Asia Pacific Metrology Programme

Final Report on APMP.T-K7.1

Comparison on water triple point cells, bilateral NMIJ-VMI

Prepared by:

Kazuaki Yamazawa[1] Tohru Nakano[1] and Pham Thanh Binh[2]

[1] National Metrology Institute of Japan (NMIJ), AIST
[2] Vietnam Metrology Institute (VMI)

1. Introduction

This bilateral comparison between National Metrology Institute of Japan (NMIJ) and Vietnam Metrology Institute (VMI) is to provide a link of the Triple point of Water (TPW) and furthermore support the CMCs related to contact thermometry of VMI. The linkage of the VMI's national reference to both the APMP.T-K7 [1] and CCT-K7 [2] is reported here.

The comparison is conducted in a manner that VMI preparing the transfer cell, compare the transfer cell with its national reference, and then send the transfer cell to NMIJ to enable the linkage to both CCT-K7 and APMP.T-K7. The cells were prepared, stored and compared following normal procedures of the laboratories. Measurements began 7 days after preparation of the cells, and continued for 2 weeks. Further details are summarized within this report.

2. Participants

Acronym	Institute	Contact persons
NMIJ/AIST (Pilot)	National Metrology Institute of Japan, AIST	Dr. Tohru Nakano tohru-nakano@aist.go.jp
VMI	Vietnam Metrology Institute	Dr. Pham Thanh Binh binhpt@vmi.gov.vn

3. Comparison method

VMI selects one of its cells for use as a transfer cell and directly compares it against its national reference. The selected transfer cell is sent together with the measurement results (attached as Appendix 1) to NMIJ where the transfer cell is compared against two reference cells. The transfer cell is sent back to the laboratory to directly re-compare with the same reference cell(s) as before to check the transfer cell stability. Based on the measurement results, the difference between the national realization at VMI and the APMP.T-K7 RV [1] is determined through the link provided by the pilot laboratory NMIJ/AIST.

4. Equipment and techniques

The TPW cells used in this comparison are listed in Table 1. The details of the measurement equipment used during this comparison are compiled into Table 2.

4.1 Equipment at NMIJ providing the linkage for this comparison

For the measurements at NMIJ, two cells among the National Reference were

selected. As reported in detail elsewhere [3], among the ensemble of NMIJ's TPW cells, cell TR0227E, which is identical to cell 4 of Ref. 3) gives an extremely close realization to the definition of the TPW and is now defined to be the National Reference of the TPW at NMIJ. Comparison results between this cell and the transfer cell provided from VMI will be reported here to establish the link for VMI. Another cell, TR0201D, is another stable cell among the cells of the National Reference. This cell had also been the National Standard at the time of CCT-K7 [2]. For the measurements at NMIJ, TR0227E, TR0201D, and the transfer cell provided from VMI were realized at the same time, held within the same ISOTECH maintenance bath. The temperatures for the three cells were measured daily. In this comparison, we merely use the data acquired from TR0201D to confirm the stability of this comparison, and we will not use the results for the linkage.

4.2 Equipment at VMI

VMI renewed their National Standard just before starting this comparison. Two quartz cells were purchased in March 2014. Measurements among the two cells were performed and among the two, Cell 1123 was selected as the National Reference at VMI and the other cell 1122 was sent to NMIJ as the transfer cell. Following the protocol, data acquired before the transportation is used for the linkage and the measurements after the transfer is merely used for the check of the stability of the transfer cell. The isotopic composition of the national reference cell at VMI is certified by the manufacturer that it is closely adjusted to the VSMOW composition. Thus, VMI performs no isotopic correction and accounts its uncertainty from the certificate.

Table 1. TPW cells used in this comparison

	NMIJ/AIST TR0227E	NMIJ/AIST TR0201D	Transfer cell	National Reference of VMI
Manufacturer	Hart Scientific	Toa Mfg.	Fluke	Fluke
Model	5901D-Q	SY-12	5901D-Q	5901D-Q
Serial number	1008	1224	1122	1123
Glass material	Quartz	Borosilicate glass	Quartz	Quartz
Depth below water surface	265 mm	280 mm	265 mm	265 mm
Note	A cell among the current National Reference. Cell number 4 within Fig. 3 of the Ref. 3). T_{natl_ref} - T_{APRV} = -2.2 μK [1]	A cell among the current National Reference. Previous National Standard at the time of CCT-K7 [2,3]	Purchased March 2014	Purchased March 2014

Table 2. Measurement Equipment

	NMIJ/AIST	VMI
Resistance bridge	ASL F18	ASL F900
Measurement current (frequency)	1 mA, $\sqrt{2}$ mA (25 Hz)	1 mA, $\sqrt{2}$ mA (75 Hz)
Reference resistor	Tinsley 5685A 25 Ω, temp. coeff. 1 ppm/°C	Tinsley 5685A 25 Ω, temp. coeff. 2 ppm/°C
Temperature control of the reference resistor	±5 mK	±5 mK
Thermometer	Chino R800-2 S/N RS993-1	Hart Scientifc 5681 S/N 1357
Technique for ice mantle preparation	Using a heatpipe cooled with liquid nitrogen	Solid CO_2

5. Measurement results at VMI

5.1 Measurements at VMI before the transportation to NMIJ

Measurement results of the temperature difference between the transfer cell and the National Standard cell at VMI before the transportation to NMIJ is shown in Appendix 1. Two mantles were formed, and the temperature differences were 0.017 mK and 0.0185 mK, respectively. The average T(VMI.S/N D-Q 1122) − T(VMI. S/N D-Q 1123) =0.0178 mK and the uncertainty of the temperature difference between the temperature realized within the transfer cell and the National Standard cell is 130 μK (k=1).

$$T_{\text{VMI.S/N D–Q1122}} - T_{\text{VMI.S/N D–Q1123}} = (0.0178 \pm 0.130)\,\text{mK} \qquad (1)$$

5.2 Measurements at VMI after the transportation back from NMIJ

Measurement results are shown in Appendix 2. The resulting temperature difference between the transfer cell VMI.S/N D-Q 1122 and the national reference (cell VMI.S/N D-Q 1123) was 0.003 mK.

5.3 Data used for the linkage

Figure 1 shows a figure provided from VMI of the temperature differences among their two cells, before and after their transportation to and from NMIJ. Each plot indicates the temperature difference measured each day, and the figure shows the results for four mantles, two mantles before transportation and the other two mantels after, during this comparison. Although the measurements before the transport appear slightly scattered compared to the measurements after, the results coincide within their measurement uncertainties. The uncertainty budget was provided and shown in Appendix 1 is for the measurement before the transportation, and furthermore, the protocol specifies the use of the data before. Thus, here in this report we will adopt the measurements before the transport (eq. (1)) which is reported in Appendix 1. As the uncertainty of the comparison at VMI is 130 μK (k=1), the difference between the two sets of measurements will not be significant.
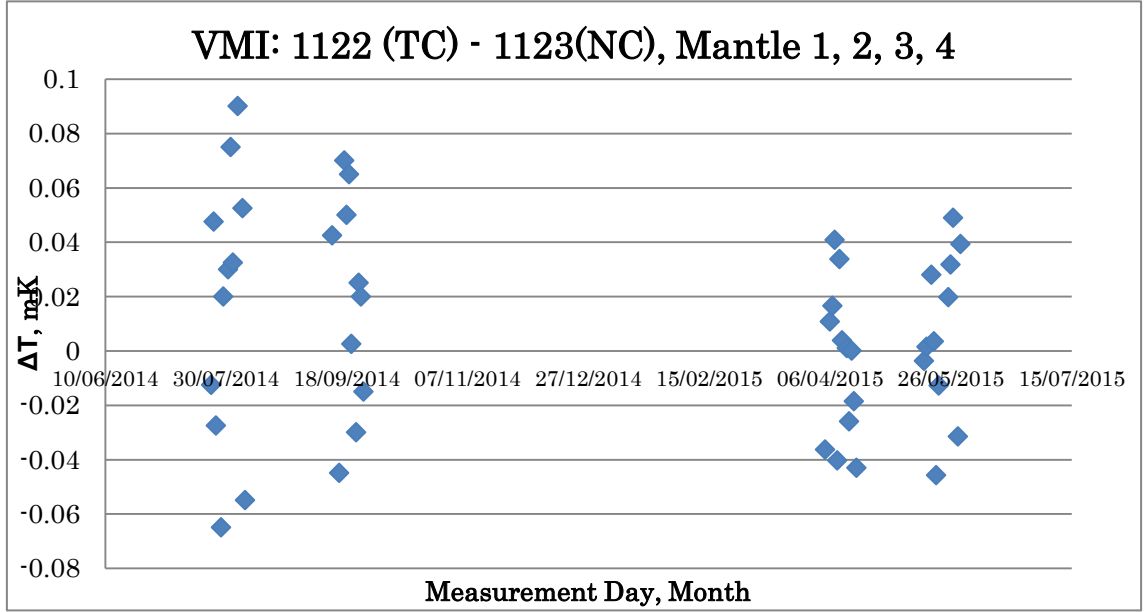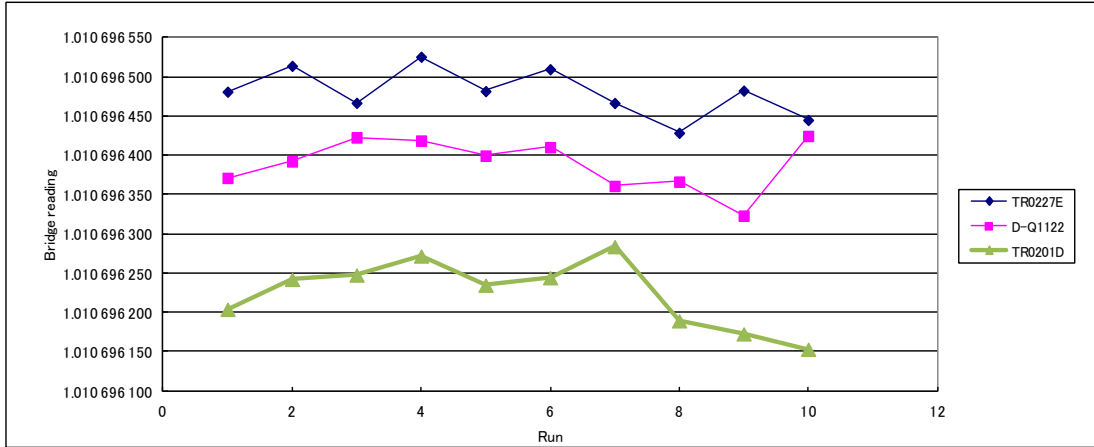
Figure 1 Temperature differences among their two cells measured at VMI, before and after their transportation to and from NMIJ.
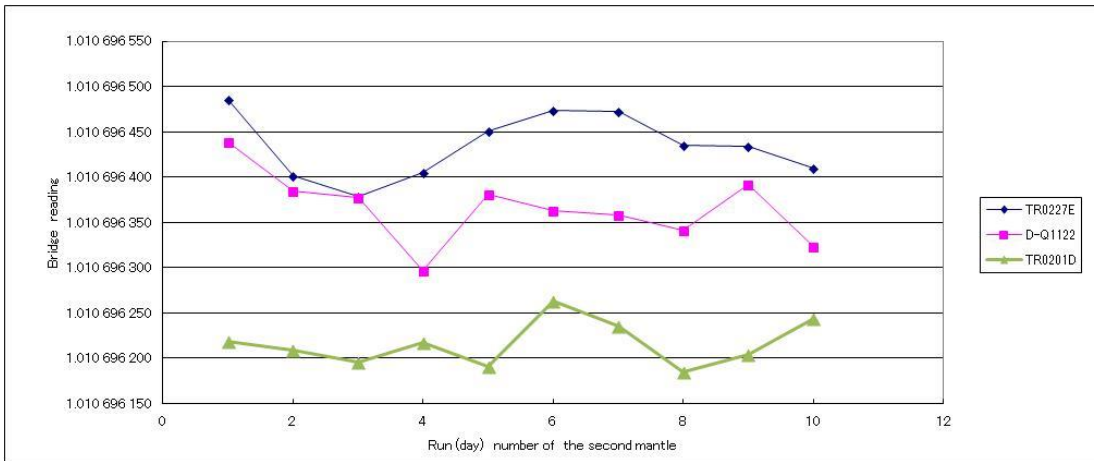
6. Measurement results at NMIJ

Figure 2 shows an example of the raw data measures at NMIJ. As already mentioned in section 4.2, we have made measurements for the VMI transfer cell and two among the NMIJ cells; TR0227E, TR0201D, and the transfer cell VMI.S/N D-Q 1122 were realized at the same time, and temperature differences were measured daily. The data acquired from TR0201D was used to confirm the stability of this comparison. As shown in figure 2, it was confirmed from the simultaneous measurement of TR0201D that the stability of the measurements was sufficient for the purpose of this comparison.

The measurement results used for the linkage are shown in Appendix 3. Taking the average of the two mantles, the resulting temperature difference between the transfer cell VMI.S/N D-Q 1122 and the national reference (cell NMIJ TR0227E) was as T(VMI.S/N D-Q 1122) – T(NMIJ TR 0227E) = -19.9 μK with the uncertainty of 46.3 μK ($k = 1$).

$$T_{\text{VMI.S/N D-Q1122}} - T_{\text{NMIJ}TR0227E} = \left(-0.0199 \pm 0.0463\right)\text{mK} \qquad (2)$$

(a) First ice mantle

(b) Second ice mantle

Figure 2 The raw data to measure the temperature differences among the cells at NMIJ.

7. Pair equivalence between NMIJ and VMI

As explained in section 4.1, TR0227E of NMIJ is an extremely close realization of the triple point of water upon the SI definition and also now defined as the National Reference of NMIJ. Here in this report, we will assume the difference between the definition and the realized temperature being negligible. Thus, the temperature difference among the transfer cell and TR0227E, T(VMI.S/N D-Q 1122) – T(NMIJ TR 0227E), will be automatically the temperature difference between the transfer cell and the National Reference of NMIJ. Since T(VMI.S/N D-Q 1122) – T(NMIJ TR 0227E) = -19.9 μK ±46.3 μK (k=1) (k=1, identical to eq. (2)), and T(VMI.S/N D-Q 1122) – T(VMI. S/N D-Q 1123) = 17.8 μK ± 130 μK (k=1, identical to eq. (1)), the VMI's National Reference is -37.7 μK ± 138.0 μK (k=1) compared to the NMIJ's

reference.

$$T_{\text{VMLS/N D–Q1123}} - T_{\text{NMIJ}TR0227E} = \left(-0.0377 \pm 0.1380\right)\text{mK} \qquad (3)$$

or, just simplifying the notation,

$$T_{\text{VMI}} - T_{\text{NMIJ}} = \left(-0.0377 \pm 0.1380\right)\text{mK} \qquad (3')$$

8. Linkage to APMP.T-K7 [1] and the CCT-K7 [3]

As shown in table 14 of the report of APMP.T-K7 (Ref. 1)), the national reference of the NMIJ is -2.2 μK ± 84.9 μK (k=2) from the APMP reference value, which is based upon the isotopic correction being applied.

$$T_{\text{NMIJ}} - T_{\text{APMP.T-K7RV}} = \left(-0.0022 \pm 0.0849\right)\text{mK} \qquad (4)$$

Combining the results from section 7 and considering the correlated factors which are those factors related to the realization of the TPW at NMIJ, the National reference of the triple point of VMI is -39.9 μK ± 142.4 μK (k=1) from the APMP reference value.

$$T_{\text{VMI}} - T_{\text{APMP.T-K7RV}} = \left(-0.0399 \pm 0.1424\right)\text{mK} \qquad (5)$$

Since the APMP reference value is reported to be 83.1 μK ± 15.2 μK (k=1) above the CCT-K7 KCRV, the national reference of the VMI could be calculated as 43.2 μK ±143.2 μK (k=1) from the CCT-K7 KCRV.

$$T_{\text{APMP.T-K7RV}} - T_{\text{CCT-K7RV}} = \left(0.0831 \pm 0.0152\right)\text{mK} \qquad (6)$$

$$T_{\text{VMI}} - T_{\text{CCT-K7RV}} = \left(0.0432 \pm 0.1432\right)\text{mK} \qquad (7)$$

The degree of equivalence is also shown in Figure 3. This result demonstrates that the degree of equivalence is sufficient for the VMI's national standard.
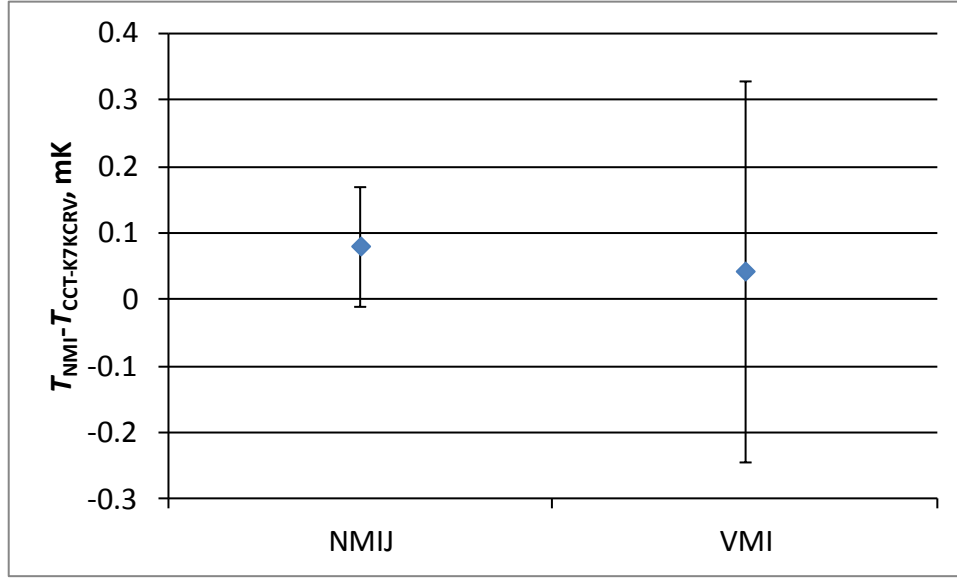
Fig. 3 Degree of equivalence for APMP.T-K7.1. Error bars indicate the expanded uncertainty ($k = 2$).

9. Bilateral equivalence

The bilateral degree of equivalence between any pair of APMP.T-K7 participants and VMI in this comparison (participant i and participant j) is expressed by the temperature difference between the national references of the two participants:

$$D_{ij} = T_i - T_j$$
$$= (T_{\text{national ref,i}} - T_{\text{national ref,j}})$$
$$= (T_{\text{national ref,i}} - T_{\text{APRV}}) - (T_{\text{national ref,j}} - T_{\text{APRV}}) \quad (8)$$

and the related uncertainty

$$U_{ij} = U(T_{\text{national ref,i}} - T_{\text{national ref,j}})$$
$$= \sqrt{U^2(T_{\text{nationalref,i}} - T_{\text{APRV}}) + U^2(T_{\text{nationalref,j}} - T_{\text{APRV}})} \quad (9)$$

The data $T_i(j)$ and $U_i(j)$ are taken from Table 14 of ref. 1 and section 8 of this report, and $U_i(j)$ is the expanded uncertainty ($k = 2$) of the participating laboratory. In Table 3, the bilateral temperature difference between the participants and the corresponding uncertainties are given above the diagonal, below the diagonal the quantified demonstrated equivalence, QDE0.95, is shown. This is a one-parameter description of equivalence. It describes the interval +/- QDE0.95 within which two

laboratories' results can be expected to agree with 95 % confidence. It is calculated as

$$QDE_{0.95}(i, j) = |D_{ij}| + \{1.645 + 0.3295 \times exp[-4.05|D_{ij}|/u_{ij}]\}u_{ij} \qquad (10)$$

Table 3 The bilateral temperature difference between the participants, the related uncertainty (above the diagonal), and the QDE between the participants (below the diagonal)   unit：μK

$j \to$ / $i \downarrow$	NMIA	SCL	KIM-LIPI	NMIJ	KRISS	SIRIM	MSL	NMC	NMISA	CMS	NIMT	VMI	
NMIA		**46.3**	**-45.9**	**15.0**	**30.5**	**-629.8**	**-4.9**	**-90.1**	**30.5**	**18.9**	**24.8**	**52.7**	D_{ij}
		135.0	301.5	101.9	146.4	209.8	66.2	190.8	152.3	85.7	163.5	153.1	U_{ij}
SCL	**279.5**		**-92.2**	**-31.3**	**-15.8**	**-676.1**	**-51.2**	**-136.4**	**-15.8**	**-27.4**	**-21.5**	**6.4**	D_{ij}
			320.6	149.2	182.5	236.4	127.5	219.7	187.3	138.7	196.5	188.0	U_{ij}
KIM-LIPI	**595.5**	**652.6**		**60.9**	**76.4**	**-583.9**	**41.0**	**-44.2**	**76.4**	**64.8**	**70.7**	**98.6**	D_{ij}
				308.1	325.6	358.6	298.2	347.8	328.3	303.2	333.6	328.7	U_{ij}
NMIJ	**201.1**	**297.8**	**613.4**		**15.5**	**-644.8**	**-19.9**	**-105.1**	**15.5**	**3.9**	**9.8**	**37.7**	D_{ij}
					159.6	219.2	91.8	201.1	165.0	106.7	175.4	165.8	U_{ij}
KRISS	**292.0**	**358.4**	**653.4**	**313.5**		**-660.3**	**-35.4**	**-120.6**	**0.0**	**-11.6**	**-5.7**	**22.2**	D_{ij}
						243.1	139.5	226.9	195.6	149.8	204.5	196.3	U_{ij}
SIRIM	**974.9**	**1065.0**	**1173.9**	**1005.4**	**1060.2**		**624.9**	**539.7**	**660.3**	**648.7**	**654.6**	**682.5**	D_{ij}
							205.1	272.2	246.7	212.2	253.8	247.2	U_{ij}
MSL	**129.9**	**269.3**	**587.9**	**183.4**	**281.3**	**962.2**		**-85.2**	**35.4**	**23.8**	**29.7**	**57.6**	D_{ij}
								185.6	145.7	73.4	157.4	146.6	U_{ij}
NMC	**413.2**	**503.7**	**684.8**	**443.9**	**502.5**	**987.5**	**400.0**		**120.6**	**109.0**	**114.9**	**142.8**	D_{ij}
									230.8	193.4	238.3	231.3	U_{ij}
NMISA	**303.3**	**367.7**	**658.5**	**324.1**	**386.3**	**1066.1**	**293.1**	**509.4**		**-11.6**	**-5.7**	**22.2**	D_{ij}
										155.5	208.8	200.7	U_{ij}
CMS	**171.4**	**276.0**	**605.5**	**209.7**	**294.0**	**997.7**	**151.0**	**433.7**	**305.4**		**5.9**	**33.8**	D_{ij}
											166.5	156.4	U_{ij}
NIMT	**322.9**	**386.3**	**666.1**	**344.5**	**402.3**	**1072.1**	**312.8**	**518.1**	**410.7**	**327.4**		**27.9**	D_{ij}
												209.4	U_{ij}
VMI	**317.1**	**369.6**	**671.4**	**332.2**	**386.0**	**1089.2**	**308.6**	**529.6**	**394.7**	**312.5**	**412.5**		D_{ij}
													U_{ij}

References

1) S. F. Tsai, R. White, J. Tamba, K. Yamazawa, M. K. Ho, C. M. Tsui, G. Zaid, A. Achmadi, K. S. Gam, H. Othman, N. M. Ali, K. H. Yuan, Y. Shaochun, H. Liedberg and C. Yaokulbodee, Final report on APMP.T-K7 key comparison of water triple point cells, Metrologia, 2016, 53, Tech. Suppl., 03004
http://www.bipm.org/utils/common/pdf/final_reports/T/K7/APMP.T-K7.pdf

2) Stock M., Solve S., del Campo D., Chimenti V., Méndez-Lango E., Liedber H., Steur P.P.M., Marcarino P., Dematteis R., Filipe E., Lobo I., Kang K.H., Gam K.S., Kim Y.G., Renaot E., Bonnier G., Valin M., White R., Dransfield T.D., Duan Y., Xiaoke Y., Strouse G., Ballico M., Sukkar D., Arai M., Mans A., de Groot M., Kerkhof O., Rusby R., Gray J., Head D., Hill K., Tegeler E., Noatsch U., Duris S., Kho H.Y., Ugur S., Pokhodun A., Gerasimov S.F., Final Report on CCT-K7: Key comparison of water triple point cells, Metrologia, 2006, 43, Tech. Suppl., 03001

3) J. Tamba et al., Int J Thermophys (2008) 29:1749–1760.

Appendix 1-revised: Measurements at VMI before the transportation to NMIJ

Measurement results on first ice mantle

Date of preparation of ice mantle of transfer cell (VMI:1122): 16/07/2014

Technique for preparation : Solid CO2

Date of preparation of the mantle of the reference cell (VMI: 1123): 16/07/2014

Date of measurement	Temperature difference from national reference (mK)	Experimental standard deviation of temperature difference from national reference (mK)	Distance from sensor midpoint to surface level of water in transfer cell (mm)	Hydrostatic-head correction for transfer cell (mK)	Self-heating correction for transfer cell (mK)
24/07/2014	**-0.0125**	**0.0028**	240	-0.1752	-1.822
25/07/2014	**0.0475**	**0.0017**	240	-0.1752	-1.788
26/07/2014	**-0.0275**	**0.0023**	240	-0.1752	-1.833
28/07/2014	**-0.0650**	**0.0017**	240	-0.1752	-1.837
29/07/2014	**0.0200**	**0.0027**	240	-0.1752	-1.791
31/07/2014	**0.0300**	**0.0015**	240	-0.1752	-1.798
01/08/2014	**0.0750**	**0.0048**	240	-0.1752	-1.812
02/08/2014	**0.0325**	**0.0021**	240	-0.1752	-1.816
04/08/2014	**0.0900**	**0.0033**	240	-0.1752	-1.805
06/08/2014	**0.0525**	**0.0025**	240	-0.1752	-1.775
07/08/2014	**-0.055**	**0.0035**	240	-0.1752	-1.800
Mean	0.017				-1.81
std. dev. of the mean	0.0154				0,006

The temperature differences should already be corrected for hydrostatic-head and self-heating effects (extrapolated to zero mA currents). To allow comparison with our measurements, the corrections should also be given separately.

Appendix 1 (Continued)-revised

Measurement results on second ice mantle

Date of preparation of　ice mantle of transfer cell (VMI: 1122)　: 05/09/2014

Technique for preparation : Solid C02

Date of preparation of the mantle of the reference cell (VMI: 1123): 05/09/2014

Date of measurement	Temperature difference from national reference (mK)	Experimental standard deviation of temperature difference from national reference (mK)	Distance from sensor midpoint to surface level of water in transfer cell (mm)	Hydrostatic-head correction for transfer cell (mK)	Self-heating correction for transfer cell (mK)
12/09/2014	0.0425	0.0030	240	-0.1752	-1.797
15/09/2014	-0.0450	0.0041	240	-0.1752	-1.855
17/09/2014	0.0700	0.0034	240	-0.1752	-1.818
18/09/2014	0.0500	0.0000	240	-0.1752	-1.817
19/09/2014	0.0650	0.0021	240	-0.1752	-1.802
20/09/2014	0.0025	0.0000	240	-0.1752	-1.809
22/09/2014	-0.0300	0.0000	240	-0.1752	-1.829
23/09/2014	0.02500	0.0020	240	-0.1752	-1.824
24/09/2014	0.0200	0.0043	240	-0.1752	-1.840
25/09/2014	-0.0150	0.0037	240	-0.1752	-1.849
Mean	0.0185				-1.82
std. dev. of the mean	0.0126				0.006

The temperature differences should already be corrected for hydrostatic head and self-heating effects (extrapolated to zero mA currents). To allow comparison with

our measurements, the corrections should also be given separately.

The resulting temperature difference between the transfer cell VMI.S/N D-Q 1122 and the national reference (cell VMI.S/N D-Q 1123) was as T(VMI.S/N D-Q 1122) – T(VMI. S/N D-Q 1123) = 0.0178   mK.
The combined standard uncertainty – including the contribution for deviation from the realization of the ideal triple point of water is estimated as 0,130 mK (k = 1).

Correction

Isotopic correction: was not applied with uncertainty 0,004 mK).

Impurity correction: was not applied with uncertainty 0,1 mK

Appendix 1 (Continued)

Equipment used for the calibration

Description of national reference:

01 cell, Hart Scientific 5901 D – Q; N⁰ 1123 (VMI: 1123)

Date   manufacturer: March 2014

Manufacturer/Type of resistance bridge, AC or DC: **ASL F900 AC**

Measurement currents: **1mA and 1,414 mA and extrapolated to zero mA (0 mA)**

Number and sampling frequency of repeated measurements: **75 Hz**

Manufacturer/Type of reference resistor: **Tinsley 5685A; 25 Ω/ Temp. coeff.: 2 ppm/⁰C**

Is reference resistor temperature controlled, if yes, stability: **± 5 mK**

Manufacturer/Type of thermometer, length of sensor: **Long stem SPRT Hart Scientific 5681, N⁰ 1357**

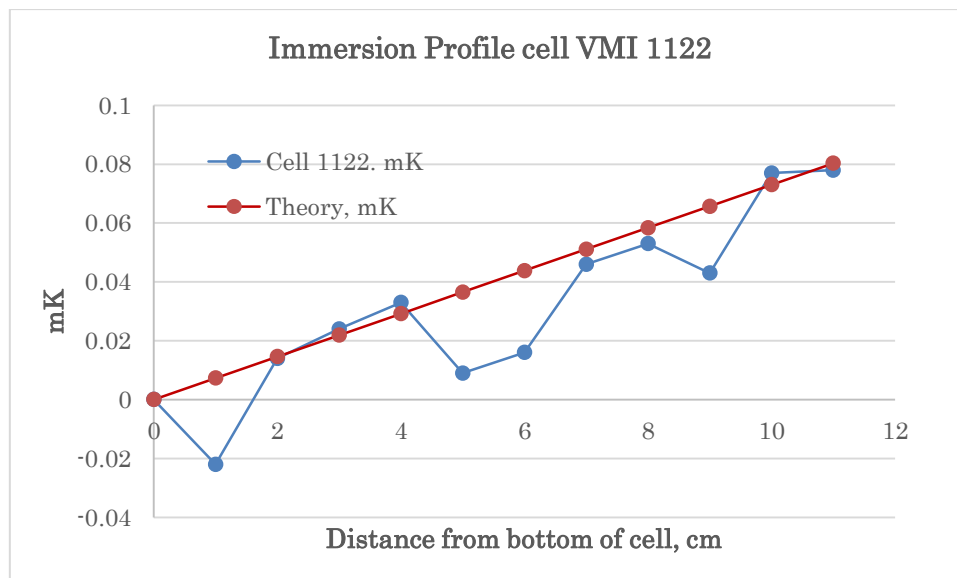Storage container for TPW cells: **Home-Made Ice Bath**

Freezing method: **Solid C02**

Immersion profile of transfer cell at measurement current 0 mA:

Distance from sensor midpoint to free surface level of the liquid water (mm)	Temperature variation (mK)
240 (0 mm)	0

230 (10 mm)	-0.022
220 (20 mm)	0.014
210 (30 mm)	0.024
200 (40 mm)	0.033
190 (50 mm)	0.009
180 (60 mm)	0.016
170 (70 mm)	0.046
160 (80 mm)	0.053
150 (90 mm)	0.043
140 (100 mm)	0.077
130 (110 mm)	0.078

The above table is for reporting measurement of the hydrostatic head effect. Measurements should be taken at a step width of 10 mm. Thermometer readings should be corrected for self-heating (extrapolated to 0 mA), measured at each position (see figure below).

$(T - T_{bottom})$/cm	0	1	2	3	4	5	6	7	8	9	10	11
Cell 1122. mK	0	-0,022	0,014	0,024	0,033	0,009	0,016	0,046	0,053	0,043	0,077	0,078
Theory, mK	0	0,0073	0,0146	0,0219	0,0292	0,0365	0,0438	0,0511	0,0584	0,0657	0,073	0,0803

Appendix 1 (Continued)

Uncertainty Budget for measurement at VMI

A	National Reference: *(Uncertainty related only to properties of the reference cell)*	Measurements: (Contribution, k=1), mK
1	Chemical Impurities	0,100
2	Isotopic Variation	0,004
3	Residual gas pressure in Cell	0,005
4	Reproducibility of Temp. Reference for two ice mantles	0,040
B	**Comparison of Transfer Cell to National Reference** *(Uncertainty related to the comparison of the two cell)*	
5	Repeatability for a single ice mantle	0,020
6	Reproducibility for difference ice mantles on Tran.Cell	0,001
7	Reproducibility for difference types of SPRT	0,019
8	Hydrostatic head of the Transfer Cell	0,004
9	Hydrostatic head of the National Cell	0,004
10	SPRT self-heating in the transfer cell and reference cell	0,008
11	Perturbing heat exchange (from immersion profile of TC)	0,024
	Others:	
12	Non linearity and precision of bridge	0,014
13	Temperature variation of standard resistor	0,040
14	Reproducibility of transfer cell	0,044
15	Influence of the technician (negligible by only one person)	0,000
	Total Uncertainty (k=1), mK:	**0,130**

Explanation of the uncertainty budget

1. Chemical impurities:

Water chemical content analysis is not available. The impurities is estimated on observation of maximum difference between the national reference cell and the transfer cell from different realized times and different dates is 0,053 mK, therefore, the standard uncertainty is not exceeded 0,053 mK/ square root 3 = 0,031 mK. This is less than the uncertainty due to impurities and isotopes as determined to be typically 0,1 mK in working Document CCT 01-02. Therefore, the corresponding uncertainty is estimated as 0,1 mK.

2. Isotopic variation:

The samples of the water was sent for Laboratory Test of the University Utah, USA for the cells of TPW (national reference cell: VMI 1123 and transfer cell: VMI 1122 are the same model Hart Scientific 5901 D-Q; year of fabrication 2012) by TPW cell manufacturer. In this comparison, the isotopic and impurity corrections were not applied. The uncertainty related isotopic composition is obtained from the report:

$(T_{v-smow} - T_{VMI1123})$ = 0,007 mK/square root 3 = 0,004 mK.

3. Residual gas pressure:

The uncertainty from residual gas pressure has been referred to Table 2 of the report CCT/01-02. This uncertainty is obtained from report: 0,005 mK.

4. Reproducibility:

Estimate of the reproducibility of the temperature reference due to changes in the following quantities: Crystal size, the age of the mantles, different mantles, the handling of the cells before preparation of the mantle.

The uncertainty of reproducibility has been taken from the raw data of 21 times measured resistance through 2 ice mantles and the aging of the two ice mantles of national reference cell. This component is estimated:

$u_{reproducibility}$ = $(0,013^2$ mK + $0,012^2$ mK+ $0,035^2$ mK$)^{1/2}$ = 0,040 mK.

5. The repeatability for a single ice mantle:

This component is obtained as experimental standard deviation of the daily obtained temperature differences between the transfer cell and the national cell, divided by square root of the number of daily results (here 11 days for the first ice mantle and 10 days for the second ice mantle).

The uncertainty of repeatability has been taken from the standard deviation of the mean of the measured resistance in each day and in 1 run. This component is estimate:

$u_{repeatability} = (0,015^2 + 0,013^2)^{1/2} = 0,020$ mK.

6. Reproducibility for different ice mantles on transfer cell:

The reproducibility for different ice mantles represents the additional variability introduced by measuring on several different ice mantles on transfer cell (probably the laboratory uses the same ice mantle of the reference cell during the time of measurements).

Temperature difference dT(ice mantle) between ice mantles of transfer cell has been taken the temperature difference between averaged temperature difference of first run comparison Mean(run 1) and second run comparison Mean(run 2):

dT(ice mantle) = Mean(run 2) - Mean(run 1) = 0,0185 mK – 0,017 mK = 0,0015 mK.

The uncertainty of the reproducibility for different ice mantles has been calculated like following equation:

u(ice mantle) = dT(ice mantle) / square root 3 = 0,001 mK.

7. Reproducibility for different types of SPRTs:

The observed temperature differences between the transfer and the reference cells could depend on type of SPRT's. This component takes into account possible SPRT internal insulation leakage.

The uncertainty of a SPRT internal insulation leakage u(leakage) has been taken from the variation of the observed temperature differences between the transfer and the reference cells. The standard deviation of the mean of the all observed temperature differences between the transfer and the reference cells is used for the u(leakage):

$u(leakage) = (0,015^2 \, mK + 0,012^2 \, mK)^{1/2} = 0,019$ mK.

8; 9.Hydrostatic head of transfer/reference cell:

The hydrostatic head is estimated to an accuracy of ± 10 mm.

10. SPRT self-heating in the transfer cell and national cell:

All the measurements are corrected for self-heating effect (calculating for 0 mA current), difference between the SPRT self-heating corrections is very small in the transfer cell and national reference cells. Self-heating is considered negligible because strongly correlated between cells. In this case the uncertainty in self-heating corrections only contributed to the type A uncertainty of the comparison of the cells, therefore, The variation of the self-heating effect has been taken for the uncertainty of the self-heating effect. The standard deviation of the mean for the self-heating effect of the reference cell and the transfer cell are combined together the uncertainty of the self-heating effect: $u(\text{self-heating}) = (0{,}006^2 \, mK + 0{,}006^2 \, mK)^{1/2} = 0{,}008 \, mK$.

11. Perturbing heat exchanges:

This component could be estimated the following:

- by comparing the deviations from expected hydrostatic pressure correction obtained in transfer and reference cells (by changing immersion depth over the length of the sensor in 50 mm)

- by modifying the thermal exchange between thermometer and its environment during the measurements on transfer and reference cells.

The uncertainty of perturbing heat exchanges has been taken from the immersion depth temperature profile. The max temperature difference between bottom and 50 mm height is 0,033 mK which shows at the table of immersion profile. The value of 0,033 mK is divided by square root 3 = 0,019 mK for using a uncertainty. The measurement of the immersion profile has been performed 5 times. From the 5 times measurements, the uncertainty of data scattering is estimated to 0,015 mK. These 2 uncertainties are combined together for the uncertainty of perturbing heat exchanges:

$u(\text{perturbing}) = (0{,}019^2 + 0{,}015^2)^{1/2} = 0{,}024 \, mK$.

12. Resistance Bridge:

The uncertainty for the ASL F900 resistance bridge were obtained from the four components: the uncertainty for the measurement precision of the bridge: This type of uncertainty is provided by the calibration certificate which is equal to +- 0,02 ppm at the confident level of 95% with coverage factor $k = 2$: $u_1 = 0{,}003 \, mK$; the uncertainty for the resolution of the bridge based on the specification of the ASL F900 bridge with 0,01 ppm error: $u_2 = 0{,}002 \, mK$; the uncertainty for the non linearity of the bridge is estimate by the temperature difference when measurement at the frequencies 25 Hz and 75 Hz: $u_3 = 0{,}012 \, mK$; the uncertainty from the quadrature effect of the ASL F900 bridge: $u_4 = 0{,}006 \, mK$.

These components of the uncertainty are combined together for the uncertainty of the ASL F900 bridge:

$$U_{bridge} = (0,003^2 \text{ mK} + 0,002^2 \text{ mK} + 0,012^2 \text{ mK} + 0,006^2 \text{ mK})^{1/2} = 0,014 \text{ mK}.$$

13. Stability of the standard resistor:

The uncertainty for the stability of the standard resistor were estimated from the three components: from the expanded uncertainty in the certificate of the used standard resistor is $u_{resistor} = U_{95}/2 = (0,3 \text{ ppm}/(2*0,10163 \text{ } \Omega.K^{-1}))*24,999945 \text{ } \Omega*10000 = 0,037$ mK; from the uncertainty of stability of liquid bath for maintaining the standard resistors was estimated 0,0014 mK and from the uncertainty for long time drift of the standard resistor in one year is 0,014 mK.

These 3 uncertainties are combined together for the uncertainty of the stability of standard resistor:

$$u_{std.resistor} = (0,037^2 \text{ mK} + 0,0014^2 \text{ mK} + 0,014^2 \text{ mK })^{1/2} = 0,040 \text{ mK}.$$

14. Reproducibility of transfer cell:

The uncertainty of reproducibility has been taken from the raw data of 21 times measured resistance through 2 ice mantles and the aging of the two ice mantles of transfer cell.

This component is estimated:

$$u_{reproducibility} = (0,014^2 \text{ mK} + 0,013^2 \text{ mK} + 0,040^2 \text{ mK})^{1/2} = 0,044 \text{ mK}.$$

Appendix 2 Measurement results at VMI after the transportation back from NMIJ

Note that the measurement result shown in this Appendix 2 is used merely to check the stability of the transfer cell according to the protocol.

Measurement report form for APMP.T-K7.1

General information of transfer cell

Laboratory: **Temperature Measurement Laboratory, VMI**

Contact person: **Pham Thanh Binh; Vu Quang Cuong**

Contact address, email： **Vietnam Metrology Institute (VMI)**
8 Str. Hoang Quoc Viet, Dict. Cau Giay, Hanoi, Vietnam
binhpt@vmi.gov.vn;   cuongvq@vmi.gov.vn

Transfer cell: manufacturer and type: **Hart Scientific; 5901 D – Q; N⁰ D-Q 1122**

Purchase or manufacture date: **March 2014**

Accessories or comments on special use: No

Inner diameter of well/mm: **12 mm**

Cell diameter /mm: **60 mm**

Depth of well below water surface /mm: **265 mm**

Appendix 2 (Continued)

Measurement results on first ice mantle (after return from NMIJ)

Date of preparation of   ice mantle of transfer cell (S/N: D-Q 1122): 26/03/2015

Technique for preparation : Solid CO_2

Date of preparation of   the mantle of the reference cell (S/N: D-Q 1123): 26/03/2015

Date of measurement	Temperature difference from national reference (mK)	Experimental standard deviation of temperature difference from national reference (mK)	Distance from sensor midpoint to surface level of water in transfer cell (mm)	Hydrostatic-head correction for transfer cell (mK)	Self-heating correction for transfer cell (mK)
4/4/2015	-0.0363	0.0027	240	-0.1752	-1.770
6/4/2015	0.0108	0.0019	240	-0.1752	-1.755
7/4/2015	0.0165	0.0049	240	-0.1752	-1.780
8/4/2015	0.0407	0.0051	240	-0.1752	-1.790
9/4/2015	-0.0402	0.0033	240	-0.1752	-1.775
10/4/2015	0.0338	0.0051	240	-0.1752	-1.788
11/4/2015	0.0038	0.0036	240	-0.1752	-1.753
13/4/2015	0.0010	0.0052	240	-0.1752	-1.768
14/4/2015	-0.0260	0.0049	240	-0.1752	-1.748
15/4/2015	0.0000	0.0031	240	-0.1752	-1.815
16/4/2015	-0.0185	0.0035	240	-0.1752	-1.755
Mean	-0.0013				
std. dev. of the mean	0.0081				

Appendix 2(Continued)

Measurement results on second ice mantle (after return from NMIJ)

Date of preparation of ice mantle of transfer cell (S/N: D-Q 1122) : 06/05/2015

Technique for preparation : Solid C02

Date of preparation of the mantle of the reference cell (S/N: D-Q 1123): 06/05/2015

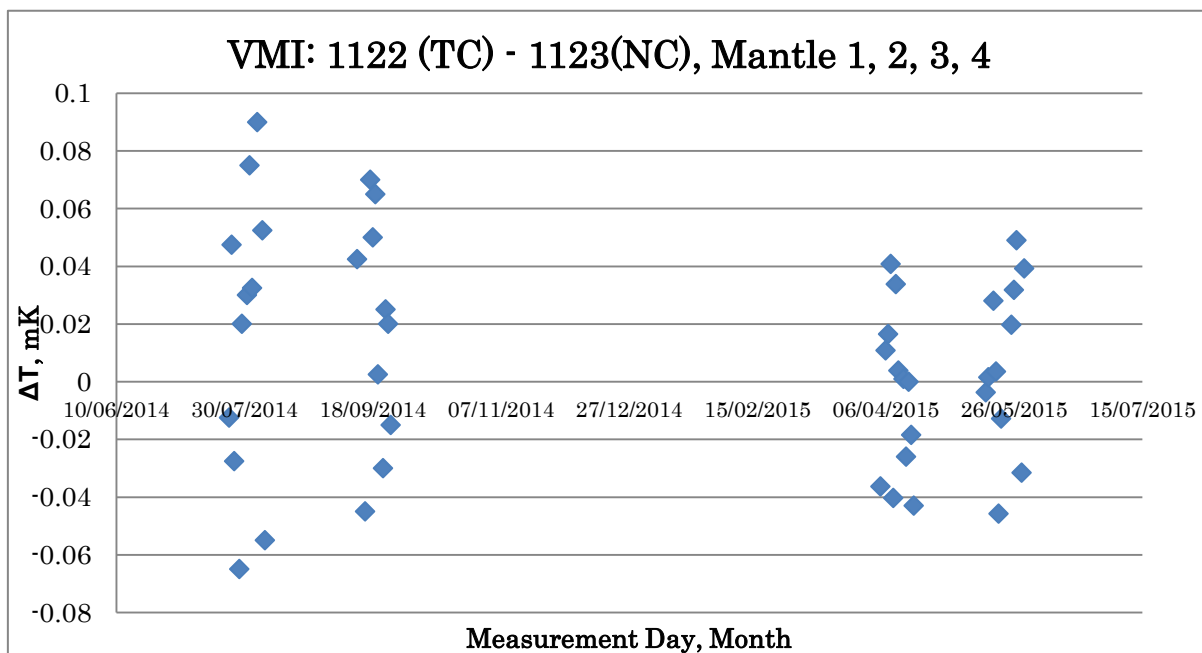| Date of measurement	Temperature difference from national reference (mK)	Experimental standard deviation of temperature difference from national reference (mK)	Distance from sensor midpoint to surface level of water in transfer cell (mm)	Hydrostatic-head correction for transfer cell (mK)	Self-heating correction for transfer cell (mK)
15/5/2015	-0.0037	0.0033	240	-0.1752	-1.770
16/5/2015	0.0015	0.0038	240	-0.1752	-1.760
18/5/2015	0.0280	0.0018	240	-0.1752	-1.730
19/5/2015	0.0035	0.0023	240	-0.1752	-1.770
20/5/2015	-0.0458	0.0034	240	-0.1752	-1.765
21/5/2015	-0.0128	0.0040	240	-0.1752	-1.750
25/5/2015	0.0197	0.0058	240	-0.1752	-1.765
26/5/2015	0.0318	0.0072	240	-0.1752	-1.741
27/5/2015	0.0490	0.0040	240	-0.1752	-1.765
29/5/2015	-0.0315	0.0029	240	-0.1752	-1.795
Mean	0.0072				
std. dev. of the mean	0.009				

The resulting temperature difference between the transfer cell VMI.S/N D-Q 1122 and the national reference (cell VMI.S/N D-Q 1123) was as T(VMI.S/N D-Q 1122) – T(VMI. S/N D-Q 1123) = 0.003 mK.

Check the Stability of transfer cell by comparison against with the National Reference after return from NMIJ:

Before (mK)	After (mK)	ΔT (mK)
0.018	0.003	0.015

APMP.T-K7.1:   VMI – Measurement Results of Four ice mantles

VMI: 1122 (TC) - 1123(NC), Mantle 1, 2, 3, 4

Appendix 3 Measurement results at NMIJ
Measurement results on first ice mantle

Date of preparation of ice mantle of transfer cell: 2014/10/31

Technique for preparation : The ice mantle is formed by using an R-134a heat pipe cooled with liquefied nitrogen, and ethanol as transferring medium.

Date of preparation of the mantle of the reference cell(s): 2014/10/31

Date of measurement	Temperature difference from national reference / mK	Experimental standard deviation of temperature difference from national reference / mK	Distance from sensor midpoint to surface level of water in tr. Cell /mm	Hydrostatic-head correction for transfer cell /mK	Self-heating correction for transfer cell /mK
2014/11/7	-0.0272	0.0020	220	0.16	1.99
2014/11/10	-0.0302	0.0023	220	0.16	1.89
2014/11/11	-0.0109	0.0019	220	0.16	1.94
2014/11/12	-0.0265	0.0026	220	0.16	1.91
2014/11/13	-0.0204	0.0021	220	0.16	1.91
2014/11/14	-0.0246	0.0020	220	0.16	1.88
2014/11/17	-0.0262	0.0026	220	0.16	1.90
2014/11/18	-0.0154	0.0025	220	0.16	1.90
2014/11/19	-0.0395	0.0019	220	0.16	1.97
2014/11/20	-0.0051	0.0044	220	0.16	1.92
mean	-0.0226				
std. dev. of the mean	0.0037				

Appendix 3 (Continued)

Measurement results on second ice mantle

Date of preparation of ice mantle of transfer cell: 2014/11/25

Technique for preparation : The ice mantle is formed by using an R-134a heat pipe cooled with liquefied nitrogen, and ethanol as transferring medium.

Date of preparation of the mantle of the reference cell(s): 2014/11/25

Date of measurement	Temperature difference from national reference / mK	Experimental standard deviation of temperature difference from national reference / mK	Distance from sensor midpoint to surface level of water in tr. Cell /mm	Hydrostatic-head correction for transfer cell /mK	Self-heating correction for transfer cell /mK
2014/12/2	-0.0117	0.0019	220	0.16	1.90
2014/12/4	-0.0042	0.0022	220	0.16	1.92
2014/12/8	-0.0004	0.0019	220	0.16	1.93
2014/12/9	-0.0268	0.0020	220	0.16	1.88
2014/12/10	-0.0174	0.0021	220	0.16	1.93
2014/12/11	-0.0275	0.0019	220	0.16	1.92
2014/12/12	-0.0285	0.0021	220	0.16	1.84
2014/12/15	-0.0233	0.0021	220	0.16	2.02
2014/12/17	-0.0104	0.0018	220	0.16	1.92
2014/12/18	-0.0214	0.0022	220	0.16	1.97
mean	-0.0172				
std. dev. of the mean	0.0037				

Appendix 3 (Continued)

Uncertainty budget for measurements at NMIJ

Origin	Contribution (k=1)
National reference	
(Uncertainties related only to properties of the reference cell)	
Chemical impurities (see explanation below)	0.020 mK
Isotopic variation (see explanation below)	0.002 mK
Residual gas pressure in cell	0.001 mK
Reproducibility [1]	0.013 mK
Comparison of transfer cell to national reference	
(Uncertainties related to the comparison of the two cells)	
Repeatability for a single ice mantel (incl. bridge noise) [2]	0.004 mK
Reproducibility for different ice mantles [3]	0.006 mK
Reproducibility for different types of SPRTs [4]	0.002 mK
Hydrostatic head of transfer cell	0.008 mK
Hydrostatic head of reference cell	0.008 mK
SPRT self-heating in the transfer cell and reference cell [5]	neglected (because of no significant differences between seven cells)
Perturbing heat exchanges [6]	0.023 mK
others	
Non linearity and precision of bridge	0.029 mK

Temperature variation of standard resistor	neglected (because of short period for comparison measurements)
Reproducibility of transfer cell	included in repeatability for a single ice mantel and reproducibility for different ice mantles
Influence of the technician	neglected (only one person)
Ambiguity of the definition of the triple point of water	0.004 mK
Total uncertainty	0.046 mK

Explanation of the uncertainty budget

[Chemical impurity]

After the temperature comparison measurements for defining the national reference, the water of one of seven cells was collected just after the cell was broken, and then analyzed to estimate the effect of the chemical impurities dissolved in the water of the cells. Quantitative analyses or qualitative analyses for 65 elements were undertaken using the actual water from the cell with an inductively coupled plasma mass spectrometer (ICPMS). The depression of the triple point of water by an impurity is estimated thermodynamically, and the standard uncertainty of the chemical impurities is evaluated as less than 0.020 mK.

[Isotopic variation]

Five cells of seven cells were manufactured with small ampoules. After removing the ampoules, the isotopic compositions of the water in the ampoules were analyzed. Two cells of seven cells were broken after the thermal measurements to analyze the water. The uncertainty of isotopic correction includes repeatability of isotopic measurements, reproducibility among measuring laboratories of the isotopic composition analyses, systematic error of measurements and correcting equation.

More details of the above chemical impurity effect and isotopic variation effect could be found in the paper, Isotopic Correction of Water Triple Point Cells at NMIJ, J. Tamba, M. Sakai, I. Kishimoto, M. Arai, Int J Thermophys, DOI 10.1007/s10765-008-0456-3.

[1] Estimate of the reproducibility of the temperature reference due to changes in the following quantities: crystal size, the age of the mantles, different mantles, the handling of the cells before preparation of the mantle.

[2] The repeatability for a single ice mantle is understood as the experimental standard deviation of the daily obtained temperature differences between the transfer cell and the national reference, divided by the square root of the number of daily results (10 for this measurement). This component takes also in account the stability of reference resistor (temperature effect).

[3] The reproducibility for different ice mantles represents the additional variability introduced by measuring on several different ice mantles on transfer cell.

[4] The component due to differences of the type of SPRT's is the same as reported for CCT K7.

[5] These uncertainties could be strongly positively correlated. All the measurements are corrected for self-heating effect. If the thermal resistances have approximately the same magnitude in transfer and reference cells the difference between the self-heating corrections is very small. In addition the uncertainties on self-heating corrections in transfer and reference cells are strongly correlated. In this case the uncertainty in self-heating corrections only contributes to the Type A uncertainty of the comparison of the cells.

[6] This component could be estimated

- by comparing the deviations from expected hydrostatic pressure correction obtained in transfer and reference cells (by changing immersion depth over the length of the sensor ≈ 5 cm)

- by modifying the thermal exchange between thermometer and its environment during the measurements on transfer and reference cells.

Appendix 3 (Continued)

Immersion profiles of the cells at NMIJ

Immersion profile TR0227E

Immersion profile D-Q1122