this research, the mass measurement in vacuum and in air of Si sphere, which is using as a density standard of KRISS, is carried out by using the precise mass comparator (Mettler-Toledo *M_one*). Si SAs are fabricated for evaluating the adsorption effect on the Si surface. Si sphere also is used as an SA.

In this paper, experimental conditions, the interim result and the uncertainty for mass measurement of silicon sphere and the adsorption effect of Si surface are described.

2. DESCRIPTION OF INSTRUMENTS

The gravimetric method is based on the weighing of two artefacts having the same mass, the same volume and the same surface finish but with very different surface areas.

Fig. 1 shows a photograph of measurement system. Measurement system is consisted of mass comparator, vacuum system and the instruments to measure environmental conditions, that is, temperature, humidity, pressure and CO_2 concentration. Measurements were performed by using the precise mass comparator (*M_one*) which has a capacity of 1 kg and a readability of 0.1 μg and the standard deviation of less than 0.5 μg. The electric weighing range is 1.5 g and its sensitivity is confirmed by a built-in wire weight of 1 g. The mass comparator has a weight-exchanger for four positions and installed in an air-tight chamber.

Fig. 1. A photograph of measurement system

Table 1. Properties of SAs and Si sphere 1

Properties	1 kg			500 g		
	SA-C	SA-D including spacers	Si Sphere	Cylinder	Disk(×6)	Difference
Conventional mass / g	999.944285	999.214751	999.838985	499.907	82.384(494.304)	
Height / mm	86.464	94.214	93.594	77.25	12.75(82.0)	
Diameter / mm	79.516	79.514(4)*+79.454 (2)+27.33(1)+2(18)	93.594	59.5	59.5	
Surface area / cm^2	311	816	275.2	198.40	77.83(466.98)	268.6
Volume / cm^3	429.33	429.02	429.29	214.71	35.37(212.22)	2.49
Roughness (Rz) / nm	26.6	26.6	-	26.6	26.6	
Purity / %	99.999	99.999	-	99.999	99.999	

The measurements were performed at normal ambient conditions, that is, at pressure between 100.256 Pa and 99.142 Pa, temperature between 19.978 ℃ and 19.834 ℃ and relative humidity between 55.6 % and 51.5 %. The weighing sequence and data logging, including the air density during weighings, are computer-controlled.

The mass comparator was installed inside an air-tight chamber connected to oil-less turbo molecular pump (Alcatel 5400CP, 400 L/s, 27,000 rpm). The pressure inside the chamber could go down to 0.1 Pa in 24 hours after pump powers on. Measurements in vacuum were carried out in the pumping state. The mass comparator in vacuum functioned well and shows standard deviation better than those in air. Compact full range controller (PKR 251) manufactured by PFEIFF Vacuum Co. is used as vacuum gauge.
Humidity, temperature and pressure sensors for measuring the ambient conditions are installed near sample inside the mass comparator. The uncertainty sources (k=2) are the 1 % R.H.(Vaisala, HMI38, readability of 0.1 %) for humidity change, 2.5 mK(ASL, F700, readability of 1 mK) for pressure and 50 ppm(Horiba, PIR-2000, readability of 1 ppm) for CO_2 concentration.

3. SURFACE ARTEFACTS

Fig. 2 shows Si SAs of 1 kg and 500 g fabricated at KRISS. Table 1 shows the properties of SAs and Si sphere. SAs are called SA-C, SA-D and Si Sphere. SA-C is cylinder type made of one piece and SA-D is consisted of 6 pieces of large disks, 1 piece of small disk, 31 pieces of small spacers and a stainless steel weight of 1 g to adjust mass difference. Small spacer (diameter=2 mm, height=1 mm) made of Si wire are used to give gap between disks. 3 pieces of spacers are used for one layer. Si sphere which is using as density standard of KRISS also is used for SA.

3.1. Cleaning

The silicon SAs and spacers were cleaned using solvents ethanol for 15 minutes in commercial ultrasonic bath (Branson 3510) and then were dried with clean nitrogen gas of purity 99.999 %[5]. Fig. 3 shows mass difference between SA-D and SA-C before and after cleaning. After first ultrasonic cleaning, mass change of approximately 238 μg showed at the mass difference between SA-D and SA-C.

Fig. 2. A photograph of Si surface artifacts (1 kg and 500 g). Inset: 1 kg Si-sphere

3.2. Dimension measurement

The surfaces are carefully polished. To measure the surface roughness of the silicon samples (disk and cylinder shape), we used a scanning white light interferometer (SWLI) which is a well-established technique for quickly determining three-dimensional surface shape over large areas without contacting a sample [6].

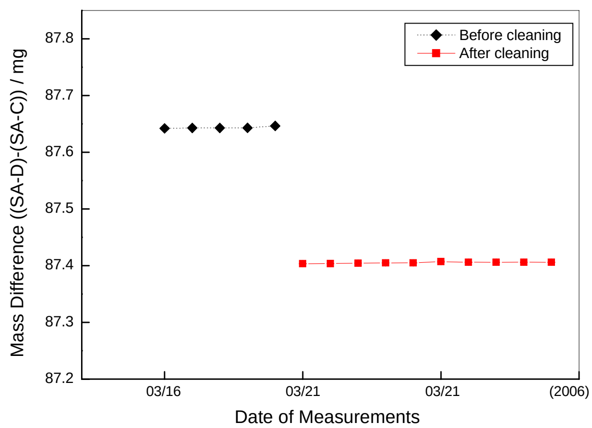

Fig. 3. Mass change between SA-D and SA-C after first cleaning

The typical scanned image by SWLI is shown in Fig. 4. The average of height roughness (R_z) of the disks was 26.6

nm with the standard deviation of 13.7 nm: the distribution of the roughness was a range of 8.07 nm to 41.28 nm.

The dimension of SAs, those are, diameter and height are measured by using 3-dimensional machine (ZEISS UMM500) at length laboratory of KRISS within the expanded uncertainty of 20 μm.

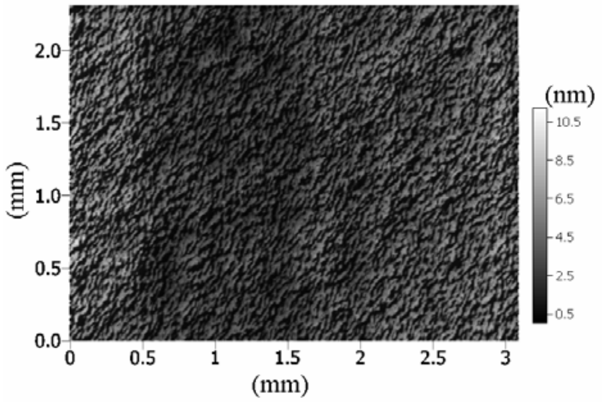

Fig. 4. The typical example of scanned image by SWLI. The gray scale represented the height amplitude (R_z) in nanometer.

The surface areas are calculated with the measured dimension. Those for SA-C, SA-D and Si sphere are obtained 311 cm^2, 816 cm^2 and 275.2 cm^2 respectively.

4. INTERIM EXPERIMENT RESULT

4.1. Mass measurement of Si sphere

Mass comparison is carried out by using the substitution method in principle, that is, Reference-Test-Test-Reference (R-T-T-R). In this experiment, one series of mass comparison between two artefacts consists of 6 measurements and one measurement consists of one R-T-T-R. Usually one group consists of 5 series of measurements and it takes about 5 hour. Sensitivity of mass comparator is checked by using the built-in wire weight of 1 g twice per group at beginning and end, as shown in Fig. 5. For performance test of mass comparator in vacuum, preliminary experiment was made with stainless steel weights (HAF, MT) and Si sphere which is using as density standard at KRISS[7,8]. The procedure to measure first is to compare between HAF and Si sphere, HAF and MT in air. Second is to compare between Si sphere and MT in vacuum. Third is to compare between HAF and Si sphere, HAF and MT in air again. As a result, true mass of Si sphere is obtained before and after vacuum as shown Fig. 6. The difference is 0.020 mg. The measurement uncertainty of Si sphere mass compared to stainless weight 1 kg is obtained as 0.120 mg at confidence level of about 95 % (k=2). Main source of uncertainty is the uncertainty due to buoyancy correction.

4.2. Bouyancy correction

The air buoyancy correction is equal to the product of the density of the ambient air by the volume difference between two masses compared. The air density is determined by the CIPM 81/91 formula with molar constant R=8.314 472 Jmol^{-1}K^{-1} and new mole fraction of argon x_{Ar}=933.150(3) mmolmol^{-1}[9]. The obtained air density shows a range of 1.186 31 kgm^{-3} to 1.173 83 kgm^{-3}.

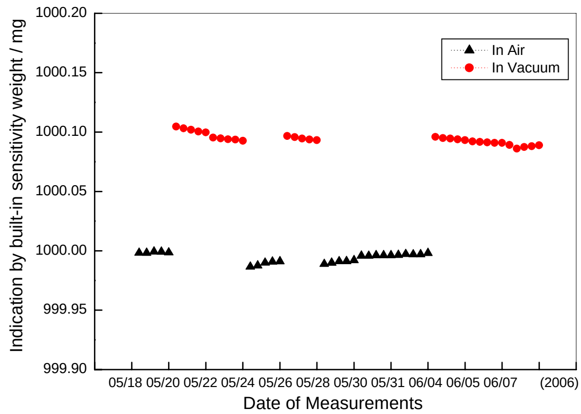

Fig. 5. Indication in air and in vacuum by built-in sensitivity weight of 1 g

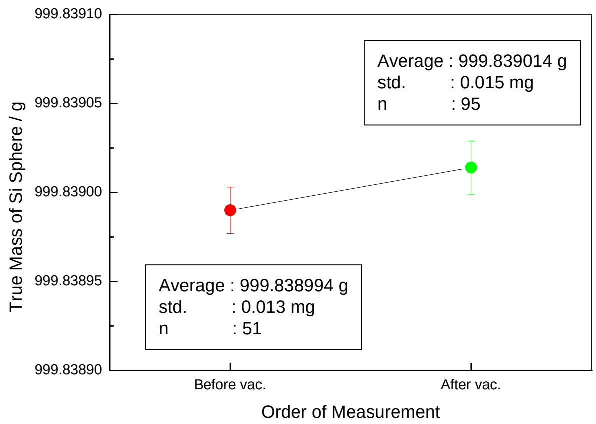

Fig. 6. True mass of Si sphere before and after vacuum

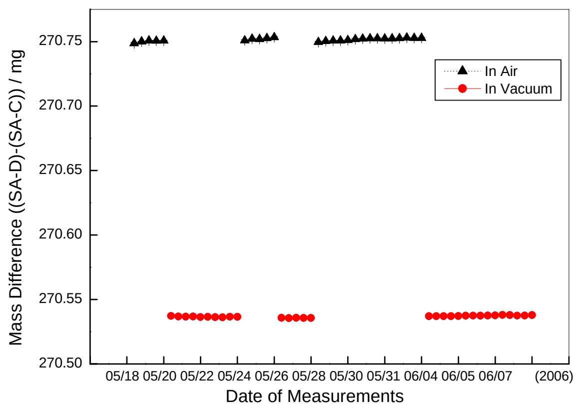

Fig. 7 Raw data for mass comparison between (SA-D) and (SA-C) in air and in vacuum

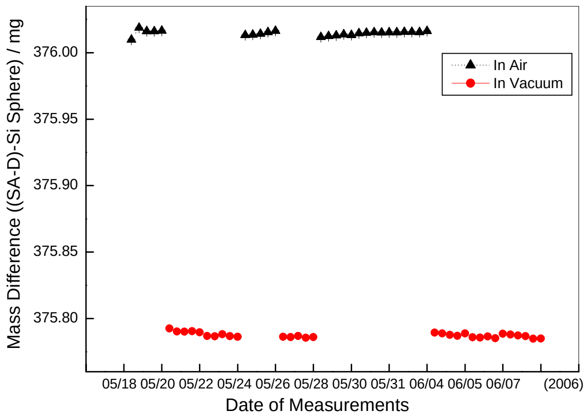

Fig. 8. Raw data for mass comparison between (SA-D) and Si Sphere in air and in vacuum

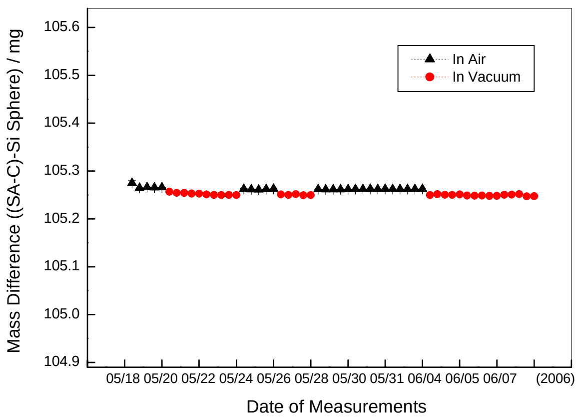

Fig. 9. Raw data for mass comparison between (SA-C) and Si Sphere in air and in vacuum

Fig. 7, Fig. 8, and Fig. 9 show the raw data for mass comparison between SA-D and SA-C, between SA-D and Si sphere, and between SA-C and Si sphere respectively.

Results are calculated by using equation (1) with data of each measurement in air and the averaged data in vacuum excluding the beginning 5 measurements. The averaged values in vacuum are as follow;

$$\Delta((SA\text{-}D)\text{-}(SA\text{-}C))_{vac} = 270.513 \text{ mg} \quad (n=25, \text{ s.d.}=0.0014 \text{ mg})$$

$$\Delta((SA\text{-}D)\text{-Si Sphere})_{vac} = 375.754 \text{ mg} \quad (n=25, \text{ s.d.}=0.0010 \text{ mg})$$

$$\Delta((SA\text{-}C)\text{- Si Sphere})_{vac} = 105.241 \text{ mg} \quad (n=25, \text{ s.d.}=0.0014 \text{ mg})$$

Where n and s.d. are the number and the standard deviation of measurement respectively.

All data are adjusted by the sensitivity of mass comparator shown in Fig. 5.

Interim results for adsorption isotherm are as follows;

$$\mu'_{((SA\text{-}D)\text{-}(SA\text{-}C))} = 0.4790 \text{ µg cm}^{-2} \quad (n=20, \text{ s.d.}=0.0017 \text{ µg cm}^{-2})$$

$$\mu'_{((SA\text{-}D)\text{-Si Sphere})} = 0.4899 \text{ µg cm}^{-2} \quad (n=20, \text{ s.d.}=0.0019 \text{ µg cm}^{-2})$$

$$\mu'_{((SA\text{-}C)\text{- Si Sphere})} = 0.6341 \text{ µg cm}^{-2} \quad (n=20, \text{ s.d.}=0.0117 \text{ µg cm}^{-2})$$

As a result, two case of μ' are similar but the other is bigger. The reason is guessed due to small difference of surface area.

5. CONCLUSION AND FUTURE WORK

The mass of Si sphere is measured before and after vacuum. The value of 999.838 994 g and 999.839 014 g is obtained for before and after vacuum respectively with the uncertainty of 120 µg. The difference is 10 µg. The results have a good agreement within the uncertainty.

The preliminary experiment with Si SAs and Si sphere were carried out for the evaluation of the adsorption effect of Si surface. As a result, adsorption mass change per area, μ', is obtained as 0.479 µg cm^{-2}, 0.490 µg cm^{-2} and 0.634 µg cm^{-2} for mass comparison between SA-D and SA-C, between SA-D and Si sphere, and between SA-C and Si sphere respectively.

In future, the experiments with SAs of 1 kg and Si SAs of 500 g according to humidity variation will be carried out to get BET parameters for multilayer adsorption.

Additionally ellipsometric system for adsorption experiment will be installed, and then both results can be compared.

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