Final report of APMP.T-S7: APMP regional comparison of Co-C eutectic melting point using Pt/Pd thermocouples

Approved by CCT WG-KC

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1. Introduction

The Co-C eutectic point (1324 ^{o}C in ITS-90) is a very promising secondary fixed-point between Cu and Pd freezing points. It is useful to calibrate a thermocouple at high temperature, and thus there is a strong need for international comparison in order to validate CMC. To meet this need, this comparison was started. The first protocol was circulated in February 2010 by the pilot laboratory, KRISS, Korea, and a final protocol (**Appendix A**) incorporating the changes raised by the participants was approved in July 2010.

After construction of the artefacts by the pilot laboratory, circulation started in September 2010. The measurement was completed in July 2014 and returned to the pilot laboratory. The calibration procedure used by the individual laboratory is given in **Appendix B**. The instruments used by each participant are given in **Appendix C**. The measurement data from the participants are given in **Appendix D**. Immersion temperature profiles of Co-C realization furnace are given in **Appendix E**, and the obtained 3 melting curves of Co-C eutectic point are shown in **Appendix F**. Uncertainty calculations as supplied by each NMI laboratory is given in **Appendix G**.

2. Participants and Measurement schedule

Table 1. List of participants and real measurement schedule

Name of Laboratory	**Contact Person**	**Real Schedule**
KRISS – Korea	Yong-Gyoo Kim dragon@kriss.re.kr	July – September 2010, Started
NIM - China	Zheng Wei zhengw@nim.ac.cn	October 2010 – January 2011
NMIJ – Japan	Hideki Ogura h.ogura@aist.go.jp	February – April 2011
NMIA – Australia	Ferdouse Jahan Ferdouse.Jahan@nmi.gov.au	May – August 2011
NPLI - India	Y.P. Singh ypsingh@mail.nplindia.org	September 2011– June 2014
KRISS – Korea	Yong-Gyoo Kim dragon@kriss.re.kr	July 2014, Finished

3. Preparation of artefacts

Two Pt/Pd thermocouples (serial number: APMP_PtPd_10_01 and APMP_PtPd_10_02) were constructed using wires of 0.5 mm diameter and 1700 mm long. Table 2 shows the source and purity of Pt and Pd wires used in this comparison. Pt and Pd wires were initially electric-annealed at about 1300 ^{o}C and 1100 ^{o}C for 24 h, respectively. And temperature was lowered to about 500 ^{o}C as-attached in wire-anneal system and annealed for 24 h. These annealed wires were inserted into alumina insulator (700 mm long, 3.2 mm diameter) having twin bores (bore diameter of 1.0 mm). The alumina insulator was baked at 1500 ^{o}C more than 1 h before use. Hot junction was made not using a strain relief coil as described in literatures [1,2]. Junction was located in Pd wire side inside the bore about 3 mm. The assembled thermocouples were secondly annealed in the vertical tube furnace at 1000 ^{o}C for 48 h followed by the furnace cooling to about 450 ^{o}C. Finally after 48 h, thermocouples were withdrawn to ambient. Figure 1 shows the assembled artefacts stored in the wooden transportation box.

Table 2. Maker and purity of Pt and Pd wires

	APMP_PtPd_10_01		APMP_PtPd_10_02	
	Pt	Pd	Pt	Pd
Source	Heraeus Co.	Heraeus Co.	Heraeus Co.	Johnson Matthey Co. (Currently Alfa Aesar)
Purity	99.9999 %	99.99 %	99.9999 %	99.997 %

Figure 1. Photo of prepared artefacts

4. Measurement results by participants

Table 3 summarizes the reported emf values at the Ag freezing point before and after measurement at the Co-C melting point. KRISS_**I** and KRISS_**F** denote for the '**I**nitial measurement' and '**F**inal measurement', respectively. After the circulation, the average emf at the Ag point were changed by -1.8 μV and -4.6 μV for APMP_PtPd_10_01 and APMP_PtPd_10_02, respectively.

Table 4 summarizes the measured emf values at the Co-C melting point. Melting point was determined from the inflection point as according to the protocol in Appendix A. APMP_PtPd_10_01 showed maximum variation of 5.5 μV between NMIs and 18.5 μV for APMP_PtPd_10_02 thermocouple, respectively.

Table 3. Summary of freezing emf at the Ag point

NMIs	Freezing emf at the Ag point /μV					
	APMP_PtPd_10_01			APMP_PtPd_10_02		
	Before	After	Difference	Before	After	Difference
KRISS_I	10786.2	10786.8	0.6	10800.8	10800.7	-0.1
NIM	10786.0	10785.6	-0.4	10799.9	10799.7	-0.2
NMIJ	10785.2	10784.8	-0.4	10800.2	10802.4	2.2
NMIA	10785.4	10784.8	-0.6	10800.2	10800.3	0.1
NPLI	10787.7	10786.5	-1.2	10803.8	10803.5	-0.3
KRISS_F	10784.8	10784.7	-0.1	10795.8	10796.4	0.6

Table 4. Summary of melting emf at the Co-C point

NMIs	Measured emfs at Co-C melting point /μV							
	APMP_PtPd_10_01				APMP_PtPd_10_02			
	1st	2nd	3rd	Average ± 1 σ	1st	2nd	3rd	Average ± 1 σ
KRISS_I	18581.6	18581.6	18581.7	18581.6 ± 0.1	18604.5	18604.6	18604.7	18604.6 ± 0.1
NIM	18582.2	18582.5	18582.6	18582.4 ± 0.2	18608.4	18608.4	18608.5	18608.4 ± 0.1
NMIJ	18581.3	18581.4	18581.5	18581.4 ± 0.1	18604.8	18605.1	18605.5	18605.1 ± 0.4
NMIA	18583.3	18584.0	18583.0	18583.4 ± 0.5	18613.0	18613.8	18613.5	18613.4 ± 0.4
NPLI	18586.6	18585.1	18584.6	18585.4 ± 1.0	18624.1	18622.6	18622.6	18623.1 ± 0.9
KRISS_F	18579.6	18579.9	18580.1	18579.9 ± 0.3	18611.0	18610.8	18610.3	18610.7 ± 0.4

5. Calculation of thermoelectric inhomogeneity

Figure 2 shows the immersion temperature profile of Co-C realizing furnace reported by each participant as in Appendix E. Temperature gradient zone of the furnace was calculated using this profile as indicated by the protocol. If the gradient zone is wide, then much longer part of the thermocouple wires are under the temperature gradient. Thus the thermoelectric inhomogeneity may become larger. The thermoelectric scanning tests for artefacts were optional and NMIA did scanning tests. So other than NMIA, inhomogeneity values were given using the KRISS scan results. Inhomogeneity at Co-C point was calculated using equation (1) below as indicated in the protocol.

$$\text{inhomogeneity} = \pm(E_x - E_{25^\circ\mathrm{C}}) \times \frac{\Delta E_{\max}(\text{within gradient zone})}{E_{200^\circ\mathrm{C}} - E_{25^\circ\mathrm{C}}} \times \frac{1}{0.95} \times \frac{1}{2} \qquad (1)$$

Figure 3 shows the thermoelectric scanning results performed by KRISS at 200 $^{\mathrm{o}}$C after the Co-C point measurements before and after the circulation. NMIA did a thermoelectric scanning in their laboratory, and calculated the inhomogeneity as shown in Figure 4. As shown in Figure 3, thermoelectric inhomogeneity was nearly same before and after the circulation. The maximum emf changes of KRISS_F due to the inhomogeneity at 200 $^{\mathrm{o}}$C were calculated to 0.4 μV for APMP_PtPd_10_01 and 2.7 μV for APMP_PtPd_10_02, respectively. These correspond to inhomogeneity of ± 0.0196 % and ± 0.132 % at 1324 $^{\mathrm{o}}$C.

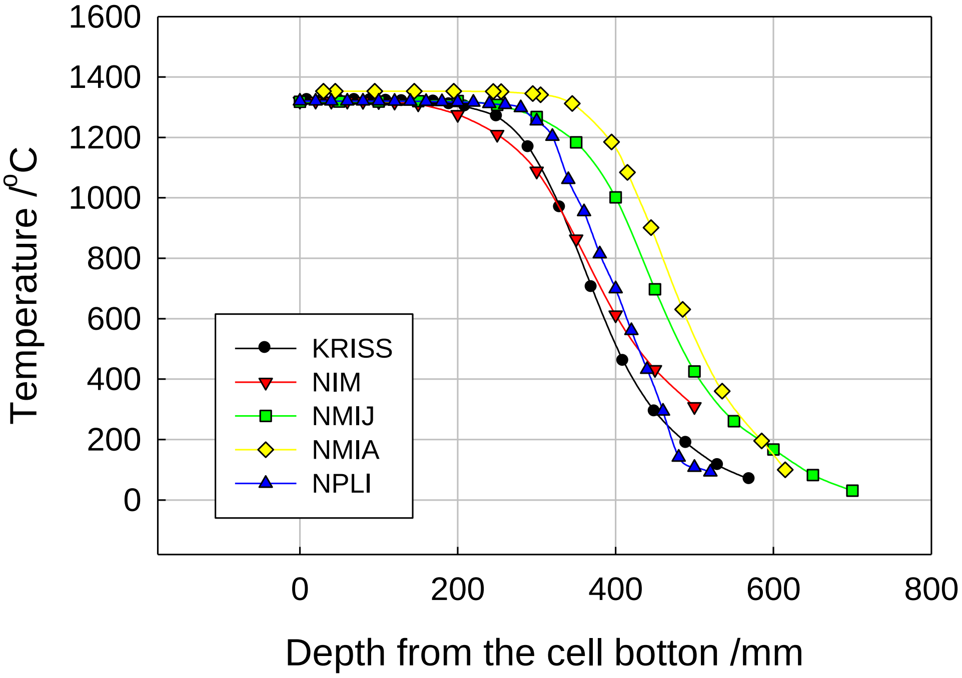
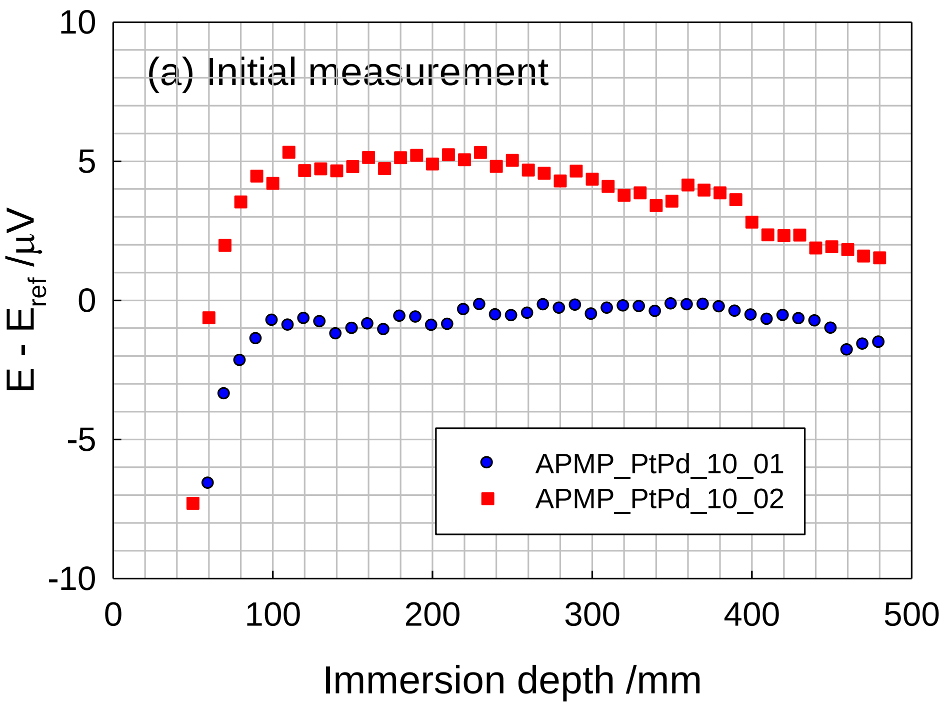


Figure 2. Temperature immersion profiles of the Co-C realization furnaces



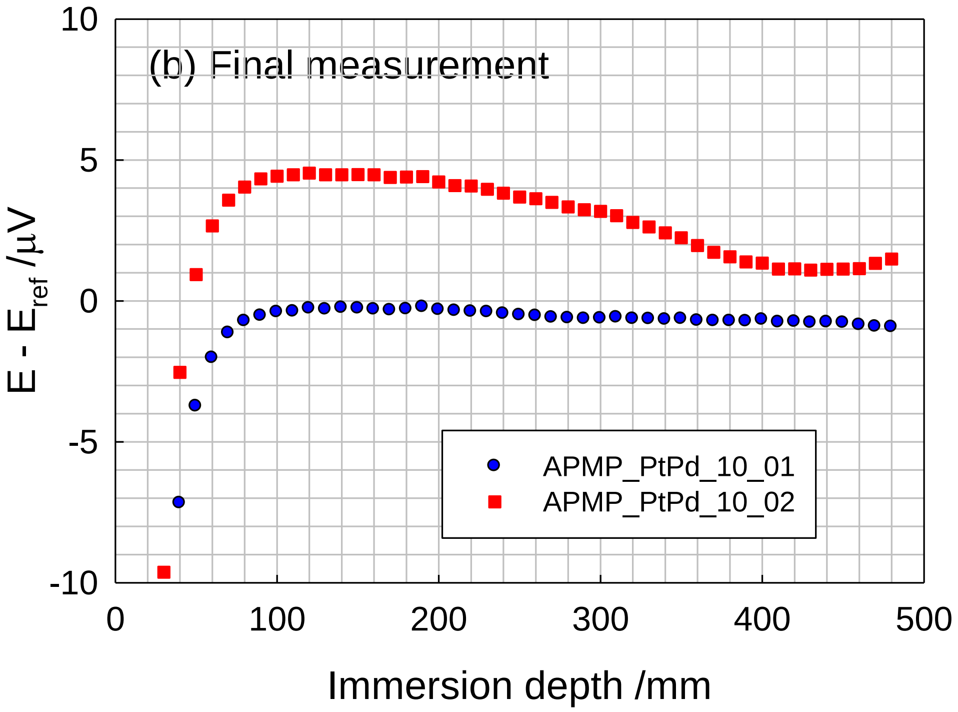
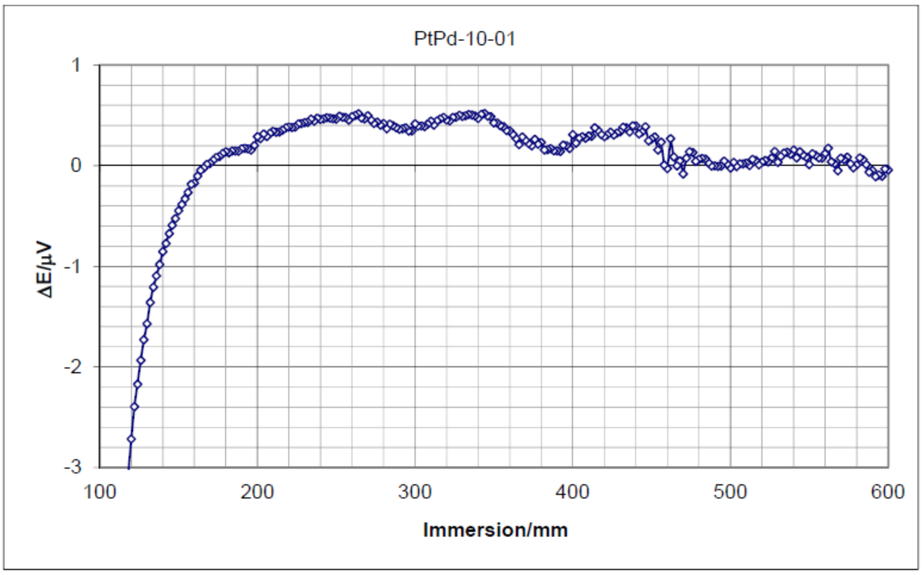
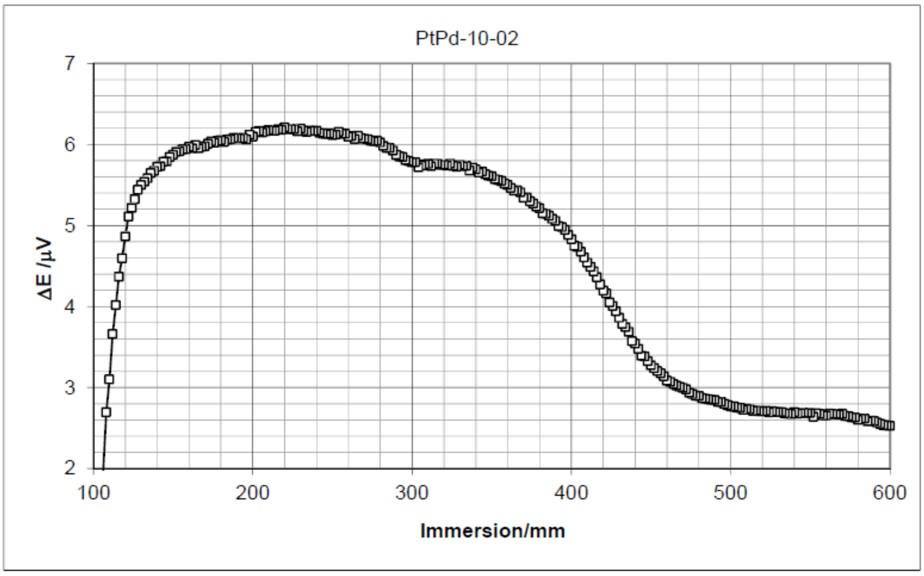


Figure 3. Thermoelectric scanning results by KRISS at 200 ^{o}C

Inhomogeneity of TCs





Inhomogeneity was calculated from 350 mm to 550 mm from the thermocouple tip using formula given below

$$\text{inhomo at 1324°C} = \pm\left(E_{1324} - E_{25}\right)\left[\frac{\Delta E}{E_{200°C} - E_{25°C}}\right] * \left(\tfrac{1}{0.95}\right) * \frac{1}{2}$$

PtPd1001	=	±	3.619 at 1324°C	ΔE=	0.4 µV from 350 to 550 mm
PtPd1002	=	±	27.143	ΔE=	3.0 µV from 350 to 550 mm

Type Pd	25	135.17
	200	1207.88
	1324	18621.6

inhomo=	0.019 %
inhomo=	0.140 %

Figure 4. Thermoelectric scanning result at 200 °C given by NMIA

Table 5. Summary of thermoelectric inhomogeneity calculations

NMI	Measured immersion length /mm	Temperature gradient zone /mm	APMP-PtPd-10-01			APMP-PtPd-10-02		
			ΔE_{Max} /μV	Inhomogeneity at 1324 °C /μV	Standard uncertainty /μV	ΔE_{Max} /μV	Inhomogeneity at 1324 °C /μV	Standard uncertainty /μV
KRISS_I	570	250 ~ 570	0.4	± 3.6	2.1	2.9	± 26.3	15.2
NIM	500	200 ~ 500	0.5	± 4.5	2.6	3.0	± 27.2	15.7
NMIJ	700	300 ~ 650	0.4	± 3.6	2.1	2.8	± 25.4	14.7
NMIA	615	350 ~ 550	0.4	± 3.6	2.1	3.0	± 27.2	15.7
NPLI	520	300 ~ 520	0.4	±3.6	2.1	2.8	± 25.4	14.7
KRISS_F	570	250 ~ 570	0.4	± 3.6	2.1	2.7	± 24.5	14.1

Table 5 shows the summary of thermoelectric inhomogeneity calculation results. Temperature gradient zone of each NMI was calculated based on the reported temperature immersion profile from the participants as described in Fig.2 of the protocol. ΔE_{Max} was calculated from the scanned data of Fig.3 at the region of temperature gradient zone. Finally inhomogeneity was calculated using eq.(1) and the corresponding standard uncertainty was obtained by assuming rectangular distribution.

6. Uncertainty calculation

Table 6 represents the calibration uncertainties calculated by the pilot laboratory using data from the participants. $U_{w/o}$ denotes for the reported uncertainty from the participants without the thermoelectric inhomogeneity factor. U_{in} denotes the contribution from the thermoelectric inhomogeneity as in Table 5. U_{drift} means the stability of artefacts during the comparison. This term was calculated using the change of emf at the Ag freezing point measured by KRISS before and after the circulation as equation (2). Expanded uncertainty, U_{total} (k=2), was calculated by using a combined uncertainty of equation (3).

$$u_{drift} = \frac{\Delta E_{Ag}}{2\sqrt{3}} \times \frac{E_{Co-C}}{E_{Ag}} \qquad (2)$$

$$u_{total} = \sqrt{u_{w/o}^2 + u_{in}^2 + u_{drift}^2} \qquad (3)$$

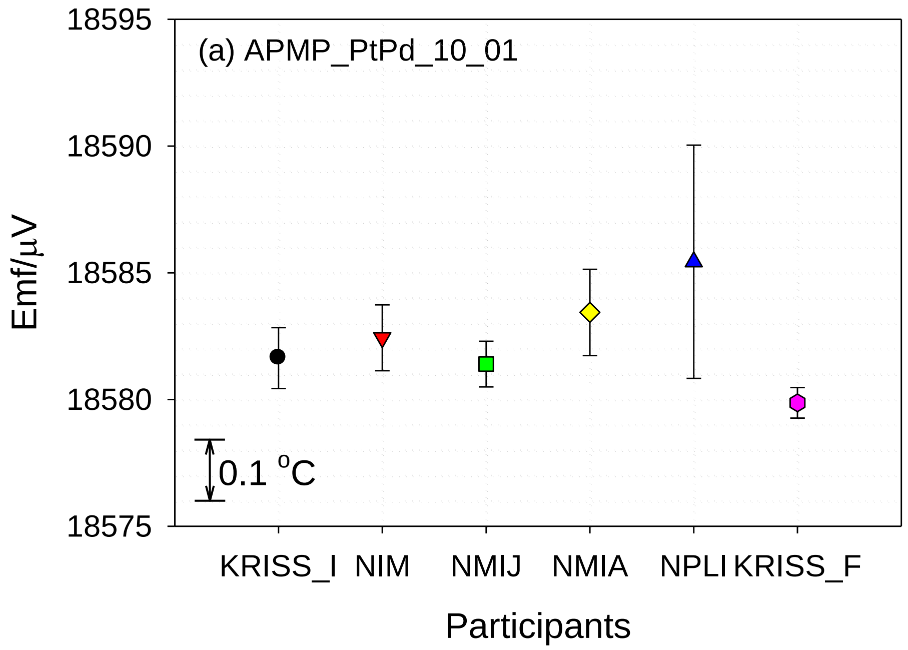
U_{total} does not include the calibration uncertainty of Co-C cell used in the comparison, NMIs who want to declare their CMC should include the uncertainty of Co-C cell (u_{cell}). To define this factor, NMIs may do another experiments through measurement with the standard radiation thermometer to determine the realization temperature of the cell in ITS-90 scale.

Table 6 Summary of uncertainty calculation

NMI	$U(k=2)$ /μV							
	APMP_PtPd_10_01				APMP_PtPd_10_02			
	$U_{w/o}$	U_{in}	U_{drift}	U_{total}	$U_{w/o}$	U_{in}	U_{drift}	U_{total}
KRISS_I	1.2	4.2	1.8	4.7	0.4	30.4	4.5	30.7
NIM	1.3	5.2	1.8	5.7	1.1	31.4	4.5	31.7
NMIJ	0.9	4.2	1.8	4.7	4.4	29.4	4.5	30.1
NMIA	1.7	4.2	1.8	4.9	1.0	31.4	4.5	31.7
NPLI	4.6	4.2	1.8	6.5	4.3	29.4	4.5	30.0
KRISS_F	0.6	4.2	1.8	4.6	1.6	28.2	4.5	28.6

7. Comparison data analysis

Figure 5 shows the plots of measured results in Table 4. Error bars denote the expanded uncertainties ($U_{w/o}$, k=2) reported by participants without inhomogeneity factor as calculated in Table 6.



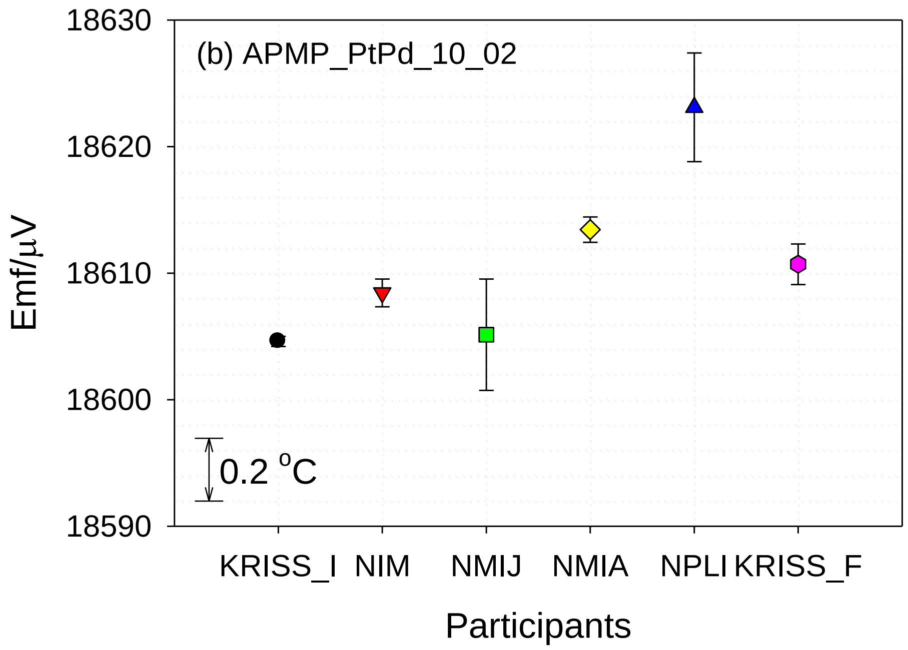


Figure 5. Plots of measured emfs given by the participants in Table 4. Error bars denote the expanded uncertainties, $U_{w/o}$, (k=2) in Table 6.

To calculate the comparison reference value, which is to be a form of the average of the obtained values (X_i) and their uncertainties (u_i), two different measures of the average were considered, the one is the (a) simple mean and the other is the (b) weighted mean. Median was not counted in this comparison because of small number of participants.

(a) Simple mean

$$X_{simple} = \sum X_i / n \tag{4}$$

$$u_{simple} = \sqrt{\sum u_i^2} / n \tag{5}$$

(b) Weighed mean

$$X_{weighted} = \sum X_i u_i^{-2} / \sum u_i^{-2} \tag{6}$$

$$u_{weighted} = \sqrt{1 / \sum u_i^{-2}} \tag{7}$$

In case of the weighted mean, Birge ratio was calculated. Birge ratio is a measure of how well estimated uncertainties explain the dispersion of the data.

$$\text{Birge ratio} = \sqrt{\sum (X_i - X_{weighted})^2 u_i^{-2} / (n-1)} \tag{8}$$

If the spread of the data points X_i is consistent, then the Birge ratio is close to 1 or less. If the spread of the data is larger than the expected from the error bars, the Birge ratio will be greater than 1 [3].

Table 7. Statistical analysis of the comparison data

		APMP_PtPd_10_01				APMP_PtPd_10_02			
		emf/μV	U (k=2)		$\lvert E_n \rvert$	emf/μV	U (k=2)		$\lvert E_n \rvert$
			μV	°C			μV	°C	
NMI	KRISS_I	18581.6	4.7	0.20	0.08	18604.6	30.7	1.30	0.19
	NIM	18582.4	5.7	0.25	0.06	18608.4	31.7	1.34	0.07
	NMIJ	18581.4	4.7	0.20	0.13	18605.1	30.1	1.27	0.18
	NMIA	18583.4	4.9	0.22	0.26	18613.4	31.7	1.34	0.07
	NPLI	18585.4	6.5	0.27	0.50	18623.1	30.0	1.27	0.37
	KRISS_F	18579.9	4.6	0.20	0.43	18610.7	28.6	1.21	0.01
simple mean /μV		18582.4 ± 5.7 (k=2)				18610.9 ± 33.4 (k=2)			
weighted mean /μV		18582.0 ± 2.1 (k=2)				18611.0 ± 12.4 (k=2)			
Birge ratio		0.3				0.2			

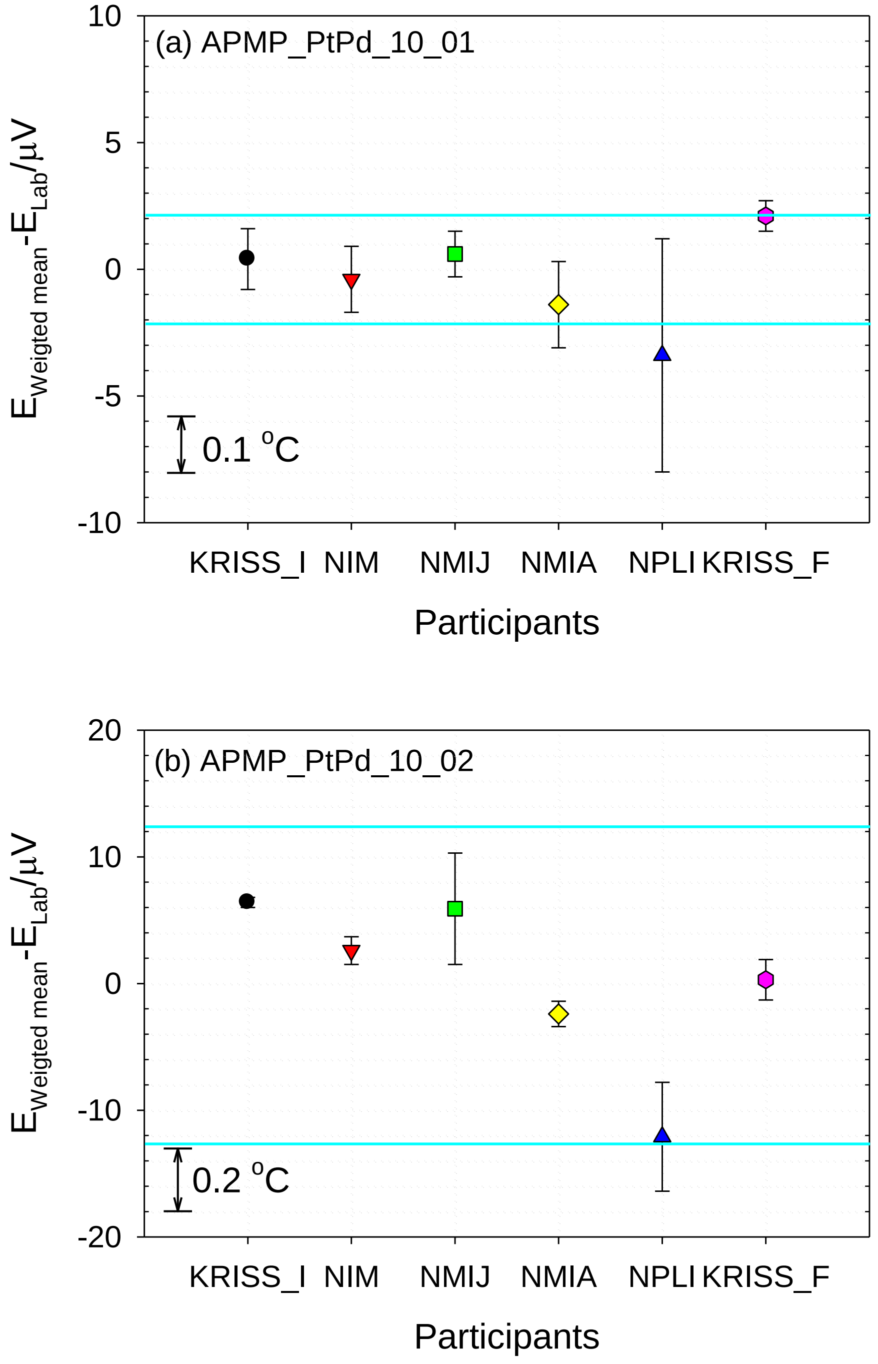


Figure 6. Plots of differences between the weighted mean and reported melting emf by the participants. Error bars denote the expanded uncertainties, $U_{w/o}$, (k=2) in Table 6. Cyan lines denote the uncertainty of the weighted mean.

The calculated Birge ratio was 0.4 and 0.3 for APMP_PtPd_10_01 and APMP_PtPd_10_02, respectively, so it was decided to use the **weighted mean as the comparison reference value** in this comparison. Figure 6 shows the differences between the weighted mean and the reported value by the participants in Table 7. Error bars denote the expanded uncertainties. Cyan lines mean the calculated uncertainty of weighed mean using eq.(7).

In order to check the discrepancies of the data from the participants, *En* number was calculated [4]. It can be useful to evaluate a participant's ability to have close to the assigned value (here, weighted mean value) within their claimed expanded uncertainty. $|E_n|$ lower than 1 can be taken as an indicator of successful performance if the uncertainties are valid and the deviation is smaller than needed by the participants.

$$E_n = \frac{(X_{lab,i} - X_{average})}{\sqrt{U^2_{lab,i}(k=2) + U^2_{average}(k=2)}} \qquad (9)$$

For two Pt/Pd thermocouples having greatly different thermoelectric inhomogeneity, *En* number were much lower than 1 as 0.24 for APMP_PtPd_10_01 and 0.15 for APMP_PtPd_10_02 in average.

As shown in Table 6, the calculated expanded uncertainty of calibration strongly depends on the thermoelectric inhomogeneity. By means of APMP_PtPd_10_01 which had smaller inhomogeneity, it was verified that the calibration uncertainty level claimed by each NMI could be achieved at the Co-C eutectic melting point for supporting of CMCs.

8. Conclusions

Using two Pt/Pd thermocouples having greatly different thermoelectric inhomogeneity, international comparison was done at the Co-C eutectic melting point. Results from all laboratories were consistent with the reference value within the calculated uncertainties. Birge number less than 1 and small *En* number of this comparison mean that the comparison successfully demonstrated the use of Pt/Pd thermocouple to compare the calibration capabilities of participating laboratories at the melting temperature of Co-C eutectic point regardless of the amount of thermoelectric inhomogeneity. Even the calculated expanded uncertainties of calibration were dominated by the thermoelectric inhomogeneity, it was verified to obtain the calibration uncertainty level of {(0.2 ^{o}C ~ 0.3 ^{o}C) + u_{cell}} (k = 2) at the Co-C eutectic melting point by means of Pt/Pd thermocouple if the inhomogeneity is small enough. Since the uncertainty budget used in this comparison does not include the uncertainty of the Co-C fixed-point cell itself, NMIs who want to use this comparison report to assess NMI's calibration capability of thermocouples, the uncertainties on the determination of the ITS-90 values of Co-C melting temperature should be added.

9. References

[1] Jahan F. and Ballico M, 2007 Stability studies of a new design Au/PT thermocouple without a strain relieving coil, *Int. J. Thermophysics* **28** 1822 – 1831

[2] Jahan F, Ballico M, Kim Y G, Liedberg H, Wang L, Ogura H and Tsui C M, 2013 Final report of APMP.T-S5: APMP regional comparison of Au/Pt thermocouples from 0 ^{o}C to 960 ^{o}C, *Metrologia Tech. Suppl.* **50** 03003

[3] Kacker R. Datla R. and Parr A, 2002 Combined result and associated uncertainty from interlaboratory evaluations based on the ISO guide, *Metrologia* **39** 279-293

[4] ISO 13528:2015, Statistical methods for use in proficiency testing by interlaboratory comparison

Appendix A: Protocol of the comparison (APMP.T-S7)

Protocol for the APMP Regional Comparison of Co-C Eutectic Melting Point using Pt/Pd Thermocouples

APMP-T-S7

July 2010

Yong-Gyoo Kim

Korea Research Institute of Standards and Science

1. INTRODUCTION

The Co-C eutectic point (1324 °C) is a very promising secondary fixed-point between Cu and Pd freezing points. It is useful to calibrate a thermocouple at high temperature, and thus there is a strong need for international comparison in order to validate CMC.

The present comparison aims to compare the melting temperature of Co-C eutectic point in APMP region using two specimens of the Pt/Pd thermocouple, which is known as a stable and robust thermometer above 1000 °C. In order to measure the stability of artifacts, Ag freezing point will be used.

The key aspects of the present comparison are as follows:

- **Co-C eutectic cell manufactured by participating labs will be used.**
- **Two Pt/Pd thermocouples will be used as transfer artifacts in a round robin comparison.**
- **Participating labs will prepare one Pt/Pd thermocouple (Other types are available.) as a monitoring thermocouple to assess heat-flux uncertainty.**
- **Participation will be restricted to the labs with existing demonstrated experience with these artifacts (to reduce chance of breakage).**
- **At each participating laboratory, Ag freezing point will be used to check the stability of thermocouples.**
- **Uncertainty due to inhomogeneity will be reduced by detailed gradient reporting.**

2. DESCRIPTION OF THE THERMOCOUPLES

Two Pt/Pd thermocouples will be supplied by pilot lab (KRISS). The thermocouple is 180 cm long from tip to the bottom of reference junction. The ice point section is 20 cm long and 5 mm in diameter. The alumina sheath of the thermocouple is 80 cm long with a diameter of 4.0 mm.

3. FACILITIES

- The participating lab should have annealing furnace with uniformity of better than ± 20 °C. The length of uniform zone should be greater than the immersion length of the thermocouple in the fixed point enclosure.
- The lab should have an Ag freezing point cell and a Co-C melting point cell with well diameter of minimum 5 mm.
- The lab should have a monitoring Pt/Pd thermocouple (Other types are available).
- The lab should have a precise digital voltmeter with a resolution of 0.01 μV.

4. CALIBRATION PROCEDURE USED IN THE COMPARISON:

- Thermocouples will be calibrated by all participants in the 450 °C annealed state.
- If the lab has facility to measure inhomogeneity, then measure the inhomogeneity at a temperature lower than 250 °C, so that no effects of heat treatment are introduced due to the measurement of inhomogeneity.
- The contribution of inhomogeneity to the comparison will depend upon the variation of applied temperature gradients fields amongst the participants. The pilot lab will use the measured inhomogeneity together with the reported gradients (Figure 2) to determine the likely maximum error in comparison due to inhomogeneity.

Note: The participating laboratory **should not dismantle** the thermocouple and should handle the thermocouples with extreme care, as they are fragile.

5. PARTICIPANTS

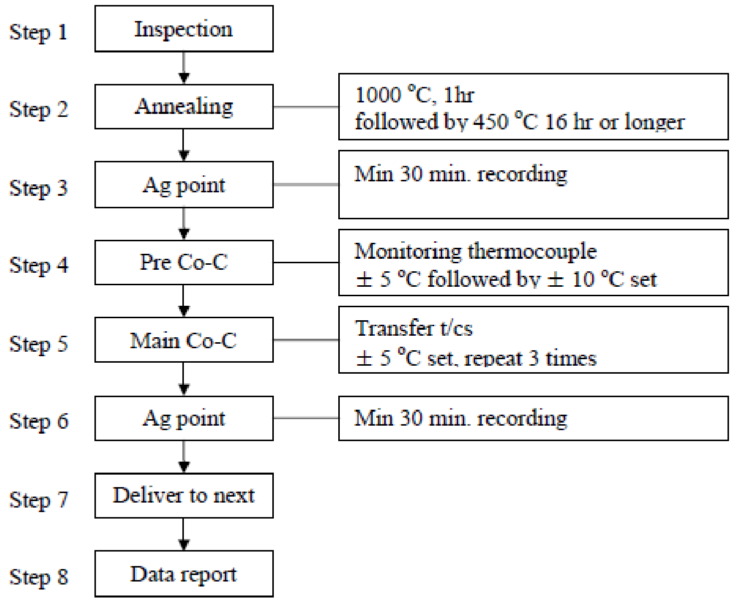
Name of Laboratory	Contact Person	Time Schedule
KRISS – Korea	Yong-Gyoo Kim dragon@kriss.re.kr	October – November '10
NIM - China	Zheng Wei zhengw@nim.ac.cn	December '10 – January '11
NMIJ – Japan	Hideki Ogura h.ogura@aist.go.jp	February – March '11
NMIA – Australia	Ferdouse Jahan Ferdouse.Jahan@nmi.gov.au	April – May '11
NPLI - India	Y.P. Singh ypsingh@mail.nplindia.org	June – July '11
KRISS – Korea	Yong-Gyoo Kim dragon@kriss.re.kr	August – September '11

*** 4 weeks for calibration and 4 weeks for transportation and customs clearances**

6. TIME SCHEDULE

- Write and approve protocol by May '10
- Construct 2 thermocouples by June '10
- Calibration by the pilot lab by November '10 and then start circulating
- Each participants calibrate within 4 weeks of receiving date
- Final Calibration by the pilot lab.

7. INSTRUCTIONS TO THE PARTICIPATING LABORATORY:



<Measurement Procedures>

- Step 1:
  - Upon receiving the transfer thermocouples, the laboratory must inspect them for damage. If there is any damage, the lab should inform the pilot lab for instruction as to how to proceed.
- Step 2:
  - If there is no damage, anneal the thermocouples at 1000 °C for 1 hour to anneal out any hysteresis or inhomogeneity introduced by the previous calibration (if any).
  - After annealing, withdraw t/cs at 1000 °C.
  - Anneal at 450 °C for longer than 16 hours to reduce the number of lattice vacancies that might be quenched into the thermoelements when the thermocouples are removed from higher temperature.

  <Optional: If the lab has facility to measure inhomogeneity, then measure the inhomogeneity of the transfer thermocouples at a temperature less than 250 °C, after annealing and before starting Step 3. Please use the measured value to calculate the uncertainty>
- Step 3:
  - Calibrate the transfer thermocouples at Ag-point. Place the thermocouple tip at 1 cm or more above the bottom of Ag cell to allow the space for the expansion.
  - Record minimum 30 min at the freezing state.

- Step 4:
  - Insert the monitoring Pt/Pd thermocouple, prepared by the participating laboratory, into a Co-C eutectic cell at room temperature, and alter the position of the tip of hot junction 1 cm from the cell bottom.
  - Elevate the furnace temperature to 1319 °C (-5 °C to melting temperature), and hold for 1 h to stabilize the Co-C cell
  - Realize the Co-C melting temperature using a monitoring thermocouple at ± 5 °C (melting at 1329 °C, freezing at 1319 °C)
  - After the melt was fully frozen, realize melting and freezing at ± 10 °C (melting at 1334 °C, freezing at 1314 °C) again.
  - Deduce the heat-flux effect from these two sets of measurement.

    $$\Delta E_{HF} = (E(+\,10\,°C) - E(+\,5\,°C))\ (S_{Pt/Pd}/S_{other\ type})$$
  - This term may also contain the impurity effects.
- Step 5:
  - Replace the monitoring t/c with one of the transfer Pt/Pd thermocouple at room temperature, and alter the position of the tip of hot junction 1 cm from the cell bottom.
  - Elevate the furnace temperature to 1319 °C (-5 °C to melting temperature), and hold for 1 h to stabilize the Co-C cell
  - Realize the Co-C melting temperature at ± 5 °C three times (melting at 1329 °C, freezing at 1319 °C)
  - Hold the fully melting state for 30 min, and 1 h of fully frozen state
  - After measuring 3 sets of melting and freezing, replace the thermocouple by another transfer Pt/Pd thermocouple at room temperature.
  - Repeat above processes using the second transfer thermocouple.
  - The participant should record full-time data for each realization.
- Step 6:
  - Repeat Step 3 measurement
  - Deduce the short-term t/c stability

    $$\Delta E_{TS} = E(Ag)_{after} - E(Ag)_{before}$$
- Step 7:
  - After completion of measurements, the lab should arrange to transfer the artifacts to the next participating laboratory.
    - Sender to pay the freight charges (to the laboratory)
    - Receiver to pay the customs clearances etc
    - Pilot lab will prepare a CARNET for applicable countries.
- Step 8:
  - The participanting laboratory should transfer the data to the pilot lab within 2 weeks
- Miscellanies
  - For each of the thermocouples, 3 different Co-C realizations are needed.
  - During calibration CJ ends of the thermocouple should be immersed in to an ice point at least up to an immersion of 180 mm.
  - The participant should record full-time data for each Co-C realization.
  - Measure the temperature profile of the furnace for Co-C realization at 1320 °C (Figure 2)

8. REPORTING DATA TO PILOT:

The participating laboratory must send to pilot lab the following information **within 2 weeks** of sending the thermocouples to next participant:

- A general outline of the calibration procedure consisting of no more than one page and send this as an electronic file named **'Procedure_NMI.doc'**.
- Details of instrumentation used in the fixed point calibration, values of calibration results, measured temperature profiles of the enclosures used, and the combined uncertainty as an Excel spreadsheet named **'Calibration Data_NMI.xls'.**
- Melting point should be determined from the inflection point of the melting curve as shown in Fig.1. Inflection point can be calculated from the second derivative of the third order polynomial fit of the measured data in range depicted in Fig.1. Report the emf at the inflection point calculated using 80 %, 60 % and 40 % melting range. (If inflection point does not appear in the specified range, then please use the median value of that range.)

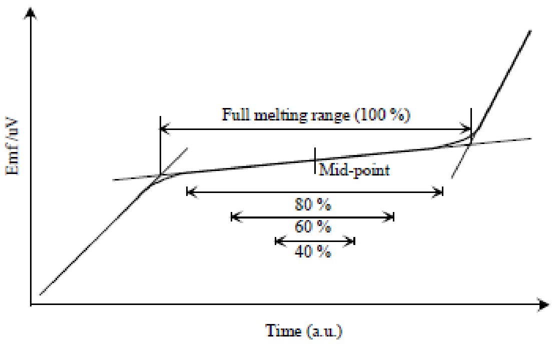


Fig.1. Schematic graph showing how to determine the melting inflection point

- If the inhomogeneity of the thermocouples is to be measured by the participant, supply the graphs of emf measurement as a function of immersion.
- The uncertainty analysis according to the 'ISO Guide to the expression of Uncertainty in Measurement' using the unit of 'microvolt'.

9. UNCERTAINTY ANAYSIS

The various uncertainty components are given below as a guide:

$$u(E_x)^2 = u(E_{RP})^2 + u(E_{IP})^2 + u(E_{HF})^2 + u(E_{IH})^2 + u(E_{CJ})^2 + u(E_{DC})^2 + u(E_{DS})^2 + u(E_{EN})^2 + u(E_{TS})^2$$

① **Measurement scatter at the fixed point, *u(E_{RP})*:** This is a type-A component. The reproducibility of EMF measurements at the fixed point. The standard deviation of 3 melting point values should be used.

② **Inflection point, *u(E_{IP})*:** This factor is for the determination of the inflection point of the melting curve. Use the maximum variation of emfs among three realization of melting.

③ **Heat flux, *u(E_{HF})*:** This is for the heat flux effect along the thermocouples. Use the emf variation of two sets of measurement using a monitoring thermocouple.

$$u(E_{HF}) = \frac{\Delta E_{HF}}{\sqrt{3}}$$

④ **Inhomogeneity of thermocouple, *u(E_{IH})*: "Exclude this component (optional)"** The inhomogeneity in Seebeck coefficient along the thermocouple being calibrated would be measured by the pilot lab using immersion-into-liquid method at 180 °C. The inhomogeneity component will be added by the pilot lab during analysis of the results from the reporting gradient zone as shown in Fig.2. 'Temperature gradient zone' is defined as the region generating 95% of the thermal emf, $E_{95\%}$, from the set temperature to 50 °C, which will be approximately the temperature of the thermometer neck of a furnace. Inhomogeneity will be counted for only 'Temperature gradient zone" using an equation below

$$\text{inhomogeneity} = \pm(E_x - E_{25°C}) \times \frac{\Delta E_{max}(\text{within gradient zone})}{E_{180°C} - E_{25°C}} \times \frac{1}{0.95} \times \frac{1}{2}$$

,

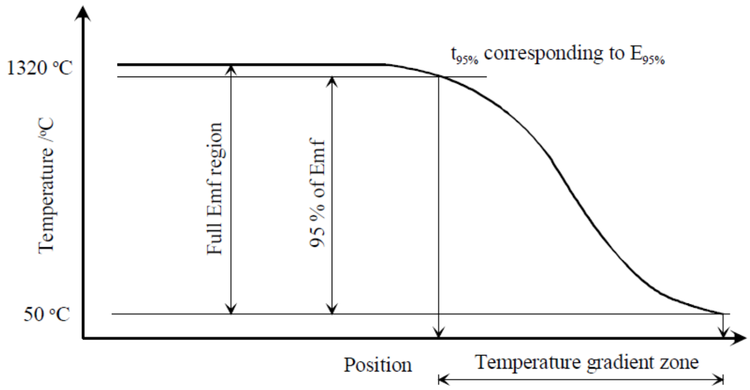


Fig.2 Schematic diagram showing the temperature gradient zone.

⑤ **CJ temperature, *u(E$_{CJ}$)*:** This component is estimated from the quality of the cold junction (ice-point) and also depends on the immersion and slight inhomogneity (if any) of this section of the thermocouples.

⑥ **DVM calibration, *u(E$_{DC}$)*:** This is calibration uncertainty of the DVM used.

⑦ **DVM short-term stability, *u(E$_{DS}$)*:** This is the drift of the DVM during use since the beginning of the measurements for the participant of this international comparison.

⑧ **Stray Emfs and Noise, *u(E$_{EN}$)*:** Any spurious emfs caused by AC pickup during measurement.

⑨ **T/C Stability, *u(E$_{TS}$)*:** Thermoelectric stability measured at the Ag freezing point.

$$u(E_{TS}) = \frac{\Delta E_{TS}}{\sqrt{3}} \times \frac{E(Co-C)}{E(Ag)}$$

9

Appendix B: Description of procedures supplied from the participants

Appendix B-1. NIM

Calibration Procedure in APMP Comparison

Inspection

The wooden box was sent to our laboratory by DHL on Dec. 1st. It was opened carefully and inspected for damage. Two transfer thermocouples and their protection tube were ok.

Annealing

Two protection tubes, with one end closed and sized 695 mm × 6.2 mm × 4.2 mm, made of pure alumina(Al_2O_3 99.7%), were trimmed and baked in 1250℃ for 2h. The Thermocouple junction tip was positioned 1 cm away from one end of the protection tube, while the transfer thermocouple was dressed into the protection tube.

Ag FP

The assembled transfer thermocouples were inserted by 600 mm into an annealing furnace, heated to 1000℃ and annealed for 1h, withdrawn at 1000℃ and inserted into the annealing furnace again at 450℃, and annealed for 16h. They were taken out of the annealing furnace at room temperature to calibrate at freezing point of silver. The assembled thermocouple was inserted carefully into the bottom of a silver cell that is in its freezing plateau. When the thermocouple was in thermal equilibrium with the cell, the electromotive voltages (emf) of thermocouple was measured using a Keithly 2182 Nanovoltmeter and recorded for 30min at freezing plateau. The immersion profile was investigated at the freezing point of Ag over a length of 13 cm too.

Co-C realization

A vertical furnace prepared for the experiment was tuned at 1320℃, the temperature uniformity was ±0.5℃ in a length of 120 mm. The DVM used for this measurement was calibrated at the electrical lab of NIM. The cell of Co-C #1—of 120 mm length, 41 mm OD, the thermometer well immersed in the fixed-point material about 80 mm deep—was installed in the furnace at 500 mm depth from the top. The assembled thermocouple was inserted to the bottom of thermometer well. The assembled thermocouple was inserted to the bottom of thermometer well. The enclosure was sealed, evacuated, and flushed with Argon 3 times repeatedly. An ice-water mixture in a Dewar vessel kept the reference junction of the thermocouple at a temperature of 0 °C. The emf of thermocouple was monitored and logged at intervals of 10s during the melting process via a terminal box connecting to the DVM, which was powered on 4h before measurement and kept at 23 °C ±3 °C during the whole measurement period. Before starting, the terminal box was in short circuit for a null measurement of the measurement system. This was used to correct the measurement data.

Firstly, a monitor Pt/Pd thermocouple of NIM 0902 was measured. The furnace was heated up to 1290 °C, and maintained at that temperature. When the furnace temperature drifted less than 0.01 °C /min, the furnace temperature was raised to 1319 °C, held at that point for 1h, and then at 1329°C for +5K, 1319°C for -5K. After the melt was fully frozen, the ±10K was applied for heat flux effects test.

Secondly, two transfer thermocouples were repeatedly tested in a condition of +/-5K in 3 times. Upon realization of Co-C, the temperature of the cell was kept at full

Appendix B-2. NMIJ

General outline of the calibration procedure

1) Both transfer-thermocouples were inserted 63 cm into the annealing furnace for one hour annealing at 1000 °C, removed from this furnace and then inserted 68 cm into the other annealing furnace for twenty hour annealing at 450 °C.
2) The transfer-thermocouples were calibrated at Ag freezing point, before and after measurements at Co-C eutectic point. Full immersion position was 2 cm above the bottom and 55 cm below the open end of the thermometer well. Instead of using alumina protective-tubes provided, a quartz protective-sheath for the thermocouples was newly prepared for exclusive use by NMIJ. During calibration, the cold-junction (CJ) end of the thermocouples was immersed 190 mm into a mixture of shaved ice and distilled water in a Dewar flask. The EMF value was the average of data measured at the full immersion position for 30 min during the freezing.
3) The heat-flux effect of the Co-C eutectic-point cell was evaluated using a monitoring Pt/Pd thermocouple, before the calibrations at the Co-C eutectic point, where the transfer-thermocouples was used.
4) One of the transfer-thermocouples was inserted 65 cm into the furnace at room temperature. To avoid a temperature overshoot, the temperature of the furnace was raised in intervals up to 1319 °C. After maintaining the furnace temperature at 1319 °C for one hour, three pairs of melting and freezing plateaux were measured. The furnace temperature was then reduced to room temperature continuously. This process was repeated using the other transfer-thermocouple. During the calibrations at the Co-C eutectic point, the CJ end of the thermocouples was immersed 190 mm into a mixture of shaved ice and distilled water in a Dewar flask.

Appendix B-3. NPLI

National Physical Laboratory (NPLI), India

Calibration Procedure for Realization of Co-C Eutectic Fixed Point by Pt/Pd Thermocouples

1. Inspection of Thermocouples: The TCs were inspected for any damage both APMP_Pt/Pd_10_01 & 02 were found to be in good condition. Monitoring thermocouple used at NPLI was Type-S thermocouple, Fluke Model 5650/9533.

2. Annealing: All the thermocouples were annealed at 1000 °C for one hour in an annealing furnace with an uniformity of ±5 °C, and withdrawn at 1000 °C. TCs were further annealed at 450 C for 20 hours.

3. Calibration at Ag Point:
The transfer thermocouples were calibrated at Ag freezing point and freezing point plateau of about 45 min was recorded. The TC was placed 1cm above the bottom of Ag point cell.

4. Calibration at Co-C Eutectic point:
First, the NPLI Type-S TC was measured at CO-C melting temperature with an increase of +5°C and freezing was recorded at -5 °C. Similarly the data was recorded for ±10 °C to deduce the heat flux effect. The melting state was held for 30 min and freezing state was held for one hour as stated in the Protocol step-4.

The transfer thermocouple APMP_Pt/Pd_10_01 was placed in Co-C cell at room temperature , TC was positioned 1-cm above the cell bottom. Measurements were performed at ±5 °C and 3-repeatetion were performed as stated in the Protocol.
Similar procedure was followed for APMP_Pt/Pd_10_02 and 3-measurement runs were carried out.

5. Calibration at Ag Point after Co-C realization:
The measurements were performed on transfer standard at Ag freezing point after Co-C. Data was recorded for 45-min in freezing state and short-term stability was evaluated.

6. Notes:
1. Three different Co-C realizations were performed for each thermocouple under comparison and full time data was recorded for each Co-C realization.
2. During calibration cold junction ends of the TCs were immersed in to an Ice-point up to the immersion of 180 mm.
3. The temperature profile of Co-C furnace was measured at 1320 C using Type-S TC.

Appendix C: Instruments used in the comparison from the participants

Appendix C-1: KRISS

NMI: KRISS

Devices	Manufacturer	Model	Serial Number	Remarks
DVM	Keithley	2182A	1232368	
Scanner (if used)	None	None	None	
Ice-point	KGW	-	-	maximum immersion depth: 285 mm
Monitoring t/c	KRISS	Pt/Pd	JPtPd2	source of wires: Alfa Aesar
Cell	KRISS	Co-C	Co-C-07-01	
Furnace	KRISS	-	KSF-V-01	

Appendix C-2: NIM

NMI:NIM

Devices	Manufacturer	Model	Serial Number	Remarks
DVM	KEITHLEY	2182	0756530	
Scanner (if used)	\	\	\	
Ice-point	NIM	TC-1	#3	250mm in depth
Monitoring t/c	NIM	PtPd	0902	thermoelements of the tc are from Alfa Aesar.
Cell	NIM	CoC	#1	
Furnace	CHINO	MAT-60SC2	070201	

Appendix C-3: NMIJ

NMI: NMIJ

Devices	Manufacturer	Model	Serial Number	Remarks
DVM	Fluke	8508A	856647857	---
Scanner	Data Proof	160B Opt.2	992	---
Ice-point	Thermos	D-6000	---	Dewar flask. The maximum depth is 250 mm.
Monitoring t/c	NMIJ	Pt/Pd	Pt/Pd CoC-1	The source of wires is Ishifuku Metal Industry Co., Ltd.
Cell	NMIJ	Co-C	CoC-a22	---
Furnace	NMIJ	---	EPF-1	3 zone furnace

Appendix C-4: NMIA

NMI: NMIA

Devices	Manufacturer	Model	Serial Number	Remarks
DVM	Agilent	34420A	LN68840	
Scanner (if used)	N/A			
Ice-point	crushed IP			Immersion in IP = 190-200 mm
Monitoring t/c	NMIA		13-0395	Sigmund-Cohn, USA
Cell	NMIA		CoC-08	
Furnace	Carbolite	TZF	20-701512	

Appendix C-5: NPLI

NMI: NPLI

Devices	Manufacturer	Model	Serial Number	Remarks
DVM	Fluke	8508A	170062540	0.01 µV; 8 1/2 digit
Scanner (if used)	NIL			
Ice-point	NPL India	NPL-THS-01		Stability 3 mK
Monitoring t/c	Fluke	Type-S, Model 5650	9533	0 to 1450 °C, Uncertainty at Ag = ± 225 m°C
Cell	NPL India	NPL_THS_Co-C_01		ID 7 mm, Length 110 mm
Furnace	Carbolite	STF/50/80/450	2302-01-09	
Annealing Furnace	Isotech	Metrology Furnace, 465	221120-1	with Alumina Annealing Block, Length 450 mm, Stability ±2 °C

Appendix D: Measurement results from the participants

Appendix D-1: KRISS

NMI: KRISS_Initial

	Emf at Ag freezing point/µV	
	APMP_PtPd_10_01	APMP_PtPd_10_02
Before	10786.2	10800.8
After	10786.8	10800.7
Difference	0.6	0.1

NMI: KRISS_Final

	Emf at Ag freezing point/µV	
	APMP_PtPd_10_01	APMP_PtPd_10_02
Before	10784.8	10795.8
After	10784.7	10796.4
Difference	0.1	0.6

NMI: KRISS_Initial

t/c No.		Melting point EMF /µV								
		1 st melting			2nd melting			3rd melting		
		80% region	60 % region	40 % region	80% region	60 % region	40 % region	80% region	60 % region	40 % region
APMP_PtPd_10_01	Measured	18581.5	18581.6	18581.7	18581.6	18581.6	18581.7	18581.6	18581.7	18581.8
	Average	18581.6			18581.6			18581.7		
	Standard deviation	0.05								
Inflection point covered in the range		Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
APMP_PtPd_10_02	Measured	18604.4	18604.5	18604.6	18604.5	18604.6	18604.6	18604.7	18604.7	18604.8
	Average	18604.5			18604.6			18604.7		
	Standard deviation	0.12								
Inflection point covered in the range		Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes

NMI: KRISS_Final

t/c No.		Melting point EMF /µV								
		1 st melting			2nd melting			3rd melting		
		80% region	60 % region	40 % region	80% region	60 % region	40 % region	80% region	60 % region	40 % region
APMP_PtPd_10_01	Measured	18579.6	18579.8	18579.4	18579.9	18579.9	18579.9	18580	18580.1	18580.2
	Average	18579.6			18579.9			18580.1		
	Standard deviation	0.25								
Inflection point covered in the range		Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
APMP_PtPd_10_02	Measured	18611.1	18611.1	18610.8	18610.6	18610.7	18611.1	18610.3	18610.4	18610.1
	Average	18611.0			18610.8			18610.3		
	Standard deviation	0.38								
Inflection point covered in the range		Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes

Appendix D-2: NIM

NMI: NIM

	Emf at Ag freezing point/µV	
	APMP_PtPd_10_01	APMP_PtPd_10_02
Before	10785.96	10799.90
After	10785.63	10799.67
Difference	-0.33	-0.23

NMI: NIM

t/c No.		Melting point EMF /µV								
		1 st melting			2nd melting			3rd melting		
		80% region	60 % region	40 % region	80% region	60 % region	40 % region	80% region	60 % region	40 % region
APMP_PtPd_10_01	Measured	18582.19	18582.23	18582.23	18582.58	18582.56	18582.48	18582.59	18582.60	18582.54
	Average	18582.2			18582.5			18582.6		
	Standard deviation	0.20								
APMP_PtPd_10_02	Measured	18608.34	18608.37	18608.36	18608.41	18608.32	18608.32	18608.48	18608.51	18608.54
	Average	18608.4			18608.4			18608.5		
	Standard deviation	0.09								

Appendix D-3: NMIJ

NMI: NMIJ

	Emf at Ag freezing point/µV	
	APMP_PtPd_10_01	APMP_PtPd_10_02
Before	10785.177	10800.218
After	10784.820	10802.404
Difference	-0.357	2.186

NMI: NMIJ

t/c No.		Melting point EMF /µV								
		1 st melting			2nd melting			3rd melting		
		80% region	60 % region	40 % region	80% region	60 % region	40 % region	80% region	60 % region	40 % region
APMP_PtPd_10_01	Measured	18581.276	18581.341	18581.425	18581.280	18581.407	18581.458	18581.454	18581.484	18581.594
	Average	18581.347			18581.382			18581.511		
	Standard deviation	0.086								
Inflection point covered in the range		Yes	Yes	Yes	Yes	Yes	No	Yes	Yes	Yes
APMP_PtPd_10_02	Measured	18604.744	18604.751	18604.861	18605.048	18605.140	18605.200	18605.454	18605.451	18605.612
	Average	18604.785			18605.129			18605.506		
	Standard deviation	0.360								
Inflection point covered in the range		Yes	Yes	Yes	Yes	Yes	No	Yes	Yes	Yes

Appendix D-4: NMIA

NMI: NMIA

Emf at Ag freezing point/µV

	APMP_PtPd_10_01	APMP_PtPd_10_02
Before	10785.43	10800.2
After	10784.8	10800.3
Difference	-0.63	0.1

NMI: NMIA

t/c No.		Melting point EMF /µV								
		1 st melting			2nd melting			3rd melting		
		80% region	60 % region	40 % region	80% region	60 % region	40 % region	80% region	60 % region	40 % region
APMP_PtPd_10_01	Measured	18583.27	18583.26	18583.25	18583.96	18583.97	18584.07	18583.04	18583.04	18583.04
	Average	18583.260			18584.000			18583.040		
	Standard deviation	0.503								
Inflection point covered in the range		Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
APMP_PtPd_10_02	Measured	18613.06	18613.01	18613.02	18613.75	18613.77	18613.77	18613.5	18613.55	18613.56
	Average	18613.030			18613.763			18613.537		
	Standard deviation	0.375								
Inflection point covered in the range		Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes

Appendix D-5: NPLI

NMI: NPLI

	Emf at Ag freezing point/µV	
	APMP_PtPd_10_01	APMP_PtPd_10_02
Before	10787.73	10803.82
After	10786.46	10803.47
Difference	-1.27	-0.35

NMI: NPLI

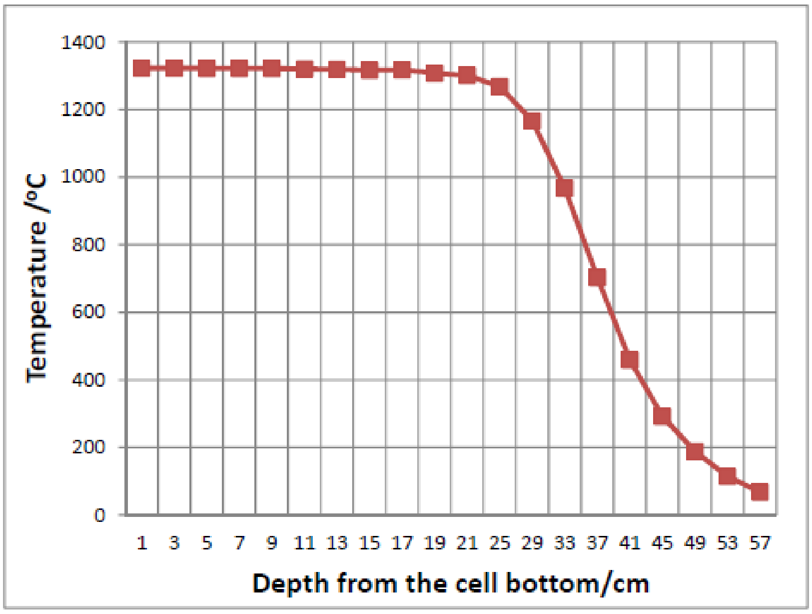
t/c No.		Melting point EMF /µV								
		1 st melting			2nd melting			3rd melting		
		80% region	60 % region	40 % region	80% region	60 % region	40 % region	80% region	60 % region	40 % region
APMP_PtPd_10_01	Measured	18587.60		18585.53	18586.07		18584.05	18585.46		18583.80
	Average	18586.57			18585.06			18584.63		
	Standard deviation	1.02								
Inflection point covered in the range		Yes	No	Yes	Yes	No	Yes	Yes	No	Yes
APMP_PtPd_10_02	Measured	18624.42	18623.76		18624.99	18620.43	18622.40	18623.87		18621.38
	Average	18624.09			18622.61			18622.63		
	Standard deviation	0.85								
Inflection point covered in the range		Yes	Yes	No	Yes	Yes	Yes	Yes	No	Yes

Appendix E: Immersion profiles of furnace from the participants

Appendix E-1: KRISS

NMI: KRISS

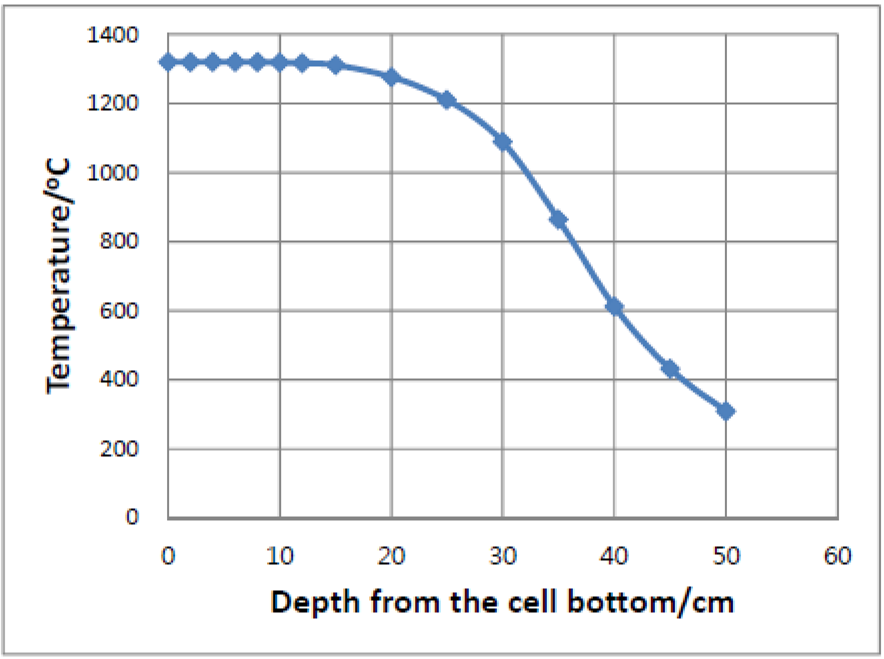
Depth from the cell bottom/cm	Temperature /°C
1	1322.63
3	1322.62
5	1322.58
7	1322.35
9	1321.8
11	1320.3
13	1318.9
15	1316.4
17	1317.7
19	1308.1
21	1301.2
25	1268.3
29	1166.5
33	967.5
37	703
41	459
45	292
49	188
53	114
57	68



Appendix E-2: NIM

NMI: NIM

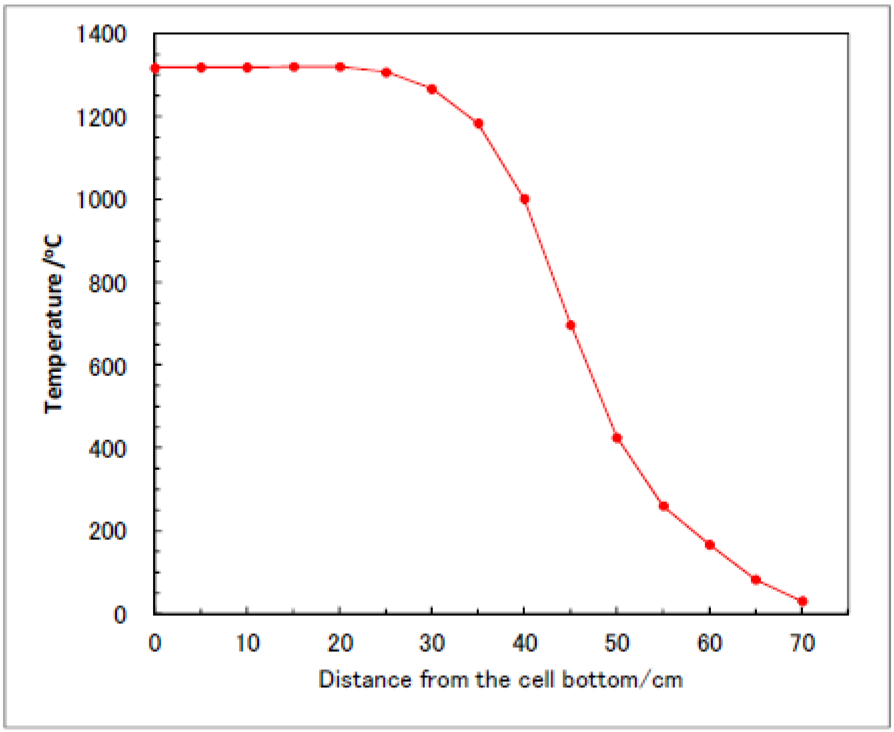
Depth from the cell bottom/cm	Temperature /°C
0	1319.7
2	1319.8
4	1320.0
6	1320.0
8	1319.6
10	1318.6
12	1316.7
15	1310.7
20	1276.1
25	1210.3
30	1088.9
35	864.3
40	612.7
45	431.9
50	309.4



Appendix E-3: NMIJ

NMI: NMIJ

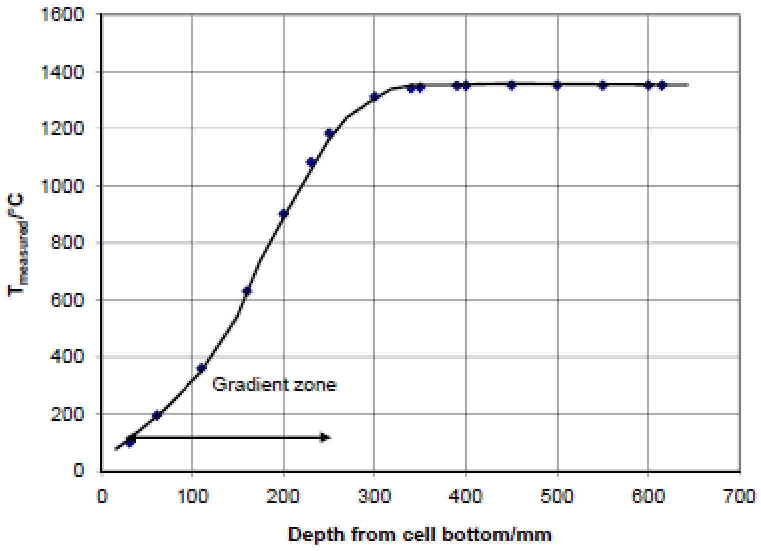
Depth from the cell bottom/cm	Temperature /°C
0	1318.2
5	1318.7
10	1319.0
15	1320.0
20	1320.4
25	1307.9
30	1267.9
35	1183.7
40	1001.7
45	697.6
50	425.5
55	260.6
60	167.4
65	82.5
70	30.7



Appendix E-4: NMIA

NMI: NMIA

Depth from the cell bottom/mm	Temperature /°C
30	100
60	195.8
110	360
160	630.8
200	901.8
230	1084.4
250	1184.8
300	1312.4
340	1341.3
350	1345.1
390	1351.7
400	1352.2
450	1353
500	1352.9
550	1352.7
600	1352.8
615	1352.8

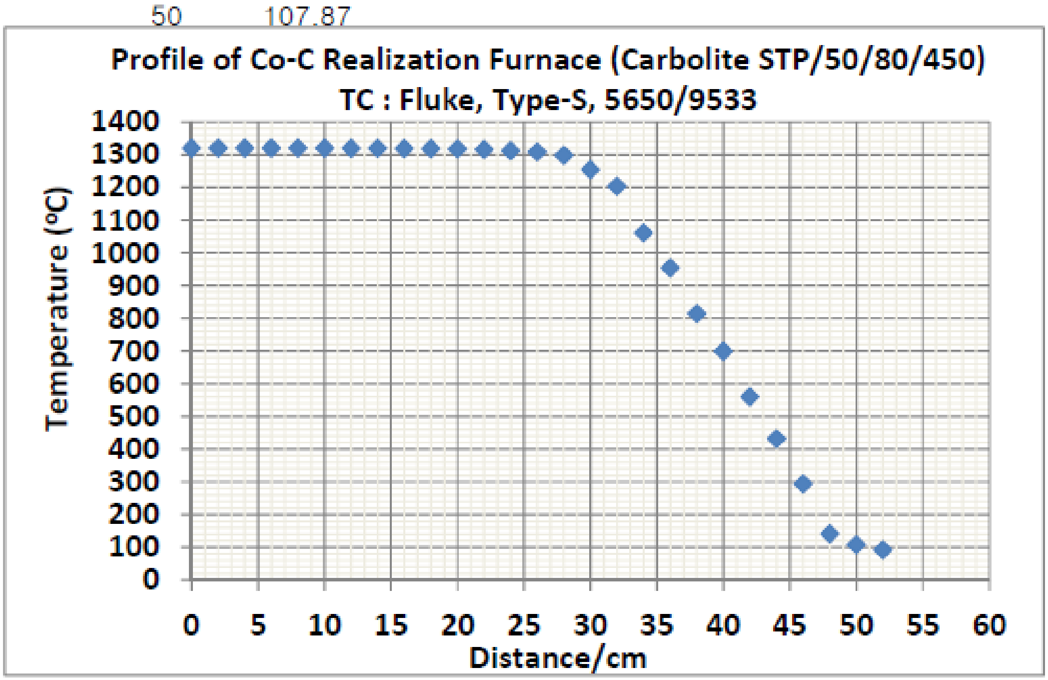


Inhomogeneity considered from 350 mm to 550 mm from tip of the thermocouples

Appendix E-5: NPLI

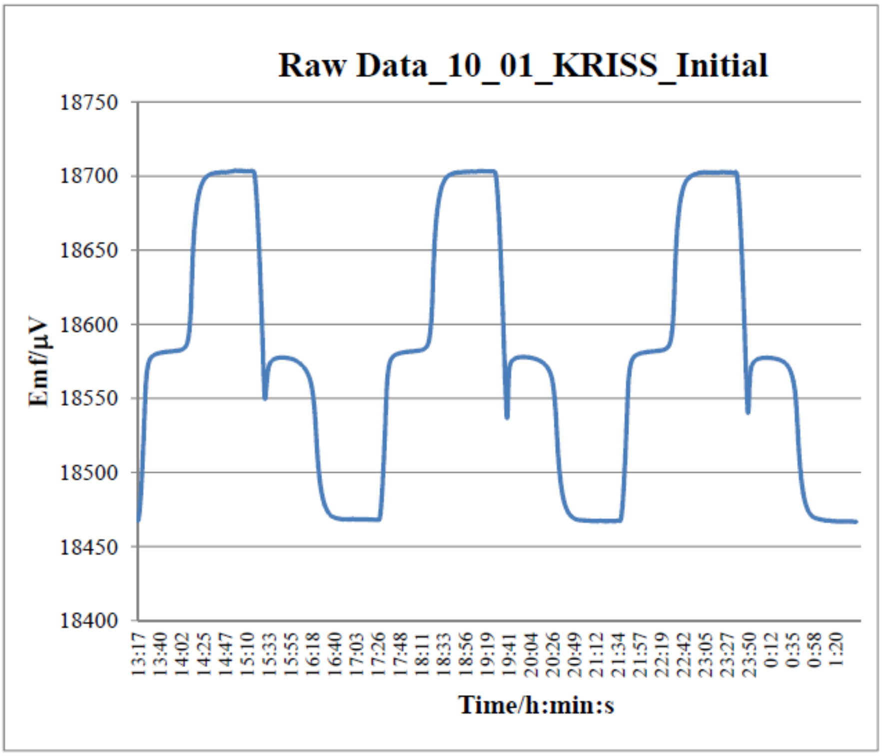
NMI: NPLI

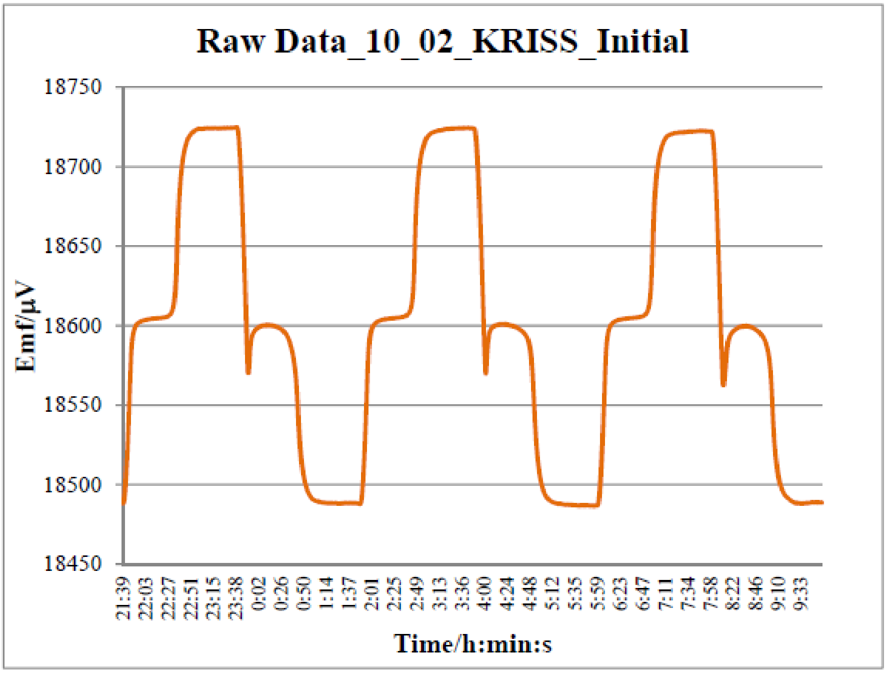
Depth from the cell bottom/cm	Temperature /°C
0	1319.83
2	1319.87
4	1319.95
6	1319.99
8	1320.01
10	1319.85
12	1319.66
14	1319.4
16	1318.93
18	1318.21
20	1317.33
22	1316.05
24	1311.91
26	1308.16
28	1298.16
30	1253.87
32	1203.4
34	1060.66
36	953.76
38	814.23
40	698.89
42	560.24
44	431.97
46	293.85
48	141.58
50	107.87



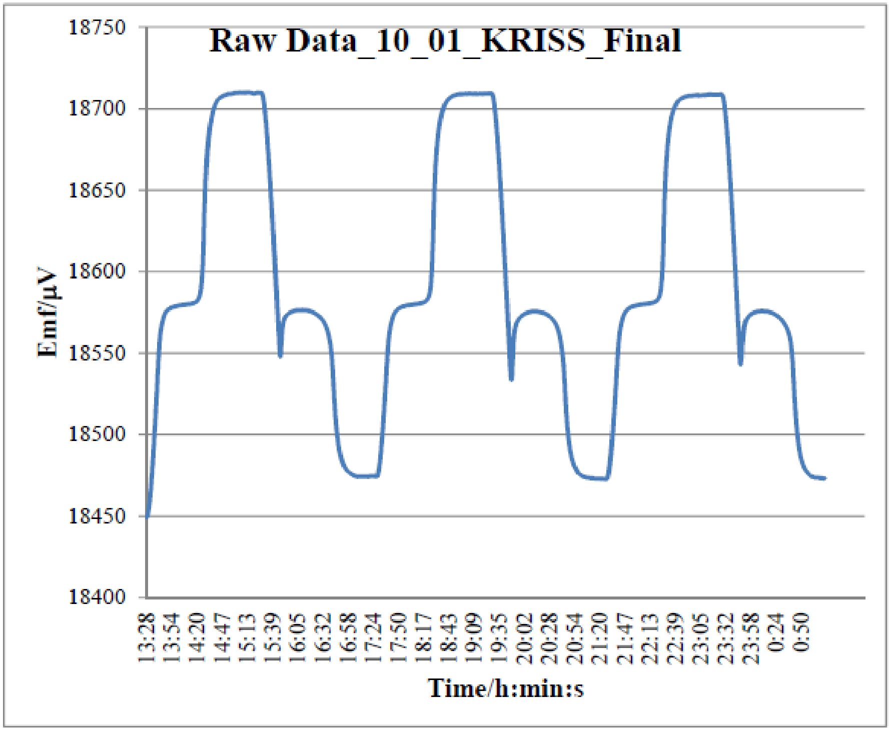
Appendix F: Melting curves from the participants

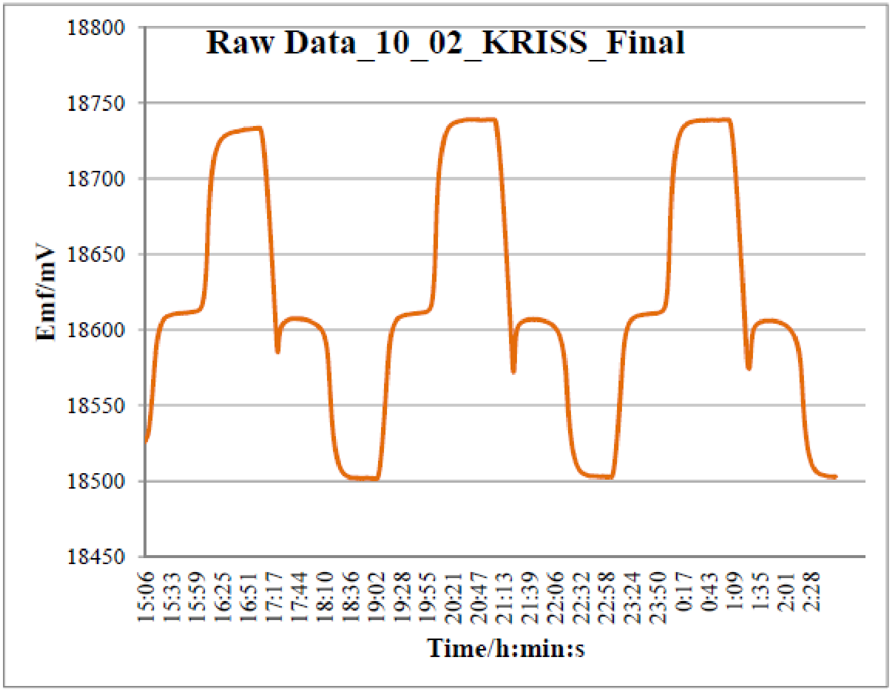
Appendix F-1: KRISS_Initial



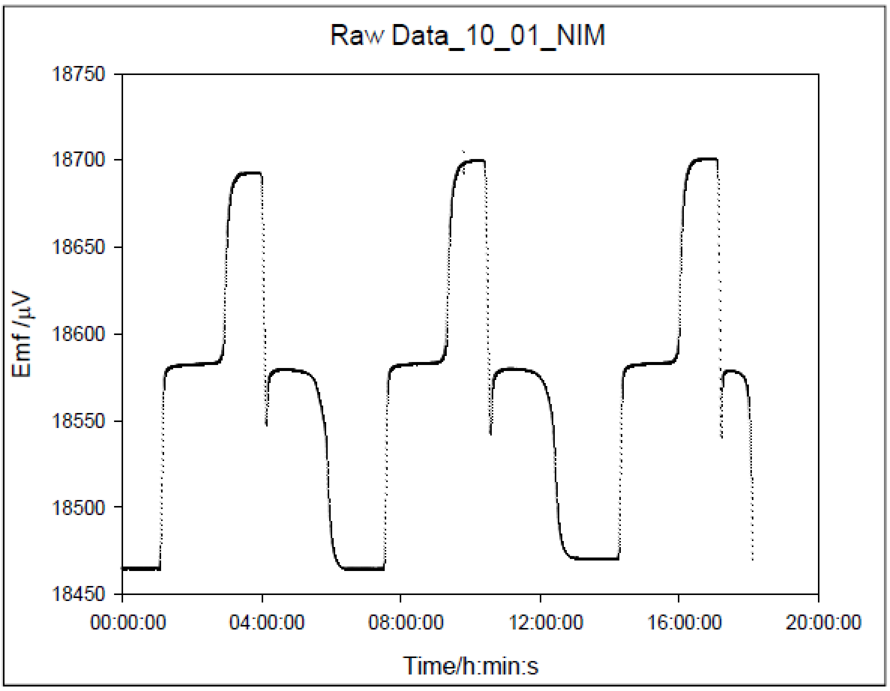


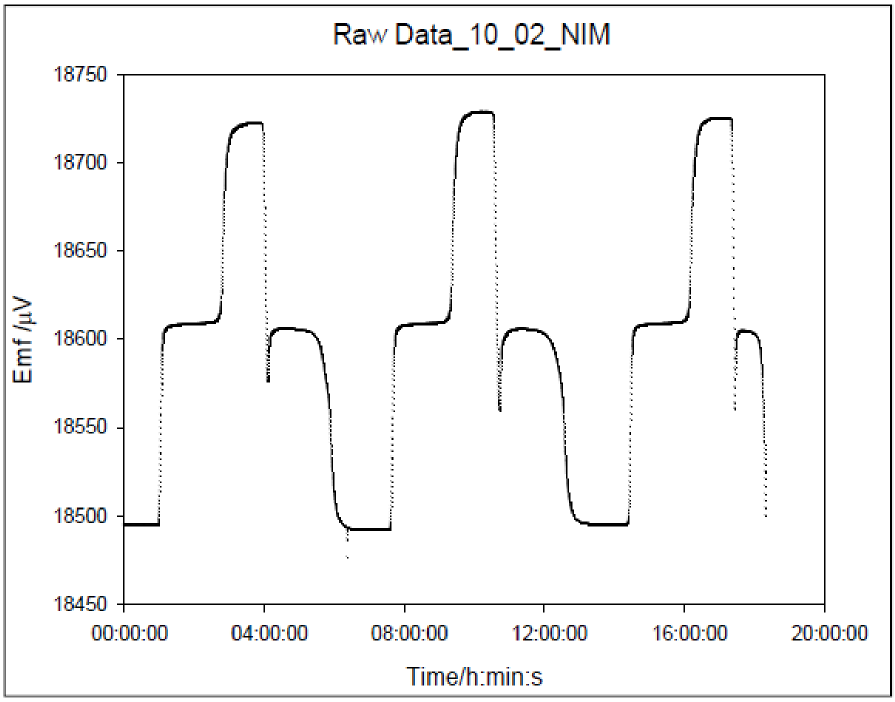
Appendix F-1: KRISS_Final



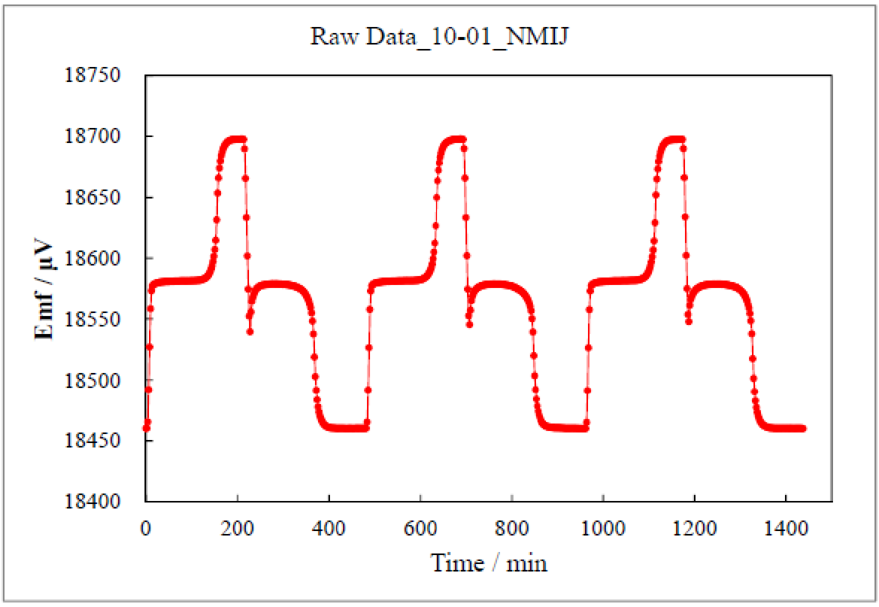


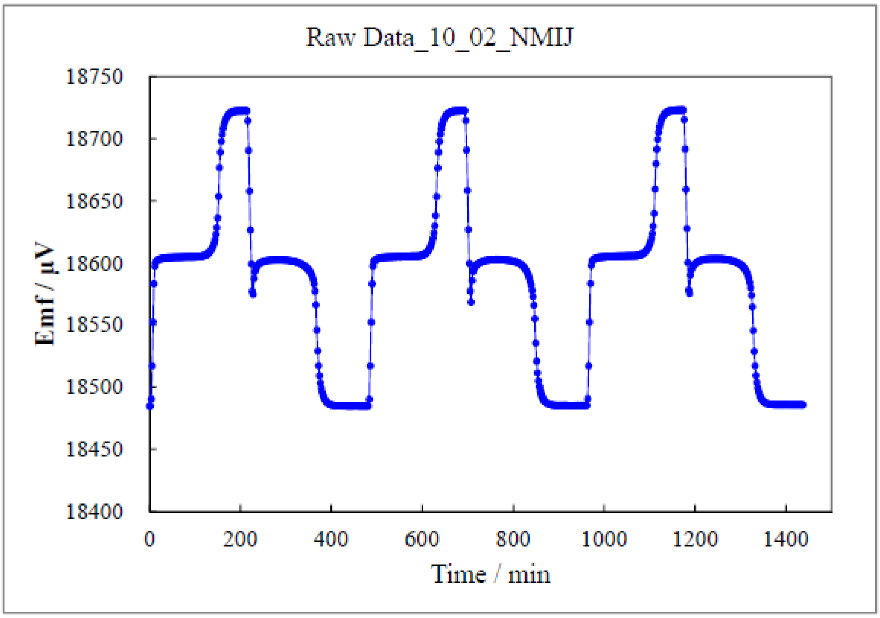
Appendix F-3: NIM



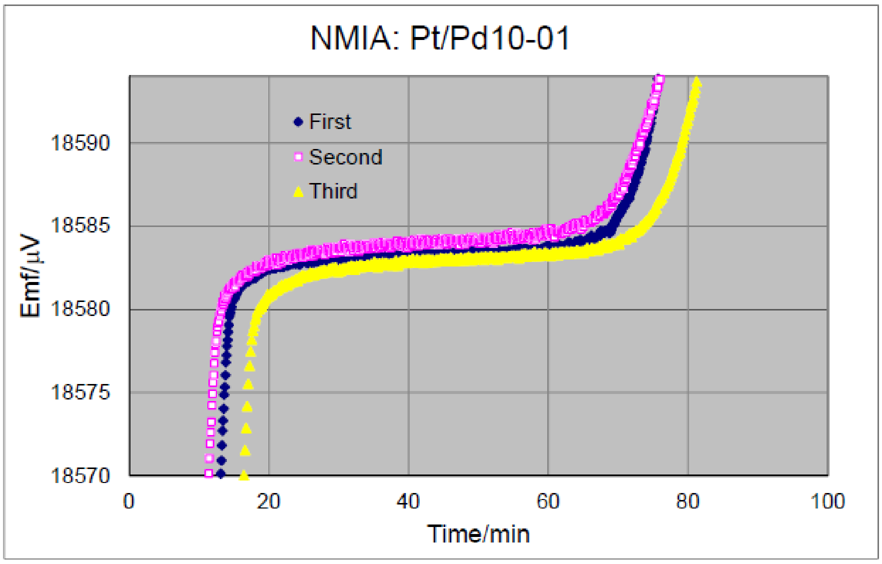


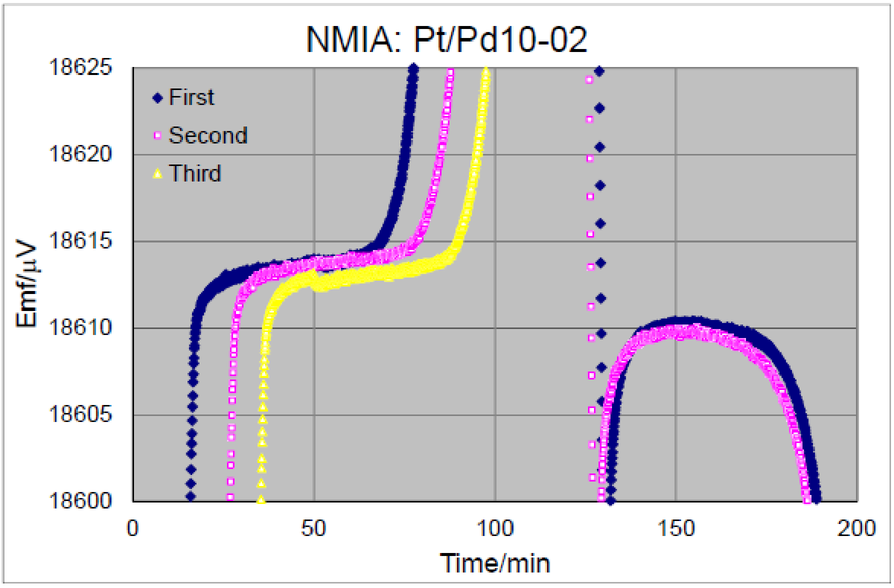
Appendix F-4: NMIJ



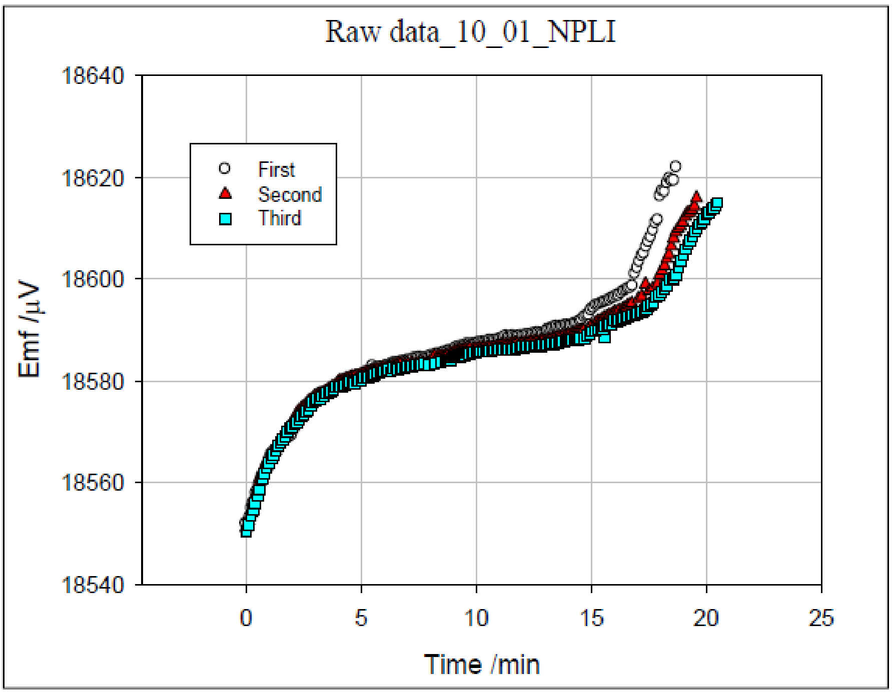


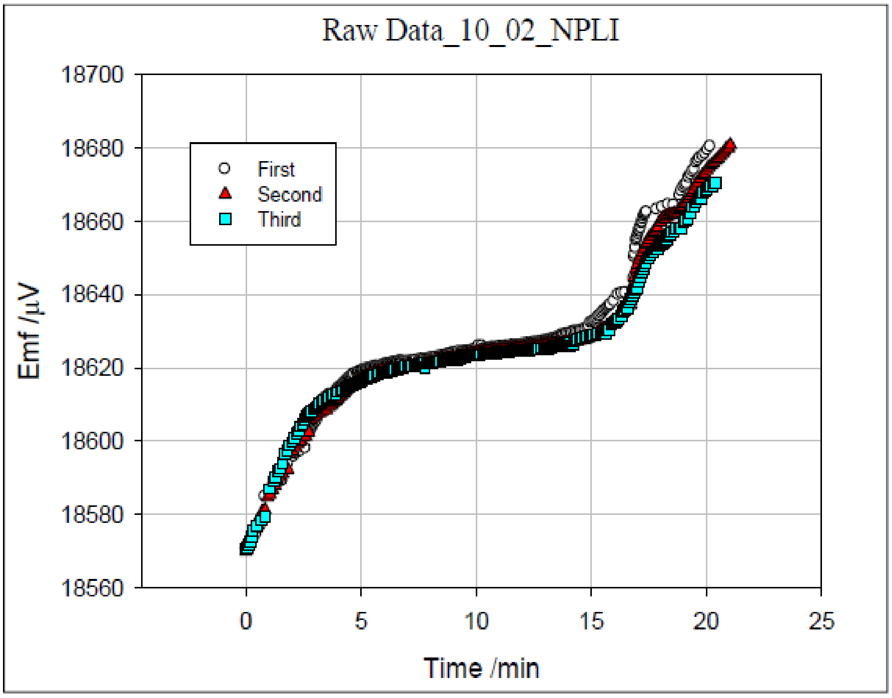
Appendix F-5: NMIA





Appendix F-6: NPLI





Appendix G: Uncertainty tables from the participants

Appendix G-1: KRISS_Initial

NMI: KRISS_Initial

Uncertainty Analysis of 10_01

Unceratiny factors	Quantity	Probability Distribution	Standard uncertainty	Sensitivity coefficient	Uncertainty contribution /μV	Remarks
1. Measurement scatter	0.05 μV	Normal	0.05 μV	1	0.05	Standard deviation
2. Inflection point	0.1 μV	Rectangular	0.06 μV	1	0.06	Maximum variation/2
3. Heat flux	0.1 μV	Rectangular	0.06 μV	1	0.06	Emf variation between ± 5 °C and ± 10 °C
4. Inhomogeneity	3.6 μV	Rectangular	2.1 μV	1	2.1	Given by KRISS
5. CJ temperature	10 mK	Rectangular	5.6 mK	5.3	0.03	Measurements
6. DVM calibration	8 μV/V at 100 mV range (*k*=2)	Normal	0.07 μV	1	0.07	certificate
7. DVM Short-term stability	0.10 μV	Rectangular	0.06 μV	1	0.06	Maximum Emf change before/after comparisons
8. Electric noise	0.05 μV	Rectangular	0.03 μV	1	0.03	Any spurious emf
9. t/c stability	0.6 μV	Rectangular	0.35 μV	1.72	0.6	Emf difference between 2 Ag freezing emf
Combined standard uncertainty /μV					2.19	

Expanded uncertainty (*k* = 2) /μV		4.38
Expanded uncertainty (*k* = 2) /°C		0.185

NMI: KRISS_Initial

Uncertainty Analysis of 10_02

Unceratiny factors	Quantity	Probability Distribution	Standard uncertainty	Sensitivity coefficient	Uncertainty contribution /μV	Remarks
1. Measurement scatter	0.12 μV	Normal	0.12 μV	1	0.12	Standard deviation
2. Inflection point	0.1 μV	Rectangular	0.06 μV	1	0.06	Maximum variation/2
3. Heat flux	0.1 μV	Rectangular	0.06 μV	1	0.06	Emf variation between ± 5 °C and ± 10 °C
4. Inhomogeneity	26.3 μV	Rectangular	15.2 μV	1	15.2	Given by KRISS
5. CJ temperature	10 mK	Rectangular	5.6 mK	5.3	0.03	Measurements
6. DVM calibration	8 μV/V at 100 mV range (*k*=2)	Normal	0.07 μV	1	0.07	certificate
7. DVM Short-term stability	0.10 μV	Rectangular	0.06 μV	1	0.06	Maximum Emf change before/after comparisons
8. Electric noise	0.05 μV	Rectangular	0.03 μV	1	0.03	Any spurious emf
9. t/c stability	0.1 μV	Rectangular	0.06 μV	1.72	0.1	Emf difference between 2 Ag freezing emf
Combined standard uncertainty /μV					15.20	

Expanded uncertainty (*k* = 2) /μV		30.40
Expanded uncertainty (*k* = 2) /°C		1.288

Appendix G-2: KRISS_Final

NMI: KRISS_Final

Uncertainty Analysis of 10_01

Unceratiny factors	Quantity	Probability Distribution	Standard uncertainty	Sensitivity coefficient	Uncertainty contribution /μV	Remarks
1. Measurement scatter	0.25 μV	Normal	0.25 μV	1	0.25	Standard deviation
2. Inflection point	0.2 μV	Rectangular	0.12 μV	1	0.12	Maximum variation/2
3. Heat flux	0.1 μV	Rectangular	0.06 μV	1	0.06	Emf variation between ± 5 °C and ± 10 °C
4. Inhomogeneity	3.6 μV	Rectangular	2.1 μV	1	2.1	Given by KRISS
5. CJ temperature	10 mK	Rectangular	5.6 mK	5.3	0.03	Measurements
6. DVM calibration	8 μV/V at 100 mV range (*k*=2)	Normal	0.07 μV	1	0.07	certificate
7. DVM Short-term stability	0.10 μV	Rectangular	0.06 μV	1	0.06	Maximum Emf change before/after comparisons
8. Electric noise	0.05 μV	Rectangular	0.03 μV	1	0.03	Any spurious emf
9. t/c stability	0.1 μV	Rectangular	0.06 μV	1.72	0.1	Emf difference between 2 Ag freezing emf
Combined standard uncertainty /μV					2.12	

Expanded uncertainty (*k* = 2) /μV	4.25
Expanded uncertainty (*k* = 2) /°C	0.180

NMI: KRISS_Final

Uncertainty Analysis of 10_02

Unceratiny factors	Quantity	Probability Distribution	Standard uncertainty	Sensitivity coefficient	Uncertainty contribution /μV	Remarks
1. Measurement scatter	0.38 μV	Normal	0.38 μV	1	0.38	Standard deviation
2. Inflection point	0.5 μV	Rectangular	0.29 μV	1	0.29	Maximum variation/2
3. Heat flux	0.1 μV	Rectangular	0.06 μV	1	0.06	Emf variation between ± 5 °C and ± 10 °C
4. Inhomogeneity	24.5 μV	Rectangular	14.1 μV	1	14.1	Given by KRISS (Optional)
5. CJ temperature	10 mK	Rectangular	5.6 mK	5.3	0.03	Measurements
6. DVM calibration	8 μV/V at 100 mV range (*k*=2)	Normal	0.07 μV	1	0.07	certificate
7. DVM Short-term stability	0.10 μV	Rectangular	0.06 μV	1	0.01	Maximum Emf change before/after comparisons
8. Electric noise	0.05 μV	Rectangular	0.03 μV	1	0.03	Any spurious emf
9. t/c stability	0.6 μV	Rectangular	0.35 μV	1.72	0.6	Emf difference between 2 Ag freezing emf
Combined standard uncertainty /uV					14.12	

Expanded uncertainty (k = 2) /uV	28.24
Expanded uncertainty (k = 2) /°C	1.197

Appendix G-3: NIM

NMI: NIM

Uncertainty Analysis of 10_01

Unceratiny factors	Quantity	Probability Distribution	Standard uncertainty	Sensitivity coefficient	Uncertainty contribution /μV	Remarks
1. Measurement scatter	0.2 μV	Normal	0.2 μV	1	0.2	Standard deviation
2. Inflection point	± 0.1 μV	Rectangular	0.06 μV	1	0.06	Maximum variation/2
3. Heat flux	0.34 μV	Rectangular	0.20 μV	1	0.2	Emf variation between ± 5 °C and ± 10 °C
4. Inhomogeneity	μV	Rectangular	μV	1	0	given by pilot lab
5. CJ temperature	± 5 mK	Rectangular	2.88 mK	5.3	0.02	Measurements
6. DVM calibration	6E-6 at 100 mV range (*k*=2)	Normal	0.07 μV	1	0.07	certificate
7. DVM Short-term stability	± 0.8 μV	Rectangular	0.46 μV	1	0.46	±0.8uV as specification in 90days
8. Electric noise	± 0.1 μV	Rectangular	0.06 μV	1	0.06	Shut off the furnace
9. t/c stability	0.33 μV	Rectangular	0.19 μV	1.72	0.32	Emf difference between 2 Ag freezing emf
Combined standard uncertainty /μV					0.64	
Expanded uncertainty (*k* = 2) /μV					1.3	
Expanded uncertainty (*k* = 2) /°C					0.054	

NMI: NIM

Uncertainty Analysis of 10_02

Unceratiny factors	Quantity	Probability Distribution	Standard uncertainty	Sensitivity coefficient	Uncertainty contribution /μV	Remarks
1. Measurement scatter	0.09 μV	Normal	0.09 μV	1	0.09	Standard deviation
2. Inflection point	± 0.1 μV	Rectangular	0.06 μV	1	0.06	Maximum variation/2
3. Heat flux	0.34 μV	Rectangular	0.196 μV	1	0.2	Emf variation between ± 5 °C and ± 10 °C
4. Inhomogeneity	μV	Rectangular	μV	1	0	given by pilot lab
5. CJ temperature	± 5 mK	Rectangular	2.88 mK	5.3	0.02	Measurements
6. DVM calibration	6E-6 at 100 mV range (*k*=2)	Normal	0.07 μV	1	0.07	certificate
7. DVM Short-term stability	± 0.8 μV	Rectangular	0.46 μV	1	0.46	±0.8uV as specification in 90days
8. Electric noise	± 0.1 μV	Rectangular	0.06 μV	1	0.06	Shut off the furnace
9. t/c stability	0.23 μV	Rectangular	0.13 μV	1.72	0.22	Emf difference between 2 Ag freezing emf
Combined standard uncertainty /uV					0.57	
Expanded uncertainty (*k* = 2) /μV					1.1	
Expanded uncertainty (*k* = 2) /°C					0.048	

Appendix G-4: NMIJ

NMI: NMIJ

Uncertainty Analysis of 10_01

Unceratiny factors	Quantity	Probability Distribution	Standard uncertainty	Sensitivity coefficient	Uncertainty contribution /µV	Remarks
1. Measurement scatter	0.09 µV	Normal	0.09 µV	1	0.09	Standard deviation
2. Inflection point	0.05 µV	Rectangular	0.03 µV	1	0.03	Maximum variation/2
3. Heat flux	0.24 µV	Rectangular	0.14 µV	1	0.14	Emf variation between ± 5°C and ± 10 °C
4. Inhomogeneity	µV	Rectangular	µV	1	0	Given by KRISS
5. CJ temperature	1.1 mK	Normal	1.1 mK	5.3	0.01	Measurements
6. DVM calibration	0.16 µV	Normal	0.16 µV	1	0.16	certificate
7. DVM Short-term stability	0.007 µV	Rectangular	0.004 µV	1	0.004	Maximum Emf change before/after comparisons
8. Electric noise	0.043 µV	Rectangular	0.025 µV	1	0.025	Any spurious emf
9. t/c stability	0.357 µV	Rectangular	0.206 µV	1.72	0.355	Emf difference between 2 Ag freezing emf
Combined standard uncertainty µV					0.43	
Expanded uncertainty (k = 2) /µV					0.85	
Expanded uncertainty (k = 2) /°C					0.036	

NMI: NMIJ

Uncertainty Analysis of 10_02

Unceratiny factors	Quantity	Probability Distribution	Standard uncertainty	Sensitivity coefficient	Uncertainty contribution /µV	Remarks
1. Measurement scatter	0.36 µV	Normal	0.36 µV	1	0.36	Standard deviation
2. Inflection point	0.05 µV	Rectangular	0.03 µV	1	0.03	Maximum variation/2
3. Heat flux	0.24 µV	Rectangular	0.14 µV	1	0.14	Emf variation between ± 5 °C and ± 10 °C
4. Inhomogeneity	µV	Rectangular	µV	1	0	Given by the pilot
5. CJ temperature	1.1 mK	Normal	1.1 mK	5.3	0.01	Measurements
6. DVM calibration	0.16 µV	Normal	0.16 µV	1	0.16	certificate
7. DVM Short-term stability	0.007 µV	Rectangular	0.007 µV	1	0.004	Maximum Emf change before/after comparisons
8. Electric noise	0.043 µV	Rectangular	0.043 µV	1	0.025	Any spurious emf
9. t/c stability	2.186 µV	Rectangular	1.26 µV	1.72	2.171	Emf difference between 2 Ag freezing emf
Combined standard uncertainty /µV					2.21	
Expanded uncertainty (k = 2) /µV					4.42	
Expanded uncertainty (k = 2) /°C					0.187	

Appendix G-5: NMIA

NMI: NMIA

Uncertainty Analysis of 10_01

Unceratiny factors	Quantity	Probability Distribution	Standard uncertainty	Sensitivity coefficient	Uncertainty contribution /µV	Remarks
1. Measurement scatter	0.473 µV	Normal	0.473 µV	1	0.473	Standard deviation
2. Inflection point	0.1 µV	Rectangular	0.1 µV	1	0.06	Maximum variation/2
3. Heat flux	0.3 µV	rectangular	0.3 µV	1	0.3	Emf variation between ± 5 °C and ± 10 °C
4. Inhomogeneity	µV	rectangular	µV	1	0	given by the pilot
5. CJ temperature	10 mK	Normal	5 mK	5.3	0.027	Measurements
6. DVM calibration	0.07 µV	Normal	0.035 µV	1	0.035	certificate
7. DVM Short-term stability	2 ppm	Rectangular	0.021 µV	1	0.021	change in calibration before/after comparisons
8. Electric noise	0.05 µV	Rectangular	0.03 µV	1	0.03	Any spurious emf
9. t/c stability	0.63 µV	Rectangular	0.36 µV	1.72	0.623	Emf difference between 2 Ag freezing emf
Combined standard uncertainty /µV					**0.842**	
Expanded uncertainty (k = 2) /µV					**1.683**	
Expanded uncertainty (k = 2) /°C					0.071	

NMI: NMIA

Uncertainty Analysis of 10_02

Unceratiny factors	Quantity	Probability Distribution	Standard uncertainty	Sensitivity coefficient	Uncertainty contribution /µV	Remarks
1. Measurement scatter	0.375 µV	Normal	0.375 µV	1	0.375	Standard deviation
2. Inflection point	0.1 µV	Rectangular	0.06 µV	1	0.06	Maximum variation/2
3. Heat flux	0.3 µV	rectangular	0.3 µV	1	0.3	Emf variation between ± 5 °C and ± 10 °C
4. Inhomogeneity	µV	Rectangular	µV	1	0	given by the pilot
5. CJ temperature	10 mK	Normal	5.6 mK	5.3	0.03	Measurements
6. DVM calibration	0.07 µV	Normal	0.35 µV	1	0.035	certificate
7. DVM Short-term stability	2 ppm	Rectangular	0.02 µV	1	0.02	Maximum Emf change before/after comparisons
8. Electric noise	0.05 µV	Rectangular	0.03 µV	1	0.03	Any spurious emf
9. t/c stability	0.1 µV	Rectangular	0.06 µV	1.72	0.104	Emf difference between 2 Ag freezing emf
Combined standard uncertainty /µV					**0.498**	
Expanded uncertainty (k = 2) /µV					**0.997**	
Expanded uncertainty (k = 2) /°C					0.042	

Appendix G-6: NPLI

NMI: NPLI

Uncertainty Analysis of APMP_Pt/Pd_10_01

Unceratiny factors	Quantity /μV	Probability Distribution	Standard uncertainty /μV	Sensitivity coefficient	Uncertainty contribution /μV	Remarks
1. Measurement scatter	1.02	Normal	0.59	1	0.59	Standard deviation
2. Inflection point	0.97	Rectangular	0.56	1	0.56	Maximum variation/2
3. Heat flux	3.20	Rectangular	1.85	1	1.85	Emf variation between ± 5 °C and ± 10 °C
4. Inhomogeneity		Rectangular		1	0.00	Given by the pilot
5. CJ temperature	0.24	Rectangular	0.14	5.3	0.72	Estimation
6. DVM calibration	0.82	Normal	0.41	1	0.41	certificate
7. DVM Short-term stability	0.20	Rectangular	0.12	1	0.12	Maximum Emf change before/after comparisons; Long term stability
8. Electric noise	0.02	Rectangular	0.01	1	0.01	Stray noise
9. t/c stability	0.64	Rectangular	0.37	1.72	0.63	Emf difference between 2 Ag freezing emf
Combined standard uncertainty /μV					2.27	
Effective Degree of freedom, ν_{eff}					328	
Expanded uncertainty (k = 2) /μV					4.55	
Expanded uncertainty (k = 2) /°C					0.19	

NMI: NPLI

Uncertainty Analysis of APMP_Pt/Pd_10_02

Unceratiny factors	Quantity /μV	Probability Distribution	Standard uncertainty /μV	Sensitivity coefficient	Uncertainty contribution /μV	Remarks
1. Measurement scatter	0.85	Normal	0.49	1	0.49	Standard deviation
2. Inflection point	0.74	Rectangular	0.43	1	0.43	Maximum variation/2
3. Heat flux	3.20	Rectangular	1.85	1	1.85	Emf variation between ± 5 °C and ± 10 °C
4. Inhomogeneity		Rectangular		1	0.00	Given by the pilot
5. CJ temperature	0.24	Rectangular	0.14	5.3	0.72	Estimation
6. DVM calibration	0.82	Normal	0.41	1	0.41	certificate
7. DVM Short-term stability	0.20	Rectangular	0.12	1	0.12	Maximum Emf change before/after comparisons; Long term stability
8. Electric noise	0.02	Rectangular	0.01	1	0.01	Stray noise
9. t/c stability	0.18	Rectangular	0.10	1.72	0.17	Emf difference between 2 Ag freezing emf
Combined standard uncertainty /μV					2.14	
Effective Degree of freedom, ν_{eff}					62	
Expanded uncertainty (k = 2) /μV					4.27	
Expanded uncertainty (k = 2) /°C					0.18	