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# REALIZATION OF NEW MERCURY TRIPLE POINT CELLS AT TUBITAK-UME

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**Abstract** – The triple point of mercury is one of the defining fixed-points of the International Temperature Scale of 1990 (ITS-90) [1]. Its value was assigned to be 231.3456 K (-38.8344°C) by ITS-90 and has an unique importance since it is the only fixed-point suggested by ITS-90 between 0.01°C and -190°C. Four mercury cells from borosilicate-glass were constructed at TUBITAK-UME Temperature laboratory. The details of construction phase then the measurement and comparison results with the reference UME cell will be given in this paper.

**Keywords:** mercury triple point, impurity, uncertainty

## 1. INTRODUCTION

The temperature laboratories of national metrology institutes must realize the triple point of mercury in order to cover long-stem standard platinum resistance thermometer (SPRT) calibrations in the sub-zero temperature range.

A variety of methods and cell materials have been utilized for realizing the mercury triple point for years [2-5]. Mainly two types of material, namely borosilicate glass and stainless steel are employed as cell material for the construction of mercury cells. UME temperature laboratory has been using a stainless-steel mercury cell as its reference cell supplied commercially from NPL to maintain the scale at -38.8344°C. A home-made mercury triple point cell from stainless-steel cell material was constructed in 2005 with the collaboration of Dr. Bonnier [6]. In 2006, it was decided to carry out the "mercury project" by using borosilicate glass due to problems experienced with the proper welding of stainless-steel tubes.

Two different batches of mercury, one with 99.9999% and the other 99.99995% purity, were used during this study. Borosilicate glass with a wall thickness of 2 mm (o.d 38 mm, i.d. 34 mm) was used for the construction of first two cells [7]. This set of cells was filled with originally 99.9999% pure mercury. The first cell of this set (BS11) was filled with mercury as obtained from supplier but a further purification process was applied on the mercury sample before filling the second cell (BS12) of this set.

During the construction of second set of cells, borosilicate glass having an outside diameter of 30 mm and a wall thickness of 2 mm was used. Adaptation of new dimension altered the amount of mercury used in the cell drastically, approximately from 2.3 kg to 1.3 kg. The second cell (BS22) of this set was filled by vacuum distillation whereas the first cell (BS21) was filled by "pour and pump" method. The purity value of the mercury stated by the supplier was 99.99995%.

The free liquid level of mercury in all cells was about 20 cm leading to a change of around 1 mK in triple point temperature of mercury.

After sealing the cells, they were put into a PTFE housing that smoothly fits to the outside diameter of the borosilicate cell. This PTFE housing which has 2 mm wall thickness also provides sort of protection of the cells. Since mercury is extremely hazardous, the utmost care and protection has been taken during the construction.

After completing the construction phase, the measurements to characterize the new cells were carried out. Finally, a comparison between new generation of mercury cells and the reference mercury cell was conducted and the uncertainty budget regarding to this comparison was formed.

## 2. PREPARATION OF THE CELLS

As mentioned in the previous section, the new mercury cells were constructed from borosilicate glass. Although glass tubes having two different outer diameters were used in this study, the size of the thermometer well (o.d 11 mm, i.d 8 mm) was same for both set of cells as well as the length of the extruding tube (20 cm) which guides the SPRT. A photograph related to the cell can be found in Fig. 1.

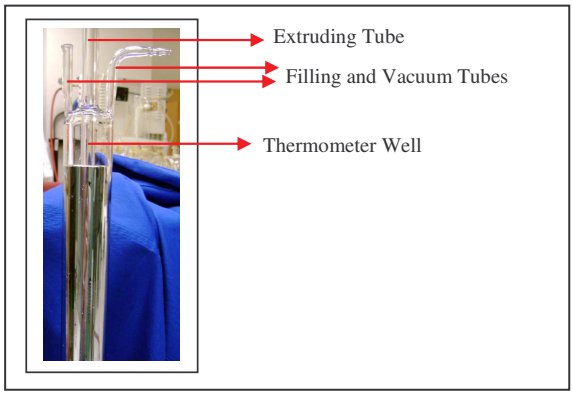


Fig. 1. The borosilicate glass cell for mercury.

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The empty cell was annealed overnight at high temperature to remove the stress occurred during cold work. After annealing, chemical cleaning phase involving washing with diluted hydrofluoric acid and undiluted nitric acid in ultrasonic bath followed by rinsing with distilled water took place. Finally the cells were steam-cleaned for 8 hours. Each cell was dried under vacuum before filled by mercury.

The first cell (BS11) was filled with approximately 2.3 kg of mercury with alleged nominal purity of 99.9999%. The mercury was directly transferred from the supplier's container to the cell without applying any purification step. After pouring all the necessary amount of mercury into the cell, the filling tube was sealed and the assembly was pumped continuously down to the level of $10^{-3}$ mbar. During evacuation lasting for 16 hours, a liquid nitrogen trap was used in order to prevent the atmosphere and the vacuum pump from mercury vapor.

A purification process was applied to the mercury sample before using it in the second cell (BS12). The purification process involved the steps filtering the mercury in order to remove the insoluble impurities floating on the surface of mercury, washing mercury with diluted potassium hydroxide followed by rinsing with distilled water and washing mercury with diluted nitric acid again followed by rinsing distilled water. During these washing steps, mercury was agitated by air bubbles. A scene from washing phase can be seen in Fig. 2.

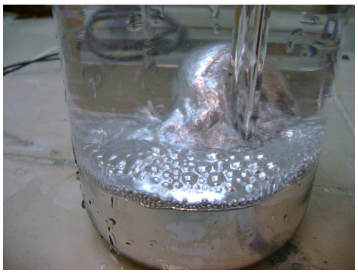

Fig. 2. Agitating the mercury in acid solution with air bubbles.

Finally a vacuum distillation was carried out aiming to leave behind the noble metal impurities. To achieve this, an amount of mercury more than needed in the cell was put into a glass beaker and boiled at approximately 300°C. The vapour of mercury condensed into liquid state while it was passing through the cold region. Then the distilled mercury was collected in the glass container and transferred to the final cell.

The mercury used in the third cell was from another batch and its purity was stated as 99.99995% with a chemical assay which was missing in the previous case. The third cell (BS21) was also filled by "pour and pump" method just as in the first cell's case.

The fourth so the final cell having same original mercury with previous one was filled by vacuum distillation method. The pressure level inside the apparatus was measured to be $9 \times 10^{-4}$ mbar. A scene from the distillation case can be found in Fig. 3.

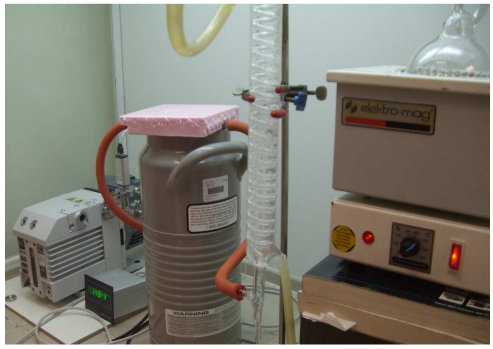

Fig. 3. The vacuum distillation apparatus for mercury.

## 3. MEASUREMENTS AND RESULTS

After constructing the new cells, a series of measurements were initiated to characterize and to compare them with TUBITAK UME reference cell. All the measurements were carried out using an ASL F18 Bridge and 25 Ω Tinsley standard resistor. A liquid bath filled with high purity ethanol was used as temperature medium. The bath was characterized beforehand and it was found to be uniform within 10 mK within an interval of 25 cm which was quite satisfactory to carry out the measurements. Two thermometers, one from Hart Scientific and the other from Tinsley were used during the experiments.

Before comparison, full plateau measurements were carried out to see the thermal environment and impurity effects. The full melting plateau obtained by BS11 can be seen in Fig. 4.

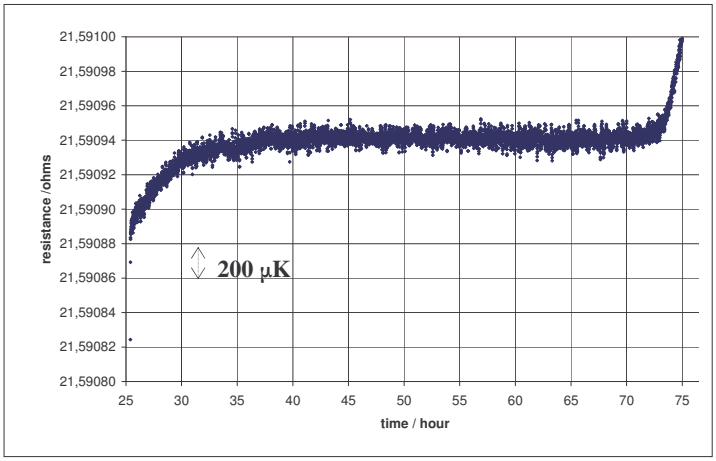


Fig. 4. The melting plateau obtained with BS11.

The duration of plateau was more than 40 hours lying within a temperature interval of 0.20 mK. The second set of mercury cells with 1.3 kg mercury inside provides a plateau of more than 25 hours depending on the rate of heating and the set point of the bath.

The immersion profiles of the new cells were studied in order to investigate heat-flux effect. Graphical presentation of the results of immersion test carried out with BS21 can be seen in Fig. 5.

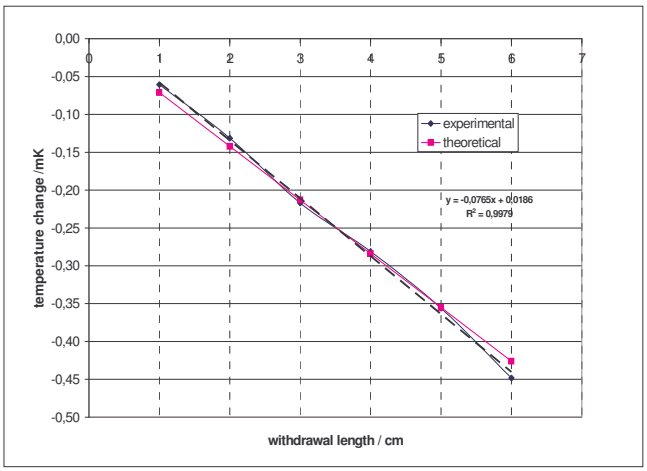


Fig. 5. The immersion profile obtained with BS21.

Measurements with this cell indicated that the largest deviation from Clasius-Clapeyron equation was 22 μK at 6$^{th}$ centimetre of withdrawal therefore the perfect conformity to the theory can easily be stated for BS21. The results of the immersion tests carried on with all cells up to 5 cm showed that the deviations from the theoretical values were not exceeding 50 μK.

After preliminary checks were completed with the new cells, a comparison with the reference mercury cell was initiated. The triple point of mercury can either be realized by freezing or by melting. For the comparison of the cells, the triple points of mercury were realized by melting and the melting was induced by inserting three warm rods successively and keeping each of them in the cell for 3 minutes at the beginning of the plateau. A graph concerning with the comparison between the cells BS11 and BS22 is given as Fig. 6. to illustrate the sequence of measurements.

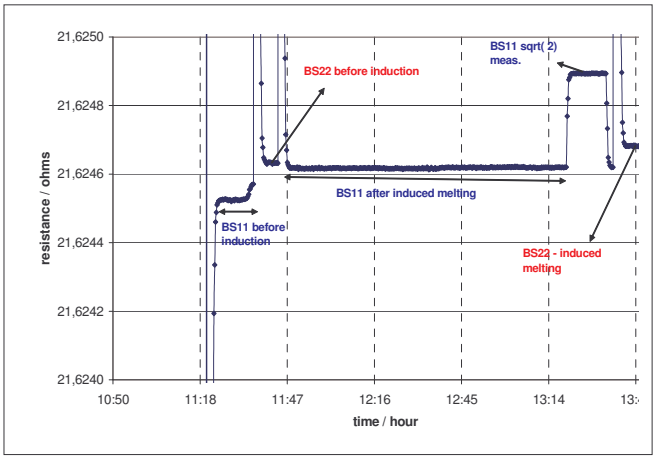


Fig. 6. Comparison measurements.

The comparison results were calculated in terms of average W values (R (Hg) / R (TPW)). The deviations from the reference value, which the value is obtained by the reference cell, are given in Table 1.

The measurement results were corrected for hydrostatic head pressure and self-heating effect.

Table 1. The comparison results.

| Mercury Cell | W ( Hg) | Deviation from the Ref. Cell / mK |
|---|---|---|
| Ref. Cell | 0,8441903 | - |
| BS11 | 0,8441869 | -0,63 |
| BS12 | 0,8441884 | -0,35 |
| BS21 | 0,8441895 | -0,20 |
| BS22 | 0,8441898 | -0,11 |

The uncertainty budget related to the comparison can be found in Table 2. Since the same SPRTs, bridge and water triple point cell were used during the comparison, the contributions arising from these items were excluded.

Table 2. The uncertainty budget.

| Quantity | Components | Standard uncertainty |
|---|---|---|
| $Q_i$ | | $u_{(Qi)}$ |
| **1** | Reproducibility | 0.10 |
| **2** | Chemical Impurities | 0.15 |
| **3** | Uncertainty linked with spurious heat fluxes | 0.03 |
| **4** | Uncertainty on the hydrostatic pressure correction | 0.04 |
| **5** | Uncertainty on the self-heating correction | 0.04 |
| **6** | Uncertainty due to the interpretation of the plateau | 0.05 |
| **7** | Stability of the standard resistor | 0.01 |
| **Combined uncertainty** | | 0.20 mK |
| | | |
| **Expanded uncertainty** | | **0.40 mK** |

The most dominant parameter in the budget appears to be uncertainty arising from chemical impurities which in our case was not assessed as absolute determination, instead only differences in the metal purity of the cells' was taken into account.

Although very reproducible results were obtained with BS11, the difference from the reference cell was calculated to be higher with this cell compared with the other mercury cells. Remembering that no purification was applied on this cell's mercury, it can be concluded that the mercury used in this cell had lower grade purity because after a purification stage, second cell (BS12) coming from the same origin yielded closer values to the reference temperature.

A depression value of 630 μK obtained with the cell BS11 indicates that the impurity level in this cell was in excess of 3 ppm considering that the cryoscopic constant of mercury is 200 μK/ ppm.

The results obtained with the second set of mercury cells and reference cell lie within a very narrow band, not exceeding 0.20 mK. The only difference between two cells of the second set was the filling technique. The cell BS22 which was filled by vacuum distillation technique yielded a little bit closer value to reference value but it can't be directly stated that this situation was related with the filling technique.

## 4. CONCLUSION

Four mercury triple point cells from borosilicate glass were constructed at TUBITAK-UME in recent years. The project was initiated to construct new batch of mercury cells being for the first time in Turkey, also to investigate the parameters that affect strongly the triple point temperature.

It can be stated that three of the home-made mercury cells were in agreement with the reference mercury cell within the uncertainty of the comparison therefore they can easily be used as reference cells in primary level laboratory activities.

The results obtained with the cells constructed from higher grade purity (99.99995%) mercury stays very close to the reference value.

The purification seemed to be working in the first set of mercury cells when the progress in deviation values from -0.63 mK to -0.35 mK before and after purification considered.

Studies on the mercury triple point continue with a focus on the comparison of the cells filled with mercury of different grade purity to analyse the effect of impurities on the triple point temperature.

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