Accurate density measurements for global environmental science at NMIJ

Naoki KURAMOTO, Yuya KANO and Yohei KAYUKAWA
National Metrology Institute of Japan (NMIJ)

Realization of the primary density standard using 1 kg Si spheres
- Mass and volume measurements
- State-of-the-art techniques developed for the redefinition of the kilogram
  → Uncertainty reduction of the primary standard

Density measurement to solve social issues
- Seawater
  → Prediction of global climate change
- Refrigerant
  → Prevention of global warming
Si single crystal as density standard

- Near-perfect crystalline structure
  → Volume and Density: Very stable
- Known accurate thermophysical properties
  - Thermal expansion coefficient in a wide temperature range
    → Accurate correction of density change due to the temperature change
- Manufacturing of artifacts with various shapes
1 kg Si sphere

Defining constants in the new SI

- Planck constant
- Speed of light in vacuum

Mass
- Mass comparison
- 1 kg reference weight

Volume
- Diameter measurement
- Laser interferometer

Primary density standard

Primary density standard of NMIJ
Volume measurement of Si sphere of NMIJ

- Diameter measurement in 1450 different directions
  → Volume
- $u$(diameter) = 0.6 nm, $u_r$(Volume) = $2.0 \times 10^{-8}$
- Laser wavelength: Traceable to an optical frequency comb (Primary length standard of NMIJ)
  → Si sphere volume: Traceable to the speed of light in vacuum
**Surface layer on Si sphere**

- **Surface layer**
  - **Thickness**: about 2 nm
  - Transparent

- **Si core**
- **Si crystal**
- **SiO₂**
- **Carbonaceous contamination layer**
- **Water**

- **Diameter measured by the laser interferometer**
  → Almost same as the diameter of Si core excluding the surface layer

- **Thickness measurement of surface layer**
  → Actual diameter including the surface layer
Surface characterization system using x-ray photoelectron spectroscopy (XPS) developed for the redefinition of the kilogram using $^{28}$Si-enriched crystals

- XPS gives information on
  - Element
  - Binding state
- Thickness of the surface layer
  - $u$ (thickness) = 0.4 nm

Laser interferometer for the Si sphere volume measurement at NMIJ

- $u$ (diameter) = 0.6 nm

Actual diameter (Si core + surface layer)
- $u$ (actual diameter) = 0.9 nm
Mass measurement of Si sphere

Vacuum balance

Si sphere

1 kg reference weight
- Stainless steel

Planck constant

Consensus value of the kilogram

National prototype of the kilogram of Japan

1 kg Reference weight
Uncertainty budget of the sphere density determination at 20 °C and 101.325 kPa

<table>
<thead>
<tr>
<th>Uncertainty source</th>
<th>Relative contribution to density determination</th>
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<tbody>
<tr>
<td>Sphere volume</td>
<td>$2.0 \times 10^{-8}$</td>
</tr>
<tr>
<td>Surface layer</td>
<td>$2.4 \times 10^{-8}$</td>
</tr>
<tr>
<td>Sphere mass</td>
<td>$2.3 \times 10^{-8}$</td>
</tr>
<tr>
<td>Relative combined standard uncertainty</td>
<td>$3.9 \times 10^{-8}$</td>
</tr>
</tbody>
</table>

- N. Kuramoto *et al., Metrologia, 57*, 025006 (2020)
- cf. $u_r$(sphere density, 2005) = $1 \times 10^{-7}$
  - Improvement towards the redefinition of the kilogram
    - Diameter measurement
    - Surface characterization
Accurate density measurement for ocean science at NMIJ

- Ocean water
  - High heat capacity much larger than atmosphere
  - Circulation of energy from the sun
    → Ocean circulation affects global climate
- Global climate change: our urgent social issue
- Simulation to understand the mechanism of global climate change
  - Seawater density
    - \( u_r < 1 \) ppm
    - SI-traceable
- Accurate seawater density measurement under the cooperation with Japan Agency for Marine-Earth Science and Technology (JAMSTEC)

Deep-ocean currents driven by difference in density of water

Strategy for density measurement of seawater

- Seawater sample
  - Collected in wide range of depth over wide area
  - Sample number: very large

- Hydrostatic weighing
  - Accuracy: high
  - Time-consuming

- Density measurement of standard seawater by hydrostatic weighing
  → Calibration of oscillating-tube densimeter

- Oscillating-tube densimeter
  - Precise density comparator
  - Rapid measurement
  - Accuracy: dependent on reference liquid used for the calibration

Standard seawater
- Reference material for salinity measurement of seawater
Weight exchange mechanism
Hydrostatic weighing

Electronic balance

Sample liquid
- Density $\rho$

Density standard: Sinker
- Mass $M$
- Volume $V$

Weight exchange mechanism

Principle of hydrostatic weighing

$$F = \rho V g = (M - M_{app}) g$$

- $F$: Buoyancy force by the sample liquid
- $M_{app}$: Apparent mass of the sinker in the sample liquid
- $g$: Gravitational acceleration

Measurement of $M_{app}$
$$\rightarrow \rho$$
Hydrostatic weighing system for seawater of NMIJ

Electronic balance
- (0.01 mg resolution up to 210 g)

Wwind shield

Syringe

Syringe trap

Seawater sample

Standard PRT

Sample liquid

Quartz-glass cell

Hollow weight1 (65 g)

Solid weight1 (122 g)

Quartz-glass cell (φ40 mm)

φ0.05 mm tungsten wire

Si sinker (100 g, 43 cm³)

Sinker exchanger (titanium)

Suspender (SUS316)

122.000 00 g

(56 + 65) g = 121.000 00 g

- Y. Kayukawa and H. Uchida, Measurement: Sensors, 18, 10200 (2021)
Density difference measurement by the pressure of floatation method (PFM)

\[ \Delta h = 1 \text{ mm} : \Delta \rho / \rho = 1 \times 10^{-8} \]

Pressure control: \( \Delta p = \sim 30 \text{ kPa} \)

\( \rho = 2329 \text{ kg/m}^3 \) (same for the density of Si crystal)

\( u_r(\text{sinker density, PFM}) = 0.2 \text{ ppm} \)

cf. \( u_r(\text{sinker density, hydrostatic weighing}) = 5 \text{ ppm} \)

- Combination of hydrostatic weighing and PFM
- \( u_r(\text{density, standard seawater}) = 0.7 \text{ ppm} \)
Density measurement of refrigerant to prevent global warming

Density measurement of refrigerant to prevent global warming

Refrigerant: Fluid used to transfer heat in refrigeration and air conditioning system

- Condensation (gas → liquid)
- Heat release
- Evaporation (liquid → gas)
- Heat removal
- Condenser
- Outdoor unit
- Door unit
- Cool air
- Evaporator

- For optimal design of the system, accurate density of refrigerant in wide pressure and temperature ranges is required.

- Completely physical properties affecting the system performance
  - Density
  - Specific heat
  - Evaporation pressure
  - Viscosity,

Thermodynamic equation of state

Pressure-enthalpy diagram generated by thermodynamic equation of state

- Refrigerant: Fluid used to transfer heat in refrigeration and air conditioning system

- Evaporation (liquid → gas)
- Heat removal

(Coefficient of performance)

\[ \text{COP} = \frac{Q}{W} \]
### Evolution of Refrigerant

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<tbody>
<tr>
<td>ODP: Ozone Depletion Potential</td>
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<tr>
<td>GDP: Global Warming Potential</td>
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- **CFC, HCFC**
  - ODP $\geq 1$
  - GWP $\geq 5000$

- **HFC**
  - ODP = 0
  - GWP $\geq 500$

- **New alternative refrigerants**
  - ODP = 0
  - GWP $\leq 10$

- **Chlorofluorocarbon CFC**
- **Hydrochlorofluorocarbon HCFC**
- **Hydrofluorocarbon HFC**
- **Hydrofluoroolefin HFO**
Magnetic suspension for density measurement in wide temperature and pressure ranges

Hydrostatic weighing with magnetic suspension

Conventional hydrostatic weighing
Hydrostatic weighing system with Si sinker using magnetic suspension

- Density accuracy: < 45 ppm
- Temperature range: −10 °C ~ 150 °C
- Pressure range: < 20 MPa


- HFO-1123 (Trifluoroethene)

Si sinker
- calibrated by PFM
- \( u_r(\text{sinker density}) = 0.4 \text{ ppm} \)

Hydrostatic weighing system with Si sinker using magnetic suspension

- \( u_r(\text{density}) < 45 \text{ ppm} \)
- Temperature range: −10 °C ~ 150 °C
- Pressure range: < 20 MPa
  - HFO-1123 (Trifluoroethene)
Contribution to development of new alternative refrigerants

- Cooperation with many universities and institutes around the world
- Thermophysical properties for some of new alternative refrigerants evaluated at NMIJ
  → NIST Reference Fluid Thermodynamic and Transport Properties Database (REFPROP)

Website of Kyushu University Research Center for Next Generation Refrigerant Properties (NEXT-RP)
  • https://i2cner.kyushu-u.ac.jp/~next-rp/en/collaborations_en
Summary

- NMIJ has realized the primary density standard using 1 kg Si sphere with a relative uncertainty of $4 \times 10^{-8}$
  - Laser interferometer for sphere volume measurement
  - XPS for sphere surface characterization
- Si artifacts traceable to the primary density standard
  - Accurate density measurement to solve social issues
    - Global climate change
    - Global warming
- To achieve accurate density measurements
  - Combination of various measurement techniques is essential
    - Hydrostatic weighing
    - Pressure of floatation method
    - Magnetic suspension densimeter