Accurate density measurements for global environmental science at NMIJ

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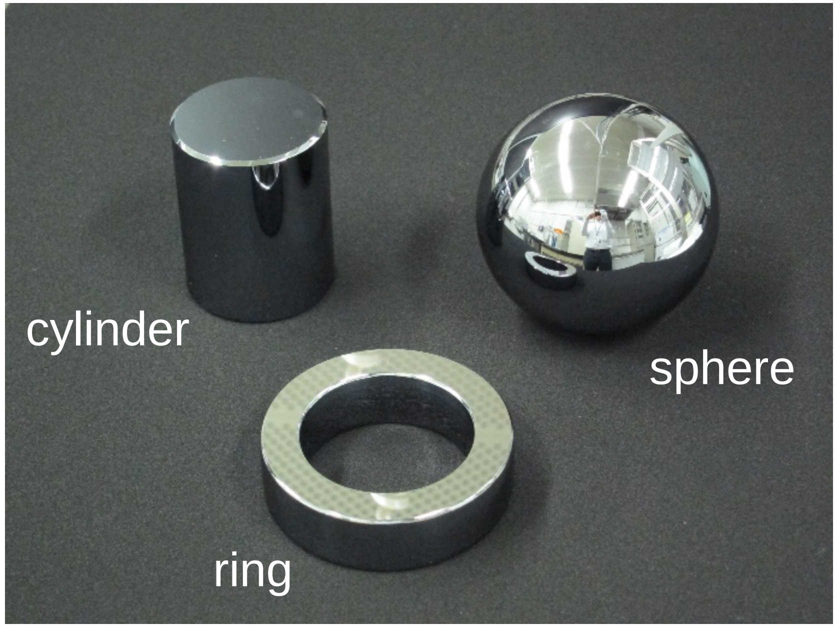
- Realization of the primary density standard using 1 kg Si spheres
  - Mass and volume measurements
  - State-of-the-art techniques developed for the redefinition of the kilogram
    → Uncertainty reduction of the primary standard
- Density measurement to solve social issues
  - Seawater
    → Prediction of global climate change
  - Refrigerant
    → Prevention of global warming

1 kg Si sphere

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



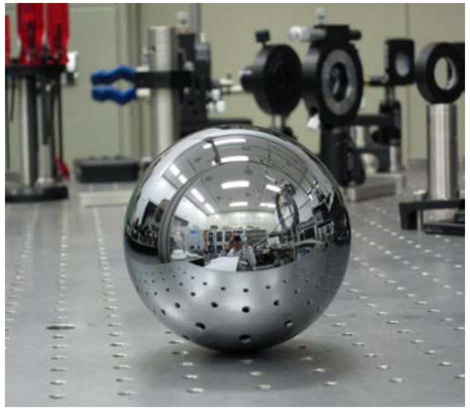
1 kg Si sphere

Defining constants in the new SI — Planck constant | Speed of light in vacuum

Mass
- Mass comparison
- 1 kg reference weight

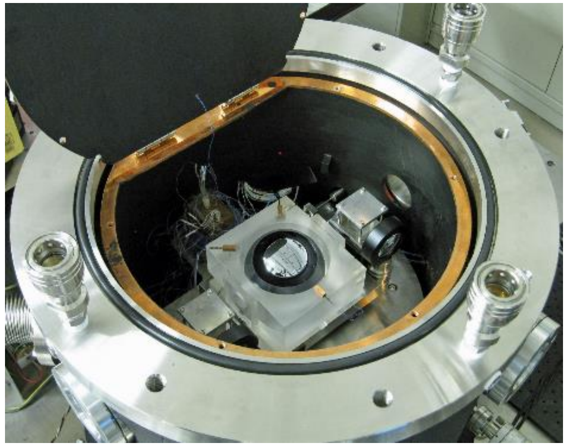
Volume
- Diameter measurement
- Laser interferometer

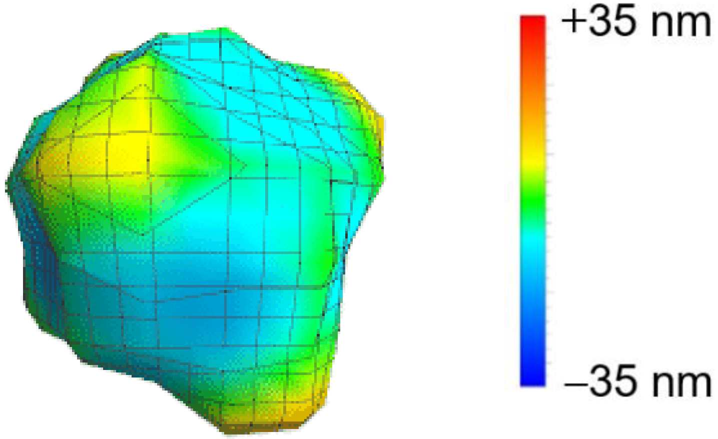
Primary density standard — Si sphere



Primary density standard of NMIJ

Volume measurement of Si sphere of NMIJ

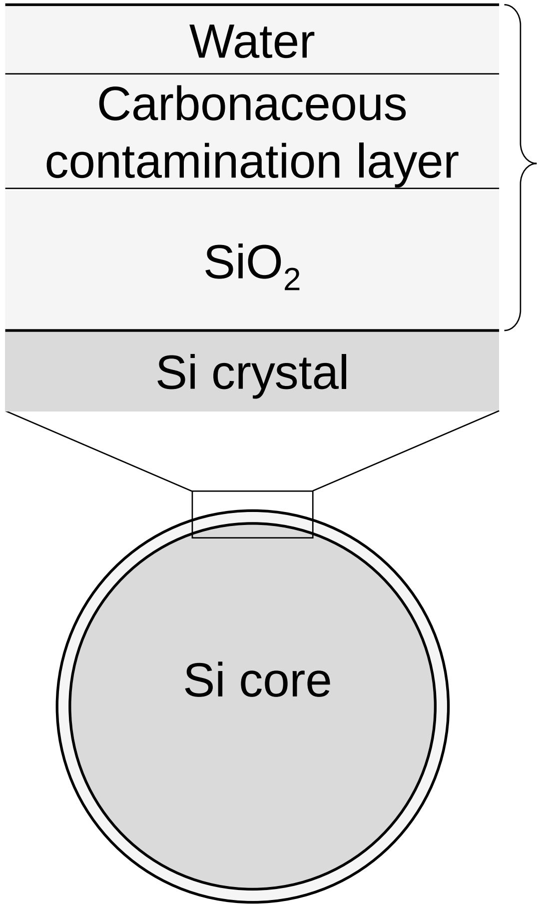




Laser interferometer for the Si sphere volume measurement developed for the redefinition of the kilogram using ^{28}Si-enriched crystals

- Diameter measurement in 1450 different directions
  → Volume
- u(diameter) = 0.6 nm, u_r(Volume) = 2.0×10^{-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 model of Si sphere

Surface layer

- Thickness: about 2 nm
- Transparent

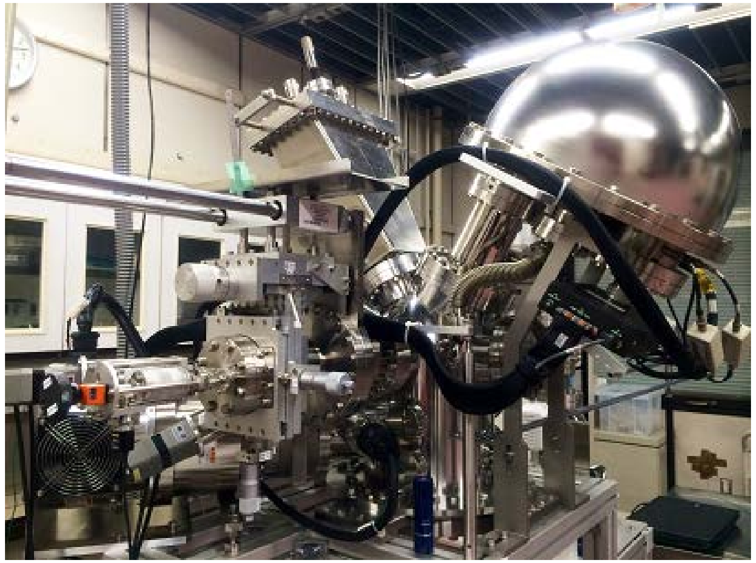
➢ Diameter measured by the laser interferometer

→ Almost same as the diameter of Si core excluding the surface layer

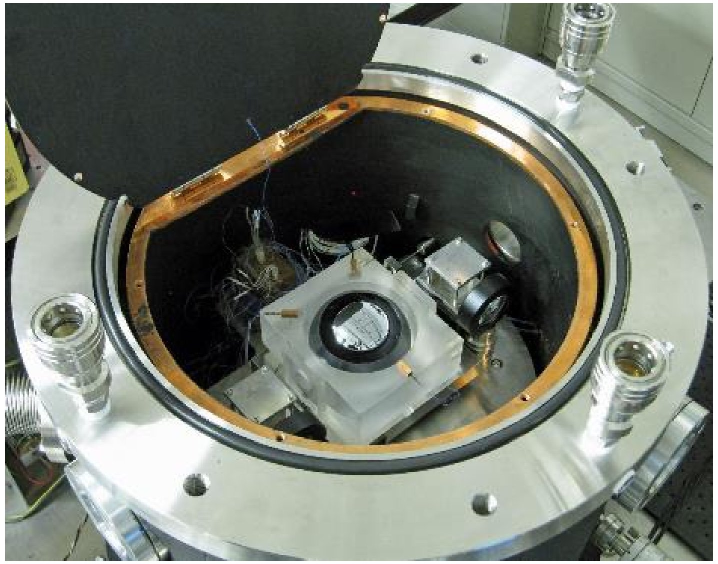
➢ Thickness measurement of surface layer

→ Actual diameter including the surface layer

Surface characterization of Si sphere



Surface characterization system using x-ray photoelectron spectroscopy (XPS) developed for the redefinition of the kilogram using ^{28}Si-enriched crystals



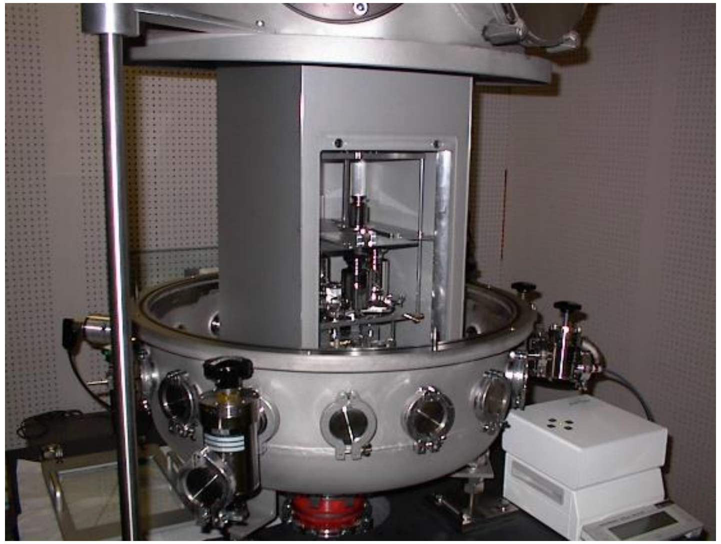
Laser interferometer for the Si sphere volume measurement at NMIJ

- u (diameter) = 0.6 nm

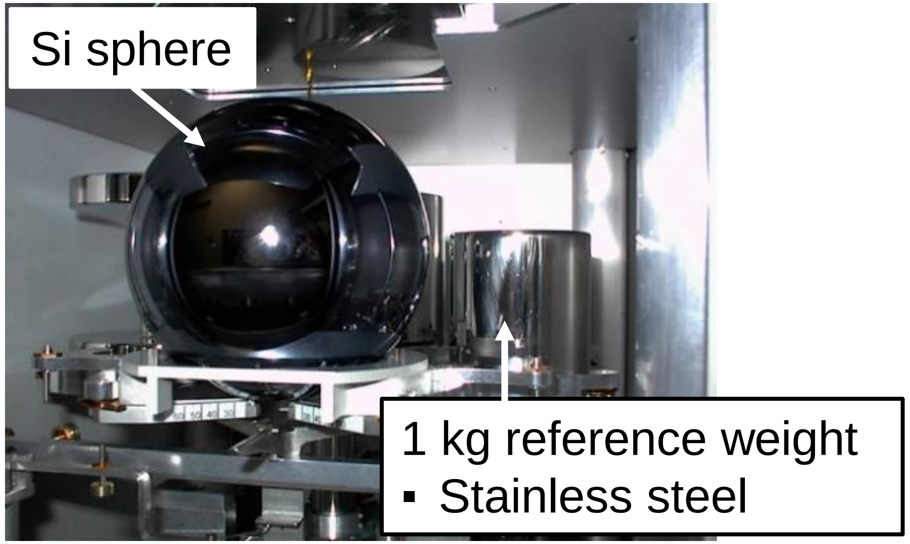
- XPS gives information on
  - Element
  - Binding state
- Thickness of the surface layer
  - u (thickness) = 0.4 nm

Actual diameter (Si core + surface layer)
- u (actual diameter) = 0.9 nm

Mass measurement of Si sphere



Vacuum balance



Si sphere and 1 kg reference weight

Planck constant ⇐ Consensus value of the kilogram ⇐

National prototype of the kilogram of Japan

⇐

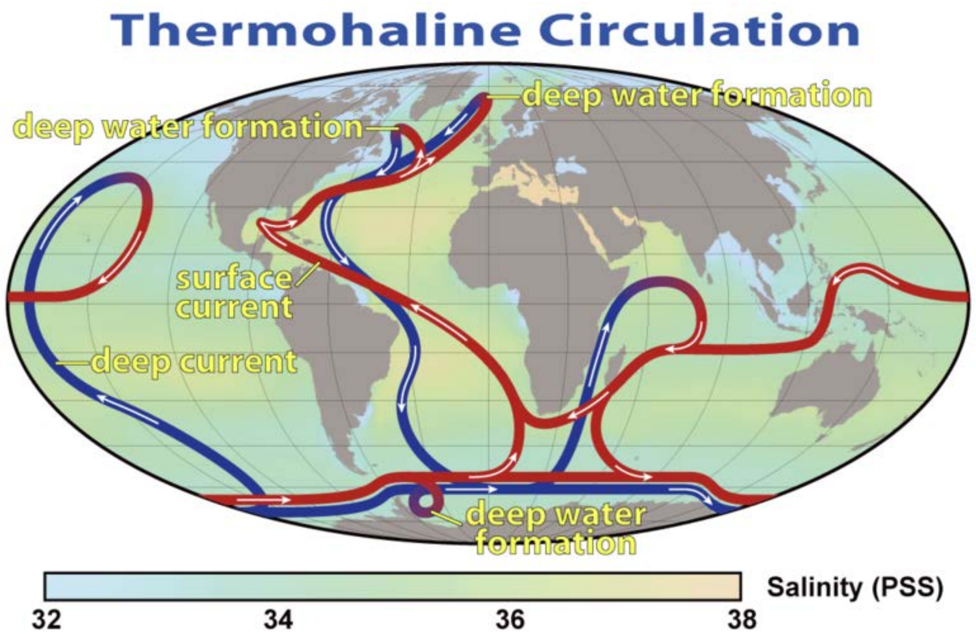
1 kg Reference weight

Uncertainty budget of the sphere density determination at 20 °C and 101.325 kPa

Uncertainty source	Relative contribution to density determination
Sphere volume	2.0×10^{-8}
Surface layer	2.4×10^{-8}
Sphere mass	2.3×10^{-8}
Relative combined standard uncertainty	3.9×10^{-8}

- N. Kuramoto *et al.*, *Metrologia,* **57**, 025006 (2020)
- cf. u_r(sphere density, 2005) = 1×10^{-7}
  - Improvement towards the redefinition of the kilogram
    - Diameter measurement
    - Surface characterization

Accurate density measurement for ocean science at NMIJ



https://en.wikipedia.org/wiki/Thermohaline_circulation

Deep-ocean currents driven by difference in density of water

- Ocean water
  - High heat capacity much lager 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)

Strategy for density measurement of seawater

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

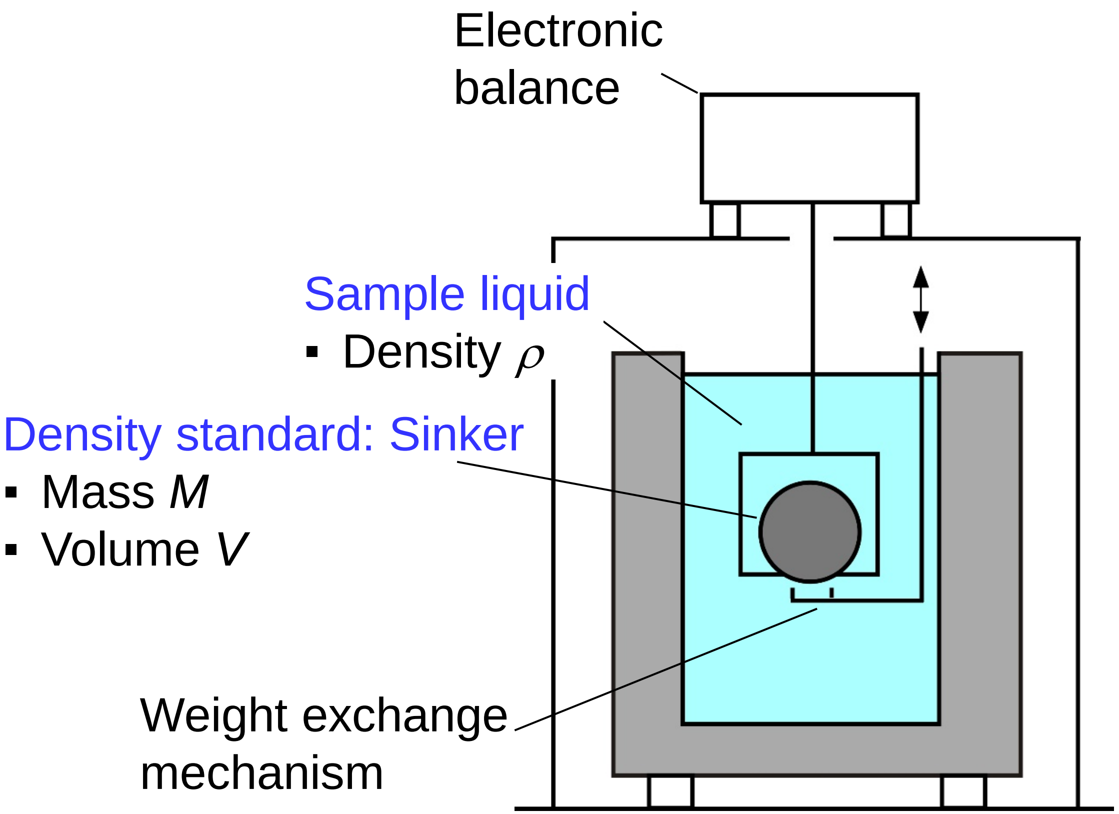
Standard seawater

- Reference material for salinity measurement of seawater

- 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

Hydrostatic weighing



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

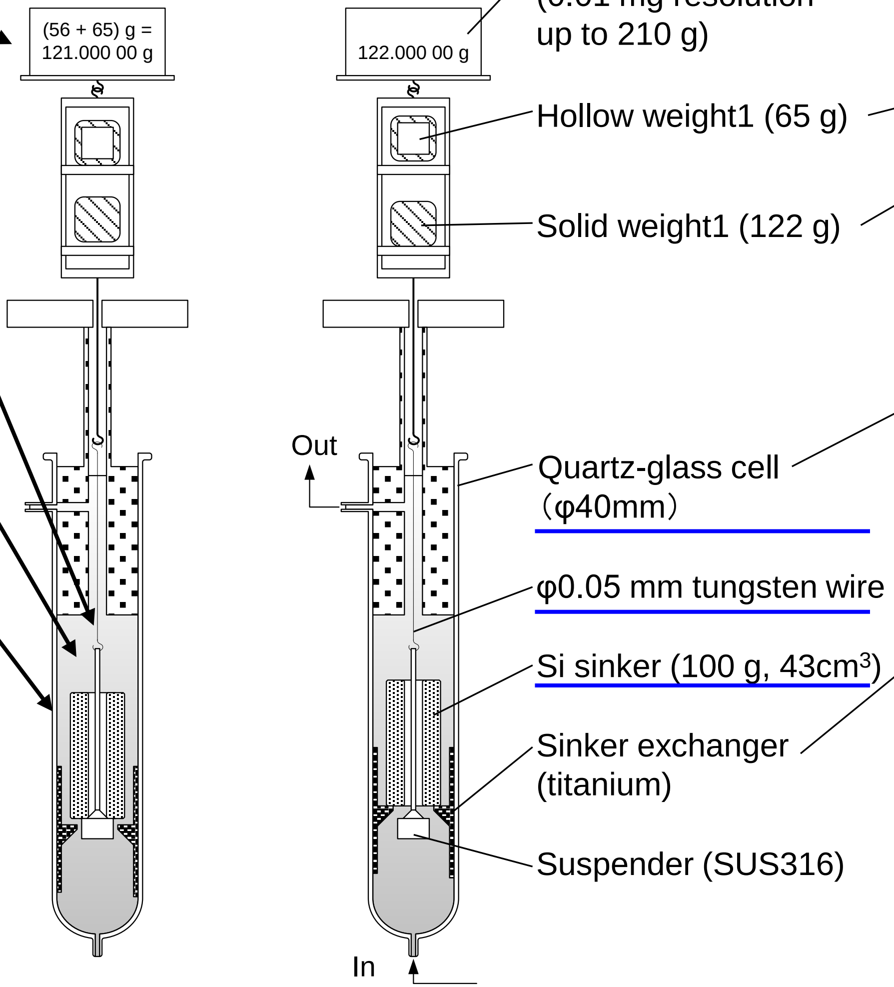
Electronic balance

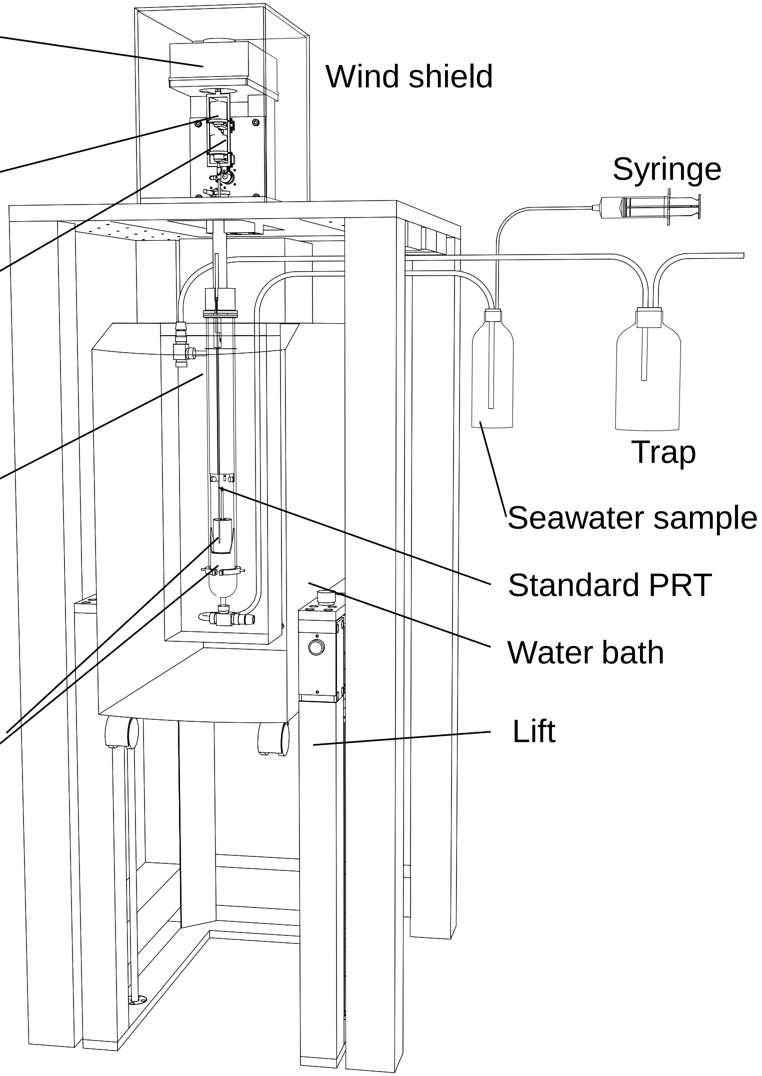
Tungsten wire
- Diameter: 0.05 mm

Sample liquid

Quartz-glass cell

Si sinker
- Shape: cylinder
- Mass: 100 g





➢ Y. Kayukawa and H. Uchida, *Measurement: Sensors*, **18**, 10200 (2021)

Density difference measurement by the pressure of floatation method (PFM)

u_r(sinker density, PFM) = 0.2 ppm

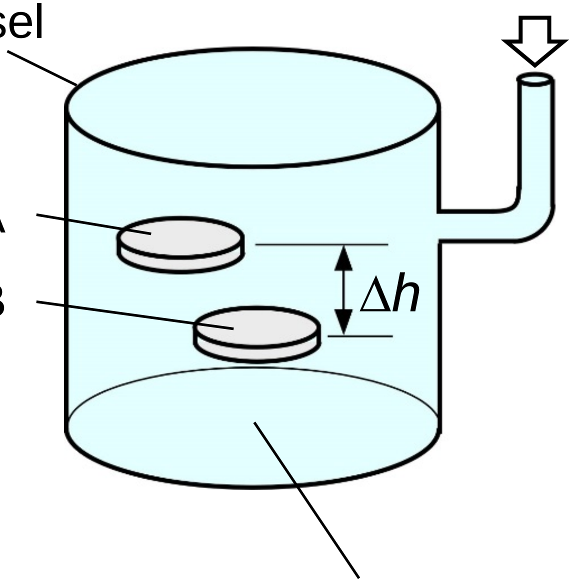
cf. u_r(sinker density, hydrostatic weighing) = 5 ppm

Closed vessel

Si sample A

Si sample B

Pressure control : $\Delta p = \sim 30$ kPa



$\Delta h =$ 1 mm : $\Delta\rho/\rho = 1\times10^{-8}$

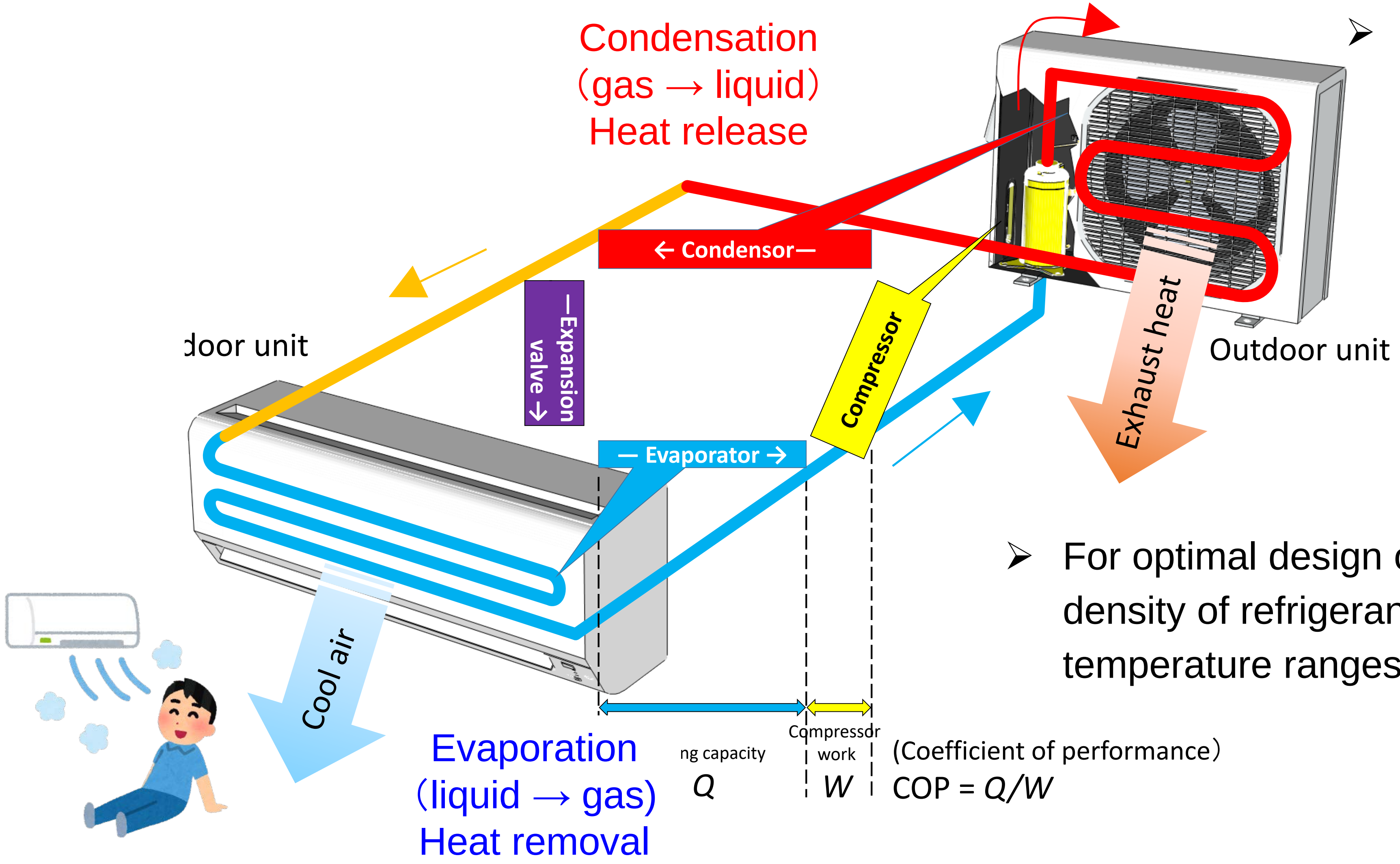
u (Relative density) = 10^{-8} order

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

- Combination of hydrostatic weighing and PFM
- u_r(density, standard seawater) = 0.7 ppm

Density measurement of refrigerant to prevent global warming

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



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

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

Evolution of refrigerant

1930s → Montreal Protocol (1987) → Kigali Amendment to Montreal Protocol (2015) →

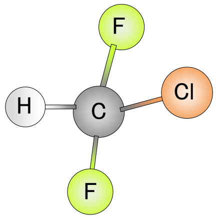
ODP: Ozone Depletion Potential

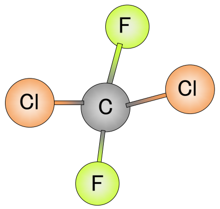
GDP: Global Warming Potential

CFC, HCFC
- ODP ≧ 1
- GWP ≧ 5000

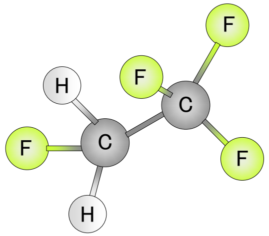
HFC
- ODP = 0
- GWP ≧ 500

New alternative refrigerants
- ODP = 0
- GWP ≦ 10

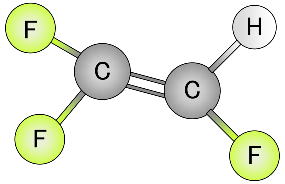




Chlorofluorocarbon CFC
Hydrochlorofluorocarbon HCFC

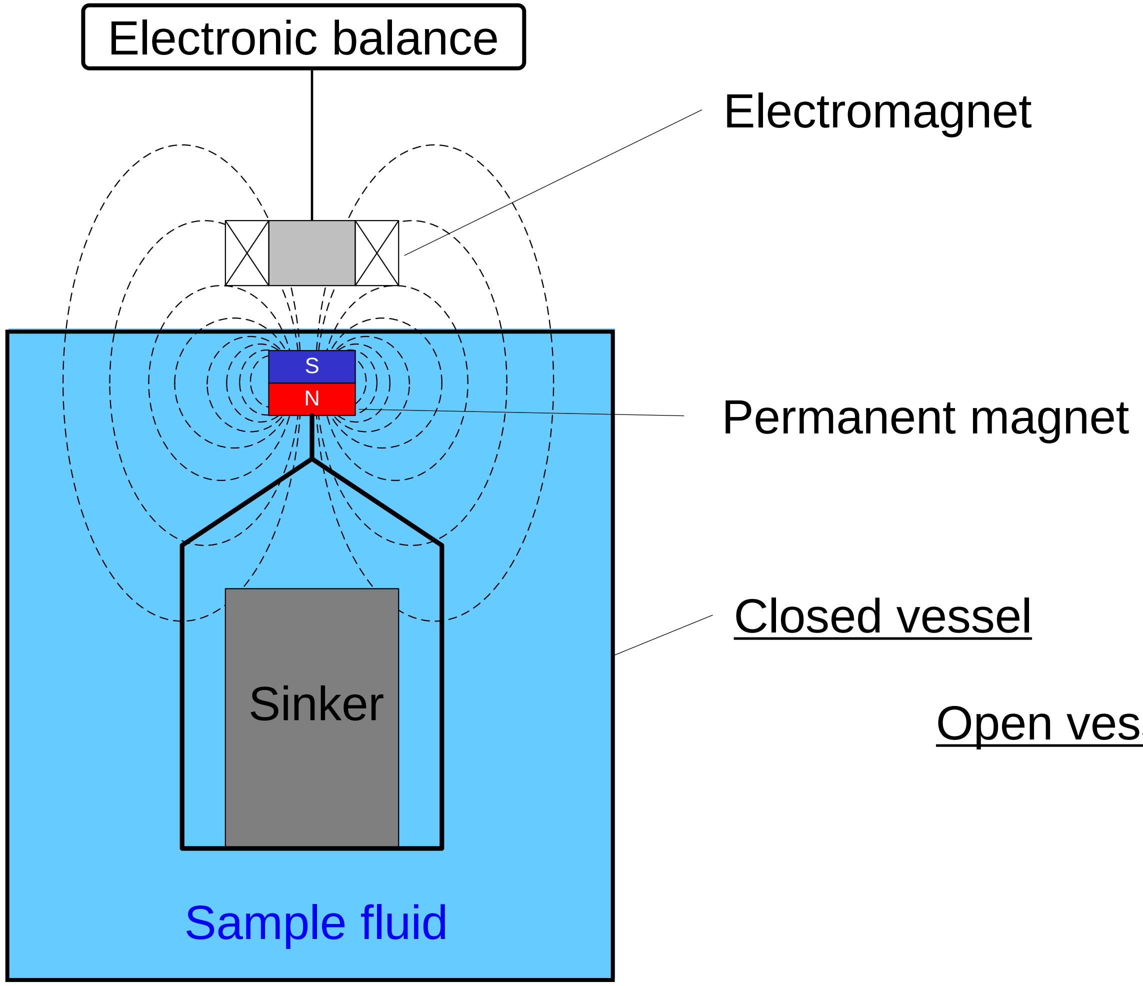


Hydrofluorocarbon HFC

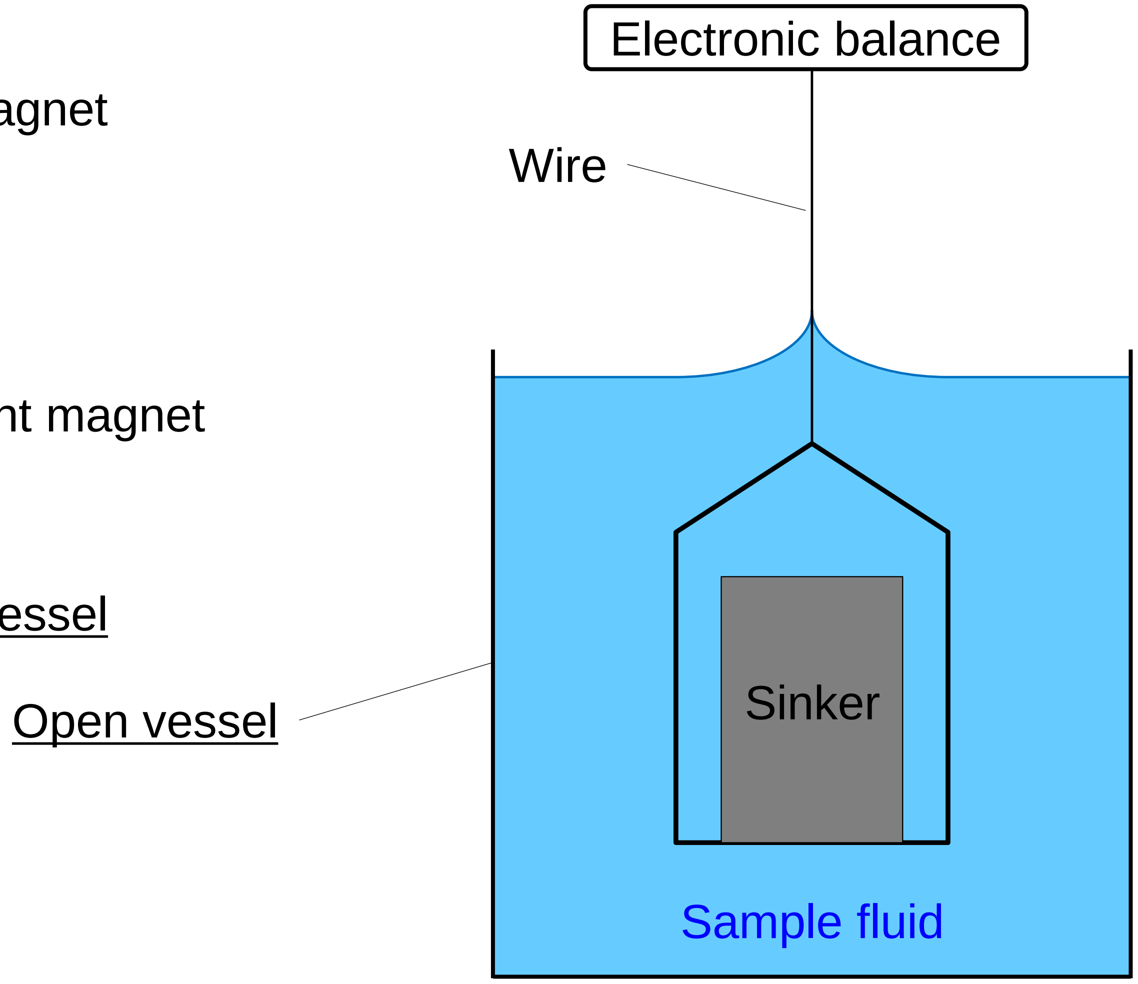


Hydrofluoroorefin HFO

Magnetic suspension for density measurement in wide temperature and pressure ranges

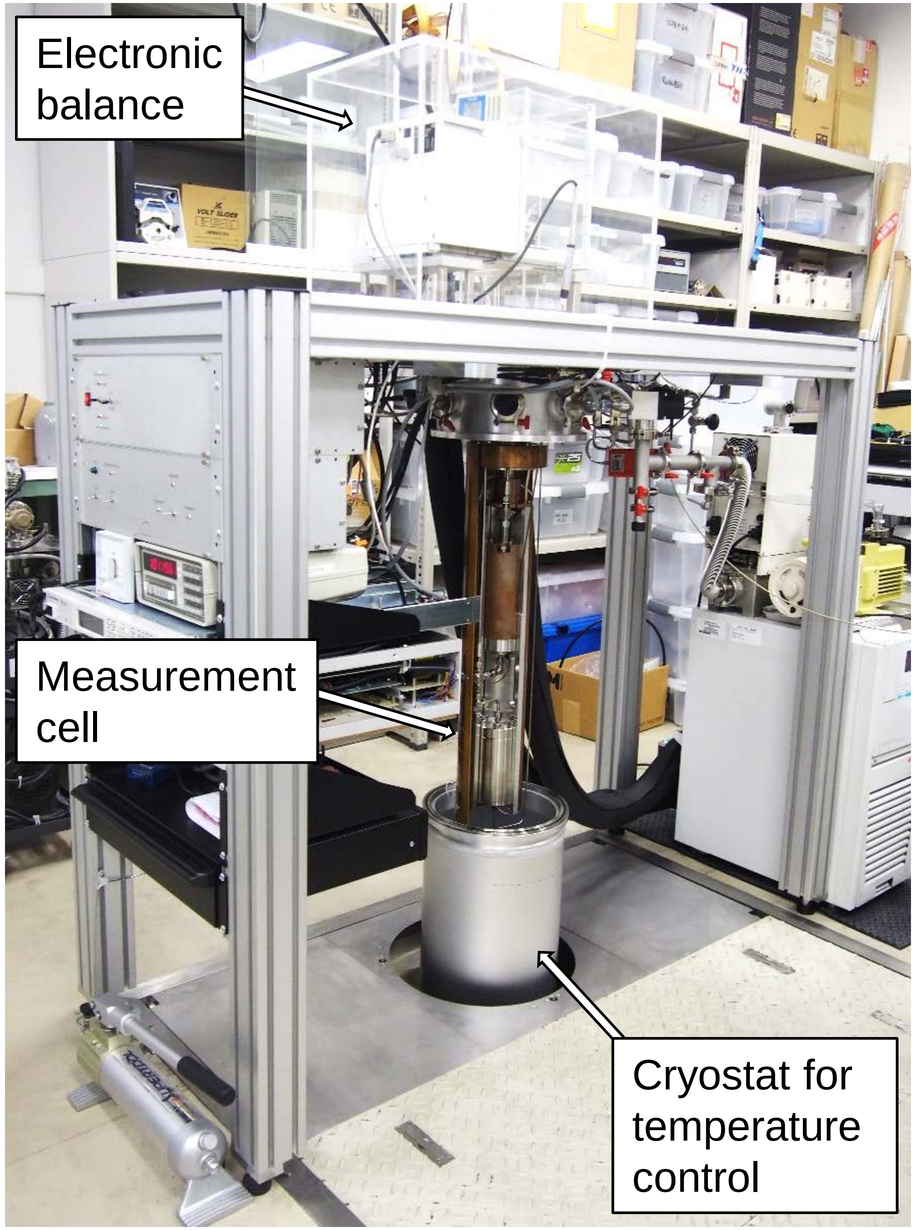


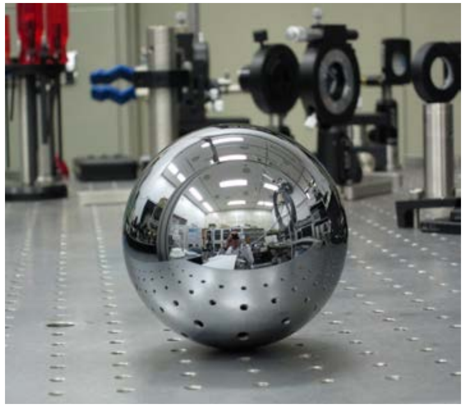
Hydrostatic weighing with magnetic suspension



Conventional hydrostatic weighing

Hydrostatic weighing with magnetic suspension at NMIJ



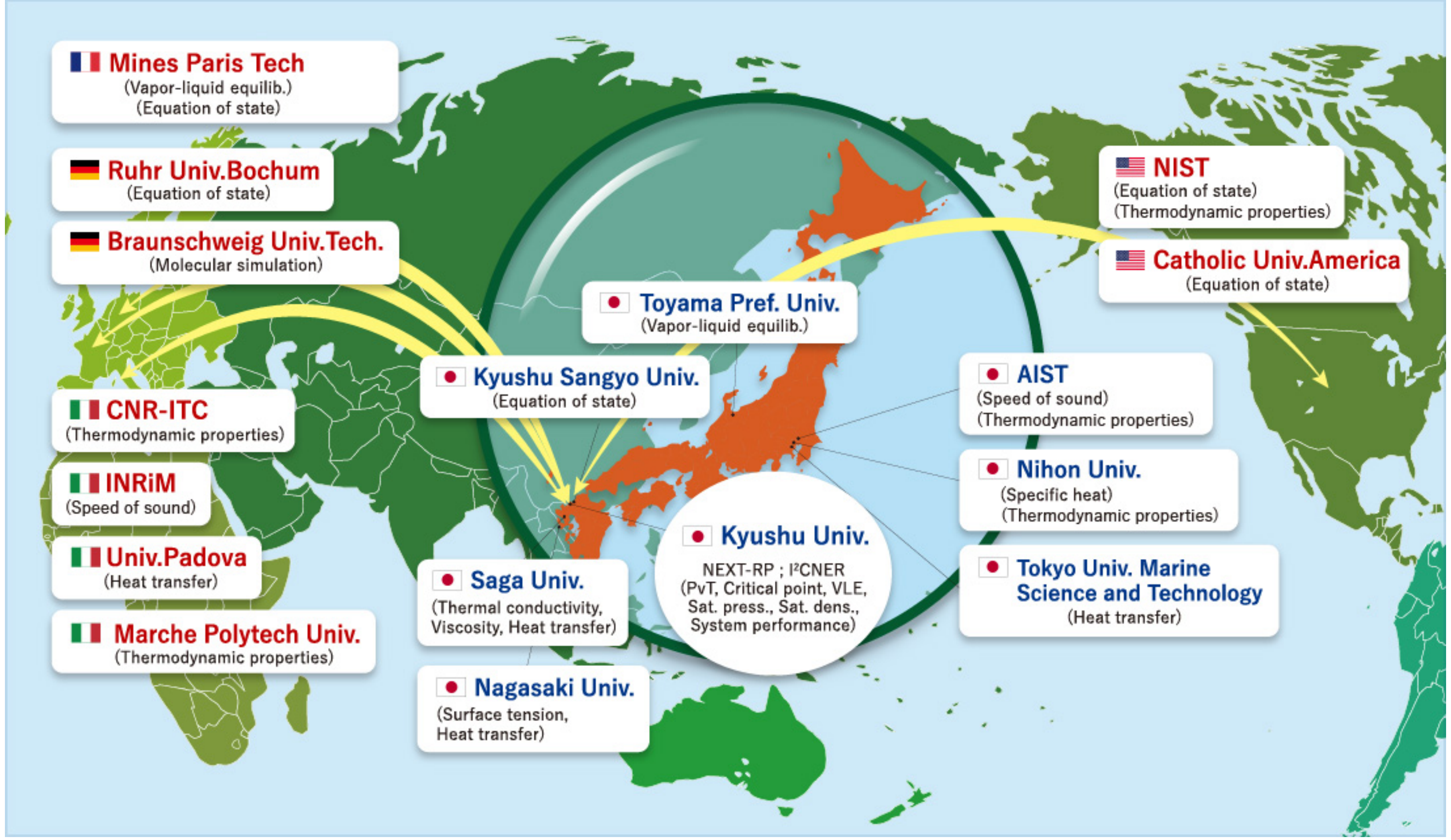


Si sinker
- calibrated by PFM
- u_r(sinker density) = 0.4 ppm

Hydrostatic weighing system with Si sinker using magnetic suspension

- u_r(density) < 45 ppm
- Temperature range: −10 °C ~ 150 °C
- Pressure range: < 20 MPa
- Y. Kayukawa, *Int. J. Refrig.*, **119**, 349–355 (2020)
  - HFO-1123 (Trifluoroethene)

Contribution to development of new alternative refrigerants



Website of Kyushu University Research Center for Next Generation Refrigerant Properties (NEXT-RP)

- https://i2cner.kyushu-u.ac.jp/~next-rp/en/collaborations_en

- 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)

Summary

- NMIJ has realized the primary density standard using 1 kg Si sphere with a relative uncertainty of 4×10^{-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