Performance of Water and Mercury Triple Points Reference Cells under Adiabatic Conditions

Mohamed Gamal Ahmed, Ahmed Ali El-Matarawy and Hoda Mohamed Abo Dorra

National Institute for Standards, Tersa St., El Haram, Giza 12211, Egypt

Abstract: Two new miniature metallic sealed-cells containing the triple point of water, WTP (273.16 K) and the triple point of mercury, HgTP (234.3156 K) have been constructed for the realization of the International Temperature Scale of 1990 (ITS-90) at the National Institute of Standards (NIS-Egypt). The two new cells, in addition to a previously realized argon and oxygen triple point cells, will provide facilities for the calibration of capsule-type standard platinum resistance thermometers (CSPRTs) at one single run. Many phase transition plateaux were carried out and compared to the laboratory large reference cells using the same thermometers in order to test the performance of the new cell.

Key words: CSPRTs, ITS-90, metallic cells, fixed points, uncertainty.

1. Introduction

The triple point of water and mercury are two of the defining fixed points of the International Temperature Scale of 1990 (ITS-90) [1], with an assigned temperature values of $T_{WTP} = 273.15$ K and $T_{HgTP} = 234.3156$ K, respectively. The mercury triple point is “critical” in the realization of the ITS-90, because the scale requires calibration at the mercury triple point temperature in all the low-temperature sub-ranges where the standard platinum resistance thermometer (SPRT) is the defining instrument and the water triple point is required to carry out the resistance ratio for each fixed point.

NIS developed miniature metallic sealed in order to have the temperature range from O₂TP [2, 3] up to WTP in one single experiment with adiabatic technique similar to those techniques reported in Ref. [4]. The cells were designed to be mounted together forming a multi-cells compartment. Performance of the new cells will be studied thorough comparing the results of the new cells with those of the laboratory large reference cells, i.e., comparing phase-transition plateaux measured

by the same thermometers at both new miniature and large reference cells. In addition, this will enable studying the thermal resistance between the sensing element of the capsule-type standard platinum resistance thermometers (CSPRTs) and solid-liquid interfaces temperatures of the substances within the cells [5].

2. Description of the Cells

The geometry of WTP cell, as shown in Fig. 1, was designed to be integrated with the multi-cells compartment, thus to have a shape similar to those of O₂TP and ArTP cells.

The HgTP cell was designed, as shown in Fig. 2, to be very close to the CSPRT shape [5, 6].

The two new cells assembled with ArTP and O₂TP to form a final multi-cells compartment.

Construction, cleaning and filling the cells with the pure samples of water and mercury are described in details in Ref. [7].

3. Experimental Arrangement

At the beginning, the CSPRT that was intended to be used in characterizing the new cells, was inserted in the laboratory reference cells. These cells are large cells used to maintain the ITS-90 [8, 9] and to calibrate

Corresponding author: Ahmed Ali El-Matarawy, assistant professor, research fields: low temperature metrology and physics. E-mail: Ahmed.matarawey@gmail.com.

Fig. 1 WTP cell.

Fig. 2 HgTP cell.

long-stem SPRTs. An alcohol bath “Fluke Model 7381” with a stability of $0.006\text{ }^{\circ}\text{C}$ was used for the realization of HgTP. Another alcohol bath “Hart Scientific Model 7012” with a stability of $0.0008\text{ }^{\circ}\text{C}$ was used for the realization of WTP.

Measurements of CSPRTs (reference thermometer “Tinsley type 5187L SN. B300”) were obtained using an F18 ASL resistance bridge in conjunction with a $100\text{ }\Omega$ Tinsley standard resistor maintained in a thermo-stated oil bath at $23\text{ }^{\circ}\text{C}$. The reference thermometer was calibrated according to the ITS-90. This thermometer was chosen after showing good stability of less than 0.1 mK over several years at the

triple point of water and mercury.

The next step was to mount the new cells with the multi-cells compartment and insert it into the adiabatic calorimeter. The cells in the adiabatic calorimeter are enclosed in an isothermal copper-can to maintain a uniform thermal condition and to avoid the effect of radiation from the outside. The top-flange of this copper-can is fixed to an outer vacuum-can. A Pt-100 sensor is fixed to this flange to monitor and control the temperature of the thermal shield through a PID regulation. More details of the calorimeter are reported in Refs. [2, 3].

4. Metrological Procedures

At the beginning, the thermometer was inserted in the large cell in order to find the repeatability and average value at each realization. Then, the CSPRT was dismounted from the large cell and inserted into the multi-cells compartment inside the calorimeter. The calorimeter inner temperature was controlled by an PID software working under LabView environment. Liquid nitrogen was used to completely freeze the HgTP and WTP cells by allowing helium as a heat-exchange gas. The copper shield temperature was controlled to some hundreds of milli-Kelvins below the triple point temperature of mercury and was left for 30 min. The temperature of the controlled shield was then raised to be few milli-Kelvins above the plateau value. The temperature of the triple point was quickly raised by powering the heater wound around the cells until melting was started; i.e., a continuous heat flux technique was used. The temperature of the shield was controlled by a Pt-100 and the cells temperature was monitored by the CSPRT.

Intermittent heat technique was also carried out on the miniature cells after removal of the exchange gas.

5. Results and Discussion

A number of 31 realizations were performed to find the best conditions for characterizations, for WTP and HgTP, for large and the new miniature cells as shown

in Table 1.

For the large mercury cell, Fig. 3 shows the measured plateaux values with the expanded uncertainty indicated as Y-bars.

For the new miniature mercury cell in the compartment, Fig. 4 shows plot of three melting curves using the same thermometer. Fig. 5 shows the measured plateaux values associated with their expanded uncertainties.

Similarly for measurements on WTP large cell, Fig. 6 shows plateaux values associated with uncertainties of three different realizations.

Figs. 7 and 8 show the melting plateaux and obtained values of the new WTP miniature cell.

Table 1 Number of the realizations in large and miniature cells.

Cell	No. of realizations
HgTP large	7
HgTP miniature	9
WTP large	7
WTP miniature	8

Fig. 3 Plateaux values with uncertainties of three realizations in HgTP large cell.

Fig. 4 Melting curves of new miniature HgTP cell.

Fig. 5 Plateaux values with uncertainties of three realizations in new miniature HgTP cell.

Fig. 6 Plateaux values with uncertainties of three realizations in large cell of WTP.

Fig. 7 Melting curves of new miniature WTP cell.

Fig. 8 Plateaux values with uncertainties of three realizations in new miniature WTP cell.

Table 2 Budget of uncertainty for realization of the WTP and HgTP for large cells (LC) and miniature multi-cells compartment (MC).

Uncertainty components	WTP (LC) (mK)	WTP (MC) (mK)	HgTP (LC) (mK)	HgTP (MC) (mK)
Plateau reproducibility	0.1	0.1	0.1	0.1
Hydrostatic pressure	0.03	0	0.03	0
Electrical measurement ⁽¹⁾	0.21	0.22	0.21	0.22
Heat flux ⁽²⁾	0.23	0.001	0.23	0.001
Impurities	0.007	0.05	0.001	0.03
Self-heating ⁽³⁾	0.02	0.02	0.02	0.02
Combined uncertainty	0.33	0.25	0.33	0.24
Expanded uncertainty	0.66	0.49	0.66	0.48

(1) Estimated from stability of the bridge, the standard resistor, multimeters and current sources; (2) estimated from the known thermal resistance between the shield and the multi-cells; (3) estimated from: $R_o = R_1 - I_1^2 \left[\frac{R_2 - R_1}{I_2^2 - I_1^2} \right]$, at 1 mA and $\sqrt{2}$ mA.

Table 3 Summary of triple point measurements of HgTP and WTP for large and miniature cells using CSPRT B300.

Plateau	Average (Ω)	Stand. Dev. (Ω)
1st HgTP LC	21.08564880	3.59025547E-6
2nd HgTP LC	21.08565141	2.84494094E-6
3rd HgTP LC	21.08565279	3.35078694E-6
1st HgTP MC	21.08568495	4.99315906E-6
2nd HgTP MC	21.08568356	3.14365499E-6
3rd HgTP MC	21.08568016	3.64312073E-6
1st WTP LC	24.97623235	2.34345063E-6
2nd WTP LC	24.97624583	2.45389732E-6
3rd WTP LC	24.97623927	2.46734945E-6
1st WTP MC	24.97619986	6.4101101E-06
2nd WTP MC	24.97620091	7.4720211E-06
3rd WTP MC	24.97620582	7.5783802E-06

Table 4 Summary of measurements of HgTP and WTP miniature cells using intermittent heat technique.

Cell	Duration (h)	Number of pulses	Total heat of pulses (J) ⁽¹⁾
WTP	24	32	3,840
HgTP	11	19	91.2

Table 3 summarizes the obtained triple point values for mercury and water in large and new miniature cells. The results show a degree of equivalence between the miniature cells and large cells beside the improvement of the uncertainty value during the measurements.

Results of the miniatures cells are those obtained by the continuous heat flux technique.

Table 4 summarizes the results obtained by the intermittent heat technique on the miniature cells. To calculate the differences ΔT between the temperature materialized by the new miniature cells and the laboratory reference large cells, Eq. (1) is used, where, T_{TP}^{LC} and T_{TP}^{MC} are the triple point temperatures of the large cell and new miniature cell of multi-cells compartment, respectively. The expanded uncertainty of the comparison between laboratory large reference cells and the new miniature cells is given by Eq. (2), where, u_{LC} and u_{MC} are standard uncertainties for triple point realizations on large and the new miniature cells, respectively. Description of the budget of these standard uncertainties is shown in Table 2.

$$\Delta T = T_{TP}^{LC} - T_{TP}^{MC} \quad (1)$$

$$U = 2\sqrt{u_{LC}^2 + u_{MC}^2} \quad (2)$$

The temperature differences were calculated from the average values of the best three realizations at each cell. As shown in Fig. 9, differences are agreed within the expanded uncertainties of the comparison.

Excluding the self-heating coming from the thermometer, total heat was estimated from:

$$Q = P \cdot t = I^2 \cdot R \cdot t_{cs} \quad (3)$$

where, I is the supplied current = 5 mA for WTP, and 1 mA for HgTP; R is the resistance of the heater wound around the cell = 160 Ω ; t_{cs} is the duration of feeding current = 5 min.

The miniature cells were filled with 11.7 g and 8.6 g for WTP and HgTP, respectively. The total quantity of

Fig. 9 Temperature differences at WTP and HgTP cells.

Fig. 10 Resistance values of HgTP cell at different melting fractions.

Fig. 11 Resistance values of WTP cell at different melting fractions.

heat required to melt the mass of the substance were 3,840 J and 91.2 J for WTP and HgTP, respectively.

The resistances of the thermometer B300 were taken during the equilibrium period after each plus especially within $20\% \leq F \leq 80\%$. Figs. 10 and 11 show the changes of resistance values during melting plateaux for HgTP and WTP, respectively.

The resistances at 50% were 24.97620246 Ω and 21.08568508 Ω for WTP and HgTP, respectively.

6. Conclusions

Performance and metrological characterization of the new metallic miniature cells for the water and mercury triple points have been discussed. It has been noted from the results that there is a high degree of equivalence between the miniature cells and the large cells, besides, having an improvement of the uncertainty values during the measurements. Realizations of fixed point in miniature cells show temperature differences of -0.32 mK and 0.37 mK with expanded uncertainties of the comparison of 0.48 mK and 0.49 mK for HgTP and WTP respectively using

CSPRTs B300. The results are very encouraging, the two new cells showed repeatabilities of 0.1 mK, reproducibility's of 0.15 mK and stabilities of 0.21 mK and 0.20 mK of the phase transitions.

Concerning the intermittent heat technique, more work still needed in order to assess other thermal parameters like cells heat capacities, thermal resistances and the temperature drifts.

References

- [1] Preston-Thomas, H. 1990. "The International Temperature Scale of 1990 (ITS-90)." *Metrologia* 27: 3-10.
- [2] Ahmed, M. G., and Hermier, Y. 2013. "Development of an Adiabatic Calorimeter in the Range 54 K-273 K in Frame of a Scientific Collaboration LNE-NIS." In *Proceedings of AIP Conf. Proc.*, 1552: 153.
- [3] Ahmed, M. G., and El Matarawy, A. A. 2012. "An Adiabatic Calorimeter for Calibrating Capsule Type Thermometers (CSPRTs) in the Range 54 K to 273 K." *Int. J. Metrol. Qual. Eng.* 3: 85-7.
- [4] Sparasci, F., Pitre, L., and Hermier, Y. "Realization of the Triple Point of Water in Metallic Sealed Cells at the LNE-INM/CNAM: A Progress Report." *Int. J. Thermophys.* 29: 825-35.
- [5] Hermier, Y., Pitre, L., Geneville, C., Vergé, A., Bonnier, G., Head, D. I., Fellmuth, B., Wolber, L., Szmyrka-Grzebyk, A., Lipinski, L., de Groot, M. J., and Peruzzi, A. 2003. "A New Generation of Multicells for Cryogenic Fixed Points at BNM/INM." In *Proceedings of AIP Conference*, 684: 179.
- [6] Lipinski, L., Manuszkiewicz, H., Szmyrka-Grzebyk, A., Steur, P. P. M., and Marcarino, P. 2001. "Comparison of Temperature Values of the Mercury Triple Point Realised in Miniature and Conventional Cells." In *Proceedings of 8th International Symposium on Temperature and Thermal Measurements in Industry and Science*, 441-6.
- [7] El Matarawy, A., and Ahmed, M. G. 2014. "New Temperature Reference Cells for Calibrating CSPRTs under Adiabatic Conditions." Presented at the 6th International Metrology Conference CAFMET, Pretoria-South Africa.
- [8] Ahmed, M. G., and Moussa, M. R. 2011. "Performance of Mercury Triple-Point Cells Made in NIS-Egypt." In *Proceedings of 15th International Metrology Congress*, Paris-France.
- [9] Quinn, T. J., and Preston-Thomas, H. 1990. *Supplementary Information for the International Temperature of 1990*. BIPM.