Comparison of Realization of the Aluminum Freezing Point

Objective: This comparison is designed to compare the realizations of the aluminum freezing point (Al FP) of the national metrology institutes (NMIs) in the Asia Pacific Metrology Programme (APMP), and to provide a linkage to the KCRV of the CCT-K4. The transfer standards will be long-stem SPRTs.

NMI Participants:

Pilot: Korea Research Institute of Standards and Science (KRISS)
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Co-pilot: National Institute of Metrology (NIM)
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Participating NMIs:

Measurement Standards Laboratory (MSL)
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National Metrology Institute of Malaysia (NMIM)
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Research Center for Metrology-LIPI (RCM-LIPI)
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Vietnam Metrology Institute, Directorate for Standards and Quality (VMI-STAMEQ)
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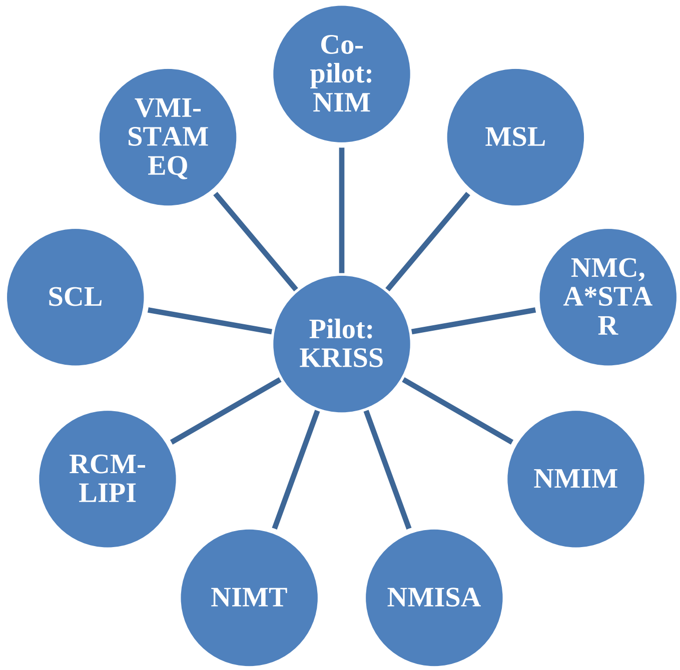
Comparison scheme: Collapsed star



Projected Timeline:

Protocol Agreement	December 31, 2017
Transfer Standards Sent to KRISS	March 31, 2018
Transfer Standards Returned to participants	December 31, 2018
Transfer Standards Re-measured by participants	March 31, 2019
Draft A Report Completed	July 31, 2019

Participants will supply the following information:

- Two SPRTs
  - NMI participants will select their own SPRTs (preferably 25 Ω SPRTs) based on their own criteria.
    - NMI participants will inform the pilot of the selection criteria and information on the artefacts (e.g. manufacturer, model, serial number, nominal TPW resistance, sheath type, sensing element length, etc.)
    - In the CCT-K4, a transfer cell (i.e. a sealed aluminum fixed-point cell) was used as the artefact. The consequence of using SPRTs as the artefacts, instead of the cell, is the addition of the measurement uncertainties related with the measurement of the resistances and the stability of the thermometers. However,

as this indicates the measurement capability of the participant more properly, it is expected to be more beneficial for the participants to claiming their CMCs.

- The participants must calibrate SPRTs at Al FP before sending the artefacts to the pilot and again on return from the pilot.
- The participants are required to hand-carry their SPRTs to and from the pilot. However, if hand carrying the artefacts is not possible due to some reasons, the participant can use a parcel delivery service with a careful packaging, but this may result in a significant change in the resistance of the SPRT; thus, this is not a recommended way to transport the artefact.
    - All the costs including the insurance on the artefacts will be paid by the participants.
    - When requested, the pilot provide proper documentation for custom formalities.

- Calibration results supplied in three resistances at Al FP and TPW (i.e. $R_{\mathrm{Al\,FP}}$ and R_{TPW}) and the resistance ratio at Al FP (i.e. W) with all corrections applied by the NMIs such that the W values are equivalent to the ITS-90 assigned temperature values for 0 mA; the calibration results should be based on at least 3 repeated measurements at Al FP (including the subsequent measurement at TPW).
    - Appendix A gives a reporting worksheet.
- The measurement equation used to compute each calibration result including the hydrostatic head and gas pressure corrections.
- Uncertainty budgets compliant with CCT WG-KC (CCT/08-19/rev) that includes degrees of freedom associated each component. Separate uncertainty budgets for each SPRT before and after the measurement at KRISS should be submitted.
    - A suggested uncertainty budget is given in Appendix B.
        - A participant can add or delete sources of uncertainty as needed.
        - A participant may choose to supply their own uncertainty budget (CCT WG-KC compliant) that includes degrees of freedom for each source of uncertainty.
        - Please identify which components of the uncertainty budget are associated with random effects and which are associated with systematic effects within this comparison.
- Immersion profile for the Al FP cell used.
    - [*R*(FP), 0 mA] and corresponding [immersion depth (sensor midpoint), cm].
- Information on instrumentation used in the comparison.
    - Tables for reporting the instrumentation are given in Appendix C.

Reporting the calibration results:

The participants should send all the results and required information to the pilot laboratory (Wukchul Joung, wukchul.joung@kriss.re.kr) after completing the 2nd round measurement at the participating NMIs without informing the results to the other participating laboratory. If there are any questions about any aspects of the protocol or about how to report something that is requested, please contact the pilot laboratory prior to submitting the report. In case of unexpected delay, the participant is also required to contact the pilot for rearrangement of the schedule; if a significant delay is expected or if it is requested by the participant, the pilot can cancel the participation of the participant. After reviewing all submitted reports, the pilot will contact the participant if there is anything that is unclear or if any additional information is needed to complete the analysis of the data.

Method of Measurement:

The following procedures are only for reference. The participating NMIs are recommended to follow their own procedures practiced for calibration of an SPRT.

1. Measure *R*(TPW) of the transfer SPRTs.
2. Insert the SPRTs into an annealing furnace preheated to 500 °C and wait for 30 minutes. Heat the annealing furnace to 670 °C for 1 hour.
3. Anneal the SPRTs for 2 hours.
4. Lower the furnace temperature down to 500 °C for 4 hours. After stabilization at 500 °C for an hour, quickly remove the SPRT to the ambient air.
5. Measure *R*(TPW) of the transfer SPRTs.
6. If the change in the resistance of the SPRTs at the TPW before and after the annealing is smaller than 0.5 mK proceed to step 7, otherwise repeat the steps from 2 to 5. In case of not fulfilling this criterion even after repeated annealing, contact the pilot.
7. Melt the sample completely by setting the furnace set value 10 K above the freezing temperature of aluminum. The sample is recommended to be molten at this temperature for more than 10 hours. After completing the melt, stabilize the molten sample at 2 K above the freezing temperature.
8. Insert the fully annealed SPRT into the annealing furnace preheated to 500 °C. Heat the annealing furnace to 660 °C for 1 hour.
9. Nucleate the sample by lowering the furnace temperature below the freezing temperature. Specific temperature difference can be different for different samples at different NMIs.

After nucleation, remove a monitor SPRT in the cell and slowly increase the furnace set value to a temperature at which the freezing temperature of aluminum is to be measured.

10. Induce an inner liquid-solid interface around the thermometer well by inserting two fused silica rods successively for 2 minutes. Specific methods can also differ from NMIs to NMIs.
11. Insert the transfer SPRT and measure *R*(Al FP) of the SPRT at two measuring currents.
12. After the calibration at the Al FP, quickly remove the SPRT from the cell and place it into the annealing furnace at 660 °C. Annealing the SPRT for an hour and lower the furnace temperature to 500 °C for 4 hours. After stabilization at 500 °C for an hour, quickly remove the SPRT to the ambient air.
13. Measure *R*(TPW) of the transfer SPRT.
14. Repeat the procedure from 7 to 13 at least 3 times for each artefact. Measurements of resistances of both the SPRTs in the same plateau is possible as long as the measurements are sufficiently fast to ensure that significant segregation of impurities does not occur during the measurements.
15. Immersion characteristics can be measured following the steps from 7 to 13 with additional measurements of the aluminum freezing temperatures at different immersion depths. A table for reporting the immersion characteristics is given in Appendix A.

Linkage Mechanism:

KRISS and NIM participated in the CCT-K4, and both NMIs will serve as the linking laboratories in this comparison. The linkage will be from the fixed-point resistance ratio for the participating NMIs to the KCRV of the CCT-K4 through the mean difference between the fixed-point temperatures of the linking laboratories and the KCRV of the CCT-K4.

$$\Delta T\left(\mathrm{NMI_{APMP.T-K4.2}} - \mathrm{KCRV_{CCT-K4}}\right) = \Delta T\left(\mathrm{NMI_{APMP.T-K4.2}} - \mathrm{KRISS_{APMP.T-K4.2}}\right) + \Delta T\left(\mathrm{KRISS_{APMP.T\text{-}K4.2}} - \mathrm{KCRV_{CCT-K4}}\right)_{\mathrm{KRISS\text{-}NIM}}$$

Where

$\Delta T\left(\mathrm{NMI_{APMP.T-K4.2}} - \mathrm{KCRV_{CCT\text{-}K4}}\right)$ is the temperature difference between the fixed-point resistance ratio of the participating NMI in the APMP.T-K4.2 and the KCRV of the CCT-K4,

$\Delta T\left(\mathrm{NMI_{APMP.T-K4.2}} - \mathrm{KRISS_{APMP.T-K4.2}}\right)$ is the fixed-point temperature difference between the participating NMI and KRISS measured in the APMP.T-K4.2,

$\Delta T(\text{KRISS}_{\text{APMP.T-K4.2}} - \text{KCRV}_{\text{CCT-K4}})_{\text{KRISS-NIM}}$ is the temperature difference between the fixed-point resistance ratio of KRISS in the APMP.T-K4.2 and the KCRV of the CCT-K4 through the simple average of the deviations of the linking laboratories from the KCRV of the CCT-K4.

The fixed-point temperature difference between the participating NMI and KRISS, $\Delta T(\text{NMI}_{\text{APMP.T-K4.2}} - \text{KRISS}_{\text{APMP.T-K4.2}})$, is defined as the average of the measured difference from the two artefacts.

$$\Delta T(\text{NMI}_{\text{APMP.T-K4.2}} - \text{KRISS}_{\text{APMP.T-K4.2}}) = \frac{1}{2}\left\{\Delta T(\text{NMI}_{\text{APMP.T-K4.2}} - \text{KRISS}_{\text{APMP.T-K4.2}})_1 + \Delta T(\text{NMI}_{\text{APMP.T-K4.2}} - \text{KRISS}_{\text{APMP.T-K4.2}})_2\right\}$$

The temperature difference between the participating NMI and KRISS for each artefact is defined as the average of the measurement results before and after the measurement at KRISS.

$$\Delta T(\text{NMI}_{\text{APMP.T-K4.2}} - \text{KRISS}_{\text{APMP.T-K4.2}})_i = \left\{W(\text{NMI}_{\text{APMP.T-K4.2}})_i - W(\text{KRISS}_{\text{APMP.T-K4.2}})_i\right\} \Big/ \frac{\mathrm{d}W_\mathrm{r}}{\mathrm{d}T}$$

Here, the subscript, *i* refers to each artefact. The resistance ratio of the participating NMI for an artefact is the average of the measurement results before and after the measurement at KRISS.

$$W(\text{NMI}_{\text{APMP.T-K4.2}})_i = \frac{1}{2}\left\{W(\text{NMI}_{\text{APMP.T-K4.2}})_{i,\text{pre}} + W(\text{NMI}_{\text{APMP.T-K4.2}})_{i,\text{post}}\right\}$$

Here, the resistance ratios $W(\text{NMI}_{\text{APMP.T-K4.2}})_i$ and $W(\text{KRISS}_{\text{APMP.T-K4.2}})_i$ are the averages from the 3 repeated measurements.

The temperature difference between the fixed-point resistance ratio of KRISS in the APMP.T-K4.2 and the KCRV of the CCT-K4, $\Delta T(\text{KRISS}_{\text{APMP.T-K4.2}} - \text{KCRV}_{\text{CCT-K4}})_{\text{KRISS-NIM}}$, is defined as a simple average of the deviations of the linking laboratories (i.e. KRISS and NIM) from the KCRV of the CCT-K4.

$$\Delta T(\text{KRISS}_{\text{APMP.T-K4.2}} - \text{KCRV}_{\text{CCT-K4}})_{\text{KRISS-NIM}} = \frac{1}{2}\left\{\Delta T(\text{KRISS}_{\text{APMP.T-K4.2}} - \text{KCRV}_{\text{CCT-K4}})_{\text{KRISS}} + \Delta T(\text{KRISS}_{\text{APMP.T-K4.2}} - \text{KCRV}_{\text{CCT-K4}})_{\text{NIM}}\right\}$$

Where

$$\Delta T\left(\mathrm{KRISS_{APMP.T\text{-}K4.2}} - \mathrm{KCRV_{CCT-K4}}\right)_{\mathrm{KRISS}}$$
$$= \Delta T\left(\mathrm{KRISS_{APMP.T\text{-}K4.2}} - \mathrm{KRISS_{CCT-K4}}\right) + \Delta T\left(\mathrm{KRISS_{CCT\text{-}K4}} - \mathrm{KCRV_{CCT-K4}}\right)$$

$$\Delta T\left(\mathrm{KRISS_{APMP.T\text{-}K4.2}} - \mathrm{KCRV_{CCT-K4}}\right)_{\mathrm{NIM}}$$
$$= \Delta T\left(\mathrm{KRISS_{APMP.T\text{-}K4.2}} - \mathrm{NIM_{APMP.T\text{-}K4.2}}\right) + \Delta T\left(\mathrm{NIM_{APMP.T\text{-}K4.2}} - \mathrm{NIM_{CCT-K4}}\right)$$
$$+ \Delta T\left(\mathrm{NIM_{CCT\text{-}K4}} - \mathrm{KCRV_{CCT-K4}}\right)$$

Here, the temperature differences of the between the fixed-point cells of KRISS and NIM in the APMP.T-K4.2 and those in the CCT-K4, which are $\Delta T\left(\mathrm{KRISS_{APMP.T\text{-}K4.2}} - \mathrm{KRISS_{CCT-K4}}\right)$ and $\Delta T\left(\mathrm{NIM_{APMP.T\text{-}K4.2}} - \mathrm{NIM_{CCT-K4}}\right)$, account for any changes in the fixed-point cells between these two comparisons. If the same fixed-point cell is to be used, this difference vanishes but only has uncertainty.

In this comparison, SPRT cutoff criteria will be used to ensure that uncertainty associated with the travel, handling, or stability of either SPRT will not dominate the standard uncertainty of the temperature difference. In this regard, the test for the stability of the travelling artefacts will be based on measurements done by the participants before and after the travel to KRISS. Following inequalities show the cutoff criteria used in this comparison, and an artefact, which meets both the two criteria, will not be included in the calculation. In case of failure of both the SPRTs, the participant will be informed of the failure of the two artefacts by the pilot and asked to repeat the measurements (possibly with different SPRTs).

$$\frac{\left|W\left(\mathrm{NMI_{APMP.T-K4.2}}\right)_{i,\mathrm{pre}} - W\left(\mathrm{NMI_{APMP.T-K4.2}}\right)_{i,\mathrm{post}}\right|}{\left(\mathrm{d}W_{\mathrm{r}}/\mathrm{d}T\right)\sqrt{u_{\mathrm{R}}^{2}\left\{W\left(\mathrm{NMI_{APMP.T-K4.2}}\right)_{\mathrm{i,pre}}\right\} + u_{\mathrm{R}}^{2}\left\{W\left(\mathrm{NMI_{APMP.T-K4.2}}\right)_{i,\mathrm{post}}\right\}}} > t_{0.95,\nu_{\mathrm{eff}}}$$

$$u\left(C_{\mathrm{SPRT},i}\right) > \frac{\sqrt{u^{2}\left(\Delta T\left(\mathrm{NMI_{APMP.T-K4.2}} - \mathrm{KRISS_{APMP.T-K4.2}}\right)_{i} - u^{2}\left(C_{\mathrm{SPRT},i}\right)\right)}}{3}$$

Where

$$u\left(C_{\mathrm{SPRT},i}\right) = \frac{\left|W\left(\mathrm{NMI_{APMP.T-K4.2}}\right)_{i,\mathrm{pre}} - W\left(\mathrm{NMI_{APMP.T-K4.2}}\right)_{i,\mathrm{post}}\right|}{\left(\mathrm{d}W_{\mathrm{r}}/\mathrm{d}T\right)\sqrt{12}}$$

In the cutoff criteria above, $u_{\mathrm{R}}\left\{W\left(\mathrm{NMI_{APMP.T-K4.2}}\right)_{i}\right\}$ is the combined standard uncertainty from all sources of random uncertainty for each SPRT, and $t_{0.95,\nu_{\mathrm{eff}}}$ is the appropriate quantile of the

Student’s *t* distribution with degrees of freedom, ν_{eff} needed to compute an approximate 95 % level of confidence for the temperature differences observed after travel to and from KRISS for each SPRT.

Appendix A: Measurement Reporting Worksheet

1. Measurement data

Participating NMI [ ]

Before sending SPRTs to pilot laboratory

Fixed-point	Artefact 1		Artefact 2	
	R_{FP} / Ω	R_{TPW} / Ω	R_{FP} / Ω	R_{TPW} / Ω
	W		W	
Al FP 1				
Al FP 2				
Al FP 3				
Average				
	U / mK		U / mK	

Final R(TPW) [ ] [ ]

On return to participating laboratory

Fixed-point	Artefact 1		Artefact 2	
	R_{FP} / Ω	R_{TPW} / Ω	R_{FP} / Ω	R_{TPW} / Ω
	W		W	
Al FP 1				
Al FP 2				
Al FP 3				
Average				
	U / mK		U / mK	

Final R(TPW) [ ] [ ]

2. Corrections

Before sending SPRTs to pilot laboratory

Fixed-point	Hydrostatic head		Gas pressure	
	Correction / mK	$u_{correction}$ / mK	Correction / mK	$u_{correction}$ / mK
Al FP				

On return to participating laboratory

Fixed-point	Hydrostatic head		Gas pressure	
	Correction / mK	$u_{correction}$ / mK	Correction / mK	$u_{correction}$ / mK
Al FP				

3. Immersion characteristics

Distance from the bottom / cm	0	1	2	3	5	7
Deviation from the bottom / mK						

Appendix B: Suggested Uncertainty Budget

Participating NMI

Type A	Al FP		TPW		Systematic or random
	mK	DF	mK	DF	
Phase transition realization repeatability					
Bridge repeatability					
Total A					
Type B					
Chemical impurities					
Hydrostatic-head					
Heat flux					
Gas pressure					
Slope of plateau					
Propagated from TPW					
Isotopic variation					
Bridge nonlinearity					
SPRT self-heating					
R_s stability					
SPRT leakage					
Total B					
Combined standard uncertainty					
Expanded uncertainty (Approx. 95 % level of confidence)					

Appendix C: Table for Instrumentation

1. Fixed-point (Al FP) cell and furnace

Laboratory	
Cell Cell manufacturer Open/closed? Pressure in cell	
Crucible Crucible material Crucible manufacturer Crucible length	
Metal sample Sample source Sample purity Sample weight	
Thermometer well Well material Well ID (mm)	
Immersion depth of SPRT[1]	
Furnace Manufacturer Control type How many zones? Heat pipe liner? Heater current (AC/DC)?	

[1] The distance from the surface of the ingot to the bottom of the thermometer well

2. Triple point of water cell

Laboratory	
Cell manufacturer	
Water source and purity	
Well diameter	
Immersion depth	
Heat transfer liquid:	
Cell maintained in: ice bath/water bath?	
Ice mantle:	
Method of preparation	
Annealing time before use	

3. Resistance measuring device

Laboratory	
Bridge manufacturer AC/DC	
If AC, give Frequency Bandwidth Gain Quad gain Output Normal measuring current Self-heating current Unity reading Zero reading Compliment check error	
If DC, give Gain Period of reversal Output	
Reference resistor Type Manufacturer Temperature Temperature coefficient	
Linearity of bridge	

4. Artefacts

Laboratory		
Artefact	Artefact 1	Artefact 2
Manufacturer		
Model		
Serial number		
Nominal resistance at TPW		
Sheath type		
Sensing element length[2]		

[2] The distance from the tip of the sheath to the mid-point of the sensing element