XX IMEKO World Congress
Metrology for Green Growth
September 9–14, 2012, Busan, Republic of Korea

REALIZATION AND UNCERTAINTY EVALUATION OF THE ITS-90 FIXED-POINTS FOR THE ESTABLISHMENT OF TEMPERATURE STANDARDS AT KRISS

K. S. Gam, I. Yang, U. C. Jeong, and Y. G. Kim

Korea Research Institute of Standards and Science, 267 Gajeong-Ro, Yuseong-Gu, Daejeon, Korea

Abstract: In past 20 years KRISS prepared the fixed-points cells for the realization of the ITS-90. Home-made fixed-points was realized using the conventional methods and were estimated the uncertainties for the realization of the fixed points. The uncertainty factors from the impurities of samples, immersion depth of sensor, pressure variation of cells, and temperature gradient was analysed in detail and especially the uncertainty of the AC thermometer bridge arising from the noise factor and non-linearity was measured. The expanded uncertainty for the fixed-points with the coverage factor k=2 was ±0.06mK at the triple point of water and, increased in accordance with the temperature increase, was ±2.34 mK at the freezing point of silver.

Keywords: the ITS-90, Fixed-point, Uncertainty, AC thermometer bridge

1. INTRODUCTION

Korea Research Institute of Standards and Science (KRISS) is responsible for establishing, maintaining and providing with measurement standards of Korea. Temperature center of KRISS has established temperature standards by the defining fixed points and standard platinum resistance thermometer (SPRT) in accordance with the International Temperature Scale of 1990 (ITS-90). During past 20 years, we have developed the open-type and the sealed type metal fixed points such as Ag, Al, Zn, Sn, In, Ga and Hg cells, and water triple-point cells. For the establishment of the temperature standards in the temperature range from -38.8344 ℃ to 961.78 ℃, we developed the sodium heat pipe furnace for the realization of Ag and Al freezing points, and the cooler for the realization of the mercury triple-point. [1] Resistance thermometry bridges, which measure resistance ratios of standard platinum resistance thermometers (SPRTs) at fixed-points to standard resistors, are important in the high precision resistance thermometry. As with other instruments in measurement chain, the resistance bridges contribute to the overall uncertainty of the measurement, and accurate assessment of the uncertainty arisen by the bridges is necessary. Particularly, as nonlinearity of the bridges only propagates into the resistance ratios and affects the measured temperature, accurate nonlinearity assessment of resistance bridges have practical importance. The nonlinearity of the resistance bridge in KRISS was assessed using the resistance bridge calibrator (RBC), and the behaviour of the bridge in terms of the nonlinearity was investigated under different combinations of gain and bandwidth.

In this papers we reports the temperature standard system at KRISS established by the realization of the fixed points of the ITS-90 and uncertainty budgets in the temperature range from -38.8344 ℃ to 961.78 ℃.

2. FIXED POINTS

2-1. Triple-point of water cell

The triple-point of water(0.01 ℃) is an important defining fixed-point for calibration of PRT's. The triple-point is realized in a sealed glass cell containing ice, water, and water vapor. When the cell is in use it may be placed in an ordinary crushed ice-water bath or a high stable water bath. KRISS TPW cell made of Pyrex glass, and cell dimension was 40 cm long and 50 mm diameter, and inner diameter of thermometer well was 12 mm. Since 1990 KRISS has been fabricated TPW cells and disseminated these cells to national calibration centers in Korea and several National Measurement Institutes(NMI). In 1997 KRISS participated in the international key comparison of triple-point of water cells organized by the BIPM [2] to confirm the quality of KRISS TPW cells. In this key comparison KRISS TPW temperature was coincident within 0.11 mK comparing to the BIPM reference value. In 2003 KRISS participated again in the CCT- K7, and the triple point of KRISS TPW cell showed 47 μK higher than the CCT-K7 KCRV.

2-2. Metal fixed-points

Mercury triple-point cell (234.3156 K) was fabricated at KRISS and a stainless steel was used as crucible and thermometer well materials. The size of cell is 39 mm of diameter and 230 mm of height. Mercury cell contained

1.60 kg of 7N pure Hg, and the specifications summarized in Table 1. The triple-point of Hg was realized using home-made dry cooler equipped with a temperature controller that had a set-point accuracy of 0.01 ℃. The core area of the dry cooler consisted of the Al equalizing block and the thermoelectric modules insulated by glass wool. To realize Hg triple-point, the cells was placed in the dry cooler, which was then set to attain a temperature of –42 ℃ to freeze the Hg. Observation of the SPRT showed that the Hg had frozen, and then the controller temperature was set to 1 ℃ lower than the Hg triple-point. The dry cooler temperature was maintained in the equilibrium state for about 2 h to obtain an equilibrated temperature in the Hg cell. The controller temperature was then set to –38.5 ℃ to obtain the melting curve of the Hg cell. Just after the Hg sample began to melt, a silica glass rod, which had been maintained at room temperature, was inserted to the thermometer well for a period of 1 min to melt the frozen Hg sample around the thermometer well. Melting temperature plateau was maintained for 6 h and the estimated average melting range was within 0.05 mK.

The gallium fixed-point is unique melting fixed-point in the ITS-90. Gallium melting point cell was made of PTFE crucible, because of its high solubility with metal and 3.1 % volume expansion on freezing. Gallium melting point realized in the liquid bath with the stability and gradient of 0.5 mK. The gallium is solidified completely by placing the cell in crushed ice for at least one hour. The solid gallium around thermometer well is then partially melted by steel rod at 42 ℃. Then the cell is placed to the liquid bath which is controlled at a temperature about 0.5 ℃ above the gallium melting point.

The metal freezing point cells for a SPRT have two types. The open-type cell is used as a standard cell at KRISS shown in Fig. 1. The open-type cell is inconvenient to carry for the international comparison and the realization for secondary standard laboratories. The sealed cell solved this problem, but the accuracy of the sealed cells is known worse than the open cell's. The indium freezing point cell was made of graphite (5N) as crucible material. Indium freezing point can be realized by using a conventional 3 zone furnace. Indium supercool by 1 K or less, so outside nucleation is usually unnecessary. After melting the ingot, the furnace temperature set to below 0.5 K from the freezing point. When the temperature indicated by a monitoring SPRT reached to the freezing point the SPRT is withdrawn and allowed to insert a cold silica glass rod in the thermometer well. This inner-induced method is sufficient to cause rapid nucleation with the formation of a thin mantle of solid indium around the thermometer well. The freezing point of a high purity sample of indium is reproducible within 0.1 mK.

The tin freezing point and the zinc freezing point are realized by using a three zone vertical furnaces. Tin sample have supercool temperature of above 10 ℃. Because of this reason, it is necessary to induce an outside nucleated slow freeze. In the case of zinc freezing point, an inner-induced method is used to obtain flat plateau. Setting procedure of furnace temperature to obtain the tin and zinc freezing points are same to that of indium. The freezing points of tin and zinc with 99.9999 % pure samples are reproducible within 0.2 mK.

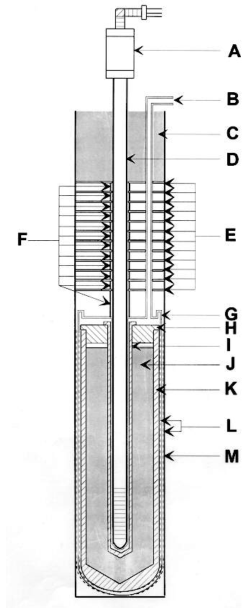

Fig. 1. Cross section of the standard open-type freezing point cell assembly. A:SPRT B:pumping tube C:Fiberfrax D:thermometer guide tube E: platinum(or Inconel) plate for radiation shield F:spacers G:envelope H:graphite cap I:graphite well J:pure metal K:graphite crucible L:silica glass wool M:Inconel tube.

The aluminium and silver freezing point cells are made of a silica glass tube. To reduce radiation losses from the light piping through the glass cell, the outside surface of the cell above 240 mm from the bottom and the thermometer guide tube were sand-blasted. The sodium heat pipe furnace was employed to realize the freezing points of silver and aluminium. Fig. 2 shows the cross section of the heat pipe furnace. The furnace consists of an axially located sodium heat pipe which is operated in the temperature range from 550 ℃ to 1050 ℃. Kanthal A-1 wire(φ1.2 mm) was used as heating element, and assembled by the ceramic tubes parallel to the long direction of the alumina tube, alternately back and forth around ceramic tubes to reduce induced magnetic fields. The freezing points of aluminum and silver with 99.9999 % pure samples are reproducible within 0.3 mK and the freezing plateau was maintained longer than 300 min. The specifications of metal fixed-point cells summarized in Table 1.

3. RESISTANCE MEASUREMENTS

The resistance measurements were performed with AC resistance bridge (ASL F900). This bridge was used to measure the ratio of SPRT resistance to that of the standard resistor. This standard resistor was maintained in an oil bath, whose temperature was controlled at 25.00±0.01 ℃. During resistance measurements of SPRT, different exciting currents and standard resistors are used

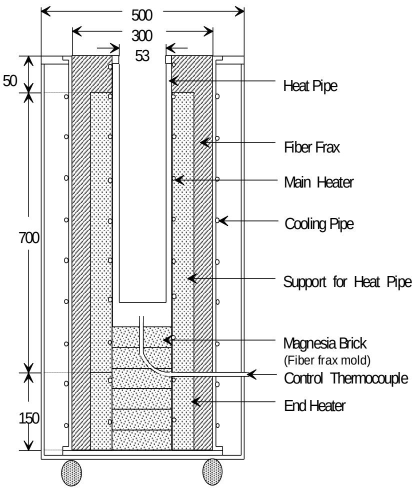

Fig. 2. Cross section of the sodium heat pipe furnace for the realization of the aluminum and silver freezing points. Dimensions are indicated in mm.

to enhance the resolution. Normally 1 mA, 3 mA and 10 mA are used for 25 Ω SPRT, 2.5 Ω HTSPRT and 0.25 Ω HTSPRT, respectively. The nominal resistances of reference standard resistors were 10 Ω for 0.25 Ω and 2.5 Ω HTSPRT, and 100 Ω for 25 Ω SPRT.To evaluate the nonlinearity of the AC resistance thermometry bridge, the nonlinearity of the resistance bridge was measured and assessed using the resistance bridge calibrator (RBC). [3] In addition to this, the behaviour of the resistance bridge in terms of the nonlinearity was investigated under different operating conditions of various gain and bandwidth combinations. The results showed that the resistance thermometry bridge marked the minimum nonlinearity of 11 ppb at 10^5 gain and 0.1 Hz bandwidth, and showed noticeable dependence on the gain.

4. RESULTS OF FIXED-POINT REALIZATIONS

4-1. Water triple-point

Water triple-point realized using dry ice powder as the coolant. Water triple-point cell is first immersed in the ice bath with the mouth of the re-entrant thermometer well above the surrounding ice-water level. The well is thoroughly dried, then filled continuously with crushed dry ice powder and maintained for about 20 min by replacing the sublimated dry ice. The fine needles quickly cover the well but soon disappear to form a clear coating of ice that will grow and become a 4 to 8 mm thick mantle in about 20 min. Finally, when the dry ice in the well is completely sublimated, the cell is located deeper into the ice bath and the well filled with icy water. A second ice-water interface is formed by melting the ice immediately adjacent to the well surface. The inner melt is made by inserting a glass rod at room temperature into the well for a few seconds. The temperature of the triple-point cell is slightly low after freezing, because of structured strains of ice that are produced when the ice is frozen. The cell should be maintained in the ice bath at least one week prior to its use.

Table 1. Specifications of the metal fixed-point cells.

Fixed-points	Sample quantity (kg)	Sample purity (%)	Impurity analysis (ppm)	Immersion depth (cm)
Hg	1.6	99.99999	Ca 0.001 Mg 0.001	13.0
Ga	1.0	99.999999	K:0.01 Ca :0.003 Zn :0.003 Cd :0.004 Sn :0.005 Hg :0.005 Pb :0.002	20.5
In	1.0	99.99995	Ca:0.003 Mg:0.03 Si:0.1	18.0
Sn	1.0	99.9999	Ag 0.1 Ca 0.1 Mg 0.1 Sb 0.3	16.5
Zn	1.0	99.9999	Not detected	16.5
Al	0.4	99.9999	Si 0.3	18.6
Ag	1.6	99.9999	Si 0.1	16.8

To correct the temperature difference of water triple-point arising from the variation of the isotopic compositions of water, the contents of δD and δ^{18}O for water filled inside water triple-point cells has been analysed. [4] Temperature deviation of the triple-point of water cells calculated by Kiyosawa's data and temperature deviation from the definition of TPW were +45.1 μK for the cells fabricated on 2002, and +25.5 μK for the cells fabricated on 2005. KRISS TPW temperature was +92 μK higher than CCT-KC 7 KCRV by the correction of the deviation of the isotopic composition from the V-SMOW. The repeatability for different ice mantles was within 0.016 mK. The combined uncertainty of water triple-point at KRISS was estimated as summarized in Table 2.

4-2. Mercury triple-point

Mercury triple-point realized by melting experiment in the dry cooler and the plateau was maintained for 6 h. The estimated average melting range of melting plateau, from 10–90 % was 0.05 mK. To confirm the long term-stability of the Hg cell, the triple-point was realized four times during August 2002 and five times during March 2004. It was observed that the SPRT resistance had changed to give a difference of –1.05 mK at the triple-point of water. The temperature reproducibility of the Hg cell was 0.074 mK during the same period. The uncertainty in the triple-point measurement of the Hg cell was evaluated from the reproducibility of Type A and Type B components. The Type B components were the chemical impurities in the Hg sample, the hydrostatic-head errors, and SPRT self-heating errors etc. The uncertainty of the realization of the

Hg triple-point is shown in Table 3.

4-3. Realization of Gallium melting point

Gallium melting point was realized at oil bath and the plateau was maintained over 20 h. The plateau of gallium melting curve from 20 % to 80 % of the molten fraction was within ±0.05 mK. The gallium melting point was reproducible within ±0.2 mK.

4-4. Realization of the freezing points of Ag, Al, Zn, Sn and In

The freezing points of Ag and Al were realized at the heat pipe furnaces and the freezing points of Zn, Sn and In were realized at the commercial Isotech 3-zone furnaces. Fig. 3 shows the freezing curves summarized from the individual metal freezing points. The freezing time of In, Sn and Zn were about 800 minutes, and plateau accuracy was within 0.3 mK. The freezing time of Ag and Al was about 300 min. and 360 minutes, and plateau accuracy was within 0.5 mK. During the freezing time we checked the immersion depth profiles of the freezing points. Fig. 4 shows the typical immersion profiles of the several samples. Immersion curves were used to evaluate the heat flux uncertainty factors.

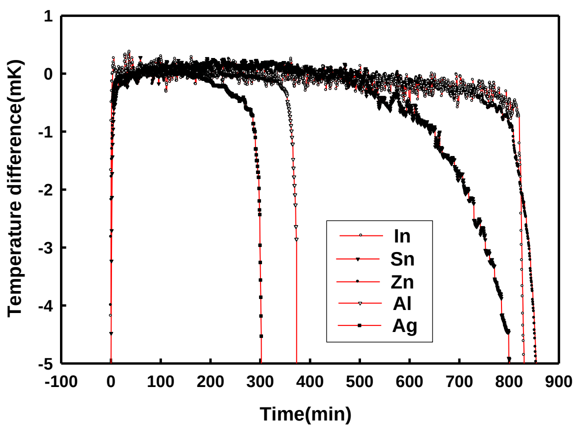

Fig. 3. Typical freezing curves of In, Sn, Zn, Al and Ag.

5. UNCERTAINTY EVALUATION

Uncertainty evaluated by the method referred to the report of the CCT WG 3. [5] The realization repeatability of the fixed-points estimated by the calculation of the standard deviation of the mean for the repeated realization. The uncertainty factors from the chemical impurities of samples are the most significant sources of uncertainty in fixed-point realization. There are several models to evaluate the uncertainty of the chemical impurity of the fixed-point cell. We used the “overall maximum estimate (OME) method” to evaluate the uncertainty of the chemical impurity of cells and calculated by the following equation;

$$u^2_{\mathrm{imp,OME}} = \frac{\left(\Delta T_{ome,\max}\right)^2}{3} = \frac{\left(c_{l,\mathrm{tot}}/A\right)^2}{3} \qquad (1)$$

Where $c_{l,\mathrm{tot}} = \sum_i c_{l,i}$ is the sum of all of the impurity concentrations, and A is the cryoscopic constant. In the uncertainty evaluation of triple-point of water, the uncertainty factor was considered when the isotopic variation corrected. The uncertainty is usually dominated by the uncertainties in δD and A_D. In the fixed-point realization the pressure effect can change the fixed-point temperature. There are two type pressure effects arising from the sample weight and the residual gas pressure difference between the control pressure and the standard pressure (101 325 Pa) defined in the ITS-90. The pressure effect arising from the weight of sample called as the hydrostatic head effect and can be estimated by the height of sample surface measured from the sensor mid-point of SPRT sensor. Vertical pressure gradient along the length of the thermometer well with the pressure determined by the depth of liquid above the sensing element of the thermometer. The temperature must therefore be corrected for the hydrostatic pressure difference between the surface of the liquid and the thermal centre of the sensing element of the SPRT. The uncertainty in the hydrostatic correction is given by;

$$u^2_{\mathrm{hyd}} = \left(\frac{dT}{dh}\right)^2 \left(u^2_{h,\mathrm{liq}} + u^2_{h,\mathrm{SPRT}}\right) \qquad (2)$$

Where $u_{h,\mathrm{liq}}$ and $u_{h,\mathrm{SPRT}}$ are the uncertainties in the elevations and dT/dh is the hydrostatic pressure coefficient defined by ITS-90. In melting and freezing points the pressure above the surface of the liquid should be the standard atmosphere, 101 325 Pa. Measurements made in cells at a different internal pressure, p_{meas}, should be corrected for the pressure difference. The uncertainty in the pressure correction is given by;

$$u^2_{T,p} = \left(\frac{dT}{dp}\right)^2 u^2_{p,\mathrm{meas}} \qquad (3)$$

Where $u_{p,\mathrm{meas}}$ is the uncertainty in the pressure inside the cell and dT/dp is the pressure coefficient defined by ITS-90. At KRISS the melting and freezing point cells are connected to the pressure control system and the uncertainty in the pressure control may be of the order of 500 Pa or lower. Heat flux error is one of the major uncertainty factors in the fixed-point realization. This error depend on the temperature gradient of the furnace (or liquid bath), the fixed-point cell design and the characteristics such as the sheath material and structure of SPRT. This error can be estimated by the immersion curves measured by moving the SPRT from the bottom to upward directions vertically. Uncertainty of Slope of plateau was estimated using the slope in the range from 10 % to 90 % of the plateau of the melting or freezing curves. Uncertainty factors of the propagation from TPW

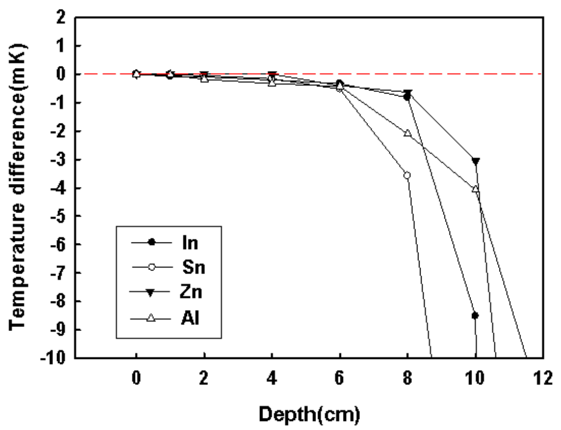

Fig. 4. Typical immersion characteristics of the metal freezing points (In, Sn, Zn, Al).

Table 2. Uncertainty budget for the water triple-point at KRISS.

Source of uncertainty	Water triple-point(mK)
Type A Realization repeatability	0.016
Type B Chemical impurity	0.030
Hydrostatic head	0.006
Heat flux	0.040
Gas pressure	0.005
Isotopic variation	0.014
Bridge nonlinearity	0.01
Bridge repeatability	0.01
Reference resistor stability	0.01
SPRT self- heating	0.005
Expanded uncertainty(*k*=2)	0.06

were calculated by the deviation function of the ITS-90, in the case of the TPW uncertainty with 0.1 mK. The major sources of uncertainty associated with the resistance measurements include the non-linearity of bridge, the reference resistor, and self-heating of the SPRT due to the sensing current. To evaluate the uncertainty of the AC thermometer bridge, we measured the nonlinearity and repeatability using RBC. Uncertainty of reference resistor was calculated using the stability of the maintenance bath with 10 mK. Other uncertainty factors were also evaluated as shown in the Table 2 and Table 3.

Table 3. Uncertainty budget for metal fixed-point at KRISS.

Source of uncertainty	Fixed-points(mK)						
	Hg	Ga	In	Sn	Zn	Al	Ag
Type A Realization repeatability	0.09	0.12	0.10	0.16	0.20	0.55	0.69
Type B Chemical impurity	0.02	0.01	0.34	0.24	0.46	0.55	0.92
Hydrostatic head	0.06	0.01	0.03	0.02	0.02	0.01	0.04
Heat flux	0.17	0.03	0.11	0.12	0.07	0.13	0.16
Gas pressure	0.01	0.01	0.03	0.02	0.02	0.04	0.03
Slope of plateau	0.09	0.09	0.32	0.16	0.13	0.16	0.17
Propagation from TPW	0.13	0.17	0.24	0.28	0.39	0.51	0.64
Bridge nonlinearity	0.13	0.13	0.14	0.14	0.15	0.16	0.18
Bridge repeatability	0.03	0.03	0.03	0.03	0.03	0.04	0.04
Reference resistor stability	0.01	0.01	0.02	0.02	0.03	0.03	0.03
SPRT self- heating	0.02	0.01	0.02	0.02	0.02	0.03	0.03
SPRT Pt oxidation	0.00	0.00	0.00	0.02	0.02	0.00	0.00
Expanded uncertainty(*k*=2)	0.44	0.30	1.04	0.70	1.06	1.62	2.34

6. CONCLUSION

In this papers, the realization of the fixed- points of the ITS-90 at KRISS and the assessments of uncertainty budgets was explained in the temperature range from -38.8344 ℃ to 961.78 ℃. The cooler and sodium heat pipe furnace for the realization of fixed-points was introduced. The uncertainty factors of the realization of the fixed-points were analysed. To confirm the bridge uncertainty, the nonlinearity of the resistance bridge was assessed using the resistance bridge calibrator (RBC), and the behaviour of the bridge in terms of the nonlinearity was investigated under different combinations of gain and bandwidth.

7. REFERENCES

[1] K.S.Gam. K.H.Kang and Y.-G.Kim.,"Investigation of new mercury triple-point cells and dry cooler made of thermoelectric modules", in *Proceeding of the 9th International Symposium on Temperature and Thermal Measurements in Industry and and Science*, Cavtat-Dubrovnik Croatia, Vol.1 , pp.307-312, 2004.

[2] R.Pello, R.Goebel and R.Köhler, *Metrologia*, **34, pp.** 393, 1997.

[3] W. Joung, K. S. Gam, I. Yang, Y.-G. Kim,"A Method for Calibrating Resistance Thermometry Bridges" in *Temperature: Its Measurement and Control In Science and Industry-2012, to be published.*

[4] K.S.Gam. K.H.Kang, Y.-G.Kim and I.Yang, Int. J. Thermophysics, DOI 10.1007/s10765-008-0414-0, 2008.

[5] CCT/08-19/rev., Uncertainties in the realization of the SPRT subranges of the ITS-90, CCT WG 3, 2008.