# Outline

## Report from CCM WG Density held on 22 April 2008 at the BIPM

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- Present state of key and supplementary comparisons
- Acceptance of CMCs on density
- Density of water
  - Clarifying Roles of CIPM and IAPWS formulations
  - New absolute measurement
- Density of air (new CIPM formulation)
- Strategic Planning and Material Metrology
- Terms of reference for WGD
- Membership

# CIPM Key and Supplementary Comparisons

| | |
|---|---|
| CCM.D-K1 | Density measurements of a silicon sphere by hydrostatic weighing (2001-2003) |
| Status | Approved for equivalence |
| Pilot | NMIJ (JP) |
| Pilot group | NMIJ (JP), METAS (CH), NRC (CA) |
| Participants | NMIJ (JP), PTB (DE), INRIM (IT), KRISS (KR), METAS (CH), NRC (CA), CEM (ES), CENAM (MX) |

| | |
|---|---|
| CCM.D-K2 | Comparison of liquid density standards (2004-2005) |
| Status | Draft A is expected for March 2007 |
| Pilot | PTB (DE) |
| Pilot group | PTB (DE), NMIJ (JP), NRC (CA) |
| Participants | BEV (AT), NRC (CA), PTB (DE), OMH (HU), NMIJ (JP), KRISS (KR), CENAM (MX), VNIIM (RU) |

| | |
|---|---|
| CCM.D-K3 | Density measurements of stainless steel weights |
| Status | Planned |
| Pilot | NMIJ (JP) |

| | |
|---|---|
| CCM.D-K4 | Hydrometers |
| Status | Planned to start in 2007 or 2008 |
| Pilot | INRIM (IT) |
| Pilot group | INRIM (IT), from SIM, from APMP |
| Participants | 4 or 5 from EUROMET, 2 or 3 from SIM, and 2 or 3 from APMP |

# RMO Key and Supplementary Comparisons

| | |
|---|---|
| EUROMET.M.D-K1 | Volume and density comparisons of three ceramic spheres (1996-1999) |
| Status | Approved for provisional equivalence |
| Pilot | METAS (CH) |
| Participants | METAS (CH), SP (SE), PTB (DE), BEV (AT), INRIM (IT), NPL (UK), SM (BE), CEM (ES), BNM-LNE (FR), FORCE (DK), OMH (HU), UME (TR) |
| Comment | No report from SM (BE) |
| | |
| EUROMET.M.D-K2 | Density of liquids (2001-2002) |
| Status | Final report accepted |
| Pilot | PTB (DE) |
| Participants | PTB (DE), MIKES (FI), BNM-LNE (FR), OMH (HU), INRIM (IT), JV (NO), GUM (PL), CSIR-NML (ZA) |
| | |
| EUROMET.M.D-K4 | Comparison of the calibrations of high resolution hydrometers for liquid density determination (2003-2005) |
| Status | Draft A in progress |
| Pilot | INRIM (IT), PTB (DE), OMH (HU) |
| Participants | BEV (AT), PTB (DE), MIKES (FI), BNM-LNE (FR), OMH (HU), INRIM (IT), GUM (PL), IPQ (PT), SMU (SK), UME (TR), VNIIM (RU) |
| | |
| EUROMET.M.D-K4.PREV | Hydrometers comparison for liquid density determination (1993-1994) |
| Status | Approved for provisional equivalence |
| Pilot | INRIM (IT) (former IMGC-CNR) |
| Participants | INRIM (IT), OMH (HU), PTB (DE), SMU (SK), IPQ (PT) |

# RMO Key and Supplementary Comparisons

| | |
|---|---|
| APMP.M.D-K4 | Comparison of calibrations of density hydrometers |
| Status | Technical Protocol in progress |
| Pilot | KRISS (KR) |
| Pilot group | KRISS (KR), NMIJ (JP) |
| Participants | NMIA (AU), CSIR (ZA), SIRIM (MY), IRL (NZ), NML (PH), NMIJ (JP), NIM (CH), NIMT (TH), NPL (IN), KRISS (KR), NMISA (SA) |
| | |
| SIM.7.33 | Comparison of the calibration of hydrometers for liquid density determination between SIM laboratories (2007-2008) |
| Status | Measurement in progress |
| Pilot | CENAM (MX) |
| Participants: | CENAM (MX), NRC (CA), NIST (USA), BSJ (JM), LACOMET (CR), CENAMEP (PA), INMETRO (BR), IBMETRO (BOLIVIA), SIC (CO), INEN (EC), INDECOPI (PE), CESMEC Ltd. (CL), LATU (UY) |
| | |
| EURAMET Project 1031 | Density comparisons of three silicon spheres (2008-2010) |
| Status | Technical Protocol completed |
| Pilot | PTB (DE) |
| Participants | BEV, DZM, NIS, MIKES, LNE, EIM, INRIM, GUM, IPQ, INM, VNIIM, CEM, METAS, UME, NPL, NMIJ |
| | |
| EURAMET Project 1019 | Density of liquids (2008-2010) |
| Status | Technical Protocol completed |
| Pilot | BEV (AT) |
| Participants | MIKES, LNE, PTB, MKEH (OMH), INRIM, JV, GUM, IPQ, INM, SMU, CEM, UME, NPL |

# Other Bilateral and International Comparisons

1) Anna M. Peuto, Attilio Sacconi, Maria Mosca, Kenichi Fujii, Mitsuru Tanaka, and Yoshiyuki Nezu, “Comparison of Silicon Density Standards at NRLM and IMGC,” IEEE Trans. Instrum. Meas., Vol. 42, No. 2, pp. 242-246, 1993.

2) Horst Bettin, Michael Gläser, Frank Spieweck, Hans Toth, Attilio Sacconi, Anna M. Peuto, Kenichi Fujii, Mitsuru Tanaka, and Yoshiaki Nezu, “International Intercomparison of Silicon Density Standards,” IEEE Trans. Instrum. Meas., Vol. 46, No. 2, pp. 556-559, 1997.

3) Kyung-Ho Chang, Yong-Jae Lee, and Jin-Wan Chung, “Final Results of Bilateral Density Comparison between NMIJ and KRISS for 1 kg Weight,” KRISS/MO-2001-058, June 2001.

4) H. Bettin, H. Toth, A. Waseda and K. Fujii, “Comparison of density difference measurements at PTB and NMIJ,” IEEE Trans. Instrum. Meas., Vol. 54, No. 2, pp. 877-881, 2005.

5) Bilateral comparison on hydrometers calibration between INRIM-Italy and CENAM-Mexico

   Status: Measurement in progress

6) SIM.7.34-B: Bilateral Comparison on volume of solids by hydrostatic weighing between CENAM-Mexico and INMETRO-Brazil.

   Status: Protocol in preparation (Report in progress)

# Other Bilateral and International Comparisons

7) Lorefice S., Heinonen M., Madec T. “Bilateral comparisons of hydrometer calibrations between the IMGC-LNE and the IMGC-MIKES,” Metrologia, 2000, Vol. 37, No. 2, pp. 141-147.

8) International comparison of absolute volume calibrations by optical interferometers at NMIJ, PTB, and NMIA (2006-2007)

   Status: Measurement in progress

9) Bilateral comparison of absolute volume calibrations by optical interferometers at NMIJ and KRISS (2006-2007)

   Status: Measurement in progress

10) Bilateral comparison of absolute volume calibrations by optical interferometers at NMIJ and NIM (2008)

    Status: Planned

11) Kari Riski, “Mass and volume comparisons at MIKES—Additional results to the EA intercomparison of weights 1 mg – 100 g (Ma1) and to the EUROMET intercomparison of ceramic spheres (EUROMET 339),” Julkaisu J4/2000

# Link between Key, Supplementary, Bilateral, and International Comparisons

| CIPM key comparison | RMO key comparison | Other bilateral and international comparisons |
|---|---|---|
| CCM.D-K1 | EUROMET.M.D-K1<br>EURAMET Project 1031 | 1), 2), 4), 6), 8), 9), 10), 11) |
| CCM.D-K2 | EUROMET.M.D-K2<br>EURAMET Project 1019 | |
| CCM.D-K3 | | 3), 11) |
| CCM.D-K4 | EUROMET.M.D-K4<br>APMP.M.D-K4<br>SIM.7.33 | 5), 7) |

EUROMET.M.D-K1 → CCM.D-K1: density of solids (silicon crystals)
EUROMET.M.D-K2 → CCM.D-K2: density of liquids (reference liquids for calibrating density meters)
RMO comparisons → CCM.D-K3: density of solids (stainless steel weights)
EUROMET.M.D-K4 → CCM.D-K4: hydrometers
APMP.M.D-K4 → CCM.D-K4: hydrometers
SIM.7.33 → CCM.D-K4: hydrometers

# “shine”: Extension of a KC to multiple CMCs

Q2 If an NMI has CMCs for both silicon crystals and stainless steel, do they have to participate in both CCM.D-K1 and CCM.D-K3 or is CCM.D-K1 sufficient?

A2 This was discussed in WGD meeting April 2008. CCM.D-K1 is used as the evidence for stainless steel weight (CCM.D-K3) because there is no completed KCs for the density of stainless steel weight. Many CMCs for stainless steel weight already exist in the BIPM website.

- Participation to CCM.D-K1 is generally regarded as an evidence to support both CMCs for silicon crystals and stainless steel, but the equivalence in stainless steel may be checked more accurately by CCM.D-K3 if this KC is available.
- Considering that the number of participants to the CCM.D-K1 is limited by practical reasons, and that the members of WGM can participate in CCM.D-K3 without using silicon density standards, having CCM.D-K3 is still useful.
- Basic idea is to accept as many CMCs as possible using available evidence in KCs.

# How to cover the variety of CMCs from limited number of comparisons

**CCM.D-K1**
**Density measurement of Si sphere by hydrostatic weighing**

$$U_r(\rho_{ref}) = 3 \times 10^{-7}$$

**CCM.D-K2**
**Density measurement of liquids by hydrostatic weighing**

$$U_r(\rho_{ref}) = 4 \times 10^{-6}$$

**CCM.D-K3**
**Density measurement of stainless steel weights**

$$U_r(\rho_{ref}) = 3 \times 10^{-6}$$

**CCM.D-K4**
**Hydrometers**

$$U_r(\rho_{ref}) = 2 \times 10^{-5}$$

- **CCM.D-K1 is apparently not satisfactory to cover the liquid density and hydrometer comparisons.**
- **Comparisons of instruments for users are still necessary.**

# How to cover the variety of CMCs from limited number of comparisons

## Other practical solutions

- Temperature range for hydrometer calibration:

  Evidence of KC at 20 °C may be used in a range 5 to 30 °C.

  Supporting documents, showing uncertainty budget and equivalence, are still necessary.

- CCM.D-K1 (1 kg silicon sphere) is used as evidence both for silicon crystals and other solid materials including stainless steel weight.

  Supporting documents, showing uncertainty budget and equivalence, are still necessary.

- For CMCs under atmospheric pressure condition (101.325 kPa), specification for pressure range is not necessary.

# CIPM Standard

- **Density of water**

| Brief history | | Method | $\rho_{max}$ at 4 °C |
|---|---|---|---|
| 1927 | BIPM | Hydrostatic weighing | 999.972 kg/m$^3$ |
| 1973 | BIPM | Correction to SMOW | 999.975 kg/m$^3$ |
| 1994 | CSIRO | Hydrostatic weighing | (999.9736 ± 0.0009) kg/m$^3$ |
| 1996 | NMIJ | Hydrostatic weighing | (999.9757 ± 0.0008) kg/m$^3$ |

Task Group on the Density of Water

CIPM formulation:Tanaka et al., Metrologia 2001, pp. 301-309.

Covered temperature range: 0-40 °C only at 101.325 kPa

$\rho_{SMOW}$(4 °C) = (999.9749 ± 0.0008) kg/m$^3$ at $k$ = 2

endorsed by the CIPM in 2001

# IAPWS Standard

## Thermodynamic properties of water

Electric Power Plant: steam turbine, boiler, aqueous solution, and etc.

1995 IAPWS-95 formulation released by IAPWS

1997 IPAWS-IF97 for industrial use

Thermodynamic Properties Working Group (TPWS)

IAPWS-95 formulation: for General and Scientific Use

Details: Wagner and Pruß: J. Phys. Chem. Ref. Data, 2002, pp. 387-535.

Covered temperature range: 251.2 K to 1273 K

Covered pressure range: up to 1 GPa

Most accurate equation of state (EOS) in the existing formulations

# IAPWS-95

## Basic structure of the formulation

Specific Helmhortz free energy

$$f(\rho, T)/(RT) = \phi(\delta, \tau) = \phi^{\circ}(\delta, \tau) + \phi^{r}(\delta, \tau)$$

$$\delta = \rho/\rho_c$$

$$\tau = T_c/T$$

$\phi^{\circ}(\delta, \tau)$: with13 coefficients

$\phi^{r}(\delta, \tau)$: with 56 coefficients

Given density $\rho$ and temperature $T$ determine pressure $p$ as

$$p = \rho^2(\partial f/\partial\rho)_T$$

# IAPWS-95 formulation

## Reference Constants

$T_c = 647.096$ K

$\rho_c = 322$ kg m$^{-3}$

$R = 0.461\,518\,05$ kJ kg$^{-1}$ K$^{-1}$

## Formulation

$$\frac{f(\rho,T)}{RT} = \phi(\delta,\tau) = \phi^{\circ}(\delta,\tau) + \phi^{\mathrm{r}}(\delta,\tau)$$

$$\phi^{\circ} = \ln\delta + n_1^{\circ} + n_2^{\circ}\tau + n_3^{\circ}\ln\tau + \sum_{i=4}^{8} n_i^{\circ}\ln\left[1 - \mathrm{e}^{-\gamma_i^{\circ}\tau}\right]$$

$$\phi^{\mathrm{r}} = \sum_{i=1}^{7} n_i\delta^{d_i}\tau^{t_i} + \sum_{i=8}^{51} n_i\delta^{d_i}\tau^{t_i}\mathrm{e}^{-\delta^{c_i}} + \sum_{i=52}^{54} n_i\delta^{d_i}\tau^{t_i}\mathrm{e}^{-\alpha_i(\delta-\varepsilon_i)^2-\beta_i(\tau-\gamma_i)^2} + \sum_{i=55}^{56} n_i\Delta^{b_i}\delta\psi$$

with $\Delta = \theta^2 + B_i\left[(\delta-1)^2\right]^{a_i}$

$$\theta = (1-\tau) + A_i\left[(\delta-1)^2\right]^{\frac{1}{2\beta_i}}$$

$$\psi = \mathrm{e}^{-C_i(\delta-1)^2 - D_i(\tau-1)^2}$$

# Estimated uncertainty in density for IAPWS-95

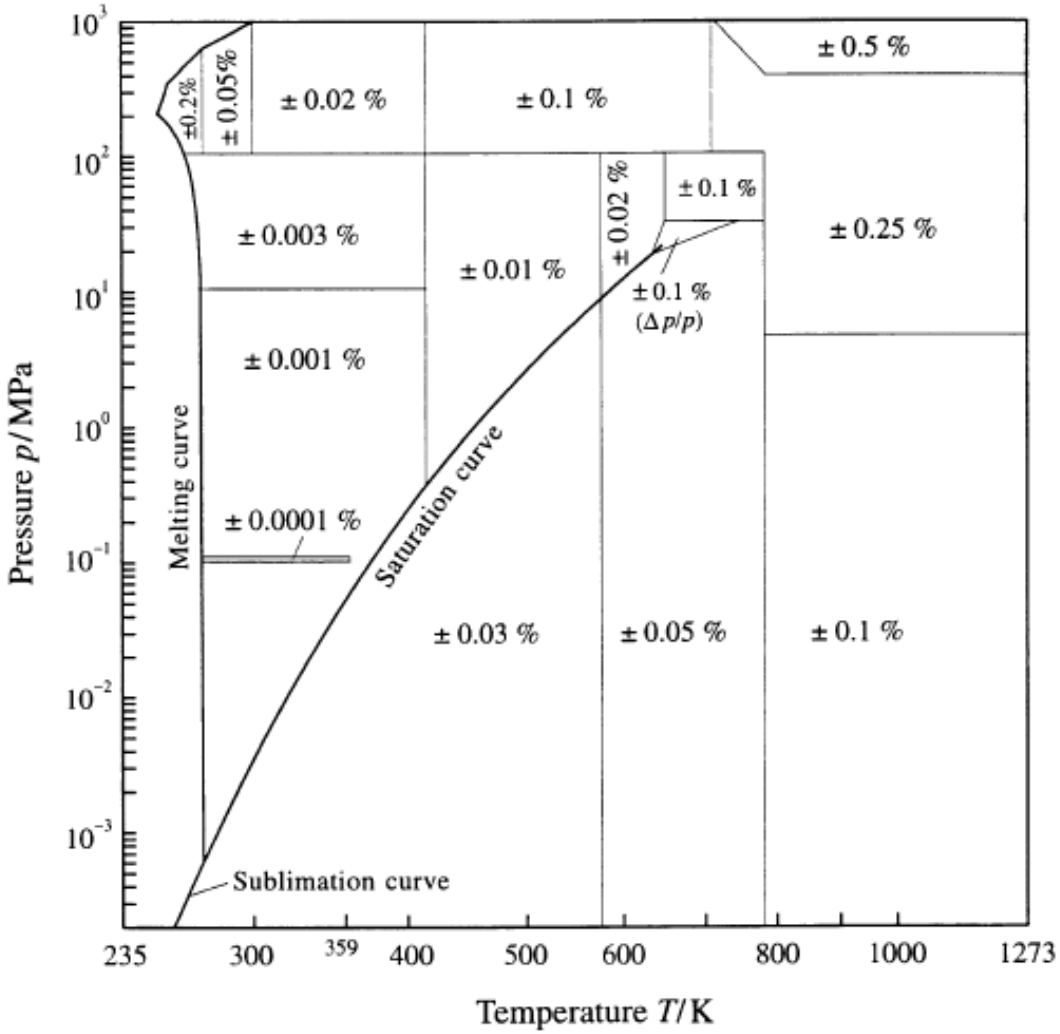
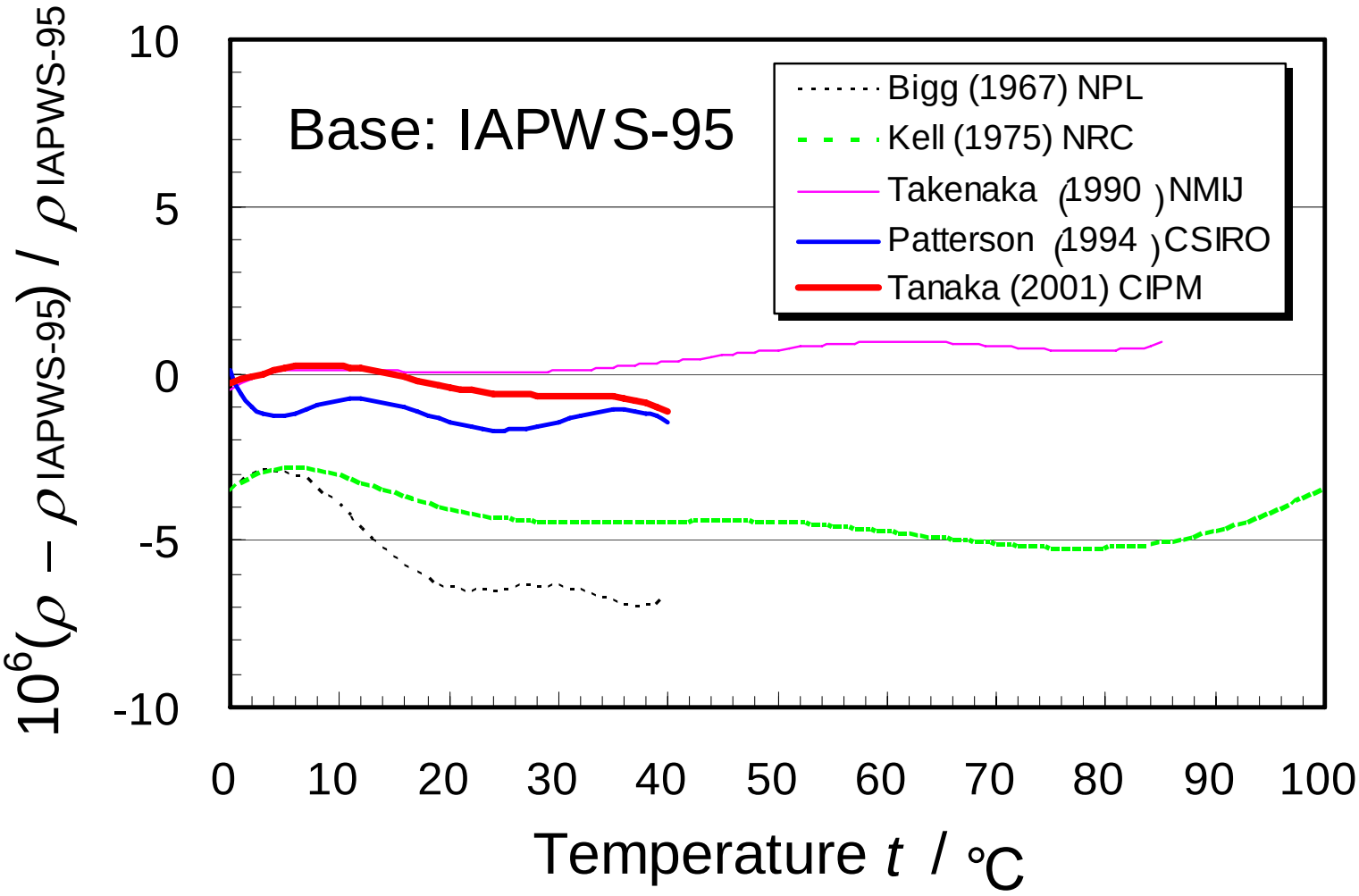



Fig. 1. Uncertainties in density, $\Delta\rho/\rho$, estimated for Eq. (4). In the enlarged critical region (triangle), the uncertainty is given as percentage uncertainty in pressure, $\Delta p/p$. This region is bordered by the two isochores 527 kg m$^{-3}$ and 144 kg m$^{-3}$ and by the 30 MPa isobar. The positions of the lines separating the uncertainty regions are approximate.

# Comparison of the reported values for the density of water



# Recommendations

- The CIPM density formulation is the preferred standard for use in metrology over its recommended range, which is liquid water from 0 °C to 40 °C at pressures near atmospheric. It should not be extrapolated outside this range.
- Densities computed from the IAPWS-95 formulation are consistent with the CIPM standard within the region of validity of the CIPM formulation. For uses outside the CIPM range of validity, the IAPWS-95 formulation is the preferred method for obtaining high-accuracy densities for water.
- For uses covering a range of conditions, some of which are inside the range of validity of the CIPM standard and some of which are not, it is generally preferable to use the IAPWS formulation for the entire calculation in order to avoid discontinuities.
- Considering that a new absolute measurement of the density of water is on-going, the covered temperature range of the CIPM formulation will be improved in the near future.

# Terms of reference for CCM WGD

- to improve techniques for realizing the SI unit of density;
- to exchange information on the density standard;
- to perform CIPM key comparisons for supporting CMCs on density;
- to coordinate RMO key and supplementary comparisons for accelerating the CIPM MRA in the field of density;
- to provide guidance to accept CMCs on density;
- to coordinate activities for density measurements at NMIs; and
- to assess needs and seeds on metrology for density.

# New membership to CCM WGD

- VNIIM (Russia): contribution for RMO key comparison on hydrometer
- BEV (Austria): contribution for RMO key comparison on liquid density