Final Report for the APMP.T-K4
(Draft B on October 27, 2011)

Comparison of Realizations of Aluminum Freezing-Point Temperatures

Prepared by K. S. Gam (coordinator) and W. Joung

Korea Research Institute of Standards and Science (KRISS)

Republic of Korea

October, 2011

Revised on March, 2013

Contents

1. Introduction

The key comparison CCT-K4 was carried out from 1998 to 2000. Following CCT-K4, the Asia-Pacific Metrology Program Key Comparison 4 (APMP.T-K4) was organized for national laboratories in the Asia/Pacific region. The participation of KRISS (South Korea) and NMIJ (Japan) provided the link between CCT-K4 and APMP.T-K4.

APMP.T-K4, taking place from December 2003 to June 2005, covers the comparison of the aluminum and silver freezing-points, using a High Temperature Standard Platinum Resistance Thermometer (HTSPRT) as an artifact. The procedure of the APMP.T-K4 was different from the procedure of the CCT-K4. In CCT-K4, the transfer Al and Ag cells, and HTSPRTs with the resistance value 0.6 Ω at the water triple point were circulated into the participants, and Al and Ag freezing-points were directly compared with the local cell's freezing-points. During the circulation of Al and Ag cells in CCT-K4, some cells were broken during the transportation. To minimize the difficulty arising from the breakage of cells, HTSPRTs were used in APMP.T-K4 as the transfer thermometers without the transfer cells. HTSPRTs used in APMP.T-K4 were same type used in the CCT-K4.

The HTSPRTs were tested and characterized by KRISS, the coordinating laboratory, before circulation. The HTSPRT was then in turn hand-carried to 7 participating laboratories, and returned after the comparison measurements at participating laboratories. The APMP.T- K4 protocol (Appendix 1) provides guidance for main features of the APMP.T-K4 such as an annealing criteria and a measurement sequence to be performed. The actual realizations of the Ag and Al freezing-points were carried out in accordance with local practices. Participants were asked to made necessary corrections to the data used to calculate the fixed point resistance ratios and to submit their results.

The comparison involves the 8 APMP NMIs, and KRISS and NMIJ were participated in CCT-K4. The organization of the comparison is shown in Fig.1.1 and the comparison was divided in 2 loops and 4 sub-loops. The participating laboratories were compared directly to KRISS.

The APMP.T-K4 report (draft A) was prepared in 2009 and the results discussed in the APMP TCT meeting, which was held at Kuala Lumpur, Malaysia from December 14 to 15, 2009. For the Ag freezing-point comparison result, the participants pointed out that the results were scattered more than expected before the program started. The chair person and participants decided that the Ag comparison results would be omitted from the report because of the instability of the HTSPRTs used in Ag freezing-point comparison. A new key comparison for Ag freezing-point is necessary to obtain acceptable CMC entry of APMP NMIs in the future.

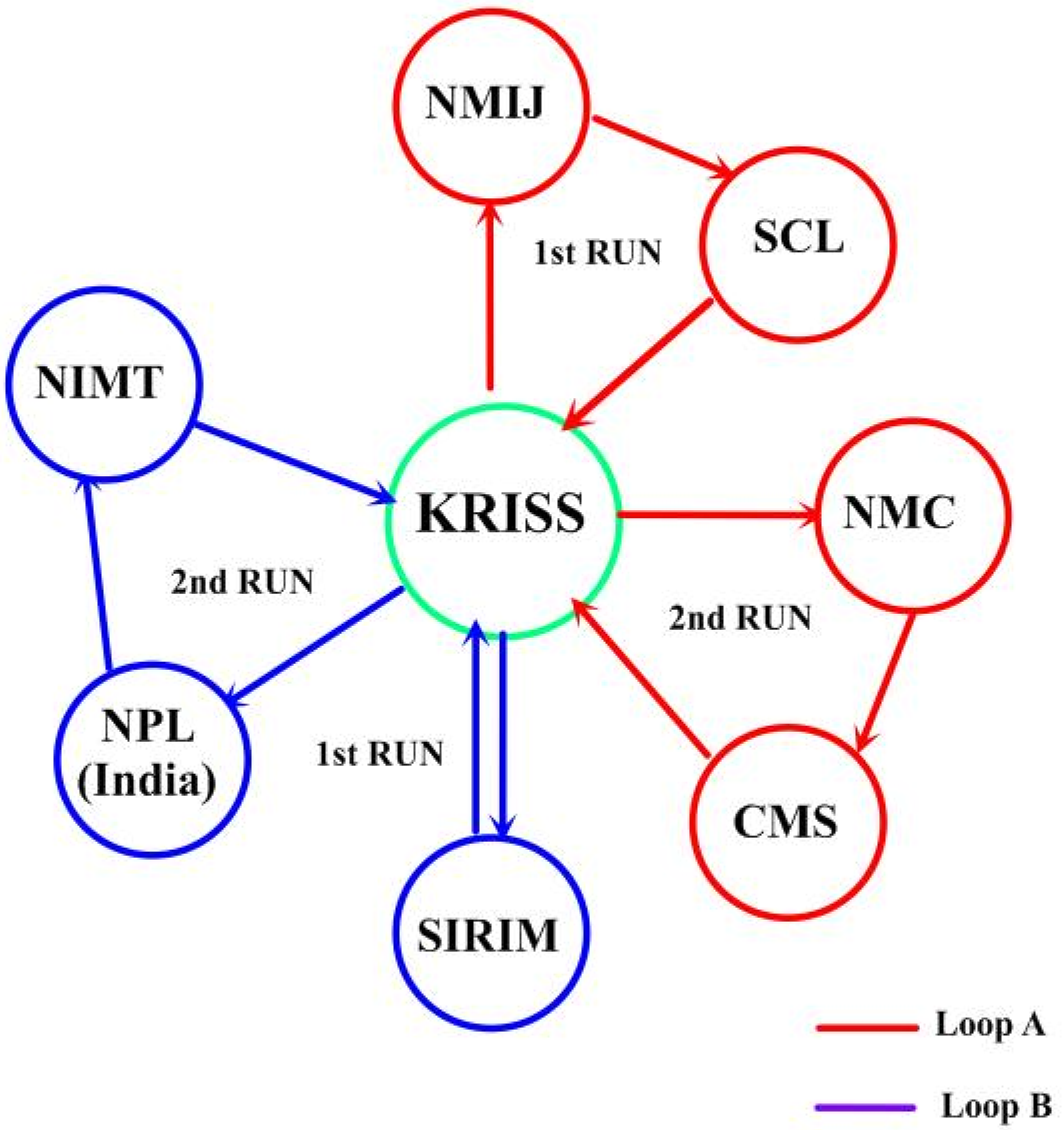


Fig. 1.1 Organization of the comparison.

2. Participating laboratories

Following NMIs participated in APMP.T-K4. Among the participants in this key comparison, KRISS and NMIJ were participated in the CCT-K4. KRISS and NMIJ provide the link between CCT-K4 and APMP.T-K4.

Table 2.1. Participating NMIs in APMP.T-K4.

Economy	Institute	Contact person
Korea	KRISS	K. S. Gam
Japan	NMIJ	K. Yamazawa
Hong Kong	SCL	C. M. Tsui
Singapore	NMC	H. Y. Kho
Taiwan	CMS	S. F. Tsai
Thailand	NIMT	U. Norranim
Malaysia	SIRIM	H. Othman
India	NPL(India)	J. K. Gupta

3. Protocol and organization of APMP.T-K4

The APMP regional comparison was initiated by APMP TCT meeting and workshop on November 5, 2001. There, KRISS was invited to be the pilot laboratory of APMP.T-K4. The procedures and instructions, which are given in appendix A, should be followed by the APMP participants in comparing the realizations of aluminum (660.323 ℃) and silver (961.78 ℃) freezing-point temperatures. In addition, each laboratory should follow its local practice in realizing the aluminum and silver freezing-points. Three HTSPRTs were used as the transfer thermometers in the aluminum freezing-point comparison and 5 HTSPRTs were used in the silver freezing-point comparison. Transfer HTSPRTs used in APMP.T-K4 were BTC-type HTSPRTs manufactured in Monitoring Ltd, Russia. The transfer HTSPRTs used in the comparison is listed in Table 3.1., and the comparison schedule is also given in this Table.
Before comparison measurements for the APMP.T-K4, the stabilities for 4 units of the BTC-type HTSPRTs (N329, N330, N334, N339) were checked by determining the change in its resistance at the triple-point of water after the anneal at 1000 ℃ for 50 h. The stabilities of HTSPRTs were distributed within 3 mK, and the stability measurement results of HTSPRTs were shown in Fig. 3.1.

Table 3.1. The comparison schedule and HTSPRTs used in the comparison.

Institute	Measurement period (MM/DD/YY)	HTSPRTs used in the comparison experiment
KRISS	12/15/03-03/27/06	All
NMIJ	01/07/04-01/19/05	Al-N329
SCL	03/05/05-03/24/05	Al-N329
NMC	04/07/05-05/06/05	Al-N358
CMS	05/06/05-12/25/05	Al-N358
NIMT	05/18/05-05/28/05	Al-N329
SIRIM	01/10/04-02/22/04	Al-N334
NPL(India)	04/07/05-05/18/05	Al-N329

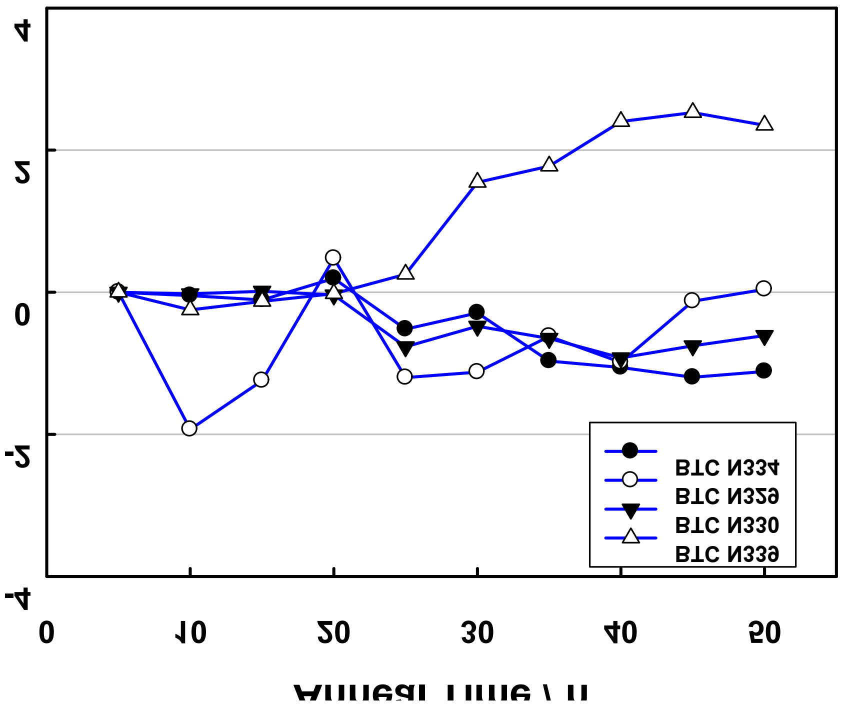


Fig. 3.1. Stability of BTC-type HTSPRTs at TPW after annealing at 1000 ˚C.

4. Results for Al freezing-point

4.1. Comparison results

Three HTSPRTs (s/n N329, N358, N334) were used in the comparison for the Al freezing-points. The W(Al) values were taken from the reports of the participating laboratories summarized in Table 4.1. The uncertainties in Table 4.1 are given for *k* = 2. The difference of W(Al) values between the pilot and the participant was calculated from the adjacent values. For example, in the case of Table 4.1.,

$W(Al)_{KRISS}$(=3.375 679 16) value was compared with $W(Al)_{NMIJ}$(=3.375 686 22), and $W(Al)_{SCL}$(=3.375 692 99) value was compared with $W(Al)_{KRISS}$(=3.375 679 60).

Table 4.1. Results for the measurements at the Al freezing-point.
Table 4.1.a.

KRISS-NMIJ- SCL-KRISS HTSPRT N329		
Participants	W(Al)	*U* / mK
KRISS	3.375 679 16	3.60
NMIJ	3.375 686 22	3.02
SCL	3.375 692 99	2.80
KRISS	3.375 679 60	3.60

Table 4.1.b.

KRISS- NMC-CMS-KRISS HTSPRT N358		
Participants	W(Al)	*U* / mK
KRISS	3.375 759 02	3.60
NMC	3.375 778 39	4.82
CMS	3.375 771 01	4.10
KRISS	3.375 771 22	3.60

Table 4.1.c.

KRISS-SIRIM-KRISS HTSPRT N334		
Participants	W(Al)	*U* / mK
KRISS	3.375 457 57	3.60
SIRIM	3.375 421 24	6.80
KRISS	3.375 454 75	3.60

Table 4.1.d.

KRISS-NPL(India)-NIMT-KRISS HTSPRT N329		
Participants	W(Al)	*U* / mK
KRISS	3.375 677 27	3.60
NPL(India)	3.375 695 94	3.63
NIMT	3.375 688 20	7.46
KRISS	3.375 689 59	3.60

The resistance ratio differences at Al freezing-point between KRISS and participants are converted to equivalent temperature differences using the following conversion equation;

$$\Delta T / \mathrm{mK} = T_{\mathrm{Lab}} - T_{\mathrm{KRISS}} = (W_{\mathrm{Lab}} - W_{\mathrm{KRISS}}) / (dWr / dT)_{\mathrm{Al}} \quad (1)$$

, where the conversion factor has the value $(dWr/dT)_{\mathrm{Al}}$ = 3.21 × 10^{-6} mK^{-1}.
Temperature differences of Al freezing-point calculated by the equation (1) are summarized in Table 4.2. and in Fig.4.1. The uncertainty *U* was calculated as the sum in quadrature from the uncertainties taken from the report of the participants, and given for *k* = 2.

Table 4.2. Temperature differences and reported uncertainties at Al freezing-point between the participants and KRISS.

Lab	T_{Lab}-T_{KRISS} / mK	*U* / mK
KRISS	0.00	5.10
NMIJ	2.20	4.70
SCL	4.18	4.56
NMC	6.04	6.02
CMS	-0.07	5.46
NIMT	-0.43	8.28
SIRIM	-11.34	7.70
NPL(India)	5.83	5.12

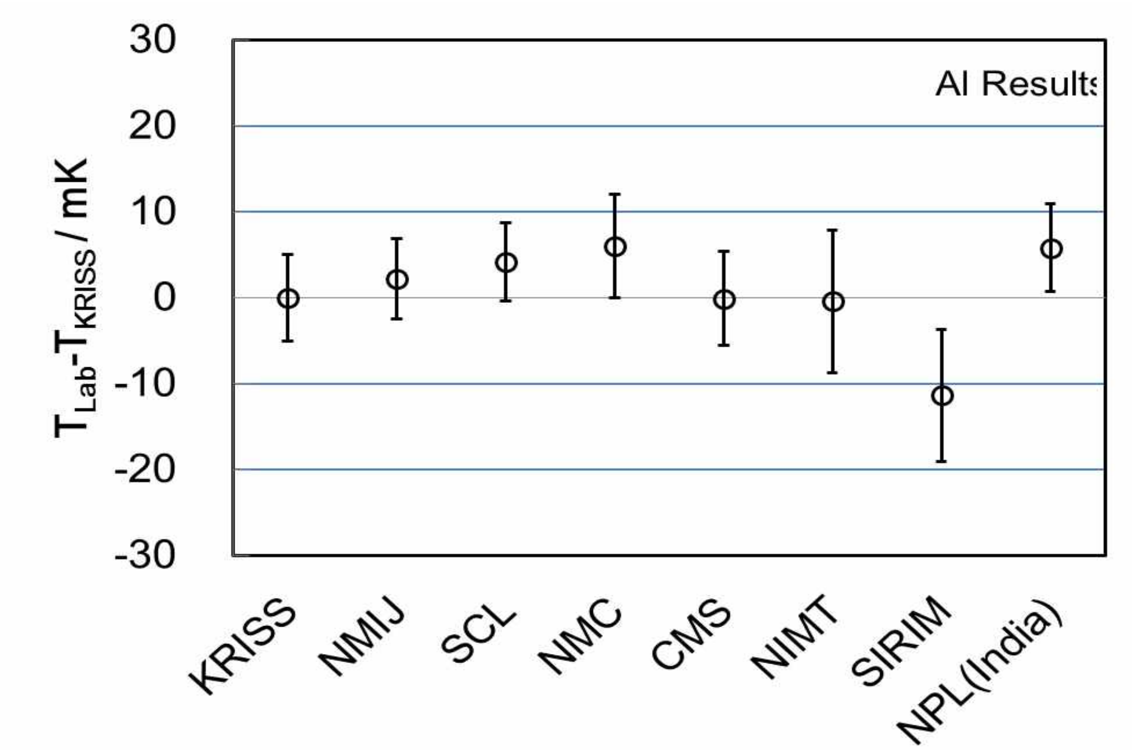


Fig. 4.1. Temperature difference at Al freezing-point between the participants and KRISS.

4.2. Linkage between APMP.T-K4 and CCT-K4

NMIJ and KRISS are two laboratories that participated in the CCT-K4 and APMP.T-K4. The APMP.T-K4 was linked to CCT-K4 via NMIJ and via KRISS consistently. In APMP.T-K4 KRISS used the Al(reference) cell participating in CCT K4. The Al(reference) cell used only to calibrate the working Al cell for calibration and maintained at maintenance box. At NMIJ Aluminium cell prepared by NMIJ for participating in CCT K4 was NRLM Al97-1. The value of this cell has been transferred to a working standard, Al No. 102, through an extensive cell comparison, including more than 15 repeated comparisons. Cell Al No. 102 was the one that was used in APMP. T-K4. The simple average of the two links was used to deliver the results for each participant laboratory relative to the CCT-K4 KCRV.

4.2.1. APMP.T-K4 linked to CCT-K4 via NMIJ

The link via NMIJ is given by the following relation;

$$\Delta T(KCRV - KRISS)_{NMIJ} = \Delta T(NMIJ - KRISS)_{APMP} - \Delta T(NMIJ - KCRV)_{CCT} \quad (2)$$

where

$\Delta T(KCRV - KRISS)_{NMIJ}$ is the difference between KRISS and the CCT-K4 KCRV via the NMIJ link,

$\Delta T(NMIJ - KRISS)_{APMP}$ is the difference between NMIJ and KRISS in the APMP.T-K4,

$\Delta T(NMIJ - KRISS)_{CCT}$ is the difference between NMIJ and the KCRV in CCT-K4.

The total uncertainty, $U(KCRV\text{-}KRISS)_{NMIJ}$ is given by;

$$U^2(KCRV - KRISS)_{NMIJ} = U^2(KCRV) + U^2(NMIJ)_{CCT} + U^2(NMIJ - KRISS)_{APMP} \quad (3)$$

Table 4.3 lists the differences and the uncertainty of individual inputs to obtain $\Delta T(KCRV - KRISS)_{NMIJ}$ using NMIJ data.

Table 4.3. Differences of APMP.T-K4 to CCT-K4 via NMIJ results and their uncertainty at *k*=2.

Items	Data source	Al FP / mK
$\Delta T(NMIJ - KRISS)_{APMP}$	APMP.T-K4	2.20
$\Delta T(NMIJ - KCRV)_{CCT}$	CCT-K4	-1.79
$\Delta T(KCRV - KRISS)_{NMIJ}$	-	3.99
$U(KCRV)$	CCT-K4	0
$U(NMIJ)_{CCT}$	CCT-K4	1.58
$U(NMIJ - KRISS)_{APMP}$	APMP.T-K4	4.70
$U(KCRV - KRISS)_{NMIJ}$	-	4.96

4.2.2. APMP.T-K4 linked to CCT-K4 via KRISS

The link via KRISS is just the negative of the value determined in the CCT-K4;

$$\Delta T(KCRV - KRISS)_{KRISS} = -\Delta T(KRISS - KCRV)_{CCT} + \Delta T\left(KRISS_{CCT} - KRISS_{APMP}\right) \quad (4)$$

where

$\Delta T(KCRV - KRISS)_{KRISS}$ is the difference between KRISS and the CCT-K4 KCRV via the KRISS link,

$\Delta T(KRISS - KCRV)_{CCT}$ is the difference between KRISS and the KCRV in CCT-K4,

$\Delta T\left(KRISS_{CCT} - KRISS_{APMP}\right)$ is the difference of the KRISS reference between CCT-K4 and APMP.T-K4, which vanishes when the same FP cell used.

The total uncertainty, $U(KCRV - KRISS)_{KRISS}$ is given by;

$$U^2(KCRV - KRISS)_{KRISS} = U^2(KCRV) + U^2(KRISS)_{APMP} \quad (5)$$

Table 4.4 lists the differences and the uncertainty of individual inputs to obtain $\Delta T(KCRV - KRISS)_{KRISS}$ using KRISS data.

Table 4.4 Differences of APMP.T-K4 to CCT-K4 via KRISS results and their uncertainty at *k*=2.

Items	Data source	Al FP / mK
$\Delta T(KRISS - KCRV)_{CCT}$	CCT-K4	-2.26
$\Delta T(KRISS_{CCT} - KCRV_{APMP})$	-	0
$\Delta T(KCRV - KRISS)_{KRISS}$	-	2.26
$U(KCRV)$	CCT-K4	0
$U(KRISS)_{APMP}$	APMP.T-K4	3.60
$U(KCRV - KRISS)_{KRISS}$	-	3.60

4.2.3. APMP.T-K4 linked to CCT-K4 via NMIJ and KRISS

The link via NMIJ and KRISS was determined by the simple average of the values obtained in the section 4.2.1 and section 4.2.2.

$$\Delta T(KCRV - KRISS)_{NMIJ\,\&\,KRISS} = (1/2)[\Delta T(KCRV\text{-}KRISS)_{NMIJ} + \Delta T(KCRV - KRISS)_{KRISS}] \quad (6)$$

The uncertainty for the link is given by;

$$U^2(KCRV - KRISS)_{NMIJ\,\&KRISS} = (1/2)^2[U^2(KCRV - KRISS)_{NMIJ} + U^2(KCRV - KRISS)_{KRISS}] \quad (7)$$

Table 4.5 summarizes the results of each of this linking mechanism.

Table 4.5. Summary of link mechanisms between APMP.T-K4 and CCT-K4.

	Via NMIJ $\Delta T(KCRV - KRISS)_{NMIJ}$		Via KRISS $\Delta T(KCRV - KRISS)_{KRISS}$		Via NMIJ & KRISS $\Delta T(KCRV - KRISS)_{NMIJ\&KRISS}$	
/mK	ΔT	$U(k=2)$	ΔT	$U(k=2)$	ΔT	$U(k=2)$
Al	3.99	4.96	2.26	3.60	3.13	3.06

4.2.4. Participant laboratory linked to CCT-K4 KCRV

The temperature difference of each APMP.T-K4 participant to that of the CCT-K4 KCRV is calculated as;

$$\Delta T(Lab_{APMP} - KCRV) = \Delta T(Lab_{APMP} - KRISS_{APMP}) - \Delta T(KCRV - KRISS)_{NMIJ\&KRISS} \qquad (8)$$

The uncertainty for the link is given by;

$$U^2(Lab_{APMP} - KCRV) = U^2(Lab_{APMP} - KRISS_{APMP}) + U^2(KCRV - KRISS)_{NMIJ\&KRISS} \qquad (9)$$

The difference between APMP.T-K4 participants and CCT-K4 KCRV are summarized in Table 4.6. The uncertainty U is given for k = 2.

Table 4.6. Differences between the APMP.T-K4 participants and the CCT-K4 KCRV. The uncertainty includes the reported laboratory uncertainty and that of the link from APMP.T-K4 to CCT-K4 KCRV.

Lab	$\Delta T(Lab_{APMP}$ - $KCRV)$ / mK	$U(Lab_{APMP}$ - $KCRV)$ / mK
KRISS	-3.13	5.94
NMIJ	-0.92	5.61
SCL	1.05	5.49
NMC	2.92	6.75
CMS	-3.19	6.26
NIMT	-3.56	8.83
SIRIM	-14.46	8.28
NPL(India)	2.70	5.96

5. Stability of the transfer HTSPRTs

HTSPRTs (BTC type) showed good stability within 3 mK before the comparison started. During the comparison measurement, HTSPRTs showed reasonable drift at water triple point before and after Al freezing-points. Appendix C is summary of HTSPRTs drift at water triple-point before and after Al freezing-points measurements. The drift values of HTSPRTs were evaluated from the differences between maximum and minimum measurement values at the water triple-points during the comparison between the participating NMIs and KRISS, and we treated these values as rectangular distribution. The drift at the water triple-point propagated at Al freezing-point temperatures. So, the uncertainty propagations of the resistance changes of HTSPRTs at water triple-point were calculated by the reference function of the ITS-90. Calculated propagation uncertainties were summarized in Table 5.1 and Table 5.2. It was well known that the instability of HTSPRTs is caused by mechanical strain and contamination of the Pt sensor through the silica glass protection tube. It is supposed that the drift at water triple-point in Al comparison measurements mainly came from the mechanical shock during the transportation. The uncertainty factor obtained from the propagation of the drift at water triple-point was combined to the uncertainty given in Table 4.6 and Table 5.1. Temperature differences of participants referring to the CCT-K4 reference value at Al freezing-point were shown in Table 5.2. and Fig. 5.1. It is concluded that Al freezing-point of participants was coincident within 4 mK except SIRIM value. Al freezing-point of SIRIM was deviated 14.46 mK from the CCT-K4 KCRV. SIRIM participated in the key comparison first time and did not have much experiences for the key comparison activity. SIRIM shall continue to carry out the bilateral comparison for Al freezing-point with the linked laboratory in near future. Although the final temperature differences and uncertainties were agreed with by almost all of the participants, CMS did not fully agree but accepted the uncertainty estimation method of including the stability of the transfer HTSPRTs. The opinion of CMS is provided in Appendix H.

Table 5.1. Resistance change of the HTSPRTs at water triple point and propagated uncertainty at Al freezing-point.

HTSPRTs	Resistance change / mK	Propagated uncertainty / mK	NMIs
N329	0.70	2.94	KRISS,NMIJ
N329	0.69	2.90	SCL
N358	1.22	5.13	NMC
N358	2.83	11.89	CMS
N329	1.80	7.56	NIMT
N334	1.26	5.29	SIRIM
N329	0.51	2.14	NPL(India)

Table 5.2. Temperature differences from the CCT-K4 KCRV at Al freezing-point and the uncertainties including the instability of the HTSPRTs.

Participant Lab	$\Delta T(Lab_{APMP}$ - $KCRV)$ / mK	$U(Lab_{APMP}$ - $KCRV)$ / mK
KRISS	-3.13	6.39
NMIJ	-0.92	6.09
SCL	1.05	5.97
NMC	2.92	7.91
CMS	-3.19	11.42
NIMT	-3.56	10.72
SIRIM	-14.46	9.31
NPL(India)	2.70	6.20

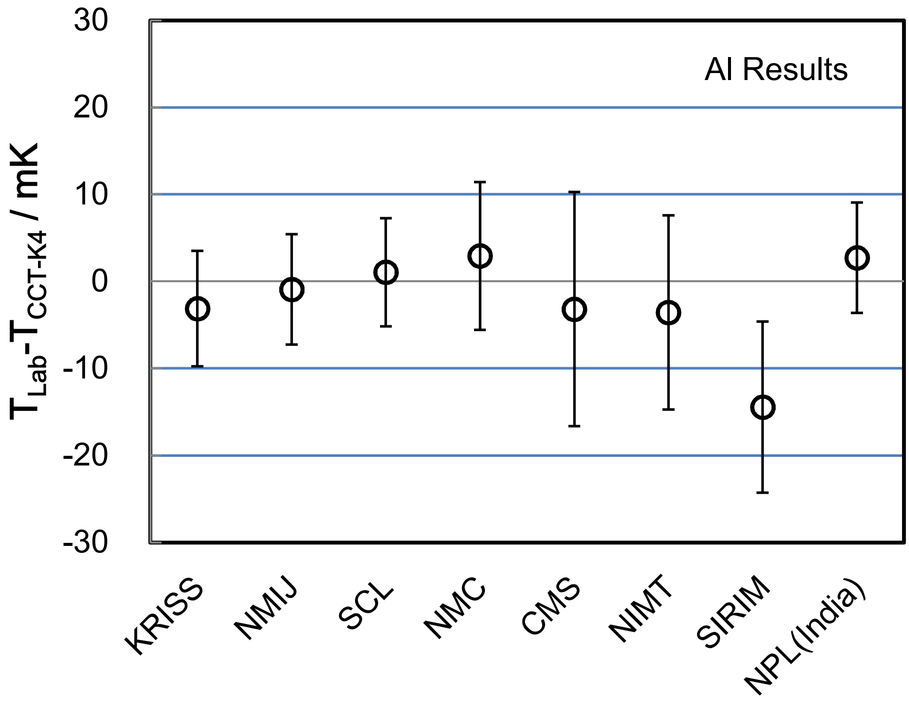


Fig. 5.1. Temperature differences refer to the CCT-K4 reference value at Al freezing-point and the expanded uncertainties (k = 2).

6. Bilateral equivalence

The degree of equivalence was assessed based on the bilateral temperature differences between the participating laboratories. The bilateral temperature difference and the corresponding uncertainties were calculated by the following equations.

$$T_{Lab,1} - T_{Lab,2} = \left(T_{Lab,1} - T_{KRISS}\right) - \left(T_{Lab,2} - T_{KRISS}\right) \quad (10)$$

$$U\left(T_{Lab,1}-T_{Lab,2}\right)=\sqrt{U^2\left(T_{Lab,1}\right)+U^2\left(T_{Lab,2}\right)} \quad (11)$$

where $T_{Lab1,i}-T_{KRISS}$ is the bilateral temperature difference between the participant and KRISS, $U\left(T_{Lab,1}\right)$ is the expanded uncertainty (k=2) of the participating laboratory. For this comparison, the bilateral temperature difference between the participants and the corresponding uncertainties are given in Table. 6.1., above the diagonal, where the uncertainties in italics. The quantifying equivalence factors $QDE_{Lab1,\,Lab2}$ as defined in Eq. (12) are given below the diagonal.

$$QDE_{Lab1,Lab2}=\left|T_{Lab1}-T_{Lab2}\right|+\left\{1.645+0.3295\exp\left(\frac{-4.05\left|T_{Lab1}-T_{Lab2}\right|}{u\left(T_{Lab1}-T_{Lab2}\right)}\right)\right\}u\left(T_{Lab1}-T_{Lab2}\right) \quad (12)$$

Table 6.1. The bilateral temperature difference between the participants (in mK, above diagonal), their expanded uncertainty (k=2, in mK, above diagonal), and the QDE between the participants (in mK, below diagonal)

Lab2 → Lab1 ↓	KRISS	NMIJ	SCL	NMC	CMS	NMIT	SIRIM	NPL (India)
KRISS		-2.2 *4.70*	-4.18 *4.56*	-6.04 *7.03*	0.07 *5.46*	0.43 *8.28*	11.34 *7.69*	-5.83 *5.11*
NMIJ	6.37		-1.98 *4.12*	-3.84 *6.75*	2.27 *5.09*	2.63 *8.05*	13.54 *7.44*	-3.63 *4.72*
SCL	8.05	5.63		-1.86 *6.66*	4.25 *4.96*	4.61 *7.97*	15.52 *7.35*	-1.65 *4.58*
NMC	12.03	9.74	7.96		6.11 *6.33*	6.47 *8.88*	17.38 *8.34*	0.21 *6.03*
CMS	5.44	6.80	8.47	11.46		0.36 *8.51*	11.27 *7.94*	-5.9 *5.48*
NMIT	8.47	9.94	11.57	14.11	8.65		10.91 *10.09*	-6.26 *8.30*
SIRIM	17.73	19.69	21.58	24.26	17.87	19.40		-17.17 *7.71*
NPL (India)	10.12	7.68	5.78	6.10	10.51	13.38	23.53	

7. References

[1] H.G. Nubbemeyer, J. Fischer: Final report on key comparison CCT-K4 of local realizations of aluminum and silver freezing point temperatures, Metrologia, 2002, **79,** Tech. Suppl. 03001

[2] M.K. Nguyen and M.J. Ballico: APMP-K3: Key comparison of realizations of the ITS-90 over the range -38.8344 ℃ to 419.527 ℃ using an SPRT, Metrologia, 2007, **44,** Tech. Suppl. 03006

[3] D. Heyer, U. Noatsch and E. Tegeler: Report to the CCT on key comparison EUROMET.T-K4, Comparison of the realizations of the ITS-90 at the freezing point s of Al(660.323 ℃) and Ag(961.78 ℃), Metrologia, 2008, **45,** Tech. Suppl. 03003

Appendix

Appendix A: Protocol of APMP.T-K4
Appendix B: Measurement data from all participants of APMP.T-K4
Appendix C: Resistance change of the transfer HTSPRTs at the triple point of water
Appendix D: Uncertainty of measurements
Appendix E: Immersion curves
Appendix F: Freezing curves of Al freezing-point cells for participating laboratories.
Appendix G: Instrumental details
Appendix H: Opinion of CMS

Appendix A: Protocol of APMP.T-K4

Protocol for APMP.T-K4

Comparison of Realizations of Aluminum and Silver Freezing-Point Temperatures

Kee Sool Gam
Korea Research Institute of Standards and Science
P.O.Box 102 Yuseong, Daejeon 305-600, Republic of Korea

INTRODUCTION

The APMP regional comparison was initiated by APMP TCT meeting and workshop during its meeting in November 5, 2001. There KRISS was invited to be the pilot laboratory of APMP-T-K4. The procedures and instructions, which are given below, should be followed by the APMP participants in comparing the realizations of aluminum (660.323 ℃) and silver (961.78 ℃) freezing-point temperatures. Each laboratory should follow its common practice in realizing the aluminum and silver freezing points. Four high temperature PRTs (HTPRTs) whose nominal resistance is around 0.59 Ω at the triple point of water, will be used as the transfer thermometer. The instructions follow the Protocols given in the Guidelines for CIPM key comparisons, Appendix F to the MRA.

LIST of PARCITIPANTS

<u>Participant list including affiliation, name and e-mail address of the contact person should appear here.</u>

KRISS (Korea)	Kee Sool Gam, Temperature-Humidity Group, ksgam@kriss.re.kr
NMIJ (Japan)	Masaru Arai, Thermometry Section, masaru-arai@aist.go.jp
SCL (Hong Kong)	C.M.Tsui, Standard and Calibration Laboratory, cmtsui@itc.gov.hk
SPRING (Singapore)	Kho Hao Yuan, Temperature and Optical Radiation Metrology Department, khohy@spring.gov.sg
CMS (Taiwan)	Shu-Fei Tsai,Temperature, Humidity & Chemical Laboratory, Shu-Fei_Tsai@itri.org.tw
NIMT (Thailand)	Uthai Norranim, Thermometry Metrology Department, uthai@nimt.or.th
SIRIM (Malaysia)	Hafidzah Othman, National Metrology Center, hafidzah_othman@sirim.my
NPL (India)	Jagdish K. Gupta, Physico-Mechanical Standards Division, jkgupta@mail.nplindia.ernet.in

APPARATUS

1. All participating laboratory must have aluminum freezing-point cell and silver freezing-point cell whose thermometer wells have inner diameter larger than 8 mm. The freezing-point cells have to be long enough to achieve a reasonable hydrostatic head.

2. All participating laboratory should prepare one and to be safer side more than one monitoring HTPRT, which will be used in the realization of the freezing points of aluminum and silver. The pilot laboratory prepares four pieces of HTPRT as transfer thermometer whose nominal resistance at the triple point of water is about 0.59 Ω. These HTPRTs should be stable during the realization of the freezing points of aluminum and silver and the suggested short-time stability before and after the freezing-point realization, approximately within 0.5 mK at the TPW.

SCHEDULE

The following schedule applies for all APMP participants being in charge to transport the transfer HTPRTs to the next participating laboratory. The transfer HTPRT must be hand-carried in their case to next participating laboratory, accompanied by its ATA Carnet. Each laboratory should complete the measurement within approximately one month. KRISS hand-carries the transfer HTPRTs to the participating laboratory, which execute the comparison experiment first in the following running schedule.

<u>Loop A (HTPRTs: BTC N335 for Ag, BTC N329 for Al)</u>

1st RUN

KRISS to NMIJ,	November 27, 2002 [1)]
NMIJ to SCL,	approximately 1 month after approval [2)]
SCL to KRISS,	approximately 2 months after approval

2nd RUN

KRISS to NMC,	approximately 3 months after approval
NMC to CMS,	approximately 4 months after approval
CMS to KRISS,	approximately 5 months after approval

<u>Loop B (HTPRTs: BTC N330 for Ag, BTC N334 for Al)</u>

1st RUN

KRISS to SIRIM,	approximately 1 month after approval
SIRIM to KRISS	approximately 2 months after approval

2nd RUN

KRISS to NPL(India),	approximately 3 months after approval
NPL(India) to NIMT,	approximately 4 months after approval
NIMT to KRISS,	approximately 5 months after approval

[1] HTPRTs (BTC N335 for Ag, BTC N329 for Al) used for Loop A has already been transported to NMIJ, when Dr. Yamazawa (NMIJ/AIST) visited KRISS to have a discussion with Dr. Gam (KRISS) concerning this Protocol.

[2] The schedule will be specified after the approval of the Protocol by CCT WG 7. All participating laboratories should submit the measurement report to KRISS by approximately 7 months after approval. The key comparison report (Draft A) will be completed until approximately 9 months after approval. It will be distributed and reviewed by all participants, upon which the Draft B will be prepared until approximately 11 months after approval. The final report will be completed by approximately a year after approval, and submitted to APMP.

DETAILED INSTRUCTIONS FOR PARTICIPATING LABORATORIES

Remarks

Each participant should follow the instructions given in (A) (Receiving the Thermometers) as soon as possible after receiving the thermometers. After this, calibrate the specified thermometers for (B) (Al Freezing Point Measurement) and for (C) (Ag Freezing Point Measurement), respectively. The sequence of (B) and (C) is mandatory. After the calibrations, pack securely the thermometers and transport them to the next participant. If any discussion upon this Protocol and the measurements during this international comparison is necessary, the participant should share the information through e-mail to all participants.

(A) Receiving the Thermometers

Procedures

1. Upon receiving the transfer HTPRTs, the host laboratory must inspect the transfer HTPRTs for damage. The host laboratory must report the condition of the HTPRT to the pilot laboratory. If there is damage, the pilot laboratory will give instructions on how to proceed.

2. If no damage is reported to the pilot laboratory, the host must measure the resistance of the transfer HTPRTs using two measuring currents (in order to determine the zero-power value) in a triple point of water (TPW) cell. The ice mantle of the TPW cell must have been prepared and aged according to the instructions in the CCT/96-8 report.

3. After completing measurements according to step 2, the 0 mA resistance value of the transfer HTPRT at the TPW (R_{TPW1}) must be communicated to the pilot laboratory before proceeding further measurements. Based on this information, the pilot laboratory will advice the host laboratory on the next step to be taken.

(B) Al Freezing Point Measurement

Remarks

Participants of Loop A and of Loop B should use HTPRT BTC-N329 and BTC-N334, respectively for measurements at the Al freezing point. Firstly, the HTPRT should be annealed according to the procedures given in the following paragraphs. If the specified criteria are fulfilled, calibrate the HTPRT using three plateaus of the aluminum freezing point. Measure the immersion characteristics using the transfer HTPRT during one of the three plateaus or in an additional fourth plateau.

Procedures

1. Anneal the transfer HTPRT before the measurement of the freezing-point temperatures of aluminum. Insert slowly the transfer HTPRT into an annealing furnace which is preheated to 500 ℃, and then increase the temperature of the annealing furnace to 675 ℃ over approximately 1 hour. Maintain the temperature at that point for 30 min, then reduce it to 500 ℃ over approximately 4 hrs. When the temperature has reached 500 ℃, remove slowly the HTPRT from the furnace directly to the room environment.

2. After the HTPRT has cooled down to room temperature, measure its resistance at the TPW (R_{TPW2}).

3. If the change of the resistance of the HTPRT at the TPW before and after annealing (R_{TPW2} - R_{TPW1}), as measured according to steps 2 and 3, is equivalent to 0.5 mK or smaller, proceed to step 4, otherwise repeat step 1 and 2.

4. After the annealing and the measurements at the TPW are completed, calibrate the HTPRT at the aluminum freezing point. It is recommended that the freezing point of aluminum is realized according to the instructions cited in the CCT/96-8 report. However, each laboratory should follow its common practice if any procedure may conflict. The monitor HTPRT should be used in the realization of the freezing point of aluminum. The transfer HTPRT must be preheated in an annealing furnace which is preheated to 500 ℃, and then the temperature is increased up to 675 ℃ over approximately 1 hour. The transfer HTPRT should be removed then from the annealing furnace, and inserted into the well of the aluminum freezing point cell and calibrated in the stable plateau of the freezing curve of aluminum.

5. After calibration measurements at two currents at the freezing point of aluminum, measure the immersion characteristics using the transfer HTPRT whenever the participating laboratory decide to measure it during this plateau. The method for measuring the immersion characteristics should follow the common procedure practiced by each participating laboratory. If the participating laboratory does not decide to measure the immersion characteristics during this plateau, proceed to step 6.

6. The HTPRT should be removed and inserted into the annealing furnace whose temperature is maintained at 675 ℃, annealed for 30 minutes and then cooled down to 500 ℃ within approximately 4 hours.

7. When the temperature of the annealing furnace (along with the HTPRT) has been dropped to 500 ℃, remove slowly the HTPRT from the furnace directly to the room environment. After the HTPRT has cooled down to room temperature, measure its resistance at the TPW (R_{TPW}).

8. Calibrate the thermometer three times by repeating steps 4 to 7.

9. If the participant decides to conduct the immersion characteristics measurement in an additional plateau, then repeat step 4, 5, 6 and 7.

(C) Ag Freezing Point Measurement

Remarks

Participants of Loop A and of Loop B should use HTPRT BTC-N335 and BTC-N330, respectively for measurements at the silver freezing point. Firstly, the HTPRT should be annealed according to the procedures given in the following paragraphs. If the specified criteria are fulfilled, calibrate the HTPRT using three plateaus of the silver freezing point. Measure the immersion characteristics using the transfer HTPRT during one of the three plateaus or in additional fourth plateau.

Procedures

1. Anneal the transfer HTPRT before the measurement of the freezing-point temperatures of silver. Insert slowly the transfer HTPRT into an annealing furnace which is preheated to 500 ℃, and then increase the temperature of the annealing furnace to 975 ℃ over approximately 2 hours. Maintain the temperature at that point for 30 minutes, then reduce it to 500 ℃ over approximately 8 hours. When the temperature has reached 500 ℃, remove slowly the HTPRT from the furnace directly to the room environment.

2. After the transfer HTPRT has cooled down to room temperature, measure its resistance at the TPW (R_{TPW2}).

3. If the change of the resistance of the transfer HTPRT at the TPW before and after annealing (R_{TPW2} - R_{TPW1}), as measured according to steps 2 and 3, is equivalent to 0.5 mK or smaller, proceed to step 4, otherwise repeat step 1 and 2.

4. After the annealing and the measurements at the TPW are completed, calibrate the transfer HTPRT at the silver freezing point. Measurement method is identical to the case of the freezing point of aluminum. The monitor HTPRT should be used in the realization of the freezing point of silver. The transfer HTPRT must be preheated in an annealing furnace which is preheated to 500 ℃, and then the temperature is increased up to 975 ℃ over approximately 2 hour. The transfer HTPRT should be removed then from the annealing furnace, and inserted into the well of the silver freezing point cell and calibrated in the stable plateau of the freezing curve of silver.

5. After calibration measurements at two currents at the freezing point of silver, measure the immersion characteristics using the transfer HTPRT whenever the participating laboratory decide to measure it during this plateau. The method for measuring the immersion characteristics should follow the common procedure practiced by each participating laboratory. If the participating laboratory does not decide to measure the immersion characteristics during this plateau, proceed to step 6.

6. The transfer HTPRT should be removed and inserted into the annealing furnace whose temperature is maintained at 975 ℃, annealed for 30 minutes and then cooled down to 500 ℃ within approximately 8 hours.

7. When the temperature of the annealing furnace (along with the transfer HTPRT) has been dropped to 500 ℃, remove slowly the HTPRT from the furnace directly to the room environment. After the transfer HTPRT has cooled down to room temperature, measure its resistance at the TPW (R_{TPW}).

8. Calibrate the thermometer three times by repeating steps 4 to 7.

9. If the participant decides to conduct the immersion characteristics measurement in an additional plateau, then repeat step 4, 5, 6 and 7.

REPORT OF RESULTS

The participating laboratories must send the followings to the pilot laboratory by the specified schedule.

1. Resistance values of the transfer HTPRT in its specified freezing-point cells [= $R(T)_{\text{in the freezing-point cell}}$] and in the TPW cell [$R$(273.16 K)], and the related resistance ratios [= $R(T)_{\text{in the freezing-point cell}}$ / R(273.16 K)] obtained after the measurement of aluminum and silver freezing point.
   The participating laboratory report to the pilot laboratory the non-corrected $R(T)/R_{\text{std}}$ data at two currents for deriving 0 mA value and the corrected values for hydrostatic head, gas pressure, and self-heating.

2. The immersion curves obtained using the transfer HTPRT for each freezing point cell in the present comparison.

3. Freezing curves of aluminum and silver cells measured by the monitor HTPRT.

4. Uncertainty analysis according to the "Guide to the Expression of Uncertainty in Measurement", ISO 1993, ISBN 92-67-10188-9. The uncertainty analysis must include the following terms and other items that the participating laboratory wants to include.

   <u>Type A</u>
   - Freeze-to-freeze repeatability with the degree of freedom

   <u>Type B</u>
   - Chemical impurities of Al and Ag cell
   - Hydrostatic-head errors
   - Bridge measurement errors
     effects of changes in reference resistors
     non-linearity of bridge
     quadrature effects in ac measurements
   - Uncertainty propagate from the TPW
   - SPRT self heating errors
   - Heat flux-immersion errors
   - Errors in gas pressure in the Al and Ag cell
   - Errors in the choice of freezing point value from plateau of the freezing curve

- High-temperature insulation degradation of the transfer HTPRT

5. Details of instrumentation and experimental techniques of the participating laboratory must be reported to the pilot laboratory

Details of instrumentation

- Bridge
  Manufacturer and model
  Frequency
  Bandwidth
  Gain
  Quad gain
  Normal measurement currents
  Self-heating currents

- Reference resistor
  Manufacturer and model
  How maintained
  Temperature control stability of maintaining bath
  Temperature coefficient of reference resistor

- Freezing point cells
  Manufacturer and model
  Type of cell (open/closed)
  Length and diameter of cell (cm)
  Crucible materials
  Source of crucible
  Sample source
  Purity of sample
  Immersion depth of HTPRT (mm)
  Thermometer well ID (mm)
  Pressure in cell (kPa)

- Furnace details
  Manufacturer and model
  DC or AC heat power
  Furnace control type
  How many zones in furnace
  Uniformity in furnace with cell
  Temperature stability over 16 h (mK)

Details of experimental techniques

- Length of time that the sample is heated above the melting point before nucleating freeze
- Method of nucleation freezes
- Duration of freeze(h)

PROCEDURES FOR THE PILOT LABORATORY

1. Before starting and after finishing each Run of each Loop, the pilot laboratory performs necessary measurements to obtain the *W* values of the transfer HTPRTs at the freezing point of aluminum or silver with instructions given in the Protocol. The obtained six data sets will be reported in the Draft.
2. The pilot laboratory receives the communications from each participant as specified in the Protocol. If necessary the pilot laboratory could give some instructions to the participants.
3. The pilot laboratory compiles the data from each participant to construct the report. The uncertainty of the transfer HTPRT due to possible drift during the transport is calculated using the data of the starting and the finishing of each Run.
4. The pilot laboratory chairs and records the discussion during this international comparison.

Appendix B: Measurement data from all participants of APMP.T-K4
Appendix B-1. Data from KRISS
Measurement Results for Al freezing-point

HTSPRTs	TPW values	W(Al)	U_{95} / mK	Compared NMIs
N329	0.604 621 49 0.604 623 61	3.375 679 16 3.375 679 60	3.60 3.60	NMIJ SCL
N358	0.604 126 91 0.604 127 77	3.375 759 02 3.375 771 22	3.60 3.60	NMC CMS
N334	0.600 590 66	3.375 457 57	3.60	SIRIM
N329	0.603 623 71 0.603 625 89	3.375 677 27 3.375 689 59	3.60 3.60	NPL(India) NIMT

Appendix B-2. Data from NMIJ
Measurement Results for Aluminum Point

1. Measurements at triple point of water

Table 1.1 Measurements before 1st Al plateau

Current, i, mA	Reading, $R(T)/R_{std}$
10	0.060463009
10√2	0.060463720

$R(T)_{corrected}$ at 0 mA = 0.604624036 Ω

Table 1.2 Measurements between 1st and 2nd Al plateaus

Current, i, mA	Reading, $R(T)/R_{std}$
10	0.060463031
10√2	0.060463779

$R(T)_{corrected}$ at 0 mA = 0.604623891 Ω

Table 1.3 Measurements between 2nd and 3rd Al plateaus

Current, i, mA	Reading, $R(T)/R_{std}$
10	0.060463006
10√2	0.060463715

$R(T)_{corrected}$ at 0 mA = 0.604624031 Ω

Table 1.4 Measurements after 3rd Al plateaus

Current, i, mA	Reading, $R(T)/R_{std}$
10	0.060463004
10√2	0.060463716

$R(T)_{corrected}$ at 0 mA = 0.604623981 Ω

2. Measurements at freezing point of aluminum

Table 2.1 First aluminum measurements

Current, i, mA	Reading, $R(T)/R_{std}$
10	0.204102764
10√2	0.204103420

$R(T)_{corrected}$ at 0 mA = 2.041020665 Ω

Table 2.2 Second aluminum measurements

Current, *i*, mA	Reading, $R(T)/R_{std}$
10	0.204102777
10√2	0.204103422

$R(T)_{corrected}$ at 0 mA = 2.04102089 Ω

Table 2.3 Third aluminum measurements

Current, *i*, mA	Reading, $R(T)/R_{std}$
10	0.204102772
10√2	0.204103418

$R(T)_{corrected}$ at 0 mA = 2.04102084 Ω

Appendix B-3. Data from SCL

SCL Al

Fixed point	Rt/Rs 10 mA	Rt/Rs 10 SQRT 2 mA	Corrected Rt	W(Al)
TPW	-	-	-	
Al	2.0410268	2.0410328	2.0410224	3.375692042
TPW	0.6046306	0.6046382	0.6046234	
Al	2.0410296	2.0410356	2.0410253	3.375693489
TPW	0.6046312	0.6046389	0.6046240	
Al	2.0410289	2.0410348	2.0410246	3.375693448
TPW	0.604631	0.6046386	0.6046238	
Mean				3.375693
S.D.				0.000009

Appendix B-4. Data from NMC

Data summary of the APMP K4 key comparison for Aluminum freezing point measured at NMC

Hydrostatic, Pressure effect and self−heating corrected

Date	BTCN358	Resistance /ohm	W
2005−04−05	Initial TPW	0.60413198	
2005−04−12	Al point (freeze)	2.03941412	
2005−04−13	TPW	0.60413173	3.37577718
2005−04−14	Al point (freeze)	2.03941378	
2005−04−15	TPW	0.60413115	3.37577989
2005−04−18	Al point (freeze)	2.03941314	
2005−04−20	TPW	0.60413128	3.37577811
		Mean :	3.37577839

Appendix B-5. Data from CMS

Table 1. Data summary of the APMP TK4 carried out at CMS.

HTPRT(BTC N358)						
	$R(T)/R_{std}$	$R(T)/R_{std}$	Hydrostatic Head effect corrected	Hydrostatic Head effect corrected	Hydrostatic Head effect corrected	Remark
Date	**R(TPW) at 0 mA**	**R(Al) at 0 mA**	**R(TPW) at 0 mA**	**R(Al) at 0 mA**	**W(Al) at 0 mA**	
2005-12-12		0.203944840		2.039364111	3.375769624	
2005-12-13	0.060414271		0.604118276			
2005-12-13		0.203944923		2.039364945	3.375771445	
2005-12-14	0.060414263		0.604118194			
2005-12-14		0.203944675		2.039362455	3.375771961	
2005-12-15	0.060414180		0.604117364			
2005-12-17	0.060414159		0.604117147			10 Ohm Standard resistor
	0.604081420		0.604115191			1 Ohm Standard resistor
					3.375771010	Mean
					0.383076218	Standard deviation of the mean (mK)
					-0.378333197	Stability (mK)

Appendix B-6. Data from SIRIM

HPRT **N334**

Date	FP	Resistance (ohm)	Stdev	Remark	W	W average	W ref	D W	mK
10-Jan-04	Wtp	0.60059347	0.03	Initial					
12-Jan-04	Wtp	0.60059305	0.03	After annealing					
10-Feb-04	Al-1	2.02724781	2.70	1st realisation of Al	3.37541004				
14-Feb-04	Wtp	0.60059126	0.12	Wtp after Al-1					
14-Feb-04	Al-2	2.02725201	1.04	2nd realisation of Al	3.37542709				
15-Feb-04	Wtp	0.60059126	0.09	Wtp after Al-2					
16-Feb-04	Al-3	2.02725171	3.98	3rd realisation of Al	3.37542659	3.37542124	3.37600860	-0.00058736	**-0.21**
16-Feb-04	Wtp	0.60059066	0.10	Wtp after Al-3					

Appendix B-7. Data from NPL(India)

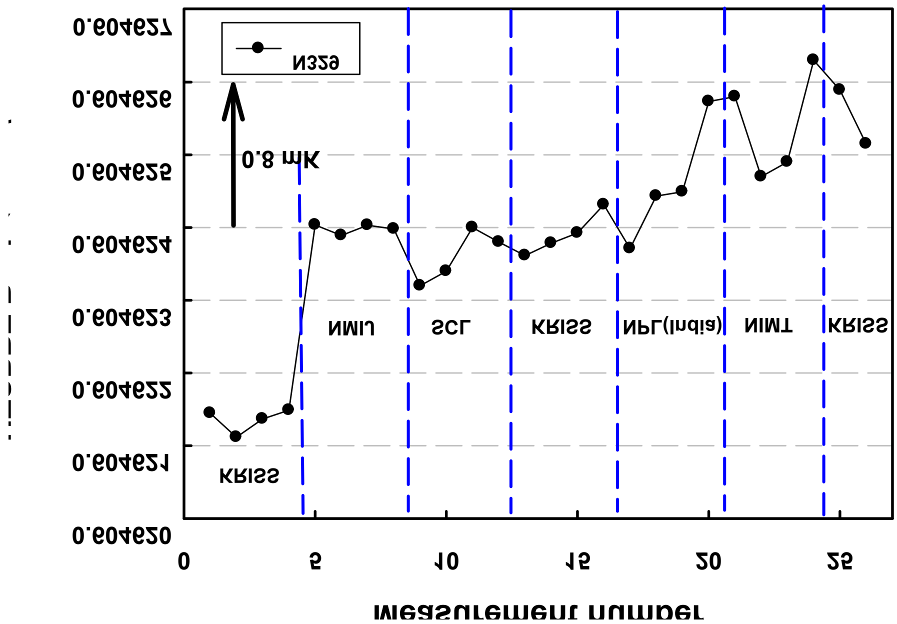
Table 1 Data Summery of APMP -TK4 Comparison Carried out at NPL(India)										
HTPRT (BTC N329) & NPL(I) Al Cell NO. AL-36										
Date	Fixed Point	Rt/Rs 10 mA	Rt/Rs 10 SQRT2mA	Self Heating	Rt/Rs at 0 mA	Rt/Rs * Value of Rs	H.H Correction	Corrected Rt	Ave. TPW	W(Fixed Point)
2005-06-04	TPW	0.060460255	0.060460992	7.37E-07	0.060459518	0.604623236	0.000000476	0.604623712		
2005-11-04	Al	0.204094189	0.204094848	6.59E-07	0.20409353	2.041030008	0.000000626	2.041029382	0.60462407	3.375699844
2005-12-04	TPW	0.060460355	0.06046112	7.65E-07	0.06045959	0.604623956	0.000000476	0.604624432		
2005-12-04	Al	0.204093842	0.204094504	6.63E-07	0.204093179	2.041026497	0.000000626	2.041025871	0.60462446	3.375691856
13/4/05	TPW	0.060460335	0.060461074	7.39E-07	0.060459596	0.604624016	0.000000476	0.604624492		
13/4/05	Al	0.204094314	0.204094972	6.58E-07	0.204093656	2.041031268	0.000000626	2.041030642	0.60462511	3.375696117
14/4/05	TPW	0.060460427	0.060461134	7.07E-07	0.06045972	0.604625256	0.000000476	0.604625732		

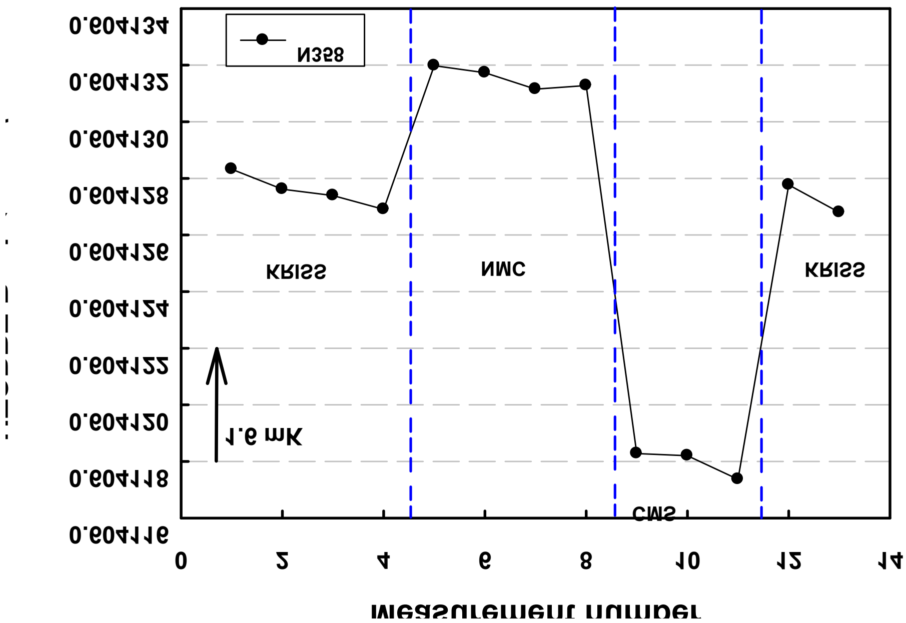
Appendix B-8. Data from NIMT

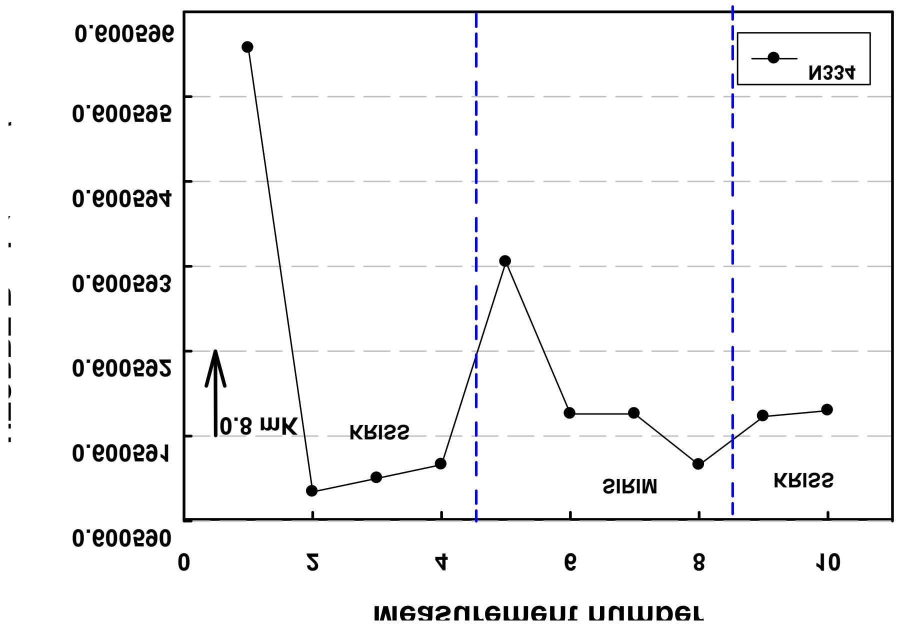
HTPRT Model: S/N: BTC N329 TL-xx-xxx

Step	Fixed Point	Temperature (oC)	Measured Value (Ω)		Measured Value (Ω)		correct self-heating	correct hydrostatic	average	correct
			Ratio(1 mA)	Ratio (1.414 mA)	R(1 mA)	R (1.414 mA)	R (0 mA)	Ratio (0 mA)	R(TPW)	Ratio (0 mA)
1	H_2O	0.01	0.6046335	0.6046405	0.60463	0.60464	0.60463	0.6046257	-	-
2	H_2O	0.01	0.6046339	0.6046410	0.60463	0.60464	0.60463	0.6046258	-	-
3	Al-1	660.323	2.0410386	2.0410457	2.04104	2.04105	2.04103	2.0410241	-	3.3756844
4	H_2O	0.01	0.6046330	0.6046402	0.60463	0.60464	0.60463	0.6046247	0.604625	-
5	Al-2	660.323	2.0410369	2.0410430	2.04104	2.04104	2.04103	2.0410250	-	3.3756885
6	H_2O	0.01	0.6046329	0.6046401	0.60463	0.60464	0.60463	0.6046249	0.604625	-
7	Al-3	660.323	2.0410431	2.0410498	2.04104	2.04105	2.04104	2.0410296	-	3.3756917
8	H_2O	0.01	0.6046344	0.6046416	0.60463	0.60464	0.60463	0.6046263	0.604626	-
9	H_2O	0.01	0.6046345	0.6046421	0.60463	0.60464	0.60463	0.6046259	-	-

Appendix C: Resistance change of the transfer HTSPRTs at the triple point of water






0.600596
0.600595
0.600594
0.600593
0.600592
0.600591
0.600590
0
2
4
6
8
10
Measurement number
N334
0.8 mK
KRISS
SIRIM
KRISS

Appendix D: Uncertainty of measurements

Appendix D-1. Uncertainty budget for measurement of Al freezing-point (KRISS)

Type A		
component	values	dimension
Freeze-to-freeze repeatability with degree of freedom:10	0.38	mK
Uncertainty due to the stability of transfer HTSPRT	0.55	mK
Type B		
Long-term drift of Al freezing-point cell	1.45	mK
Uncertainty due to the reproducibility of the plateau in aluminum cell	0.10	mK
Uncertainty due to the choice of freezing-point value from plateau in aluminum cell	0.10	mK
Uncertainty due to the uncertainty propagation of the fixed point in water triple point cell	0.43	mK
Uncertainty due to the chemical impurities	0.67	mK
Uncertainty due to the gas pressure correction	0.05	mK
Uncertainty due to the error in resistance measurements by the measuring bridge	0.03	mK
Uncertainty due to the heat flux or immersion profile in aluminum cell	0.08	mK
Uncertainty due to the hydrostatic-head correction in aluminum cell	0.02	mK
Uncertainty due to the self-heating correction in aluminum cell	0.11	mK
Uncertainty due to the insulation degradation of the transfer HTSPRT	0	mK

Combined uncertainty U = 1.80 mK
Expanded uncertainty U = 3.60 mK (k = 2)

Appendix D-2. Uncertainty budget for measurement of Al freezing-point(NMIJ)

Type A			
symbol	component	values	dimension
$u_{c1,2}$	Freeze-to-freeze repeatability with degree of freedom: 2	0.09	mK
$u_{c1.3}$	Uncertainty due to the stability of transfer HTSPRT	0.10	mK
Type B			
$u_{c2.1}$	Uncertainty due to the calibration against the national standard open cell	0.49	mK
$u_{c2.2}$	Uncertainty due to the repeatability of the plateau in aluminum cell	0.12	mK
$u_{c2.3}$	Uncertainty due to the choice of freezing-point value from plateau in aluminum cell	0.06	mK
$u_{c2.4}$	Uncertainty due to the repeatability of the fixed point in water triple point cell	0.17	mK
$u_{c2.5}$	Uncertainty due to the chemical impurities and isotopes of water	0.34	mK
$u_{c2.6}$	Uncertainty due to the gas pressure correction in water triple point cell	0.34	mK
$u_{c2.7}$	Uncertainty due to the error in resistance measurements by the measuring bridge	1.31	mK
$u_{c2.8}$	Uncertainty due to the heat flux or immersion profile in aluminum cell	0.03	mK
$u_{c2.9}$	Uncertainty due to the hydrostatic-head correction in aluminum cell	0.02	mK
$u_{c2.10}$	Uncertainty due to the self-heating correction in aluminum cell	0.02	mK
$u_{c2.11}$	Uncertainty propagated from the heat flux or immersion profile in water triple point cell	0.12	mK
$u_{c2.12}$	Uncertainty propagated from the hydrostatic-head correction in water triple point cell	0.04	mK
$u_{c2.13}$	Uncertainty propagated from the self-heating correction in water triple point cell	0.04	mK
$u_{c2.14}$	Uncertainty due to the insulation degradation of the transfer HTSPRT	0	mK

Combined uncertainty u_c = 1.51 mK
Expanded uncertainty U_c = 3.02 mK (k = 2)

Appendix D-3. Uncertainty budget for measurement of Al freezing-point(SCL)

Table 1
Uncertainty Analysis

Uncertainty Components	Type	Standard Uncertainty Ui	Sensitivity Coefficient Ci	CiUi	Degrees of Freedom Vi
Freeze-to-freeze repeatability	A	4.62E-07	312015	0.144 mK	2
Chemical impurities of the aluminium cell	B	1 ppm	0.674	0.674 mK	50
Hydrostatic-head error	B	0.046 mK	1.000	0.046 mK	50
Bridge measurement errors at the freezing-point of aluminium	B	0.12 ppm	1.053	0.126 mK	50
Bridge measurement errors at triple-point of water (TPW)	B	0.12 ppm	-1.053	-0.126 mK	50
Uncertainty propagated from TPW cell	B	0.15 mK	-4.201	-0.630 mK	50
HTPRT self-heating error	B	0.30 mK	1.000	0.300 mK	50
Heat flux-immersion error	B	0.40 mK	1.000	0.400 mK	50
Error in gas pressure inside the aluminium cell	B	0.61 mK	1.000	0.606 mK	50
Error in the choice of freezing point value from plateau of the freezing curve	B	0.50 mK	1.000	0.500 mK	50
High-temperature insulation degradation of the transfer HTPRT	B	0.50 mK	1.000	0.500 mK	50

Combined standard uncertainty (Uc)	1.42 mK
Effective degree of freedom(Veff)	307
Coverage factor (k)	1.97 (95 % level of confidence)
Expanded uncertainty (U = kUc)	2.80 mK
	or 0.00000897 (resistance ratio)

Appendix D-4. Uncertainty budget for measurement of Al freezing-point (NMC)

No.	Sources of uncertainty	Type	Uncertainty Value (mK)
1	Chemical impurities	B	2.00
2	Hydrostatic head of reference cell	B	0.01
3	Residual gas pressure in cell	B	0.02
4	Standard Resistor	B	0.24
5	Bridge measurement	B	0.42
6	Propagation from TPW	B	1.17
7	Self-heating error	B	0.03
8	Immersion error	B	0.23
9	Error in choice of FP from plateau	B	0.14
10	High temperature insulation degradation	B	0.29
11	Freeze to Freeze repeatability with degree of freedom 2	A	0.22
		Combined uncertainty	2.41 mK
		Expanded uncertainty (k = 2)	4.82 mK

Appendix D-5. Uncertainty budget for measurement of Al freezing-point (CMS)

symbol	component	values	dimension
Type A			
$u_{c1,2}$	Freeze-to-freeze repeatability with degree of freedom:2	0.38	mK
$u_{c1.3}$	Uncertainty due to the stability of transfer HTSPRT	0.47	mK
Type B			
$u_{c2.1}$	Uncertainty due to the reproducibility of the plateau in aluminum cell	0.73	mK
$u_{c2.2}$	Uncertainty due to the choice of freezing-point value from plateau in aluminum cell	0.87	mK
$u_{c2.3}$	Uncertainty due to the uncertainty propagation of the fixed point in water triple point cell	0.34	mK
$u_{c2.4}$	Uncertainty due to the chemical impurities	1.50	mK
$u_{c2.5}$	Uncertainty due to the gas pressure correction	0.02	mK
$u_{c2.6}$	Uncertainty due to the error in resistance measurements by the measuring bridge	0.08	mK
$u_{c2.7}$	Uncertainty due to the heat flux or immersion profile in aluminum cell	0.08	mK
$u_{c2.8}$	Uncertainty due to the hydrostatic-head correction in aluminum cell	0.01	mK
$u_{c2.9}$	Uncertainty due to the self-heating correction in aluminum cell	0.12	mK
$u_{c2.10}$	Uncertainty due to the high-temperature insulation degradation of the transfer HTPRT	0.03	mK
	Combined uncertainty u_c	2.05	mK
	Expanded uncertainty Uc (k = 2)	4.10	mK

Appendix D-6. Uncertainty budget for measurement of Al freezing-point (NIMT)

symbol	component	values	dimension
Type A			
	Freeze-to-freeze repeatability with degree of freedom:2	0.56	mK
	Uncertainty due to the stability of transfer HTSPRT	0.47	mK
Type B			
	Uncertainty due to the calibration	0.76	mK
	Uncertainty due to the reproducibility of the plateau in aluminium cell	0.73	mK
	Uncertainty due to the choice of freezing-point value from plateau in aluminium cell	0.12	mK
	Uncertainty due to the uncertainty propagation of the fixed point in water triple point cell	1.95	mK
	Uncertainty due to the chemical impurities	1.50	mK
	Uncertainty due to the gas pressure correction	2.49	mK
	Uncertainty due to the error in resistance measurements by the measuring bridge	0.08	mK
	Uncertainty due to the heat flux or immersion profile in aluminium cell	0.08	mK
	Uncertainty due to the hydrostatic-head correction in aluminium cell	0.01	mK
	Uncertainty due to the self-heating correction in aluminium cell	0.12	mK
	Uncertainty propagated from the heat flux or immersion profile in water triple point cell		mK
	Uncertainty propagated from the hydrostatic-head correction in water triple point cell		mK
	Uncertainty propagated from the self-heating correction in water triple point cell		mK
	Uncertainty due to the insulation degradation of the transfer HTSPRT	-	mK

Combined uncertainty u_c = 3.73 mK
Expanded uncertainty U_c = 7.46 mK (k = 2)

Appendix D-7. Uncertainty budget for measurement of Al freezing-point (SIRIM)

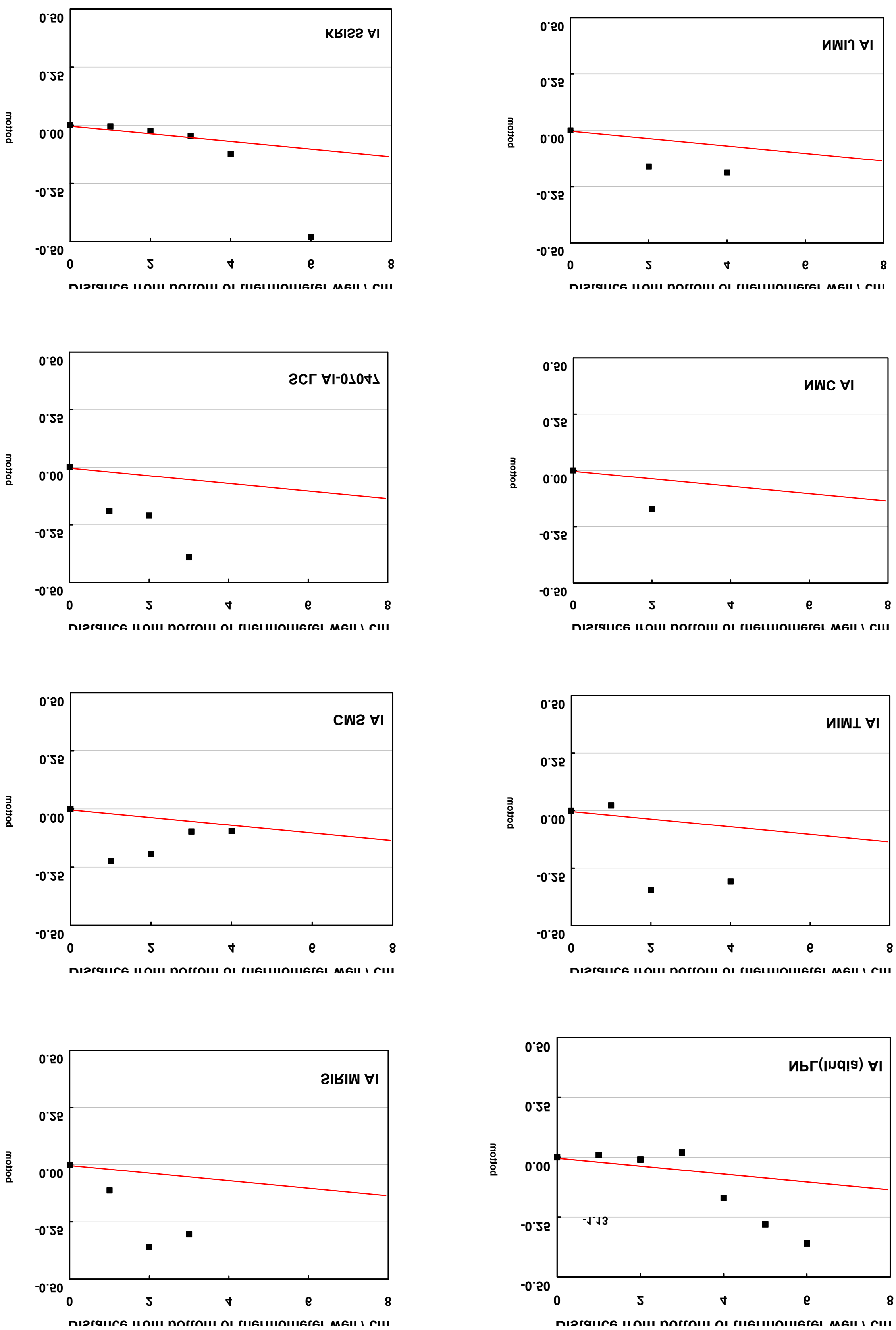
component	values	dimension
Type A		
Freeze-to-freeze repeatability with degree of freedom:3	0.98	mK
Uncertainty due to the stability of transfer HTSPRT	0.50	mK
Type B		
Long-term drift of Al freezing-point cell	-	mK
Uncertainty due to the reproducibility of the plateau in aluminum cell	-	mK
Uncertainty due to the choice of freezing-point value from plateau in aluminum cell	-	mK
Uncertainty due to the uncertainty propagation of the fixed point in water triple point cell	0.38	mK
Uncertainty due to the chemical impurities	1.00	mK
Uncertainty due to the gas pressure correction	0.14	mK
Uncertainty due to the error in resistance measurements by the measuring bridge	0.20	mK
Uncertainty due to the heat flux or immersion profile in aluminum cell	3.00	mK
Uncertainty due to the hydrostatic-head correction in aluminum cell	0.20	mK
Uncertainty due to the self-heating correction in aluminum cell	0.32	mK
Uncertainty due to the insulation degradation of the transfer HTSPRT	-	mK

Combined uncertainty U = 3.40 mK
Expanded uncertainty U = 6.80 mK (k = 2)

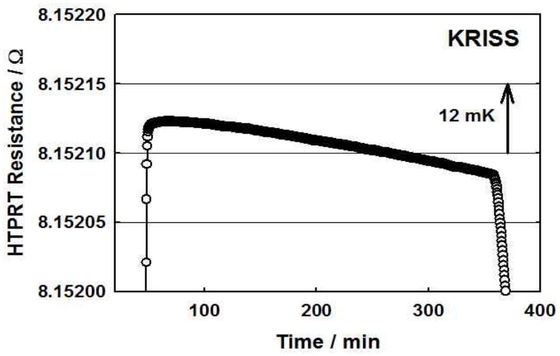
Appendix D-8. Uncertainty budget for measurement of Al freezing-point (NPL(India))

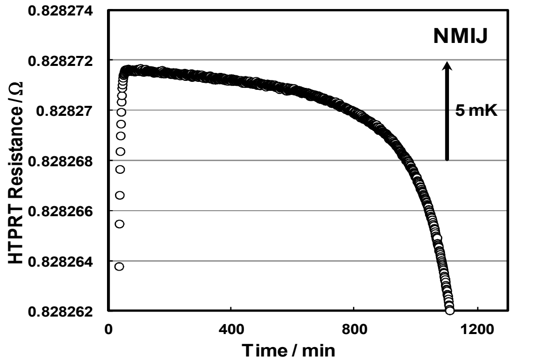
Fixed Points → **Uncertainty Components** ↓	**Al**
Type 'A' Unc.Comp. (mK)	
Freeze to freeze repeatability with degree of freedom :2	0.58
Type'B' Uncertainty Component (mK)	
1. Chemical Impurities (rectangular distribution)	0.87
2. Hydrostatic head error (rectangular distribution)	0.01
3. Error in gas pressure (5 Torr) (rectangular distribution)	0.03
4. Standard Resister (From Cal. Report) (normal distribution)	1.25
5. Effect of Bath on Std. Resistor(rectangular distribution)	0.17
6. Bridge measurement/ Linearity (rectangular distribution)	0.06
7. Quadrature effects in ac measurements(rectangular distribution)	0.01
8. Uncertainty propagation from TPW(rectangular distribution)	0.72
9 Self heating error(rectangular distribution)	0.12
10. Heat flux immersion error(rectangular distribution)	0.23
11. Choice of fixed point value(rectangular distribution)	0.17
Standard combined Uncertainty (mK)	1.82
Expanded Combined Uncertainty, *k*=2 (mK)	3.63

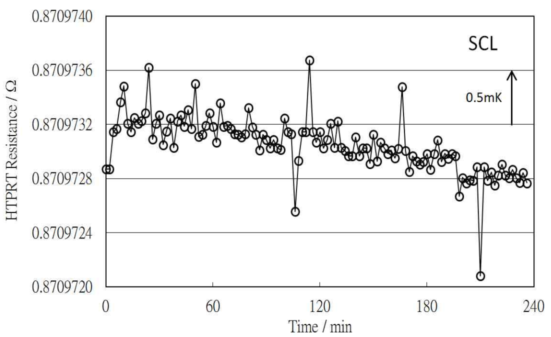
Appendix E: Immersion characteristics of Al freezing-point cells for participating laboratories.

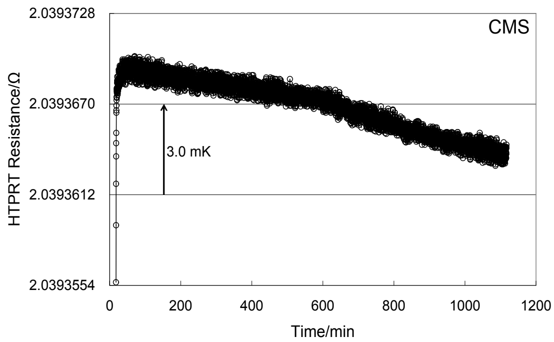


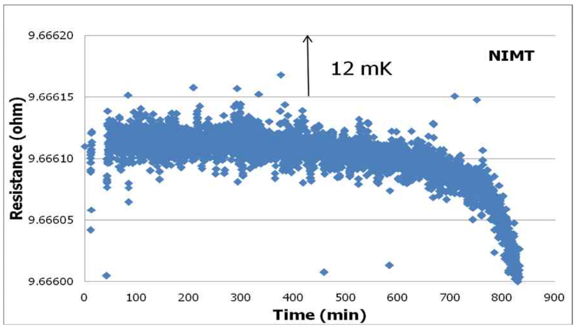
Appendix F: Freezing curves of Al freezing-point cells for participating laboratories.

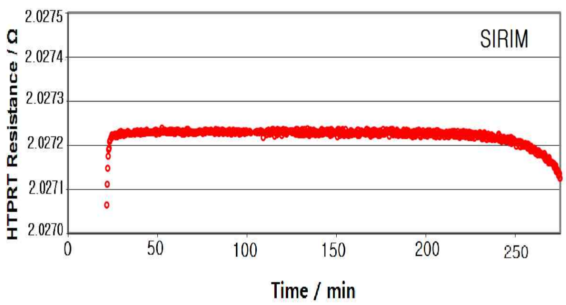


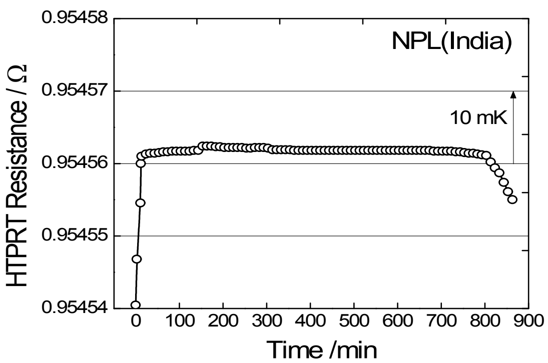












Appendix G: Instrumental details

Instrumentation	KRISS	NMIJ	SCL	NMC
Bridge Manufacturer	ASL F900	ASL F18	ASL F18	DC Bridge MI6010A
AC/DC	AC	AC		
If AC, give				
Frequency	30 Hz	low	75 Hz	
Band width	0.1 Hz	0.1 Hz	0.02 Hz	
Gain	10^4	10^4	10^4	
Quad gain	10	10	10	
Read manually or off IEEE-488	IEEE-488			
Normal measurement currents	10 mA	10 mA	10 mA	
Self-heating currents	14.14 mA	14.14 mA	14.14 mA	
Unity reading	1			
Zero reading	0.000 000 001			
Compliments check error	0.02 ppm			
If DC, give				
Gain				NA
Period of reversal				8 s
Read manually, off strip chart, or off IEEE-488				IEEE-488
Reference resistor type	Wilkins 5685A	Wilkins 1Ω, 10 Ω	Wilkins 5685A	Wilkins 5685A,10 Ω
Reference resistor manufacturer	Tinsley	Tinsley	Tinsley	Tinsley
Reference resistor - how maintained	in oil bath	Air controlled bath	in oil bath	Air Bath
Reference resistor - temperature control	±10 mK	±0.1 °C	±20 mK	23.15 +/- 0.15 °C
Reference resistor - temperature coefficient	1.25 ppm/℃	±1 ppm/℃	±2 ppm/℃	1.25 ppm / °C
RBC evaluation of resistance bridge	Yes			Yes
RBC evaluation result of linearity of resistance bridge	4.31×10^{-8}			P = Pr
Normal standard deviation of measurement set with RBC	0.03 ppm			0.0000007299

Instrumentation	CMS	NIMT	SIRIM	NPL(India)
Bridge Manufacturer	ASL	MI	ASL F18	ASL F900
AC/DC	AC	DC	AC	ac
If AC, give				
Frequency	30 Hz		25 Hz	25 Hz/75 Hz
Band width	0.1 Hz		0.1 Hz	0.1,0.2,0.5 Hz
Gain	10^4		10^4	10^5
Quad gain				100
Read manually or off IEEE-488	IEEE-488		IEEE-488	manually
Normal measurement currents	10 mA		5 mA	10 mA
Self-heating currents	14.14 mA		SQRT(2)x5mA	14.14 mA
Unity reading	1.000 000 1			0.999 999 998
Zero reading	0.000 0001			0
Compliments check error				0.000 000 004
If DC, give				
Gain		100		
Period of reversal		10 s		
Read manually, off strip chart, or off IEEE-488		IEEE-488		
Reference resistor type	Wilkins 5685A	1Ω	AC/DC	Wilkins 5685A, 10 Ω
Reference resistor manufacturer	Tinsley	Tinsley	Tinsley	Tinsley
Reference resistor - how maintained	in oil bath	in oil bath	in oil bath	in oil bath
Reference resistor - temperature control	control at 20 °C	23 °C	25 ℃	20 ℃±0.01 ℃
Reference resistor - temperature coefficient	2 ppm/℃	2 ppm/℃		3 ppm/℃
RBC evaluation of resistance bridge	yes	RBC 100		
RBC evaluation result of linearity of resistance bridge	4.781×10^{-8}	4.365×10^{-7}		
Normal standard deviation of measurement set with RBC	0.03 ppm			

Fixed-Point Crucible/Container Details

	KRISS	NMIJ	SCL	NMC
Cell commercial/Lab made	Al-KC4-97 /lab made	Al No.102 /Isotech	Al-07047 /Hart Scientific	Al9302 /NIM, China
Crucible material (graphite, etc.)	Graphite	Carbon	Graphite	Graphite
Source	Ultra carbon	Isotech	Carbon of America	NIM
Purity/how purified	99.999 %			Not available
Length / cm	25.5	28	29	25
Diameter / mm	44	50	48	45
Thermometer well material	graphite			Quartz
Thermometer well ID / mm	11	8	8	8.2
Metal sample source	JM	no information	Honeywell	NIM
Metal sample purity	99.9999 %	99.9999 %	99.9999 %+	99.9999 %
Metal sample weight / kg	0.5			Not available
Crucible container material	silica glass			Quartz
Open or closed cell	open	closed	closed	Closed
Pressure in cell	-	undetected	85.2 kPa	99464 Pa
Immersion depth of SPRT / cm	16.1	not necessary	19.5	19
Crucible container OD / mm	51			49
Furnace details				
Furnace or bath?	furnace	furnace	furnace	Furnace
Commercial/Lab made	lab made	lab made	Isotech ITL17702	Lab made (NIM)
DC or AC heater power	AC	DC	AC	AC
Furnace control type	PID		PID	PID
Furnace controlled by temperature sensor or by power settings	temperature sensor			temperature sensor
Temperature stability over 16 hrs. / mK	50	10	within 120 mK	500
How many zones in furnace	2		1	3
Heat pipe liner/working material	sodium heat pipe	sodium heat pipe	potassium heat pipe	No
Uniformity in furnace (without cell)	0.1 ℃	±10 mK (fixed-point cell within)	within 20 mK	500
Temperature distribution over ingot with sample a few kelvins below or above melting temperature	0.01 ℃			

	CMS	NIMT	SIRIM	NPL(India)
Cell commercial/Lab made	Al 2005-1 /Lab. made	Al No.154 /Isotech	447RT0009 /NPL, UK	Al-36 /Isotech
Crucible material (graphite, etc.)	graphite	graphite	graphite	graphite
Source	Ultra carbon		NPL, UK	not known
Purity/how purified	99.999 %	99.999 %	pure grade	high purity
Length / cm	25.5	24.7	24	24.2
Diameter / mm	48	49.4	43.5	44
Thermometer well material	silica glass		quartz	quartz
Thermometer well ID / mm	8	8	8	8
Metal sample source	JM		JM	Leico
Metal sample purity	99.9999 %	99.999 %	99.9999 %	99.9999 %
Metal sample weight / kg				500 g
Crucible container material	silica glass		quartz	quartz
Open or closed cell	closed	closed	closed	closed
Pressure in cell	-	1 atm	1 atm	1 Bar
Immersion depth of SPRT / cm	22.3	20.9	15.4	20
Crucible container OD / mm			50	50
Furnace details				
Furnace or bath?	furnace	furnace	furnace	furnace
Commercial/Lab made	YSI	Isotech	Carbolite	Isotech
DC or AC heater power	AC	AC	AC	DC
Furnace control type	PID		three term controller(715E)	PID
Furnace controlled by temperature sensor or by power settings	temperature sensor	temperature sensor	temperature sensor	Type R t/c
Temperature stability over 16 hrs. / mK	3.2	4		
How many zones in furnace	1	1	1	1
Heat pipe liner/working material	sodium heat pipe	heat pipe	heat pipe	Sodium heat pipe
Uniformity in furnace (without cell)	± 82 mK over 18 cm			
Temperature distribution over ingot with sample a few kelvins below or above melting temperature		0.004 ℃		

Nucleation of Freezes or Preparation of Melts, Duration of Freeze of Melt, etc.	

	KRISS	NMIJ	SCL	NMC
Procedure (freeze or melt)	freeze			Freeze
If by freezing, give				
Length of time sample heated above melting point before nucleating freeze	overnight			>3 hrs
Method of nucleation freeze or melt	slow cooling			Cool furnace temperature to approx 1°C below freeze point
Method of forming inner liquid/solid interface	induced			Induced
If by chilling, give				
Method (glass rods, gas, etc.)	glass rod			steel rod
If by heating, give				
Method (glass rods, heater, etc.)				
Fluid used in thermometer well for thermal contact	air			
Liquid fluid level in thermometer well				
Use of bushing with REC SPRT?	no			
If yes, specify the material				
Duration of freeze or melt				3 hrs
Was cell used for freezing point? Melting point? Triple point?	freeze			freeze

SPRT treatment				
Was SPRT heated to about 675 °C in pre-heat furnace before being transferred to Al freezing-point cell?	yes			yes
If yes, how many hours to reach 675 °C?	1			1
After Al freezing point measurement, was SPRT transferred directly to annealing furnace at approximately 675 °C and then cooled over several hours to 500 °C before removing to room temperature?	yes			yes
If yes, how many hours?	3			4
If no, how was SPRT heat treated?				

Nucleation of Freezes or Preparation of Melts, Duration of Freeze of Melt, etc.	

	CMS	NIMT	SIRIM	NPL(India)
Procedure (freeze or melt)	freeze	freeze	freeze	freeze
If by freezing, give				
Length of time sample heated above melting point before nucleating freeze	overnight	3 hours	2 hours	4 hours
Method of nucleation freeze or melt	slow cooling	freeze	Induce-take out PRT for 3 mins	freeze
Method of forming inner liquid/solid interface	induced	chilling	induce	Cooling
If by chilling, give				
Method (glass rods, gas, etc.)	quartz rod	quartz rod	Brass rod in silica tube	quartz rod
If by heating, give				
Method (glass rods, heater, etc.)				
Fluid used in thermometer well for thermal contact	air		no fluid	air
Liquid fluid level in thermometer well				not applicable
Use of bushing with REC SPRT?	no	no	no	no
If yes, specify the material				
Duration of freeze or melt	depends on the designated temp. range	8 hours	2 hours	11 hours
Was cell used for freezing point? Melting point? Triple point?	freezing point	freezing point	freezing	freezing point

SPRT treatment				
Was SPRT heated to about 675 °C in pre-heat furnace before being transferred to Al freezing-point cell?	yes	yes	yes	yes
If yes, how many hours to reach 675 °C?	1 hour	1 hour	3 hours	1 hour
After Al freezing point measurement, was SPRT transferred directly to annealing furnace at approximately 675 °C and then cooled over several hours to 500 °C before removing to room temperature?	yes	yes	yes	yes
If yes, how many hours?	675 ℃ for 0.5 hour and 500 ℃ for 4 hours	675 ℃ for 1/2 hour and 500 ℃ for 4 hours	4 hours	4 hours from 675 ℃ to 500 ℃
If no, how was SPRT heat treated?				

Triple Point of Water Cells				
	KRISS	NMIJ	SCL	NMC
Manufacturer	KRISS			Jarrett-Isotech
Well diameter / mm	13			11
Water source and purity?	filtered & distilled			Jarrett-Isotech
Immersion depth of SPRT in the cell / cm	26.1			29
Heat transfer fluid?	water			Distilled Water
Heat transfer fluid level in thermometer well / cm	30			Level with cell water level after inserted SPRT
Use of metal bushing?	Al bushing			No
How are mantles prepared?	dry ice			dry ice
How long are mantles prepared before use?	10 days			> 3 weeks
How are mantles maintained - ice or stirred bath	ice			stirred bath

Triple Point of Water Cells				
	CMS	NIMT	SIRIM	NPL(India)
Manufacturer	Hart Scientific	Isotech	NPL, UK	Locally made
Well diameter / mm	12	11	12	10
Water source and purity?			NPL, UK	Distilled,deionised, ≥18 MΩ
Immersion depth of SPRT in the cell / cm	26.5	37.1	22.0	30
Heat transfer fluid?	Pure water	water	distilled water	distilled water
Heat transfer fluid level in thermometer well / cm	Level with the cell water level after inserted SPRT	27	7 to 8	30
Use of metal bushing?	no	no	no	no
How are mantles prepared?	dry ice	dry ice	dry ice	Immersion cooler with liquid nitrogen
How long are mantles prepared before use?	1 week	2 days	3 days	1 week
How are mantles maintained - ice or stirred bath	Maintenance bath	stirred bath	ice bath	ice bath

Appendix H: Opinion of CMS

Dear Dr. Gam,

Thank you for your response.

In reply to your comments
1. I understand your opinion that the HTSPRT resistance difference at the TPW during the comparison between the participating lab and KRISS caused by the mechanical shocks and the differences of the measuring system including the calibration values of the standard resistor.

However, even though mechanical shock is a stronger factor than the calibration uncertainty of standard resistor, the latter is still a competed factor in our case. Furthermore, if mechanical shock is a dominated factor, why the TPW difference between KRISSi and KRISSf through a long trip of (KRISSi-NMC-CMS-KRISSf) comparison procedure is less than 1 mK (about 0.83 mK according to my calculation)? Besides, we suggest such important resistance changes at TPW in appendix C should also represent by digital values apart from representing in graphical form.

2. I agree that the artifact HTSPRT circulated as KRISS-Lab 1-Lab 2-KRISS in APMP. T-K4, while the artifact differently circulated as PTB-Lab 1-Lab 2-Lab3- ....-Lab 6-PTB. Nevertheless, an interesting issue is why the evaluated uncertainties originated from instability of artifact HTSPRT in APMP. T-K4 are almost much greater than in EUROMET. T-K4 even though their artifact travelled through many more labs than ours? I strongly believe it involve whether appropriate evaluation is applied on to prevent overestimating or underestimating.

As a participating laboratory of APMP.T-K4, I really hope you could consider over our opinion again. If it unfortunately happens that you insist keeping the original evaluation model, CMS requires that our opinion above should be included in the appendix or be noted by an appropriate manner in the final report.