Uncertainty reevaluation in determining the volume of a silicon sphere by spherical harmonics in an Avogadro project*

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To determine the Avogadro constant with a target relative uncertainty of 2×10^{-8}, the uncertainty component of the silicon sphere's volume introduced by the spherical harmonics method, which is usually used in determining the sphere's volume, is reevaluated. By means of representing the shape of the silicon sphere by an ellipsoid with Gaussian white noise in its diameters, the uncertainty of the current mapping methods based on the spherical harmonics theory can be estimated theoretically. It is evidenced that the uncertainty component attributed to the current mapping method is underestimated. To eliminate this effect as much as possible, the number of mapping points should be increased to more than before. Moreover, a new mapping method is proposed to accomplish the equal-area mapping with large number points on the silicon sphere.

Keywords: metrology, Avogadro constant, silicon sphere, spherical harmonics

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1. Introduction

The current aim of the International Avogadro Coordination is to determine the Avogadro constant ($N_{\rm A}$) with a relative uncertainty of 2.0×10^{-8},[1] so that $N_{\rm A}$ may be applied to redefine the kilogram. $N_{\rm A}$ is defined as $N_{\rm A} = M_0/\rho V_{\rm a}$, where M_0 and $V_{\rm a}$ are the molar mass and atomic volume, respectively, and ρ is the macroscopic density. The density is determined by measuring the mass m and volume v of a nearly perfect single crystal silicon sphere with a diameter of nearly 94 mm. To satisfy the demand of redefinition, among all the quantities, the volume v of a silicon sphere is expected to be determined with a relative uncertainty of 1×10^{-8}, which means that the uncertainty of the mean diameter should be better than 0.3 nm. Recent results have shown that a relative uncertainty of 3×10^{-8} in volume is achievable.[2,3] However, the effects of the methods on the estimate of the volume by measuring diameters on discrete positions of the silicon sphere, which are usually ignored before, should be reevaluated carefully when considering the most accurate target.

The shape of the real sphere is always imperfect owing to the technique of fabrication. Therefore, for a real sphere with large sphericity, the volume determined by measuring only one diameter will not be accurate enough. In 1974, Johnson[4] concluded that for a sphere with a diameter of 94 mm, the N-point mean of some discrete diameters can represent the average diameter of the sphere approximately. There are two routes to obtain the volume of an approximate sphere: estimating its average diameter or average breadth (to avoid confusion, the term 'mean' refers to the experimental value of a quantity and 'average' refers to its theoretical value). Nevertheless, things are not as trivial as they seem. In fact, we can only measure the diameters in some, but not all, finite positions of the sphere in experiment. Therefore, how to sample the points and then estimate the mean value so that the average diameter can be evaluated accurately is still a problem. In 1994, Mana[5] extended Johnson's work further in two aspects. (i) If the approximate sphere can be represented by spherical harmonics (SH), then the coefficient of the zero-order of the SH is exactly

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the average diameter of the sphere. (ii) Providing a mapping theorem. According to this theorem, the average diameter of an approximate sphere having a bandwidth-limited spectrum can be obtained by the N-point mean of a specific set of diameters. Almost at the same time, Giardini and Ha[6,7] described an experimental setup capable of furnishing the roundness and sphericity measurements, as well as an algorithm to calculate the volume of sphere.

Nowadays, methods of an N-point mean based on Johnson and Mana's theories are widely applied in order to determine the volume of a silicon sphere.[2,8−13] However, these theories are based on the hypothesis that the sphericity of the sphere can be represented by a bandwidth-limited SH exactly, which is just a mathematical approximation and not a fact. Actually, experiments have shown that artificial spheres are not scratch free in nanometer scale,[12] which means that the bandwidth of the real sphere should be unlimited or unknown in nanometer scale. Thus the estimated uncertainty based on the N-point mean method should be reevaluated carefully.

In this article, efforts are made to reevaluate the methods for estimating the uncertainty of the average diameter. We will show that with the invalid hypothesis of Johnson and Mana, the uncertainty of the average diameter evaluated previously is underestimated. Consequently, the current mapping numbers should be increased greatly according to the features of the real sphere.

2. Theory

2.1. An uncertainty component that cannot be ignored

The sphere's volume can be described as

$$V = \frac{4\pi}{3}r_0^3 + r_0^2\int_{\rm s}\delta {\rm d}\Omega + r_0\int_{\rm s}\delta^2{\rm d}\Omega + \frac{1}{3}\int_{\rm s}\delta^3{\rm d}\Omega, \quad (1)$$

where r_0 is the average radius of the sphere and δ is the deviation of the radius at different solid angles Ω. According to the definition, $\int_{\rm s}\delta{\rm d}\Omega = 0$ and $\frac{1}{3}\int_{\rm s}\delta^3{\rm d}\Omega$ can be ignored because it is very small. Thus, Eq. (1) reduces to

$$V = \frac{4\pi}{3}r_0^3 + r_0\int_{\rm s}\delta^2{\rm d}\Omega. \quad (2)$$

According to Johnson and Mana's theories, the volume can be estimated by the first part of Eq. (2) and the second part is considered to be the systematic error, which is used for the uncertainty estimation. In fact, however, only finite numbers of radii can be measured in experiment, so that the measured mean result $\bar{r}$ is just an approximation of the average radius r_0, usually $\bar{r} \neq r_0$ on the nanometer scale. Suppose the discrepancy between them is Δr, namely, $\bar{r} = r_0 - \Delta r$, then $\int_{\rm s}\delta{\rm d}\Omega$ in Eq. (1) will not be equal to zero but Δr and Eq. (2) should be reserved as follows:

$$V_{\rm exp} = \frac{4\pi}{3}\bar{r}^3 + 4\pi\bar{r}^2\Delta r + \bar{r}\int_{\rm s}\delta^2{\rm d}\Omega. \quad (3)$$

The subscript "exp" represents the situation in experiment. Therefore, the relative error introduced to the volume should be $\Delta V/V \approx 3\Delta r/\pi r_0$. For a sphere with a diameter of 94 mm, let Δr be 1 nm, then the relative error of the volume is up to about 3×10^{-8}. This error cannot be ignored when considering the current measurement target.

2.2. Estimating the uncertainty by the SH

The SH are applied widely to represent the diameters of the sphere because they, similar to the expansion of the Fourier series, can describe the sphericity of the sphere approximately by a finite series combination of Laplace functions.[4] If an artificial sphere can be represented by SH with order m and degree l, its mean diameter can be described as

$$\langle D\rangle = b_{0,0} + \sum_{l=1}^{L}\sum_{m=-l}^{l} b_{l,m}({\rm Y}_l^m, {\rm Y}_0^0), \quad (4)$$

where $\langle D\rangle = \frac{1}{N}\sum_{i=1}^{N} D_i$ is the N-point mean of a set of measured diameters, ${\rm Y}_l^m$ is the SH component, $b_{l,m}$ is the coefficient of the SH, and the round brackets represent the scalar product of the two functions; $b_{0,0}$ is the average diameter defined as

$$b_{0,0} = \frac{1}{4\pi}\int_0^{2\pi}{\rm d}\phi\int_{-1}^{1} D(\zeta,\phi){\rm d}\zeta. \quad (5)$$

According to Eq. (4), if we want the mean diameter $\langle D\rangle$ to approach the average diameter $b_{0,0}$ as closely as possible, the optimal mapping rule on the sphere can be obtained by trying to make the experimental $({\rm Y}_l^m, {\rm Y}_0^0)$ equal zero, and its actual value is adopted to evaluate the uncertainty of the mean diameter due to the imperfect mapping.

However, this theorem is based on the hypothesis that the sphere has a bandwidth-limited spectrum. It means that the real sphere can be described by a

finite order of the SH exactly, which is just an approximation and not the fact, as it is limited by the current fabrication technique. Therefore, the symbol $b_{0,0}$ in Eq. (4) is misused when considering its original definition in Eq. (5).

We briefly describe the process to approximate the real sphere and evaluate its average diameter by the SH below.

Step 1: approximating the real sphere by a finite series of the SH and obtaining a sphere with a bandwidth-limited spectrum, we call it the math sphere.

Step 2: mapping a set of discrete diameters on the math sphere's surface and constructing an ideal sphere whose diameter is the mean value of this mapping set.

Step 3: adopting the ideal sphere with the diameter of the mean value obtained in Step 2 as the approximation of the real sphere.

According to the definition, the real sphere is represented by the SH with degree ∞ and average diameter $b_{0,0}$. When using a math sphere with limited bandwidth to approximate the real sphere, its average diameter, if represented by $b^*_{0,0}$, is the approximation of $b_{0,0}$. Even for the math sphere, we cannot determine its average diameter $b^*_{0,0}$ by integration but only by the N-point mean $\tilde{b}^*_{0,0}$ of a set of mapped diameters. Therefore, Eq. (4) should be revised as

$$\langle D\rangle = \tilde{b}^*_{0,0} = b^*_{0,0} + \sum_{l=1}^{L}\sum_{m=-l}^{l} b^*_{l,m}(\mathrm{Y}_l^m, \mathrm{Y}_0^0). \quad (6)$$

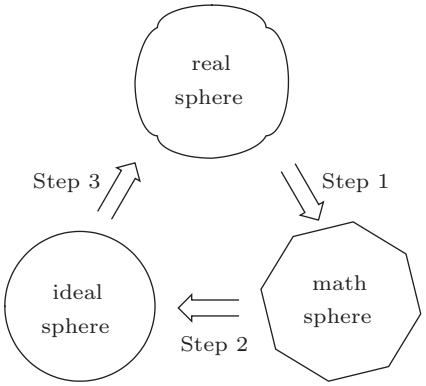


Fig. 1. Process of approximating the real sphere by the SH.

The error sources of this estimation consist of two parts. One is the imperfect mapping, which has been shown in Ref. [5] and considered to be the only error source there. The other is the limited bandwidth approximation, represented by $\left|b^*_{0,0} - b_{0,0}\right|$, which is dependent on the sphericity of the sphere[6] and ignored in Ref. [5]. Therefore, the uncertainty of the average diameter should be evaluated by

$$u(b_{0,0}) = \sqrt{u\left(\sum_{l=1}^{L}\sum_{m=-l}^{l}\left|b^*_{l,m}(\mathrm{Y}_l^m, \mathrm{Y}_0^0)\right|^2\right) + u\left(\left|b^*_{0,0} - b_{0,0}\right|^2\right)}, \quad (7)$$

where u stands for the standard uncertainty of the quantity in the round brackets. The calculation method of $u(|b^*_{0,0} - b_{0,0}|)$ can refer to Ref. [9]. This uncertainty component cannot be ignored for the current target, just as we have shown in Subsection 2.1.

Different from Mana, Fujii *et al.*[10] used the SH to fit the mapped data by a least square method, and evaluated the uncertainty of the mean diameter by determining the standard deviation of the fitted parameter $b_{0,0}$, which is much more straightforward. As a matter of fact, the best sphericity of the real sphere nowadays is no better than 50 nm,[1] which cannot avoid the discrepancy on nanometer scale from the math sphere having a bandwidth-limited spectrum. With discrete mapped points, the results may be influenced by the features of the real sphere. However, the large deviation of the fitted results presented in Ref. [3] shows that the number of mapping points may not be sufficient when considering the target uncertainty.

3. Uncertainty estimation by numerical simulation

3.1. Method

To test the validity of the methods used nowadays,[3,5] we construct an approximate sphere by

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{c^2} = 1, \quad (8)$$

which is an ellipsoid in the Cartesian coordinates. If we set the parameters $2a$, $2b$, nd $2c$ to be 94000000 nm, 94000025 nm and 94000050 nm, respectively, an approximate sphere with a diameter of nearly 94 mm and a maximum sphericity of 50 nm can be obtained. According to the volume formulas of mathematic ellipsoids and spheres, the average diameter of the sphere with the same volume as the ellipsoid can be easily deduced approximately as 94 000 025 nm with a dis-

crepancy of 2.3×10^{-6} nm.

All the mapping theories mentioned above are based on the consideration of distributing the mapped points on the sphere as uniformly as possible so that all the points have the same weight in the mean. In fact, a similar application has been appeared in geography for many years and is called equal-area map projection,[14] which can project the Earth on a map in equal area. The projection we used is called cylindrical equal-area projection, whose transformation formula is

$$\begin{cases} \phi = x/\sin(y), \\ \theta = y, \end{cases} \tag{9}$$

where (x, y) are points in a 2D rectangle with $x \in [-\pi \sin(y), \pi \sin(y)]$, $y \in [-\pi/2, \pi/2]$ and (θ, ϕ) are points in spherical coordinates. One projection example is demonstrated in Fig. 2. Figure 3 shows the 70 directions generated by this projection method.

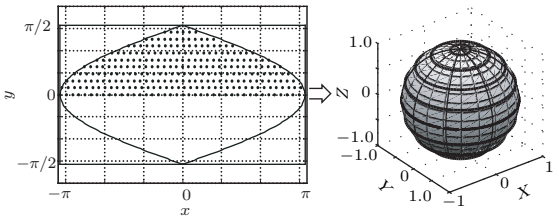


Fig. 2. Example of cylindrical equal-area projection.

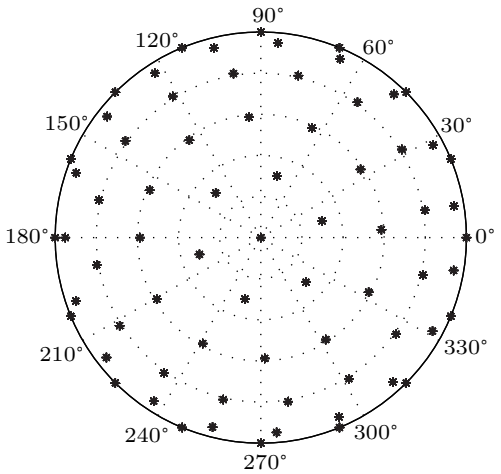


Fig. 3. 70 points distributed uniformly on the sphere.

A real sphere can be described approximately by the SH with degree of L

$$D(\theta, \varphi) = \sum_{l=0}^{L} \sum_{m=-l}^{l} b_{l,m} \mathrm{Y}_l^m(\theta, \varphi). \tag{10}$$

Because the measurement data are point-symmetric, the value of the odd degree of l is zero. In addition, only the real parts of Y_l^m are meaningful for this application and defined as

$$\mathrm{Y}_l^m = \begin{cases} \cos(m\varphi)\mathrm{P}_l^m(\cos\theta) & (m \geq 0) \\ \sin(|m|\varphi)\mathrm{P}_l^{|m|}(\cos\theta) & (m < 0), \end{cases} \tag{11}$$

where $b_{0,0}$ is the average diameter of the sphere with spectrum bandwidth L. Generally, $b_{0,0}$ can be obtained from fitting the mapping points to the SH by the least square method. The objective function to be minimized is

$$\chi^2 = \sum_{i=1}^{N} \left(\frac{1}{\sigma_i^2} \left(D(\theta_i, \varphi_i) - D_i \right)^2 \right), \tag{12}$$

and the uncertainty of the fitted parameters can be estimated by their covariances matrix and sample variance for the fit.[15]

3.2. Simulation results

The generated ellipsoid has two pairs of lobes so that the SH of 2-degree can represent it exactly, which means that the ellipsoid is bandwidth-known. The results fitted by SH are shown in Fig. 4, the fitted $b_{0,0}$ equals 94000025 nm with bias of $\pm 1.8 \times 10^{-5}$ nm, whose uncertainty can be ignored completely.

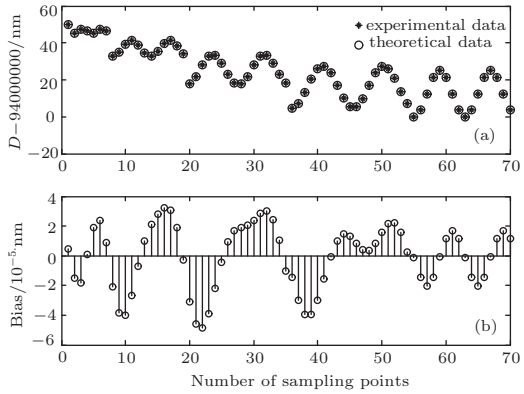


Fig. 4. Fitted results of an ellipsoid by 2-degree SH. (a) Theoretical and experimental data of D; (b) bias of the fitted results.

However, the features of the real sphere are by no means as perfect as for mathematic ellipsoid. Owing to the limitation of the manual fabrication technique, the shape of the real sphere will inevitably deviate from the mathematic sphere. In order to simulate the influence on the fitted result caused by the shapes of real sphere, a Gaussian white noise with null mean and

specific standard deviation is added to the 70 directions of the ellipsoid to represent a real sphere. The standard deviation of the noise varies from 1 nm to 10 nm, then 5000 spheres are generated and fitted by the SH each time. The results are shown in Fig. 5.

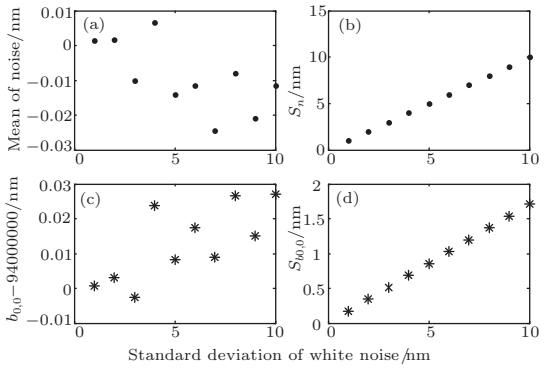


Fig. 5. Simulated results of the ellipsoid with white noise. S_n and $S_{b0,0}$ are standard deviations of the generated white noise and fitted $b_{0,0}$, respectively. (a) and (b) are the mean and standard deviations of the generated white noise, respectively. (c) and (d) are the mean value and standard deviation of the fitted results of $b_{0,0}$, respectively. All the horizontal axis of the subfigures is the theoretical standard deviation of the white noise.

The noise with null mean will not change the average diameter of the ellipsoid but influence the fitted results. As shown in Fig. 5(a), all the means of the noise do not exceed 0.025 nm. However, even the fitted result of $b_{0,0}$ almost has no change, the uncertainty of the mean $S_{b_{0,0}}$ is increased along with the growth of standard deviation of the noise S_n.

The relation between S_n and $S_{b_{0,0}}$ is described in Fig. 6.

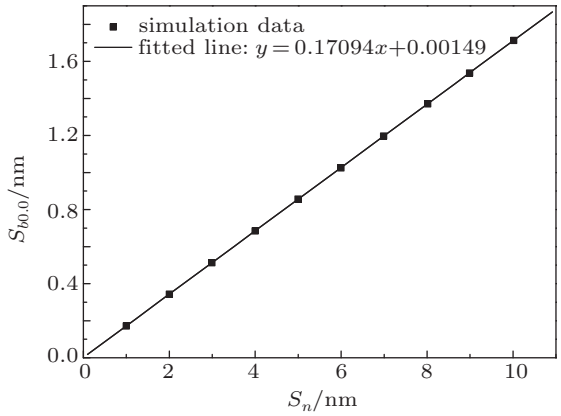


Fig. 6. Relationship between the standard deviation of the white noise and that of $S_{b0,0}$.

A straight line can fit the simulation data perfectly, so the influence of the noise on the uncertainty of the fitted $b_{0,0}$ can be expressed as

$$S_{b_{0,0}} \approx 0.17 S_n. \tag{13}$$

With $S_n = 10$ nm, the sphericity of the generated sphere is about 80 nm, close to the current fabrication level. However, the uncertainty of the mean is up to 1.7 nm, which results in the relative uncertainty of 5.4×10^{-8} in volume.

To observe the influence of the degree of the SH, higher degrees of the SH are also applied to fit the generated sphere with noise of $S_n = 10$ nm. The results are listed in Table 1.

Table 1. Fitted results of the SH by 70 points.

Degree of SH	Fitted results/nm	
	$b_{0,0}$	$S_{b_{0,0}}$
2	94000025.00	1.71
4	94000024.98	1.71
6	94000024.98	1.72
8	94000024.97	1.73

Table 1 shows that the fitted result does not improve but actually worsens again with the increase of degree. The reason can be explained as follow: the noise may be related to the higher degree of SH, whereas the number of fitted parameters is also increased with the degree. For SH of degree N, there are $(N+2)(N+1)/2$ parameters to be fitted. With the limited number of mapping points, the freedom of the fitting will decrease with the increase of degree of SH, which prevents the uncertainty of the fitted results from improving.

Several published data have provided evidence to our conclusion.[3,10,13] For instance, the best standard deviation of the mean diameter obtained by Fujii *et al.*[3] on 70 points is 1 nm for a silicon sphere with sphericity of about 70 nm.

For further discussion, the fitted results of the approximate sphere with 10-nm white noise by using 223 points (the distribution is shown in Fig. 7) are summarized in Table 2.

Table 2. Fitted results of the SH by using 223 points.

Degree of SH	Fitted results/nm	
	$b_{0,0}$	$S_{b_{0,0}}$
2	94000025.01	0.95
4	94000025.01	1.00
6	94000024.96	1.06
8	94000024.98	1.14

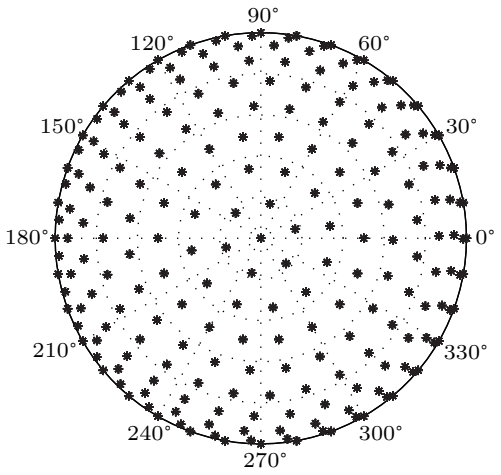


Fig. 7. 223 points distributed uniformly on the sphere.

Comparing Table 1 with Table 2, we can conclude that even though the spectrum bandwidth of the real sphere is unknown, the increase of mapping points can improve the estimated uncertainty of the mean diameter. The reason can be explained as follows: with the same degree of the SH, the freedom of the fitting grows with the number of mapping points. However, the values of the mean diameter are not sensitive to the fine structure of the sphere, which means that we cannot evaluate the fitted results only by the repeatability of the mean value when using the least square method.

For the sphere S4 in Ref. [10], its uncertainty of the mean is 0.7 nm, similar to the generated sphere with about 4-nm white noise. When we use 223 points to fit the average diameter, the uncertainty can be reduced to 0.38 nm, which is very close to the target uncertainty.

4. Practical mapping method

For a spherical interferometer,[2] it is easy to map large number points on the sphere because of the two-dimensional measurement principle. However, for a plane interferometer, it can only measure one position each time. Therefore, increasing mapping numbers is easy for mathematic simulation but difficult to be realized in practice, especially for the plane interferometric setup,[2,13,16] since the distribution of the spherical angles are not uniform for the equal-area mapping. However, equal-spherical angle mapping can be carried out easily by the rotating system. However, the possible problem with the equal-spherical angle mapping is that the mapped points are not distributed uniformly on the surface of the silicon sphere. A practical mapping method named weighted mean-based on equal-spherical angle mapping is proposed to evaluate the mean thickness of the mapped points.

According to this method, two steps are necessary to obtain the mean value of the measured discrete diameters on the silicon sphere, i.e., mapping the surface of the silicon sphere by the equal-spherical angle at first, and then calculating the weighted mean of the mapped points according to the theory of equal-area projection.

The weight of the mapped points can be deduced directly from Eq. (9) as

$$\overline{D} = \frac{\sum\limits_{j=1}^{N}\sum\limits_{i=1}^{M} D(\theta_j, \phi_i)\sin\theta_j}{M\sum\limits_{j=1}^{N}\sin\theta_j}, \tag{14}$$

where $M \times N$ are mapped points on the surface of the sphere. This mapping method can be realized and extended easily in experiment as it is insensitive to the angle resolution of the rotating system.

5. Conclusions

The SH method is widely used in estimating the volume of a silicon sphere in the Avogadro project. However, for the current target of 0.3-nm uncertainty in diameter of the silicon sphere, the method of estimating the uncertainty of the average diameter based on previous theory should be reevaluated carefully. In this paper, the revised formula for the uncertainty estimation of the SH method is deduced and a simple simulating method for evaluating the uncertainty is presented. In addition, a relationship between the feature of the sphere and the estimated uncertainty of the fitted mean diameter is deduced. It is evidenced that the uncertainty of the sphere's volume (or diameter) attributed to the previous N-point mean method is underestimated. Thus, the number of mapping points on the sphere should be increased to more than used before. By means of the spherical interferometry, Bartl and Nicolaus[17] mapped hundreds of thousand points on the silicon sphere and concluded that the mapped number should be several hundreds experimentally, which is consistent with the conclusion presented here. Finally, a practical mapping method is proposed for a large number of mapping points on a sphere.

References

[1] Becker P, Friedrich H, Fujii K, Giardini W, Mana G, Picard A, Pohl H J, Riemann H and Valkiers S 2009 *Meas. Sci. Technol.* **20** 092002

[2] Nicolaus R A and Fujii K 2006 *Meas. Sci. Technol.* **17** 2527

[3] Kuramoto N, Fujii K, Azuma Y, Mizushima S and Toyoshima Y 2007 *IEEE Trans. Instrum. Meas.* **56** 476

[4] Johnson D P 1974 *J. Res. Natl. Bur. Stand.* A **78** 41

[5] Mana G 1994 *Metrologia* **31** 289

[6] Giardini W and Ha J 1994 *Meas. Sci. Technol.* **5** 1049

[7] Ha J, Giardini W and Zosi G 1995 *Metrologia* **32** 111

[8] Nicolaus R A and Bönsch G 1997 *IEEE Trans. Instrum. Meas.* **46** 563

[9] Sakuma A, Fujii K and Tanaka M 1994 *Meas. Sci. Technol.* **5** 1233

[10] Fujii K, Tanaka M, Nezu Y, Sakuma A, Leistner A and Giardini W 1995 *IEEE Trans. Instrum. Meas.* **44** 542

[11] Fujii K, Tanaka M, Nezu Y, Nakayama K, Fujimoto H, de Bièvre P and Valkiers S 1999 *Metrologia* **36** 455

[12] Nicolaus R A and Bönsch G 2005 *Metrologia* **42** 24

[13] Luo Z, Gu Y, Zhang J, Yang L and Guo L 2010 *IEEE Trans. Instrum. Meas.* **59** 2991

[14] Snyder J P 1987 *Map Projections- a Working Manual* (Washington: US Government Printing Office) pp. 76–81

[15] Bevington P R and Robinson D K 1969 *Data Reduction and Error Analysis for the Physical Sciences* (New York: McGraw–Hill) pp. 222–226

[16] Luo Z, Yang L and Chen Y 2005 *Acta Phys. Sin.* **54** 3051 (in Chinese)

[17] Bartl G and Nicolaus A 2009 *Meas. Sci. Technol.* **20** 065104