# 絶対塩分評価のための密度・屈折率測定技術の開発

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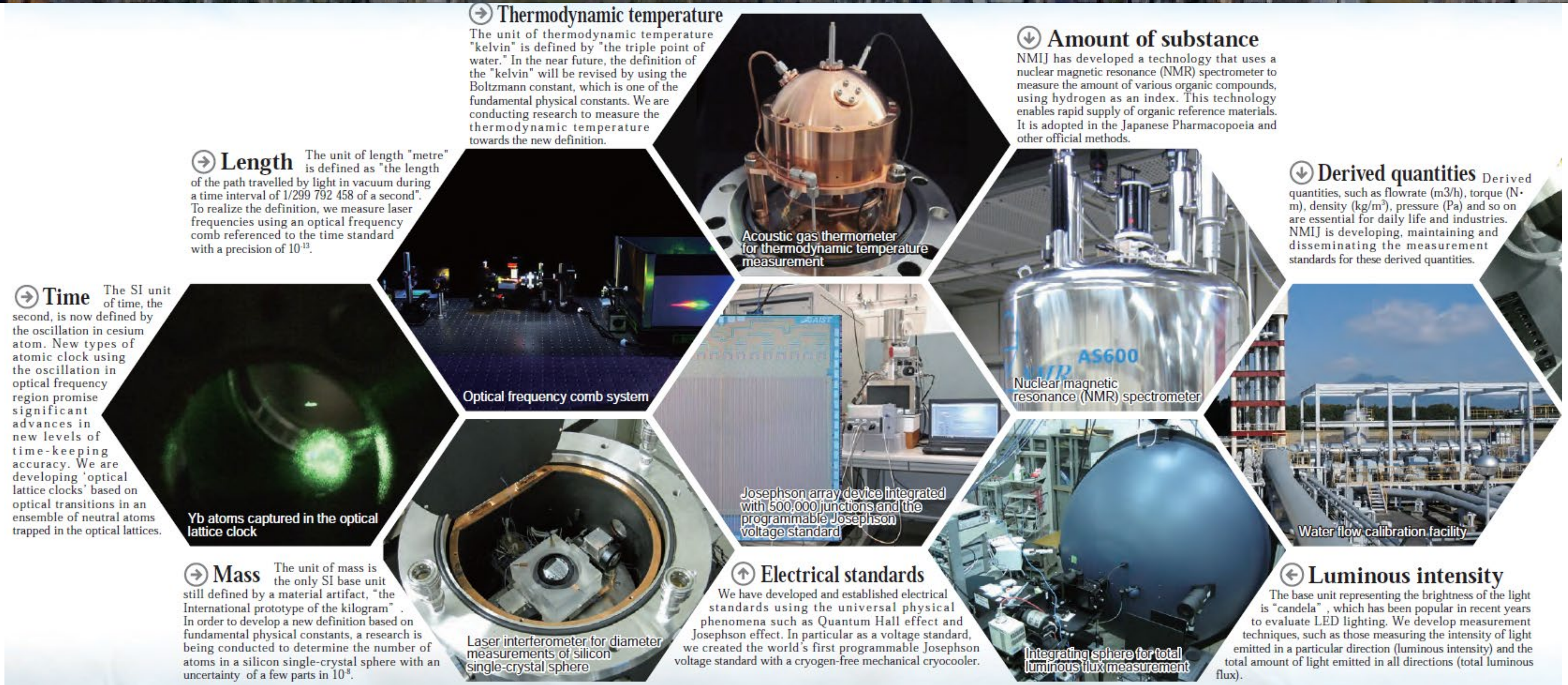


# 液体密度の標準：純水

CIPM/CCM による推奨式（Tanaka 2001）
$U(\rho)/\rho$ = 0.83 ppm@20 ºC, 0.1MPa

metrologia

Recommended table for the density of water between 0 °C and 40 °C based on recent experimental reports[1]

M. Tanaka, G. Girard, R. Davis, A. Peuto and N. Bignell

**Abstract.** Experimental results from four recent research reports on the determination of the density/temperature relationship of Standard Mean Ocean Water (SMOW) under a pressure of 101 325 Pa are analysed and a new formula is recommended for metrological applications. This paper determines the formulae of density and relative density, with their uncertainties, in the temperature range 0 °C to 40 °C. The uncertainty estimation of one of the reports included in the analysis has been re-evaluated. Effects on water density due to isotopic mixtures other than SMOW, ambient pressures different from 101 325 Pa, and the presence of dissolved air, are also reviewed.

**1. Introduction**

***1.1 Background***

Water is a ubiquitous liquid whose physical properties serve as references in many areas of science (particularly in the fields of oceanography and chemistry). Its density is a widely used reference for determinations of unknown densities and volumes. Tables for the relative density[2] of water between 0 °C and 40 °C have been deduced from measurements carried out by Thiesen et al. [1] and by Chappuis [2] at the beginning of the twentieth century. Most other tables in the literature [e.g. 3-7] are derived from this early work. Note that the relative density tables given in [1] and [2] are consistent to within 1 part in $10^6$ only in the range of temperatures 0 °C to 16 °C. At 40 °C, the tables have diverged by almost 10 parts in $10^6$.

Once the relative density has been established over a range of temperatures, knowledge of the density at one temperature within the range is sufficient to fix the density over the entire range. The density of water was calculated from the measurements at the BIPM, also carried out by Chappuis [2], which found the maximum density $\rho_{max}$ of distilled tap water, free of dissolved gases and at a pressure of 101 325 Pa, to be 999.972 kg $m^{-3}$. The density maximum occurs at approximately 4 °C. However, these density measurements were made at a time when the existence of isotopes was unknown and, therefore, the uncertainty from this source alone is insufficient for the most demanding modern use.

By 1965, the problem of water density drew the attention of the Association Internationale pour les Sciences Physiques de l'Océan and its recommendation was adopted by the International Union of Geodesy and Geophysics (IUGG) in 1971 (Resolution 18). The Resolution called for the determination of the density of water, in terms of the International System of Units (SI), at 0 °C and 20 °C and for the determination of the relative density of water between 0 °C and 40 °C.

At the same time, Commission I.4 (Commission on Physico-Chemical Measurements and Standards) of the International Union of Pure and Applied Chemistry (IUPAC) took up the same question. In 1973, IUPAC issued a Recommendation [8] asking for the following:

- that absolute determinations of the density of water, whose isotopic composition is as close as possible to Standard Mean Ocean Water (SMOW) be undertaken with the goal of a final uncertainty no greater than 0.001 kg $m^{-3}$ at two or three well-defined temperatures in the range between 0 °C and 40 °C;

M. Tanaka: National Metrology Institute of Japan (NMIJ), Umezono 1-1-4, Tsukuba, Ibaraki, Japan.
G. Girard (retired) and R. Davis: Bureau International des Poids et Mesures (BIPM), Pavillon de Breteuil, 92312 Sèvres Cedex, France.
A. Peuto: Istituto di Metrologia "G. Colonnetti" (IMGC), Strada delle Cacce 73, 10135 Turin, Italy.
N. Bignell: CSIRO National Measurement Laboratory (NML), PO Box 218, Lindfield, NSW 2070, Australia.

1. This report was prepared by a Task Group formed by the Working Group on Density, Consultative Committee for Mass and Related Quantities (CCM). The Working Group has accepted the report, which will be submitted for final approval to the International Committee for Weights and Measures (CIPM) at its meeting in October 2001.
2. The term "relative density" refers to the ratio of water density at a given temperature to the maximum density, which occurs near 4 °C. The term "thermal dilatation" is sometimes used to designate a related quantity, which is the ratio of water volume at a given temperature to the volume at 4 °C.

*Metrologia*, 2001, **38**, 301-309 301

**2つの絶対測定結果に基づいている：**

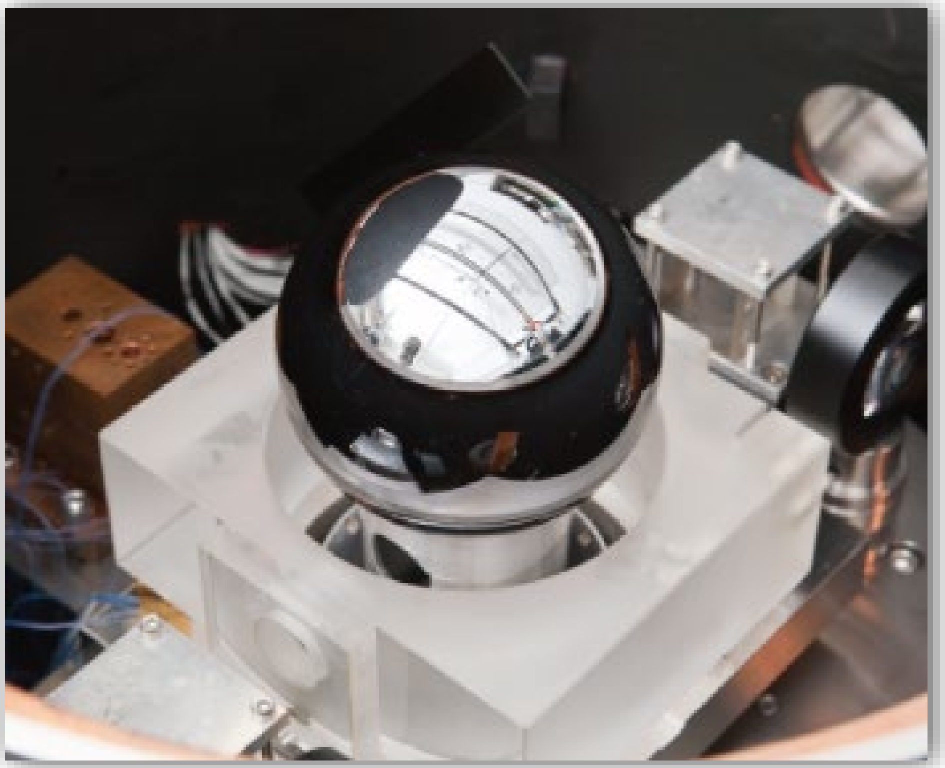
Patterson and Morris (1994)
- 中空ガラスシンカーを用いた液中秤量
- 光波干渉による直径測定
- 質量測定

Fujii and Takenaka (1995)
- 溶融石英球を用いた液中秤量
- 光波干渉による直径測定
- 質量測定

**密度標準として用いるには補正が必要：**
- 同位体補正(約3.0 ppm)
- 溶存空気 (約2.6 ppm@20 ºC)

# 密度の1次標準（国家標準）：シリコン単結晶

1 kg原器に（ほぼ）直結した質量測定

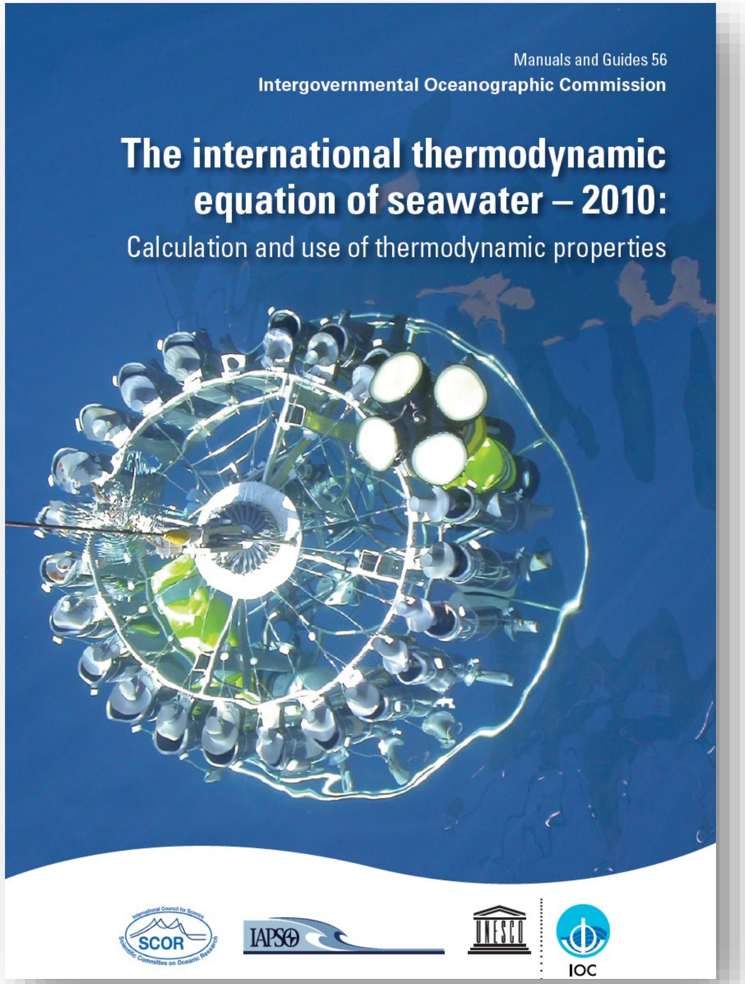


レーザー干渉計によるシリコン球の直径測定

# 海水密度の標準 TEOS-10

TEOS-10 manual

$U(\rho)/\rho$ = 8 ppm@(0 to 40）ºC, 0.1MPa




**<u>2つの絶対測定結果に基づいている:</u>**

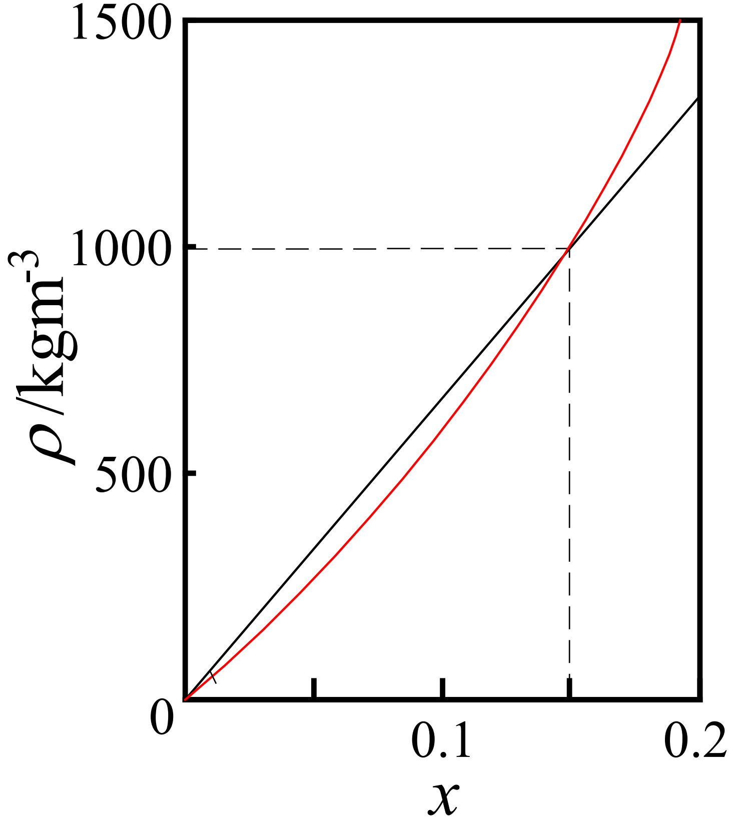
Millero et al. (1976)

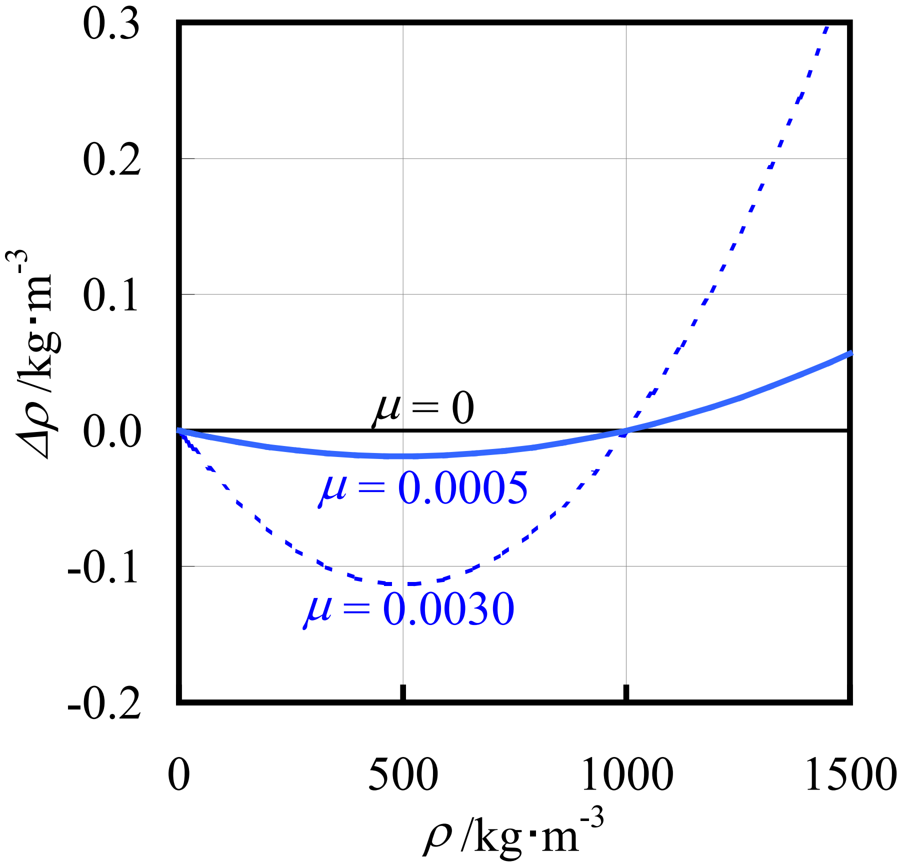
- 磁気密度計
- 純水密度で校正
- IAPSO P63 およびその希釈
- $U(\rho)/\rho$ = 2 ppm

Poisson et al. (1980)

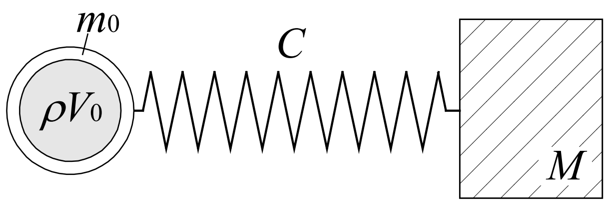
- 中空ガラスシンカーを用いた液中秤量測定
- 純水密度で校正
- $U(\rho)/\rho$ = 5 ppm

# 振動密度計における課題：非線形性




Resonance model:




$$\rho = A\frac{(1+\mu)x}{1-\mu x} \qquad \mu = \frac{m_0}{M}$$

! Studied by Kayukawa et al.(2003) for DMA 512HP

# 研究課題と数値目標

- 海水密度の絶対測定手法の開発

- 密度の不確かさの目標値:

  $U(\rho_{\text{TEOS-10}}) \fallingdotseq 0.000\,001\ \text{g cm}^{-3}$

- 海水標準物質に関する密度絶対測定の実施

- TEOS-10の信頼性に関する定量的評価を行う

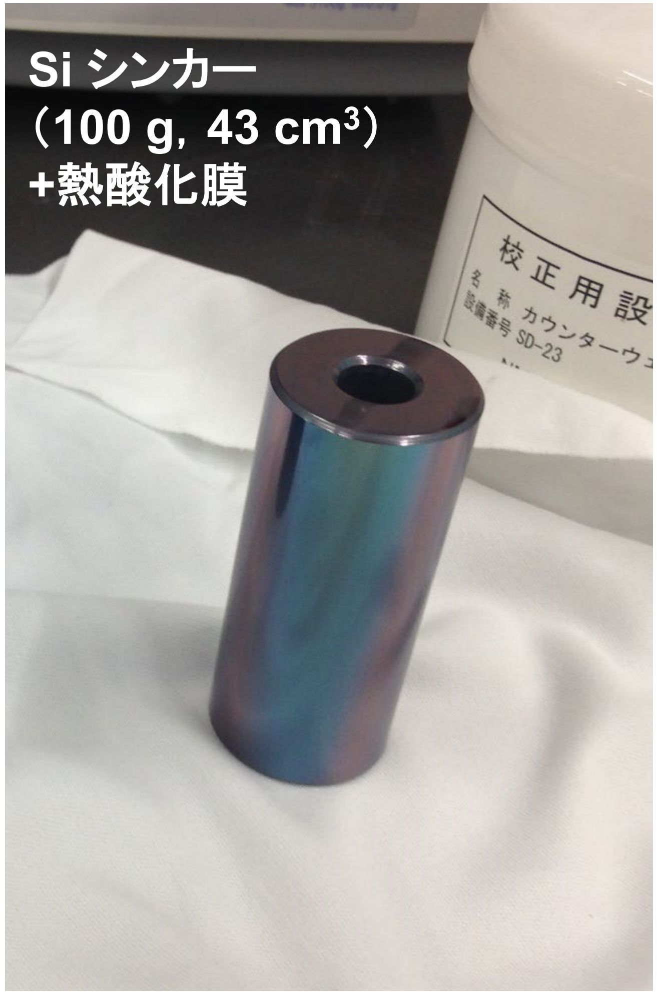
# 各国標準研の液体密度測定能力（BIPM CMC DB）

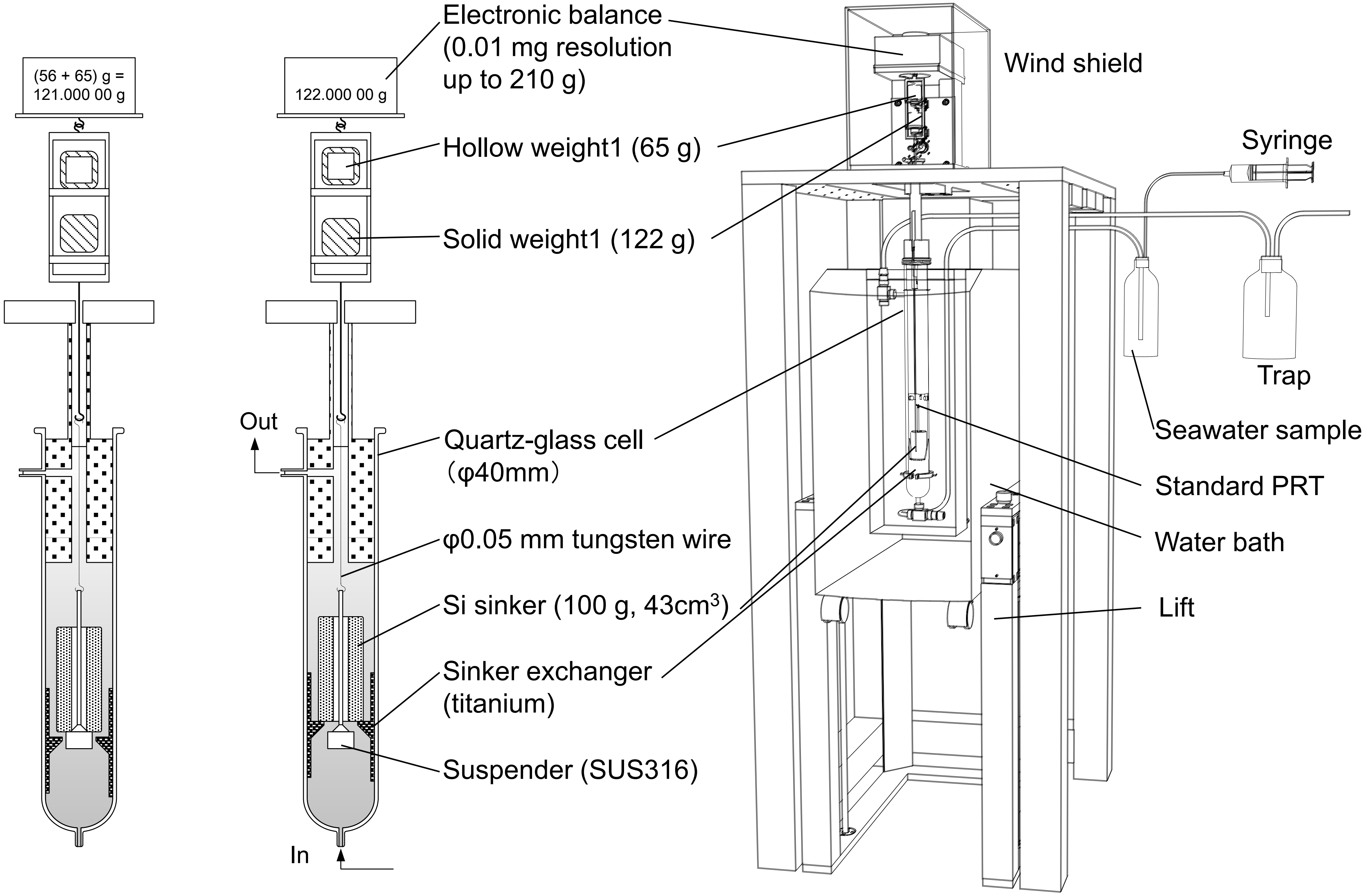
| NMI, country | Method | Range | $U(\rho)/(\mathrm{kg\ m^{-3}})$ |
|---|---|---|---|
| NRC, Canada | HW | 630 to 2,000 | 0.10 |
| PTB, Germany | HW | 600 to 2,000 | 0.004 to 0.018 |
| NMIJ, Japan | MSD | 600 to 1,700 | 0.015 to 0.021 |
| KRISS, Korea | HW | 600 to 2,000 | 0.005 |
| NPL, UK | HW | 750 to 1,000 | 0.006 to 0.008 |
| NIST, US | HW | 600 to 2,000 | 0.01 |
| NMIA, Australia | HW | 500 to 2,000 | 20 ppm |
| NIM, China | HW | 500 to 3,000 | 0.08 to 0.2 |
| INRiM, Italy | HW | 800 to 2,000 | 24 ppm |
| MSL, New Zealand | HW | 600 to 2,000 | 20 ppm |
| VNIM, Russia | HW | 600 to 2,000 | 0.010 to 0.013 |

HW: 液中秤量法, MSD: 磁気懸架式密度計

# 水溶液密度の絶対測定のための液中秤量装置

## $U(\rho)$=0.001 3 kg m$^{-3}$




(56 + 65) g =
121.000 00 g
122.000 00 g
Electronic balance
(0.01 mg resolution
up to 210 g)
Hollow weight1 (65 g)
Solid weight1 (122 g)
Out
In
Quartz-glass cell
（φ40mm）
φ0.05 mm tungsten wire
Si sinker (100 g, 43cm³)
Sinker exchanger
(titanium)
Suspender (SUS316)
Wind shield
Syringe
Trap
Seawater sample
Standard PRT
Water bath
Lift

# ppm精度で海水密度測定する際の課題

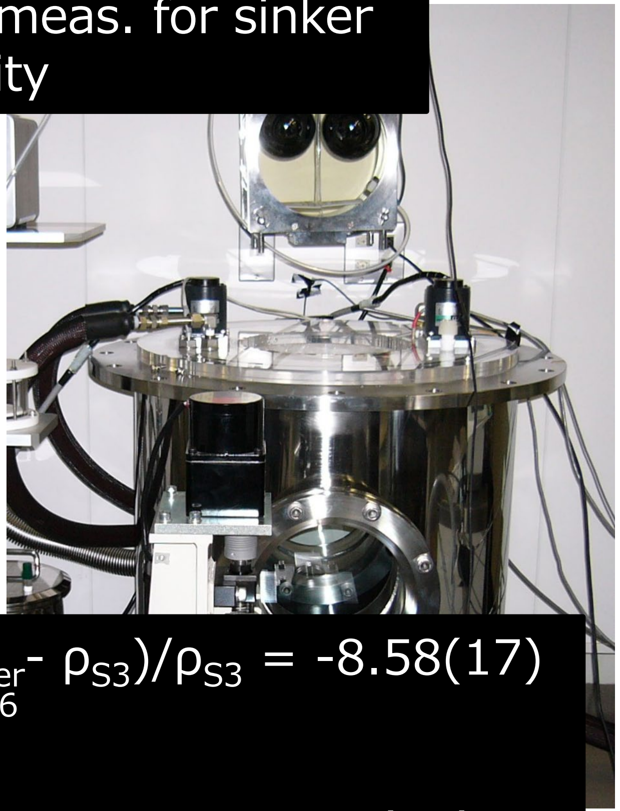
- 低減すべき不確かさ要因
  - シンカー密度校正
  - シンカー質量校正
  - 気泡付着の影響

- 密度測定値のドリフト
  - 要因1
  - 要因2
  - 要因3

# Challenges in sea-water density measurements

- 低減すべき不確かさ要因
  - シンカー密度校正
  - シンカー質量校正
  - 気泡付着の影響

PFM meas. for sinker density



$(\rho_{sinker} - \rho_{S3})/\rho_{S3} = -8.58(17) \times 10^{-6}$

$\rho_{sinker} = 2.329\ 052\ 77(56)\ g\ cm^{-3}$

# Challenges in sea-water density measurements

- 低減すべき不確かさ要因
  - ~~シンカー密度校正~~
  - シンカー質量校正
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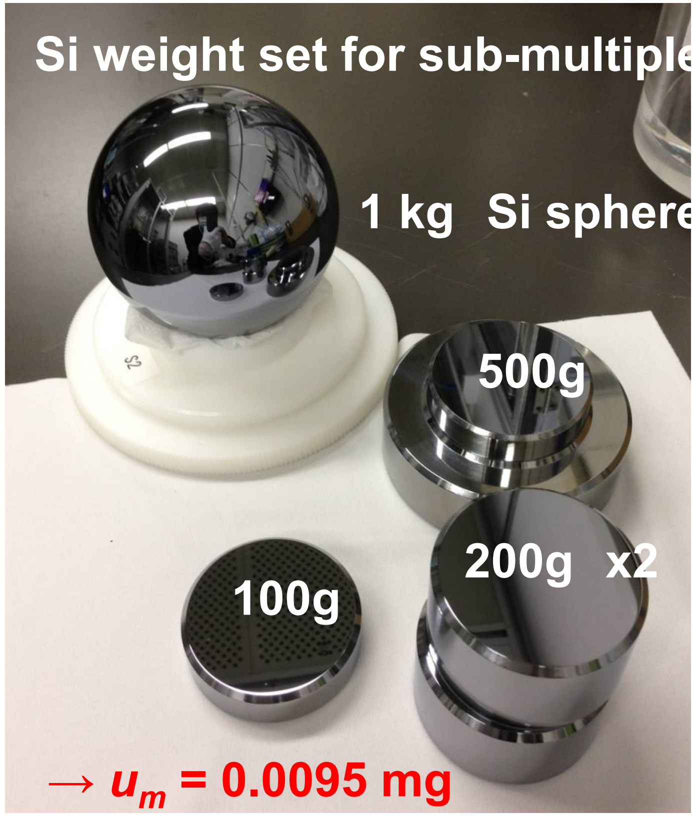
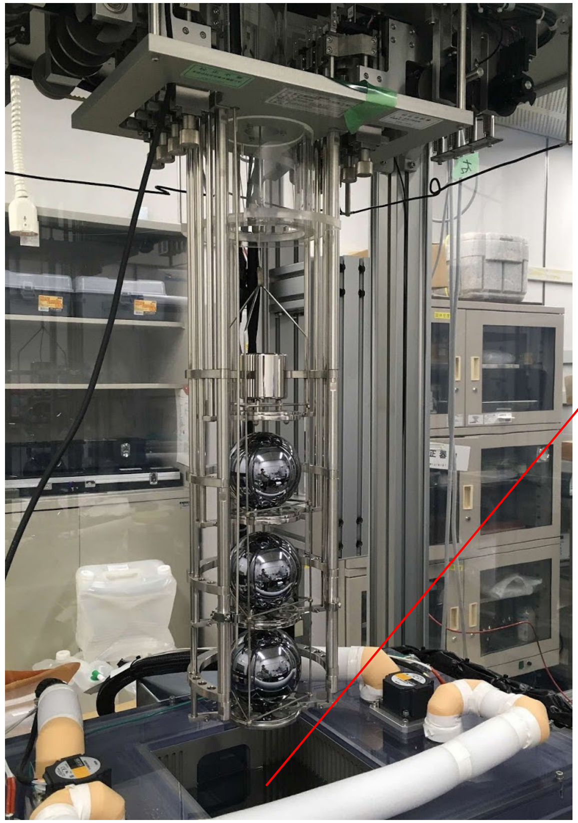


# n-トリデカンを用いた妥当性確認



NMIJ の固体密度校正設備（シリコン球を用いた液中秤量装置）

By 1 kg Si spheres

$\rho_{tridecane}$= 0.756 4311 g cm$^{-3}$

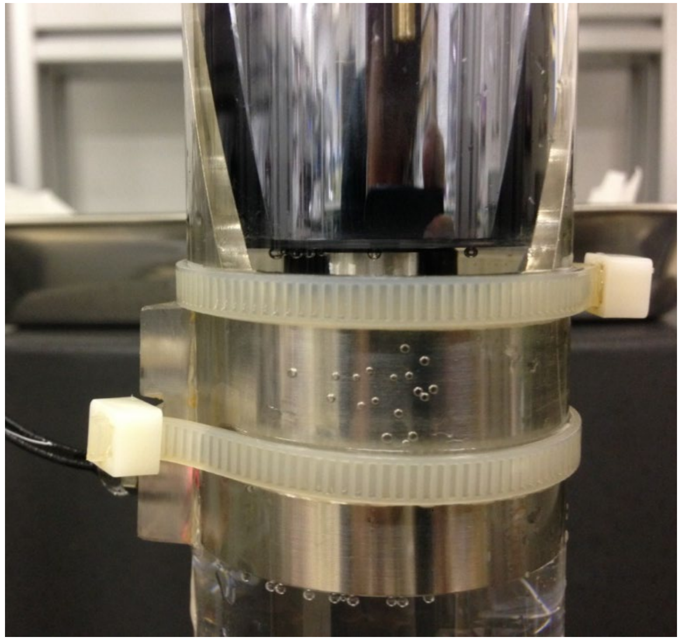
By 100 g Si sinker (this work)

$\rho_{tridecane}$= 0.756 4301(13) g cm$^{-3}$(Run 1)

$\rho_{tridecane}$= 0.756 4299(13) g cm$^{-3}$(Run 2)

# Challenges in sea-water density measurements

- 低減すべき不確かさ要因
  - ~~シンカー密度校正~~
  - ~~シンカー質量校正~~
  - 気泡付着の影響



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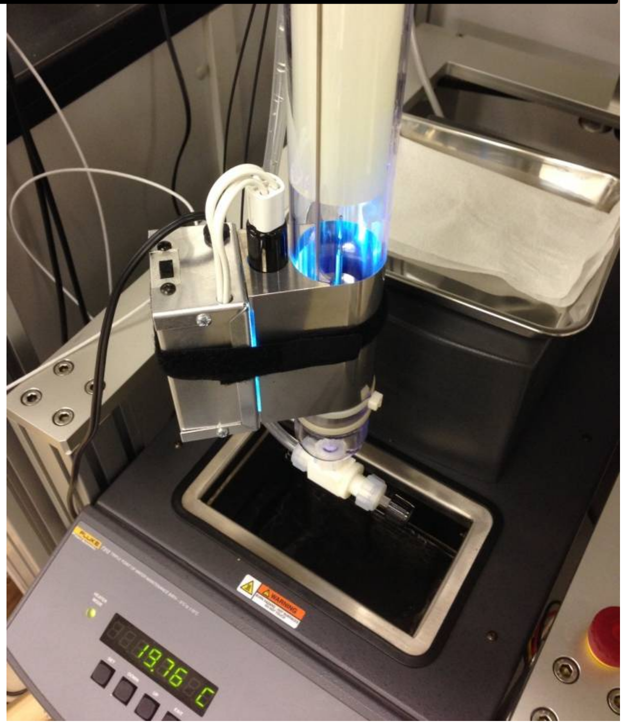
- 低減すべき不確かさ要因
  - ~~シンカー密度校正~~
  - ~~シンカー質量校正~~
  - ~~気泡付着の影響~~

UV light to make the sinker surface
→hydrophobic



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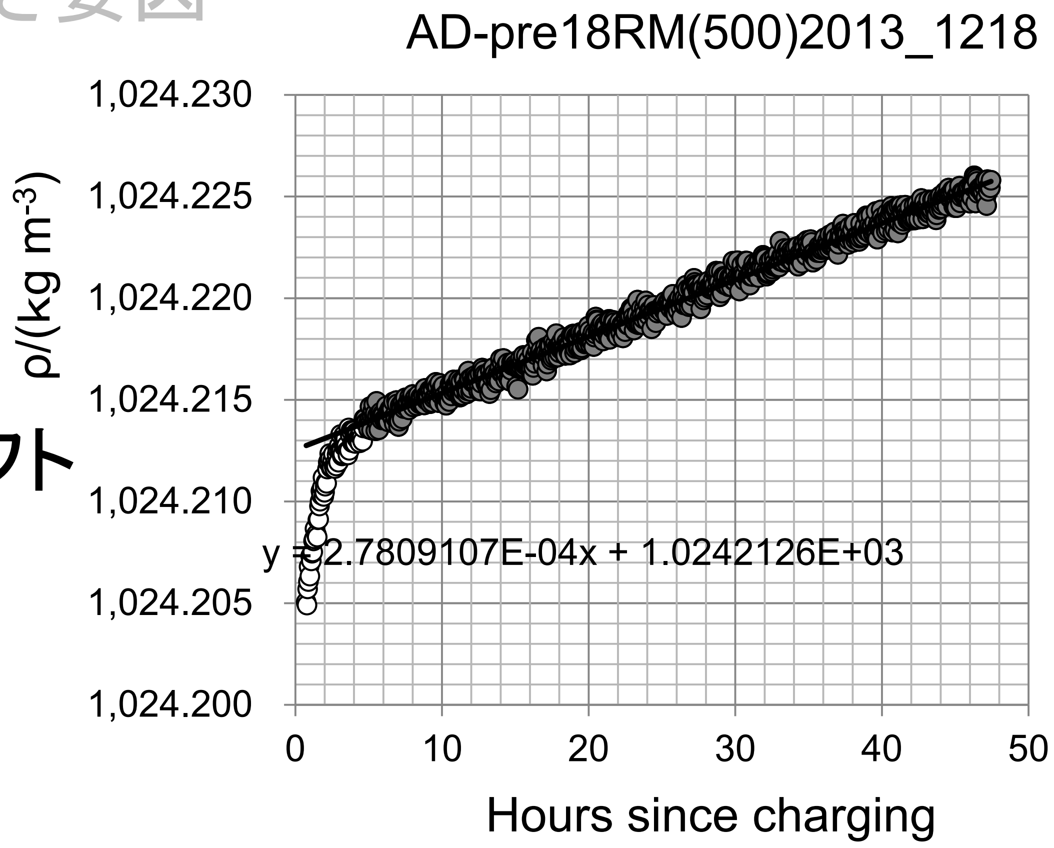
  - ~~シンカー密度校正~~
  - ~~シンカー質量校正~~
  - ~~気泡付着の影響~~
- 密度測定値のドリフト
  - 海水の蒸発？



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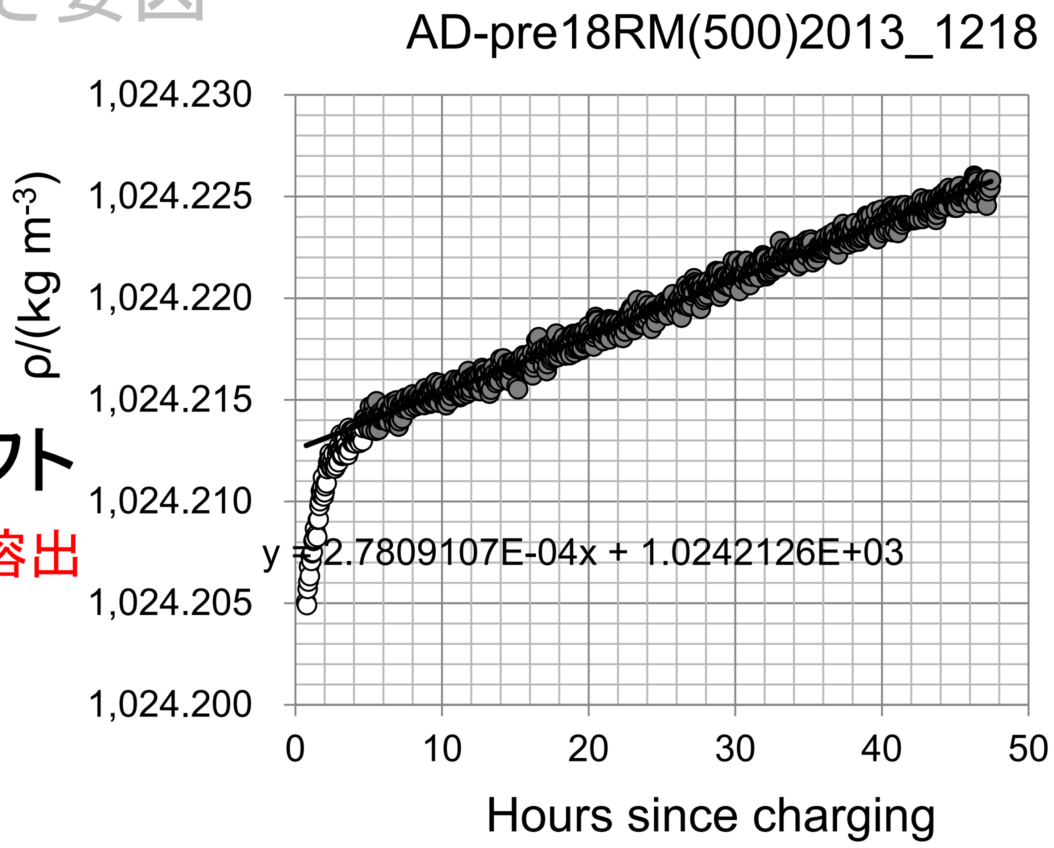
  - ~~シンカー密度校正~~
  - ~~シンカー質量校正~~
  - ~~気泡付着の影響~~
- 密度測定値のドリフト
  - ~~海水の蒸発？~~シンカー溶出



# Challenges in sea-water density measurements

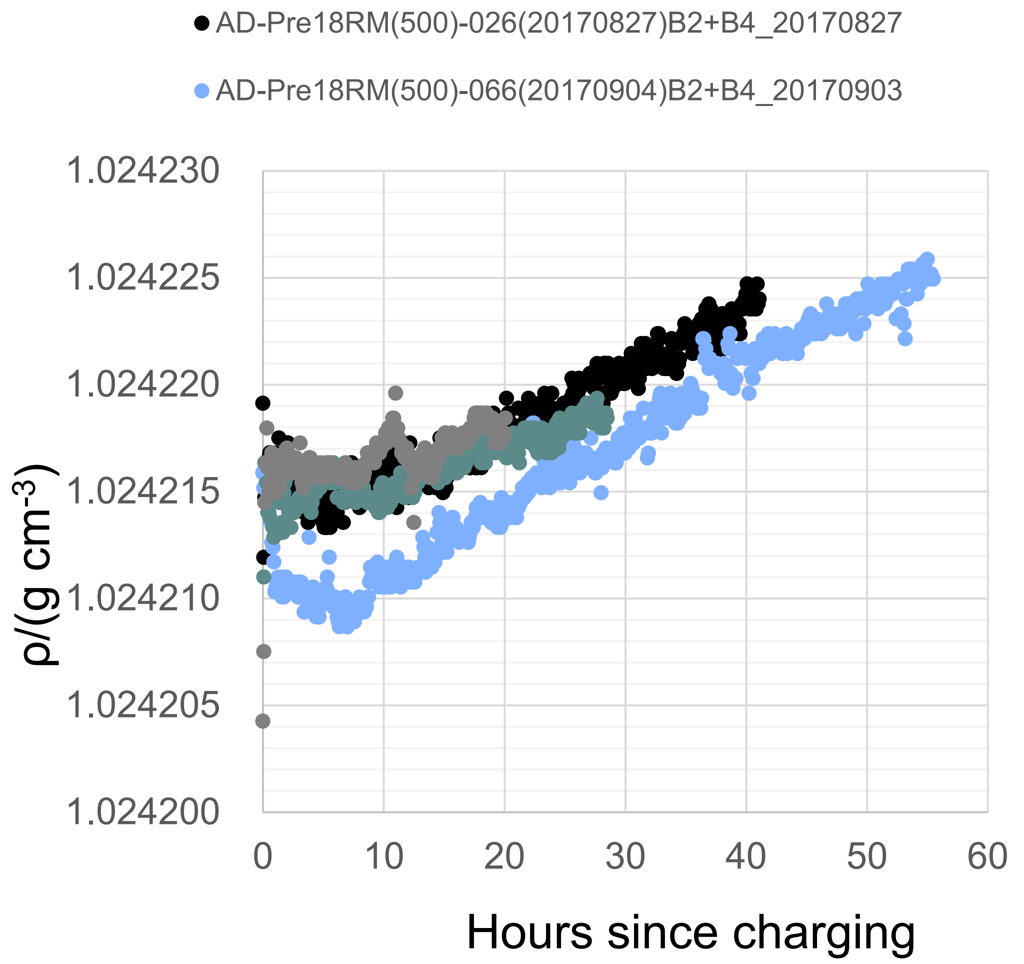
- 低減すべき不確かさ要因
  - ~~シンカー密度校正~~
  - ~~シンカー質量校正~~
  - ~~気泡付着の影響~~

Thermal oxidation（TO) layer (thickness: 100 nm) to prevent Si dissolution from the surface

- 密度測定値のドリフト
  - ~~海水の蒸発？~~シンカー溶出

# Challenges in sea-water density measurements

- 低減すべき不確かさ要因
  - ~~シンカー密度校正~~
  - ~~シンカー質量校正~~
  - ~~気泡付着の影響~~
- 密度測定値のドリフト
  - ~~シンカー溶出~~
  - 海水の蒸発



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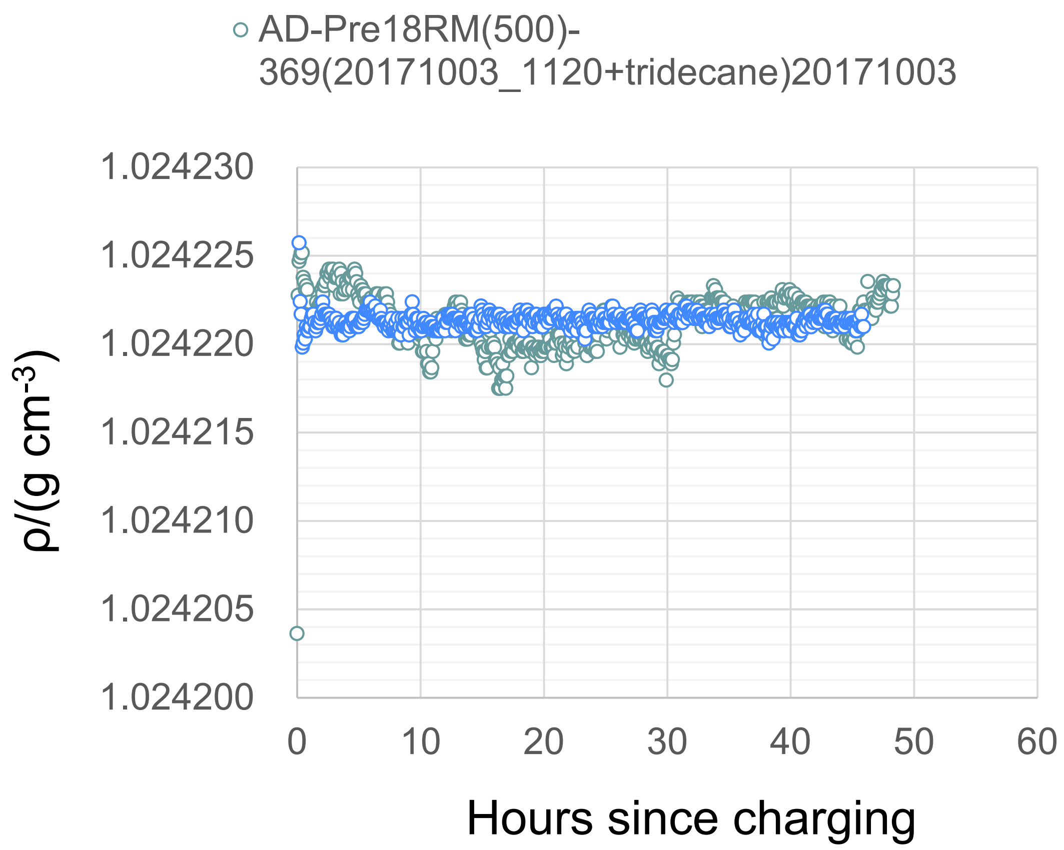
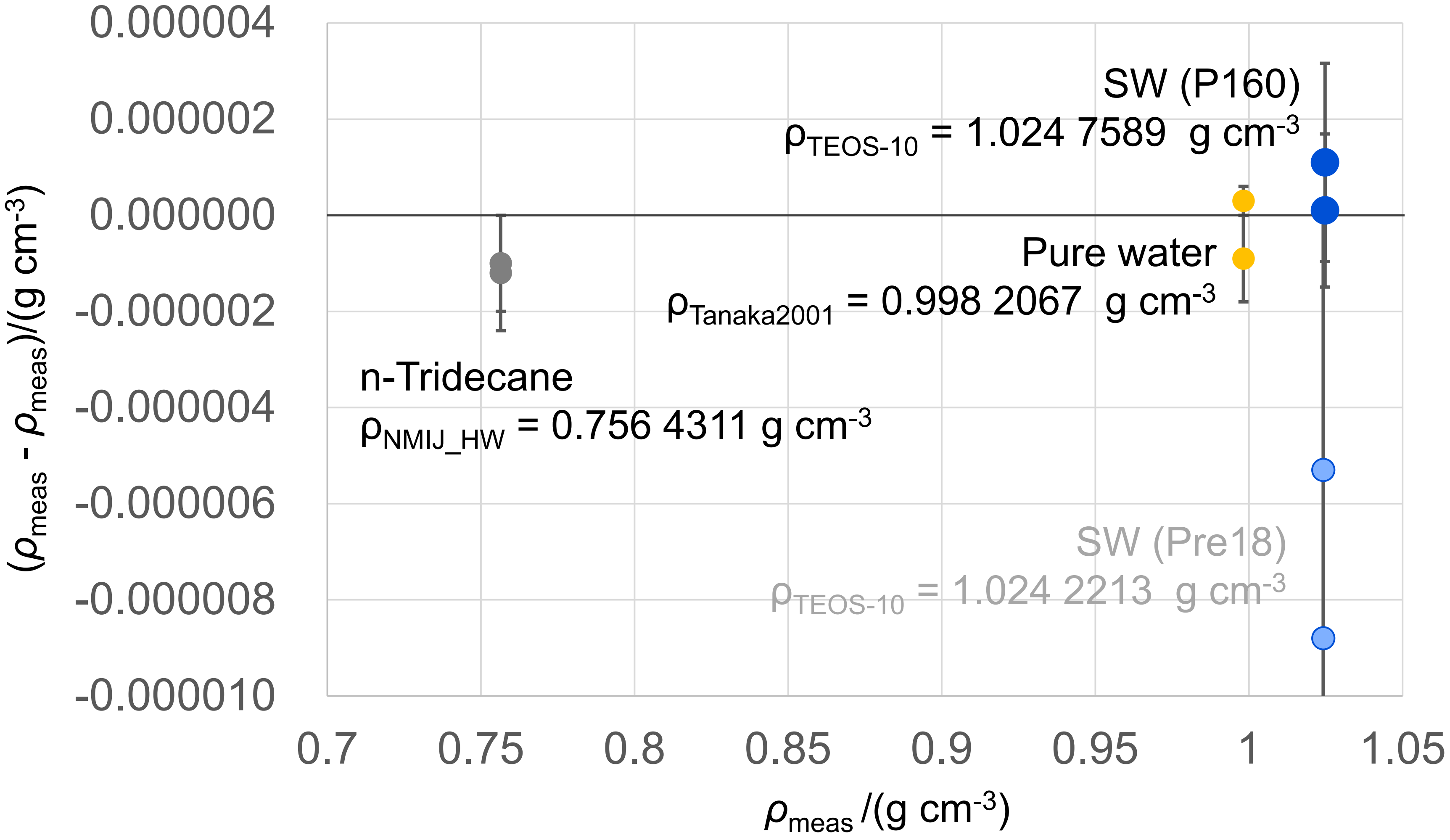
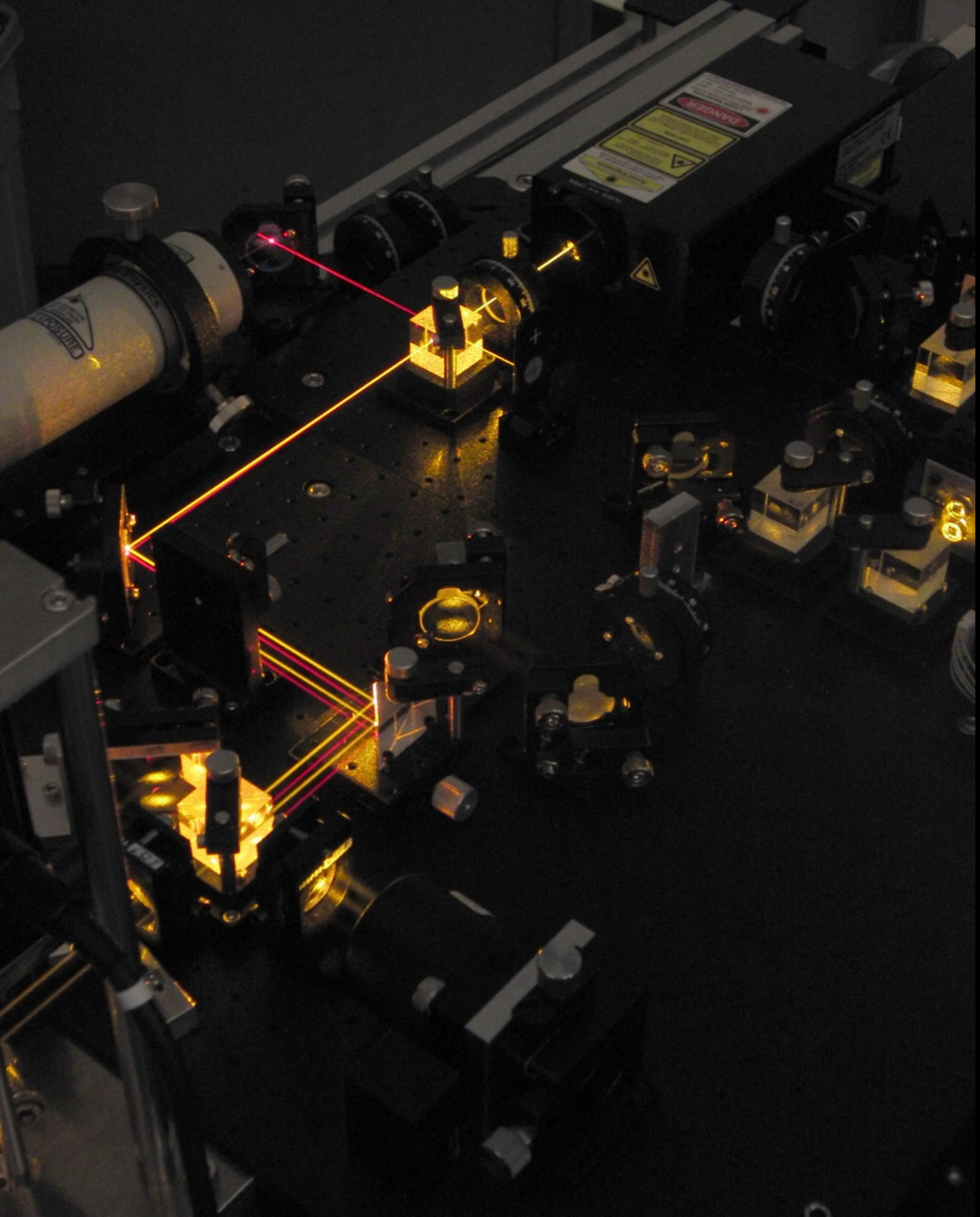
- 密度測定値のドリフト
  - ~~シンカー溶出~~
  - ~~海水の蒸発~~



# 測定結果



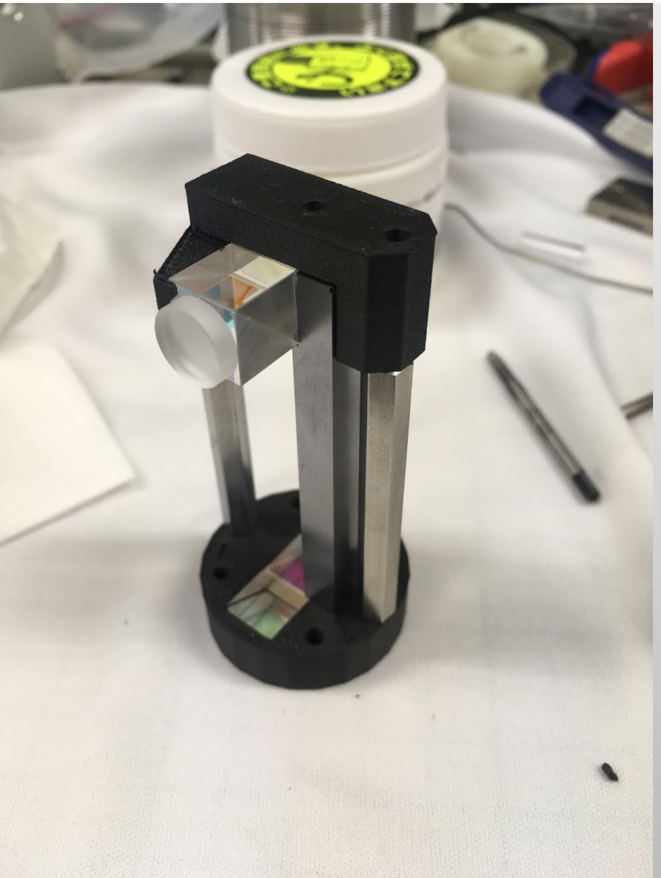
0.000004
0.000002
0.000000
-0.000002
-0.000004
-0.000006
-0.000008
-0.000010
0.7
0.75
0.8
0.85
0.9
0.95
1
1.05
$\rho_{meas}$ /(g cm$^{-3}$)
($\rho_{meas}$ - $\rho_{meas}$)/(g cm$^{-3}$)
SW (P160)
$\rho_{TEOS-10}$ = 1.024 7589 g cm$^{-3}$
Pure water
$\rho_{Tanaka2001}$ = 0.998 2067 g cm$^{-3}$
n-Tridecane
$\rho_{NMIJ\_HW}$ = 0.756 4311 g cm$^{-3}$
SW (Pre18)
$\rho_{TEOS-10}$ = 1.024 2213 g cm$^{-3}$

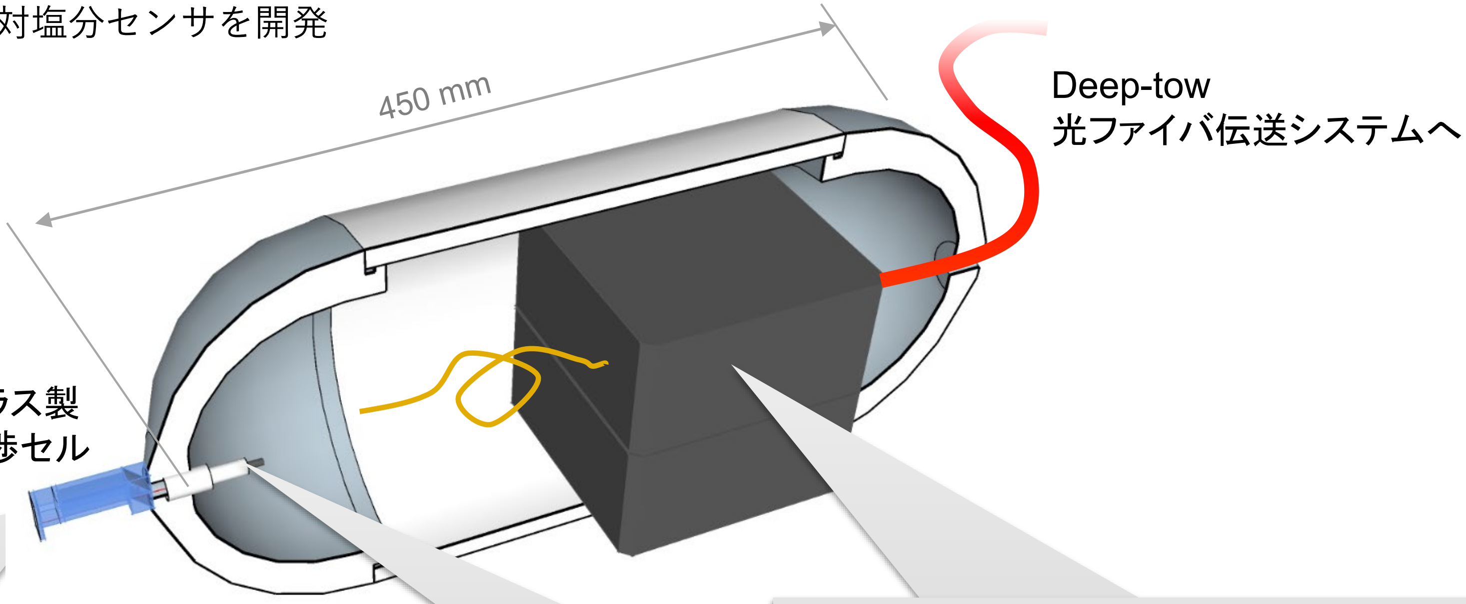


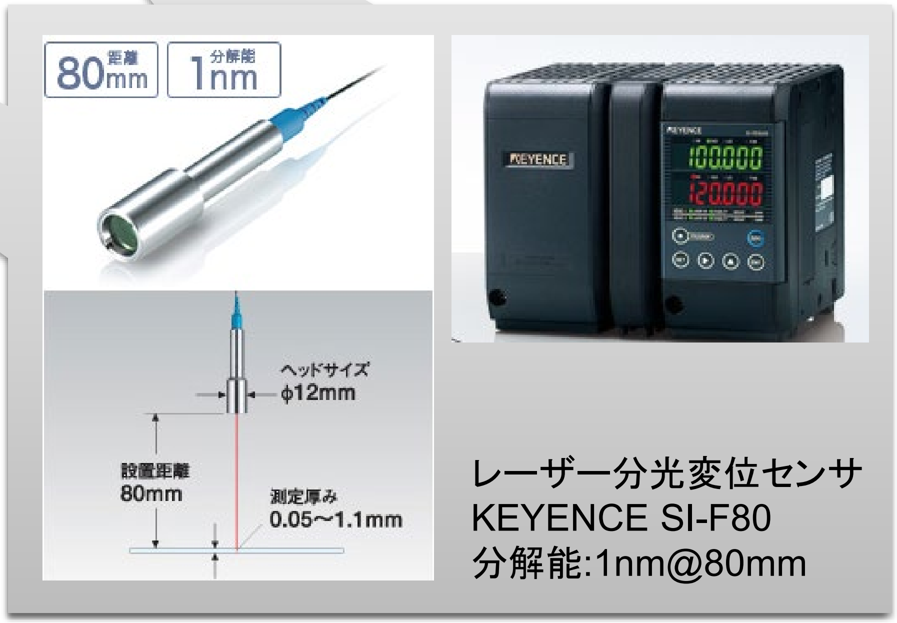
# 屈折率による絶対塩分測定

# 屈折率を用いた絶対塩分センサの開発

最大深度10,000 m、相対分解能$10^{-8}$を持つ絶対塩分センサを開発






This work
Valeport CTD(C)
Valeport (sound velocity)

# 屈折率を用いた絶対塩分センサの開発

最大深度10,000 m、相対分解能$10^{-8}$を持つ絶対塩分センサを開発

JAMSTECにおいて耐圧試験を実施し
20 Mpa（水深2,000 m）をクリア


Deep-tow（AIST）に搭載