A new density standard replaced from water

— Using silicon single-crystals as the top of traceability in density measurement —

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Water is conventionally and widely used as a reference standard to measure physical quantities such as the density, volume, internal volume, and concentration. Water is also used as a standard for other physical properties such as the specific heat and surface tension. However, water density is influenced depending on its isotopic composition and content of dissolved gases. Researches on density measurement using solid material with stable density such as silicon single-crystals were therefore started in the 1970s. Demands have been raised from industry for densimetric technology to improve reliability of product and to maintain traceability of measurement. With this background, AIST established a new density standard using silicon single-crystals. Shifting the density standard from liquid to solid will not only improve the accuracy but also promotes development of new material evaluation technology for thin films as well as metrological standard technology for next generation.

Keywords : Density, standard, water, silicon single-crystals, traceability, Avogadro's constant

1 Introduction

Water has been used as a density standard since ancient time. The International Prototype of the Kilogram (IPK) currently used as the standard of mass was originally defined as the mass of one litter of water measured using the Prototype Meter created at the end of the 18th century[1]. In the International System of Units (SI, from Le Système International d'Unités)[2], the unit of density (kg/m^3) is the SI derived units composed from the SI base units, kilogram (kg) and meter (m). To measure the density according to the definition of SI, only mass and length standards are needed, and it seems there is no necessity to establish a new standard for density. However, to start from absolute measurements of mass and length to measure the physical quantity of density, large-scale measurement facility is required and measurements are extremely difficult, and it is much easier to make a relative density measurement of unknown material with respect to the density of material whose absolute value is already known accurately. Therefore, general method used is to measure the absolute value of density of a widely available material with high reproducibility, and then to make relative measurement of unknown material using this substance as a reference standard. The material that serves as the standard for density is called density reference material or density standard material[3][4].

Water is a density standard material that was used first, and has been used widely to calculate the density and volume of other materials. The absolute measurement of the density of water was done by the Bureau International des Poids et Mesures (BIPM) around 1890 to 1910[5]. Since this measurement was conducted before the discovery of isotopes, the issue of uncertainty caused by the ambiguity of isotropic composition of water remained. Therefore, several international organizations such as the International Union of Pure and Applied Chemistry (IUPAC) issued a recommendation to re-measure the absolute value of the density of water with known isotropic compositions at the relative combined standard uncertainty less than 1×10^{-6} in density. In response, the Australian Commonwealth Scientific and Industrial Research Organisation (CSIRO)[6] and the National Metrology Institute of Japan (NMIJ, formerly the National Research Laboratory of Metrology)[7] conducted independent absolute measurements of the density of chemically pure water with isotropic composition equivalent to the standard mean ocean water (SMOW)[8] in 1990s. The independent absolute measurements were thus obtained by Australia and Japan. Since there was a relative density difference of 2.1×10^{-6} that is greater than the uncertainty between the two values, the two data were analyzed by the Working Group on Density (WGD) of Comite Consultatif pour la Masse et les Grandeurs Apparentèes (CCM), Comité International des Poids et Mesures (CIPM), and recommended values for the density of water having isotopic compositions equal to SMOW have been issued in a range 0 to 40 °C with the absolute value of 999.9749(8) kg/m^3 at 4 °C and 101.325 kPa[9]. The number in parenthesis expresses the expanded uncertainty (k=2) of the last digit. This value is widely used as the internationally recommended value. However, the density of water changes due to effects of dissolved gases and isotropic compositions, and several corrections are necessary depending on the actual condition of the water sample.

Other than water, mercury has been used as a standard for high density. Absolute measurement for the density of mercury was conducted by the National Physical Laboratory (NPL) of UK in 1957 and 1961 to establish the standard for pressure[10][11]. When the average values of

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these measurements are converted to ITS-90, the current temperature scale, the density at 20.000 °C and 101.325 kPa is 13 545.854(3) kg/m^3 [12]. Although the relative combined standard uncertainty of the measurement is reported to be 0.2×10^{-6}, due to differences in isotropic compositions, there are relative deviations of about 1.7×10^{-6} in the density of mercury samples from different places of origin. Therefore, the relative combined standard uncertainty of the density of non-calibrated mercury is thought to be larger than 1×10^{-6} [13]. The uncertainty of the density of mercury not only affects the pressure standard[14], but also remains as the major uncertainty source in the absolute measurement of the universal gas constant R determined by the spherical resonator[15] and absolute measurement of Josephson constant $K_J = 2e/h$ (here, e is the elementary charge and h the Planck constant) determined by the mercury electrometer[16].

Since conventionally used liquid density standards have problems caused by inconsistencies in the measurements and uncertainty in the isotropic compositions, it is extremely difficult to construct a density standard with a relative uncertainty smaller than 1×10^{-6} from these data. On the other hand, the demands to accelerate the global Mutual Recognition Arrangement (MRA) and to clarify traceability of measurement have increased in the field of measurement standard. Particularly, there is increasing necessity for measuring the density in a way traceable to the definition of SI. In industry, density sensors with high-sensitivity such as vibrating tube densimeters are already used widely, but it has become difficult to provide sufficiently accurate density standard from conventional testing and certification for hydrometer calibration conducted under Measurement Law. Particularly in the brewing industry, alcohol concentration of alcoholic beverages are determined by density measurement using the alcohol table, and introduction of vibrating tube densimeters allowing automatic and high precision measurement had been considered. Therefore, there was increasing demand for building a traceability system in the Japan Calibration Service System (JCSS) established in the Measurement Law.

Recently, high precision density standard has been required from science and technology such as the redefinition of SI and the determination of fundamental physical constants. Particularly, experimental research to redefine the kilogram, which is the only SI base unit still defined by material artifact, is being conducted by NMIJ and other national metrology institutes[17]. In the x-ray crystal density (XRCD) method to determine the Avogadro constant from absolute measurements of the density, lattice constant, and molar mass of silicon single-crystals, an absolute measurement of the density of isotopically enriched silicon single-crystals at a relative standard uncertainty of 1×10^{-8} is required[18].

Considering these circumstances, AIST decided in 2001 to build a new density standard with silicon single-crystals as the top of traceability, and started providing reference standards for solid density that could not be handled by conventional measurement methods. To date, we have provided a new density standard traceable to the definition of SI to industries and users by developing new calibration technologies for hydrometer, density standard liquid, vibrating tube densimeter, solid material, thin film, and PVT properties.

2 Need for new density standard

2.1 Social demand

In petroleum, alcohol, brewing, and food industries, density of liquids is measured during manufacturing process and for quality control. Particularly, accurate measurement of alcohol concentration is essential for quality control of alcoholic beverages, ingredient labeling, distribution, and fair assessment of alcohol tax. In the Measurement Law, Specific Measuring Instruments are set for important measurements in certain economic activities and services, and Type Approval is conducted for the structure and specification of the measuring instruments. For the density measurement of liquids, standards are provided for density, specific gravity, and alcohol hydrometers. Hydrometer, also called the "float," is a measuring instrument for density, and the scale of the alcohol hydrometer is calibrated using the alcohol table[19] that shows the relationship between the alcohol concentration and the density. Hydrometer scale was conventionally calibrated using the density of water. However, due to its structure, it is easily influenced by the surface tension of the liquid sample, so the relative standard uncertainty of density measurement by hydrometer is limited to be about 0.01 %. The relative standard uncertainty of alcohol concentration measurement based on this measurement is therefore about 0.1 %. Although this method is inexpensive, its scale must be read visually by the operator, and cannot be readily automated.

The measurement method most widely used by the National Tax Agency (NTA) for assessing alcohol tax was the alcohol concentration measurement using alcohol hydrometers. Alcohol hydrometers certified according to the Measurement Law must be used in the Official Analysis Method of the NTA. This is because the data used for tax assessment must be fair, and the alcohol hydrometers certified by the Measurement Law was the only available alcohol measuring instrument with third-party verification.

On the other hand, the demand for more precise density measuring instrument had increased in the brewing industry to improve quality control and to introduce automation. The industrial demand was to measure alcohol concentration at an uncertainty of 0.05 % for fine control of manufacturing process, and it was therefore necessary to supply a new density standard traceable to the national standard with an uncertainty of 0.005 %.

Vibrating tube densimeter is a density measuring instrument with extremely high resolution, and the most stable instrument can measure the liquid density with a reproducibility of 10^{-6} to 10^{-7}. Although vibrating tube densimeters had already been introduced experimentally in the brewing industry when the issue was first investigated, it was necessary to calibrate the relationship between the density and vibration frequency using density standard liquids. It was necessary to supply such density standard liquids with third-party certification at a relative standard uncertainty of about 0.001 %, but there was no system for providing traceable density standard liquids in Japan.

2.2 Scientific needs

Speed of light in vacuum c, the Planck constant h, elementary charge e, and the Avogadro constant N_A are fundamental physical constants that are used to described nature. If such fundamental physical constants are determined in conformity with the definition of SI, various fundamental physical constants can be derived from them. Because the values of fundamental physical constants are of primary importance for science and technology, the Task Group on Fundamental Constants that was established in the Committee on Data for Science and Technology (CODATA) of the International Council for Science (ICSU) summarized the recommended values of fundamental physical constants through a process of adjustment so that rigorous relationships among them are kept in a consistent way [20].

The Avogadro constant is important not only for adjustment of the fundamental physical constants, but also to define the unit mole (mol) for the amount of substance. Moreover, if the Avogadro constant can be determined with a sufficiently small uncertainty, it will become possible to redefine the kilogram, the only SI basic unit still defined by material artifact, based on mass of an atom or fundamental physical constants [21][22]. Therefore, Conférence Générale des Poids et Mesures (CGPM) that was organized under Convention of Meter recommended experimental studies to redefine several SI basic units including kilogram using fundamental physical constants and to evaluate the mass stability of the International Prototype of the Kilogram (IPK) under cooperation of national metrology institutes throughout the world.

Technology to measure the density of silicon single-crystals with a small uncertainty plays an important role in the determination of the Avogadro constant by the x-ray crystal density (XRCD) method. In the XRCD method, the Avogadro constant N_A is derived by $N_A = 8M/(\rho a^3)$ from absolute measurements of the density ρ, molar mass M, and lattice constant a of silicon single-crystals. In 2005, the NMIJ, the Physikalisch-Technische Bundesanstalt (PTB) of Germany, and the Institute of Reference Materials and Measurement (IRMM) of the Europe Joint Research Center collaborated to measure the Avogadro constant from silicon single-crystals with natural isotropic compositions, and achieved a relative standard uncertainty of 3×10^{-7}, which is the highest accuracy achieved by the XRCD method[23]. In 2007, the International Avogadro Coordination (IAC) Committee organized by the CIPM, under cooperation of eight research institutes around the world including NMIJ, prepared a single-crystal from highly enriched silicon isotope ^{28}Si for improving the uncertainty of the Avogadro constant to 2×10^{-8}, and the research continues toward the redefinition of the kilogram. To achieve this goal, it is necessary to determine the density of silicon single-crystals with a relative standard uncertainty of 1×10^{-8}.

The Avogadro constant determined from silicon single-crystals is also used to verify theories in the AC Josephson and quantum Hall effects[20]. The electric potential difference generated by the AC Josephson effect is expressed as $U = nf/K_J$ (n is integer, f is frequency of microwave irradiated onto the Josephson junction device, $K_J = 2e/h$ is the Josephson constant), and the electrical resistance realized by the quantum Hall effect is expressed as $R = R_K/i$ (i is integer, $R_K = h/e^2$ is the von Klitzing constant), and these are important fundamental theories in establishing the electrical standards. However, since whether the electric potential difference and the electrical resistance are exactly quantized by $2e/h$ or h/e^2 cannot be proven by theories, work to verify the theory in the range of uncertainty of experiment is conducted by comparing and investigating with values such as h and e obtained from experiments that do not depend on the AC Josephson and quantum Hall effects. In the Task Group on Fundamental Constants of CODATA, the value for the Avogadro constant obtained by the XRCD method is used as an input quantity because the value for h is obtained from the Avogadro constant without relying on the AC Josephson or quantum Hall effects. From these investigations, it is now verified that the AC Josephson and quantum Hall effects are correct with an uncertainty of about 10^{-7} [20].

2.3 Scenario for achieving the goal

It is necessary to clarify the R&D policy to achieve the goal by satisfying both the demands from society and science. The policies are summarized as follows:

(1) To set the National Primary Standard (the highest order standard in Japan) for density that is traceable to the definition of the SI basic units.
(2) The primary standard of density must have function that can meet the demands from society as well as future needs in science.
(3) To be able to calibrate the users' measuring instrument such as hydrometer, density standard liquid, and vibrating tube densimeter by unbroken chain linked to the primary standard of density.
(4) To create a system where the density calibration service can be provided by registered calibration service

provider certified according to ISO/IEC17025 standard used in the Japan Calibration Service System (JCSS).
(5) To ensure that the highest order standard of registered calibration service is sufficiently stable, and does not require frequent calibration by the primary standard owned by the AIST.

When working on (1) of the above policies, we considered designating water as the standard of density by determining the purification method, purity analysis, and isotropic composition measurement of water. However, despite maximum technological effort, it is still extremely difficult to have a relative uncertainty of better then 1×10^{-6}. On the other hand, densimetric technology for silicon single-crystals, which was developed at the AIST for determination of the Avogadro constant, had already reached the level of 1×10^{-7}. Therefore, we selected the density standard system with silicon single-crystals as the top of traceability. Item (5) was an important factor when considering the necessary work at the registered calibration service providers. We discussed this point with candidates of service providers, and reached conclusion that even if the initial investment for calibration facilities was somewhat high, in middle to long-term, it would be easier for the service providers to have their own stable density standard for maintaining reliable calibration, as they would be freed from frequent calibrations of their own density standard. Based on these considerations, AIST started working on the new density standard system.

3 Development of new density standard system

Since density of silicon single-crystals is extremely stable, the National Institute of Standards and Technology (NIST) of the USA considered using it as a solid density standard for first time in the 1970s[24]. When the CSIRO developed the technology of polishing a 1 kg sphere from silicon single-crystals in 1987[25], it became possible to directly determine the density from mass and dimensional measurements, and thus it opend a new way for substantially reducing the uncertainty of density measurement. Conventionally, the density of silicon single-crystals had been calculated from buoyancy force measurement in a liquid[24], using the volume standard realized by steel spheres whose volumes had been determined from dimensional measurements. By polishing silicon single-crystals into spherical form, the absolute value of the density could be obtained directly without buoyancy force measurement. In order to use the silicon sphere for determination of the Avogadro constant and not just for a density standard, CSIRO developed a new manufacturing process using mechano-chemical polishing as well as mechanical polishing at the final phase, to prevent crystal damage near subsurface[26]. In cross-sectional observation near the sphere surface by transmission electron microscope, it was verified that crystal structure was maintained until it transformed to surface oxide layers. Using this polishing technology, it is now possible to obtain a sphere with a diameter about 94 mm, mass about 1 kg, sphericity (maximum deviation from mean diameter) 50 nm, and surface roughness 0.1 nm. AIST noticed the excellent characteristic of the silicon solid density standard when the polishing technology was first developed at the CSIRO, and started working on a new density standard system that will replace water[27]-[30].

3.1 Characteristic of silicon solid density standard

Silicon is a fundamental material in the semiconductor industry, and highly pure, dislocation-free, large size single-crystals are obtained readily. Since there are three isotopes ^{28}Si, ^{29}Si and ^{30}Si, the density of individual silicon crystal may relatively vary about 1×10^{-5} due to variations in natural isotropic compositions and mass fractionation effect during the crystal growth, but their mean density value is about 2329 kg/m^3 at 20.000 °C and 101.325 kPa. Followings are outstanding characteristics when silicon single-crystals are used as a density standard.

(1) Since silicon has near-perfect crystalline structure, its density is extremely stable once it is measured.
(2) While water and mercury are liquid, and silicon single-crystals are solid, there is much less effect for silicon single-crystals due to degradation of chemical purity and changes in isotropic composition when they are used for calibrating densities of other materials.
(3) Although the surface is covered with oxide layers, the density of the oxide layers is close to that of substrate silicon single-crystals, and thus the density change due to progressive oxidation is extremely small.

Particularly, (2) is major motivation in promoting the development of a new density standard system replaced from water. Silicon solid density standard is not only highly precise, but it also has excellent usability unseen in the liquid density reference materials in terms of maintenance and management as well as actual operation conducted by the calibration service provider.

3.2 Development of absolute measurement technology for density

Figure 1 shows the laser interferometer developed for absolute measurement of the volume of silicon single-crystals[31]. Since the size is selected so that the mass of the silicon sphere is to be about 1 kg to realize mass measurement traceable to the Prototype Kilogram of Japan, the diameter is about 94 mm. The volume of the sphere with low sphericity can be calculated accurately from the mean diameter by measuring its diameters from many orientations. Therefore, silicon spheres with a sphericity better than 100 nm are used for the solid density standard.

The SI base unit for length, meter (m), is defined by the speed of light and the wavelength of a light beam determined by

optical frequency measurement, so the frequency of laser source used for the interferometer must be calibrated using the method traceable to the definition of second (s). However, since it is difficult to make absolute measurement of optical frequency each time measurements are made, CIPM set recommended wavelengths of frequency-stabilized lasers where the frequency was absolutely measured beforehand by the method traceable to the definition of second. In the diameter measurement of silicon spheres, we maintain the traceability to the definition of meter by using a laser diode as the light source, whose frequency is calibrated using recommended wavelength of I_2 stabilized He-Ne laser,.

For accurate diameter measurement by optical interferometry, it is important to evaluate the thickness of oxide layers on the sphere surface and to evaluate the phase shift when the incident light beam is reflected on the sphere surface. Particularly, to redefine the SI basic unit, kilogram, by determining the Avogadro constant, the diameter of the silicon sphere must be measured with subnanometer accuracy. The surface of the silicon sphere is normally covered by oxide layers with a thickness of about 3 nm, so it is necessary to implement a surface analysis technology. Traditionally, ellipsometry has been used for silicon spheres, but recently, more accurate and reliable surface measurement techniques are employed using new surface analysis methods such as the x-ray reflectometry (XRR) and x-ray photoelectron spectroscopy (XPS). Since silicon single-crystals have certain coefficient of thermal expansion, it is necessary to measure the sphere temperature with an uncertainty of about 1 mK. Therefore, improvements are made by introducing active radiation shield to realize stable temperature condition in a vacuum chamber.

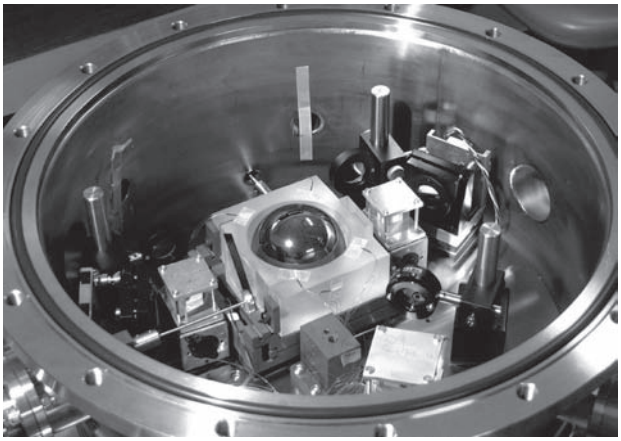

Fig. 1 Laser interferometer for measuring the diameters of silicon spheres.

Table 1 shows the elemental technology for the absolute measurement of the density of silicon single-crystals. To establish the solid density standard traceable to the definition of SI, several measurements standards, such as optical frequency, temperature, surface analysis, and mass are required. The new density standard was built by combining these standards.

3.3 Development of measurement technology for density comparison

To provide traceable hydrometer, density standard liquid, and vibrating tube densimeter to users, new measurement technologies are necessary to compare the densities. Therefore, AIST developed a new hydrostatic weighing apparatus, hydrometer calibration system, and magnetic suspension densimeter as shown below.

Table 1. Elemental technology developed for absolute measurement of density of silicon single-crystals.

Elemental of technology	Development goal	Elemental technology developed to achieve goal
Measurement and control of optical frequency	Nanometre measurement of diameters using gas lasers with fixed frequency (goal when it was impractical to control optical frequency in a wide range)	Modulation and analysis of interference fringe by mechanical scanning of etalon: achieved diameter measurement precision of 3 nm (1994)
	Wideband control of optical frequency and complete automated measurement of diameters by introducing laser diode	Measurement and control of optical frequency at 20 GHz band
		Complete automated measurement of diameters by the phase shifting method: improved diameter measurement precision to 1 nm (2007)
	Diameter measurement at subnanometre precision	Interference fringe measurement by the dark fringe method: improved performance to the quantum noise limited interferometry (development in progress)
Surface analysis	Evaluation of thickness of oxide layers on the surface of silicon spheres	Spectroscopic ellipsometry of sphere surface (from 1996)
		Combination of XRR and XPS (2007)
Measurement and control of temperature	Precision measurement of temperature of silicon sphere in vacuum	Temperature control of vacuum chamber by circulation of temperature-controlled water: achieved temperature measurement with an uncertainty of 5 mK by evaluating temperature distribution by thermocouples and temperature measurement based on ITS-90 (1994)
		Achieved temperature measurement with an uncertainty of 1 mK by introducing radiation shield and its active temperature control (2008)
Orientation control of sphere	Diameter measurement from multiple orientation in vacuum	Development of automatic control mechanism of orientation of sphere in vacuum and its computer control (1994)
Mathematical derivation of volume	Mathematical determination of volume of imperfect sphere	Establishment of volume derivation method by geometric consideration
Mass measurement	Mass evaluation of silicon sphere in vacuum	Introduction of sinker system for precise air buoyancy correction
		Evaluation of adsorption coefficient at silicon sphere surface

3.3.1 Density calibration of solid material by hydrostatic weighing

Figure 2 shows the structure of hydrostatic weighing apparatus that was developed to calibrate the density of solid materials using silicon spheres[32]. Tridecane, (n-$C_{13}H_{28}$) that has low surface tension and stable density, is used as a working liquid. Density difference is measured with a relative standard uncertainty of 4×10^{-8} by alternately weighing the silicon spheres and the solid sample in the liquid. To correct the effect of density gradient due to temperature distribution and gravity in the liquid, the solid sample is placed between the two silicon spheres placed in vertical direction. This apparatus is now used to calibrate the density of arbitrary solid materials such as stainless steel weight, glass, semiconductor crystal, and precious metals. The density of silicon single-crystals used as secondary standard in JCSS is also calibrated with this apparatus. Figure 3 shows a photograph of the apparatus and density-calibrated silicon single-crystals.

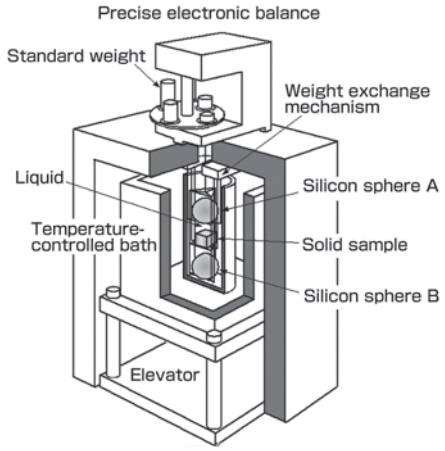

Fig. 2 Structure of hydrostatic weighing apparatus.

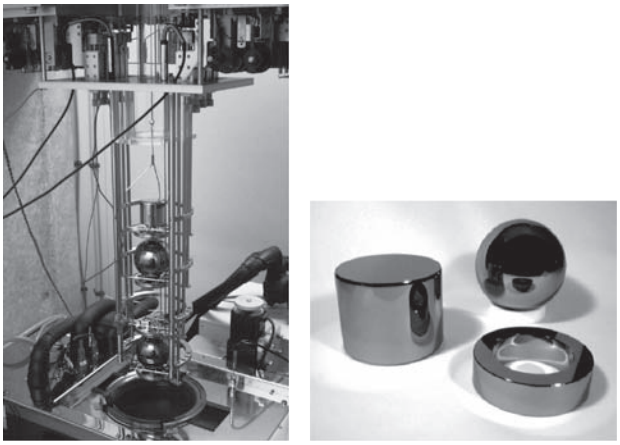

Fig. 3 Hydrostatic weighing apparatus (left) and silicon single-crystals calibrated for density as National Secondary Standard (right). Other than sphere, silicon single-crystals of various forms such as cylinder and ring are used as Secondary Standard.

3.3.2 Hydrometer calibration by the weighing method

Figure 4 shows the principle of scale calibration for hydrometers by hydrostatic weighing. By measuring the buoyancy force acting on the hydrometer in a working liquid using electronic balance, the scale on the stem of hydrometer can be calibrated[33]. In the conventional weighing method where water was used as the density standard, it was difficult to calibrate the hydrometer scale with a small uncertainty since the surface tension of water is high and sensitive to surface contamination. Currently, tridecane is used as the working liquid instead of water. Therefore, the method involves calibrating the density of tridecane by hydrostatic weighing using a ring-shaped silicon single-crystals with calibrated density (National Secondary Standard). It measures the density of the working liquid near the body of the hydrometer. Standard Instrument Testing according to the Measurement Law and hydrometer scale calibration in JCSS are conducted using this method.

3.3.3 Calibration of density standard liquid using magnetic suspension densitometer

Vibrating tube densimeters[34] are used in various fields including petroleum, alcohol, brewing, food industries, as well as for medical testing as a high-sensitivity density measuring device. Normally, since calibration is done using only water and air as the density reference materials, the uncertainty of the density measurement is relatively large when used in a range that departs from the density of the reference materials. Therefore, reliability and traceability of the vibrating tube densimeters can be maintained by supplying several density standard liquids in a range of about 0.5 g/cm^3 to 2.0 g/cm^3.

Figure 5 shows the magnetic suspension densimeter developed at the AIST to calibrate the density standard liquids[35]. This densitometer measures density of fluid according to the same principle as the hydrostatic weighing shown in Figure 2. Since it uses non-contacting mechanism

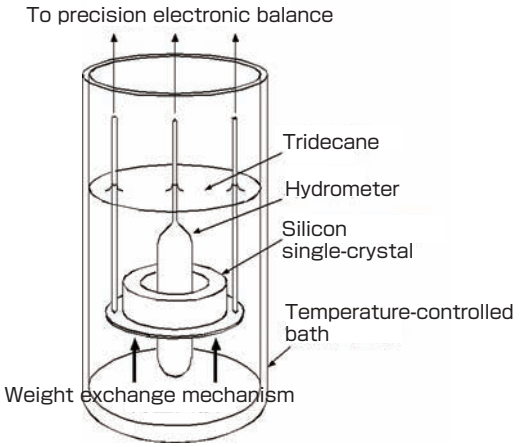

Fig. 4 Ring shaped silicon single-crystal used for calibrating hydrometers.

using magnetic suspension, it can measure the density of fluids under high-pressure and liquids with high vapor pressure without influence of surface tension at meniscus.

By using silicon single-crystals as a sinker, and calibrating its density by hydrostatic weighing, traceable density standard liquids can be supplied in a wide temperature and pressure range. The relative standard uncertainty of the density standard liquids calibrated by this principle is 7×10^{-6}. The measurement result at AIST is used as a reference value when conducting performance test to verify the correctness of measurements of registered calibration service providers of JCSS.

4 Investigation for uncertainty and international equivalence

As mentioned in Section 3.2, in Japan, the density of silicon spheres is determined by absolute measurements of their diameters and masses, and they are designated as the National Primary Standard of density by Measurement Law. The values of the National Primary Standard and uncertainty are shown in Table 2. This is based on the absolute measurements of the density conducted by AIST until 2005, and the relative combined standard uncertainty of the density is 1.2×10^{-7}.

To verify the correctness of the absolute values and uncertainty of Japanese solid density standard and to confirm the international equivalence are important issues in advancing MRA of measurement standard and to demonstrate the reliability of Japanese density measuring instruments. Therefore, the author distributed questionnaires to national metrology institutes of various countries and surveyed the density calibration method and the status of density reference in each country as key comparison study for the Working Group on Density of the CCM. As a result, it was found that although there were very few national metrology institutes that have independent standard for absolute value of density like AIST, many countries have already started to establish traceability based on solid density standard such as silicon single-crystals instead of water. In this key comparison, designated as CCM.D-K1, a silicon sphere of NMIJ was transported to participating countries from 2001 to 2002, to evaluate the international equivalence of the density standards. The participating countries measured the density of the silicon sphere by hydrostatic weighing and the values were compared.

The measurements at national metrology institutes of eight countries including NMIJ are shown in Figure 6. The value of NMIJ showed smallest uncertainty, and the values of other participating countries fell in the range of uncertainty. The reference value calculated from the weighted mean of these values is most reliable as an absolute density value traceable to the definition of SI. The value of NMIJ agrees very well also with the reference value. This verifies the high reliability of the absolute and relative density measurements conducted at the NMIJ.

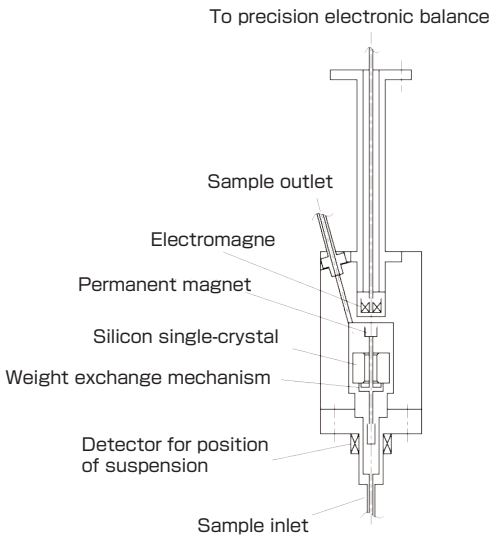

Fig. 5 Magnetic suspension densitometer.

Table 2. Absolute values of the volume, mass, and density of Primary Standards S4 and S5 at 20 °C and 101.325 kPa.

Physical quantity	Unit	Sphere S4	Sphere S5	Relative combined standard uncertainty $u_{cr}/10^{-6}$
Volume	cm^3	429.601242	429.615 387	0.119
Mass	g	1000.578 619	1000.612 019	0.016
Density	$kg{\cdot}m^{-3}$	2329.086 89	2329.087 95	0.120

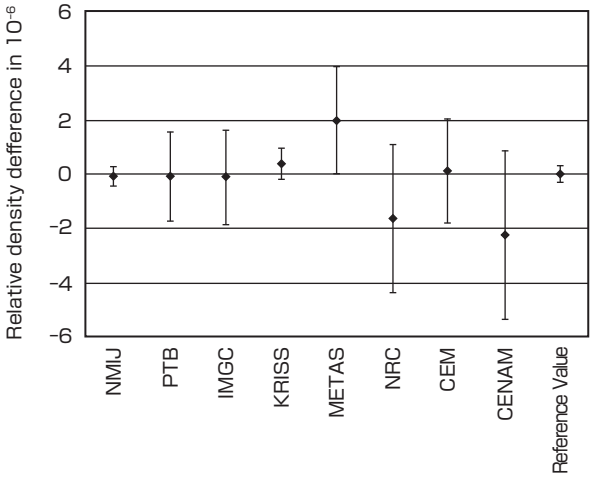

Fig. 6 Measurement result of the key comparison CCM. D-K1 organized by the Working Group on Density of the CCM, CIPM. A 1 kg Silicon sphere was transported as a travelling standard to NMIs of participating countries, and the density of the travelling standard was measured using hydrostatic weighing apparatus using solid density standard of the participating institute. Error bar expresses the expanded uncertainty (k=2). Participating metrological institutes were NMIJ (Japan), PTB (Germany), IMGC (Italy, currently INRIM), KRISS (Korea), METAS (Switzerland), NRC (Canada), CEM (Spain), and CENAM (Mexico). Reference value is the weighted mean of measurements of all participants.

For the density standard liquids, key comparison CCM.D-K2 lead by the Working Group on Density of the CCM was conducted and completed in 2005. International equivalence for the calibrations at the NMIJ was thus verified also in this key comparison.

5 Establishment of traceability system for density and contribution to society

AIST cooperated with the National Institute of Testing and Evaluation (NITE), which is the accreditation body of JCSS, since 2000, and started creating guideline for technological application necessary for implementing calibration service for density based on ISO/IEC 17025 standard. This guideline describes the methods for: maintaining traceability from silicon spheres designated as the National Primary Standard; calibration method of hydrometer, density standard liquid, and vibrating tube densimeter, and the frequency of calibration. Considerations and investigations were conducted as joint work with several candidate calibration service providers. In preparing the guideline, as much freedom as possible was given to the calibration system built by registered calibration service providers, while ensuring accurate evaluation of the uncertainty of the calibration, to allow evolution of density calibration service into various forms in the future. From 2001 when the first technological application guideline for the density calibration service was set up, AIST personnel cooperated as technical advisor in the certification process conducted by NITE.

Figure 7 shows the traceability system constructed on the absolute and comparative measurements for density. The silicon spheres S4 and S5 for which the absolute measurement of density were conducted are set at the top of traceability (National Primary Standard), and silicon single-crystals calibrated by hydrostatic weighing (see Figures 2 and 3) are used as the Secondary Standard at the registered calibration service. In JCSS, registered calibration service provider that fulfilled the ISO/IEC 17025 standard may use the Secondary Standard to calibrate the users' measurement instruments such as hydrometer, density standard liquid, and vibrating tube densimeter.

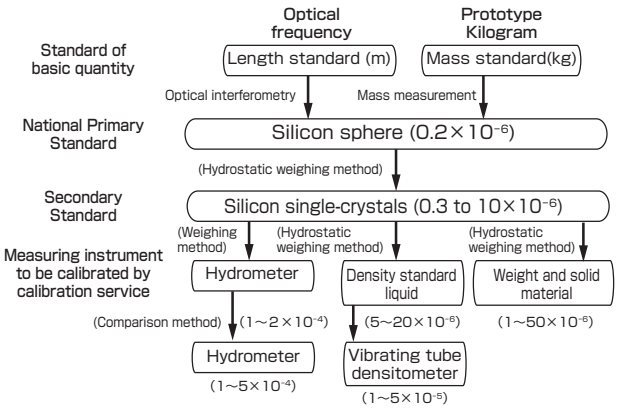

Fig. 7 Traceability system with density of silicon sphere at the top.
Values in parentheses show the estimated relative expanded uncertainty at 95 % confidence level.

The number of provision of density standard by JCSS increased drastically since 2001, and in 2007, about 6,000 calibration certificates were issued for a year for users' density measuring instruments. Particularly, for alcohol concentration measurement of alcoholic beverages, "measurement of alcohol concentration using vibrating tube densimeter" was conventionally approved for use as "method that is deemed practical and accurate, although it is listed in the Official Analysis Method of the National Tax Agency," and application to the National Tax Agency was required to use the vibrating tube densimeter. Also, for alcohol table to convert density to alcohol concentration, values were provided by the Official Analysis Method, and it was necessary for AIST to compare the values with the alcohol table used in Measurement Law before introducing the vibrating tube densimeters calibrated according to JCSS for use in assessing alcohol tax. Therefore, AIST collaborated with the National Tax Agency and disclosed the alcohol table used by AIST on the website, and the people in the brewing industry can readily refer to the AIST alcohol table. It was now possible to use the alcohol concentration measured by the vibrating tube densimeters calibrated according to JCSS as basis of tax assessment by Alcohol Tax Law. Hence, vibrating tube densimeters came into wide use, and in 2007, the National Tax Agency decided to deregulate, and "measurement of alcohol concentration by the vibrating tube densimeter" was included in the Official Analysis Method. As long as the vibrating tube densimeters are calibrated by the density standard liquids provided by the registered calibration service certified by JCSS, it may be used for measurement of alcohols concentration for tax assesment. The Japanese government thus recognized the reliability of the densimeters approved by JCSS, and the use in the brewing industry is increasing steadily.

6 Development into new measurement evaluation technology

The comparative measurement technology for density employed by JCSS is described in Section 3.3, and AIST is developing other new density comparison technologies for material science and energy conservation. Comparison of the densities between silicon single-crystals using the pressure-of-flotation method[36] is a technology originally developed to improve the accuracy of the Avogadro constant. It detects very small density distribution in the crystal, and now it is applied to density measurement of thin films[37], since the measurement sensitivity is extremely high and can detect a relative density difference of 10^{-7} to 10^{-8}. The density of thin

films with 10 to 100 nm thickness formed on silicon substrate is successfully measured with a relative uncertainty of about 0.1 %. Using this principle, it became possible to evaluate the density of oxide films that are vapor-deposited by different methods, and to specify a particular film manufacturing condition that gives highest density for the oxide films[38].

Moreover, improvements were made to the magnetic suspension densitometer mentioned in Section 3.3.3, and a new PVT property (pressure-density-temperature relation) measurement technology was developed at the AIST[39]. It cancels out the effect of diamagnetism of the sample fluid itself near-completely. This new magnetic suspension densitometer employs dual sinkers using germanium single-crystals that has different density from that of silicon single-crystals. They are used as sinkers, and measurements of PVT properties for working fluids and alternative refrigerants are being conducted with high accuracy.

Table 3 shows the examples of application of these measurement technologies used in the silicon density standard. Thy were created only after the density standard using silicon single-crystals became available, and it would have been extremely difficult to develop them from a standard system based on water.

7 Conclusion

Since silicon single-crystals with near-perfect crystalline structure have excellent properties such as form stability and density stability, it can be used as the material for the solid density standard. AIST developed the technology for the absolute measurement of density from diameter and mass measurements of silicon spheres, and constructed a new density standard system replaced from water, through integration of comparative measurement techniques of density. These density measurement technologies were not only employed in the Standard Instrument Testing and certification according to Measurement Law, but also realized the traceability of the density measurement in JCSS. It is now contributing to maintenance of traceability for densimeters used in industry. The number of calibrations of density measuring instruments by JCSS is thus increasing steadily.

Table 3. Development and application of new measurement technology for density comparison.

Measurement method	Characteristics	Examples for application
Pressure-of-flotation method	Detection of small density difference among silicon samples Uncertainty of measurement of relative density difference is 10^{-7} to 10^{-8} Require extremely precise temperature control (10 to 100 μK)	Evaluation of density distribution in silicon crystals Evaluation of defect in silicon crystals
	Density measurement of thin films	Evaluation of thin film manufacturing process Evaluation of density of SAW device Evaluation of density of flexible print substrate
Magnetic suspension method	Precise measurement of PVT properties Possible to measure density by cancelling out the effect of diamagnetic properties of fluids with unknown magnetic susceptibility Employ double sinker method with silicon and germanium single-crystals	Density measurement of gas and liquid Evaluation of thermophysical properties of working fluids and alternative refrigerants Development of energy conservation technology Protection of earth environment Control of carbon gas emission

Future issue is to advance this solid density standard system by integrating it with new evaluation technologies for material science and thermophysical properties, and to actively apply them for semiconductor industry and energy conservation.

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Terminology

Term 1. Relative combined standard uncertainty: The concept that expresses the quality of measurement was formerly called error. It is now summarized in the *Guide to the Expression of Uncertainty in Measurement* in ISO/IEC. The standard uncertainty of a quantity x is expressed as $u(x)$ which is the variation in measurement of a certain quantity x, and it is determined by the standard deviation of the measurement. The relative combined standard uncertainty $u_{c,r}(y) = u_c(y)/y$ is expressed as a relative quantity of the combined standard uncertainty $u_c(y)$ where the standard uncertainties of multiple input parameters are combined by error propagation equation.

Term 2. MRA (Mutual Recognition Arrangement): In measurement standard, the equivalence of standard provided by the national metrology institutes (NMIs) of countries or regions is mutually recognized, and calibration certificates issued by the NMIs are mutually recognized. The measuring instrument calibrated by a certain NMI can be used in other countries or regions without recalibration, to ensure one-stop service for users. Based on the TBT agreement, transparency in imposing mandatory regulation, voluntary regulation, or compatibility evaluation procedures is maintained, and international accord is promoted by international

standards and international guidelines to remove as much as possible the standards and certifications that may remain as trade barriers.

Term 3. Traceability: This is a general term for measurement management system where the chain of comparisons (calibrations) using international and national standards reaches the measuring instrument at user level. In ISO/IEC 17025 standard, primary standard realized according to the definition of the International System of Units (SI) must be used at the top of traceability.

Term 4. Japan Calibration Service System (JCSS): This originated as Japan Calibration Certification System for calibration service providers according to Measurement Law in November 1993. In July 2005, it became a system to register calibration service providers after screening them for compatibility with requirements for testing and calibration laboratories (ISO/IEC 17025) set by International Organization for Standardization (ISO) and International Electrotechnical Commission (IEC).

Term 5. ISO/IEC 17025 standard: International standard document on quality control for services provided by testing and calibration laboratories. Physical standards provided by NMIJ, AIST are subjected to quality control and third-party verification based on this standard.

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Discussion with Reviewers

1 On manufacture of sample and importance of evaluation

Question (Norimitsu Murayama)

The success of this research was achieved by successful manufacture of high-quality silicon single-crystal sphere, along with development of various elemental technologies for absolute measurement of density. I think the synthesiological value of this paper will increase if you describe the manufacturing process and quality evaluation (purity, crystal imperfection, and etc.) of the silicon sphere.

Answer (Kenichi Fujii)

Since development of technology to polish silicon single-crystals into 1 kg sphere with high sphericity by CSIRO of Australia was major motivation for establishing new density standard to replace water, I added the manufacturing procedure and quality evaluation to the beginning of Section 3. Also, I added Reference [26] for details of polishing method. If the sphere was to be used only for density standard, it was not important to evaluate the purity or defect in the silicon spheres, and it would have been sufficient simply to guarantee the stability of the density by measurement. However, for determining the Avogadro constant, it was essential to correct the effect of impurities on density and lattice constant, to quantify the concentration of defects and atomic vacancies, and to accurately evaluate the average number of atoms in the unit cell. If the sphere was polished by conventional mechanical polishing, crystal defects occurred near the surface and it would be difficult to accurately determine the Avogadro constant. Therefore, CSIRO employed a mechano-chemical polishing method that incorporated chemical polishing at the final phase of polishing to minimize the subsurface damage in the crystal. By taking such polishing process, not only geometric perfection of the sphere, but also the crystallographic perfection can be guaranteed.

2 Technical terminologies

Question (Norimitsu Murayama, Mitsuru Tanaka)

I think readers from other fields will be able to understand better if you provide definitions and concepts for “relative combined standard uncertainty” and “the standard traceable to the definition of SI.”

Answer (Kenichi Fujii)

I added a Terminology section after Acknowledgements to explain relative combined standard uncertainty and traceability.

3 Scientific demand

Question (Mitsuru Tanaka)

The description about demands in fundamental physical constants in 2.2 Scientific demand does not necessarily cover scientific demands, so I think you should give other examples. Perhaps you may discuss “verification of theory for the von Klitzing constant R_K (or the fine structure constant α).”

Answer (Kenichi Fujii)

I added importance of verification for theories used in the Josephson and quantum Hall effects as scientific demand for measuring the Avogadro constant in Section 2.2.

4 Scientific issues to be positioned as *Type 1 Basic Research* that composes *Full Research*

Question (Mitsuru Tanaka)

The study to determine the Avogadros constant by silicon single-crystals is described as starting point. Rather, it may be easier for people to understand, if volumetric technology of sphere is set as *Type 1 Basic Research*. Since scientific output is included as goal of *Full Research*, I think it makes it difficult to understand if you start from determination of the Avogadro constant from

silicon single-crystals.

Answer (Kenichi Fujii)

For *Type 2 Basic Research* scenario, when we started research to improve uncertainty of volumetric technology for spheres around 1984, it was necessary to conduct volume measurement of quartz spheres for absolute measurement of the density of water that was being conducted at the former National Research Laboratory of Metrology. While the volumetric accuracy needed for this study was about 10^{-7}, the reason for obtaining volume at higher accuracy was to improve the uncertainty of the Avogadro constant. Although development of volumetric technology required for density standard can be considered *Type 1 Basic Research*, the reason for improving volumetric accuracy to 10^{-8} was the development of polishing technology for silicon spheres at the CSIRO in 1987, and this development was also aimed at improving the uncertainty of the Avogadro constant.

5 Description of *Product Realization Research* in society and industry

Question (Mitsuru Tanaka)

The Author contributed greatly to the dissemination of research result through instructions to registered calibration service providers, certification process, and creation of technological standard for certification. I think you should also mention the relationship between the AIST's advice and the National Tax Agency's notification on alcohol table. Also, I think you should including international activities such as the Working Group on Density of the CCM.

Answer (Kenichi Fujii)

In Section 4, I added that the author et al conducted CIPM key comparison for density for first time in the world to verify the international equivalence of the density standard, as well as our contribution to activities in the WGD/CCM/CIPM.

In Section 5 Establishment of traceability system for density and contribution to society, I added our contributions including technical advice to registered calibration service providers, work on JCSS certification process, and creation of technology standard of JCSS certification. Much time were spend on these activities, and I held several meetings and sessions to make sure people working on calibration services would correctly understand the key points in conducting traceable measurement. Also, talking to the people in calibration service was extremely useful opportunity to know which technologies and information were desired by end users, and I think this is important process for AIST to make contributions to the society.