Performance of Mercury Triple Point Cells Made in Brazil

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Abstract. Fixed–points cells are primary standards in ITS-90. They contain reference material with a purity of 99.999 % or more. The gallium in a melting–point cell, for example, can reach a purity of 99.99999 %. This level of purity is not easy to obtain. However, substances like water and mercury can be purified by means of distillation and chemical procedures. This paper presents the results of mercury triple–point cells made in Brazil that were directly compared to a mercury triple–point cell of 99.999% purity. This reference cell, made by Isotech (England), was previously compared to cells from CENAM (Mexico) and NRC (Canada) and the maximum deviation found was approximately 0.4 mK. The purification stage started with a sample of mercury 99.3 % pure, and the repeated use of both mechanical and chemical processes led to a purification grade considered good enough for calibration of standard platinum resistance thermometers. The purification procedures, the method of construction of the cell, the laboratory facilities, the comparison results and the budget of uncertainties are described in this paper. All of the cells tested have a triple-point temperature within 0.25 mK of the triple-point temperature of the Inmetro reference cell.

INTRODUCTION

The mercury triple–point (Hg TP) is one of the seventeen fixed points of the International Temperature Scale of 1990 (ITS-90) given in BIPM reference [1]. This fixed point is used in all ITS-90 sub-ranges below 273.16K [2]. In these sub-ranges, Hg TP measurements are used to determine the coefficients in deviation equations for SPRT calibrations. Usually, the resistance measurement values in Hg TP have uncertainties lower than ±0.5 mK (k=2). Mercury as a reference substance can be purified and distilled up to 99.9999 % purity or better. For Hg TPs of 99.999999 % purity, melting and freezing plateaux yield triple point values within 0.1 mK over most of the liquid–solid range [3].

Although this purity can be obtained, with a sealed mercury triple–point cell of 99.999 % purity it is possible to perform SPRT measurements with uncertainties within ±0.5mK (k=2) [4, 5].

This work presents the results of two Hg TP cells made with mercury of 99.99 % certified purity and two other cells made with purified mercury, starting with a sample of 99.3 % purity. We refer to these cells as the "test" cells.

MERCURY PURIFICATION AND DISTILLATION

Initially, the glassware were washed with distilled water and cleaned with ultrasonic sound waves (84 kHz). The mercury sample of 99.3% purity was poured in a glass funnel with nitric acid P.A. (HNO_3) as shown in Figure 1. After mixing the Hg and HNO_3 for two minutes, the funnel glass valve was opened and the mercury was filtered and collected in a beaker. The impurities, contained in the funnel and filter, were removed to another receptacle and kept in a glass bottle.

Then, the mercury sample, with a mass of approximately 1.2 kg was distilled in vacuum.

The whole process was repeated three times.

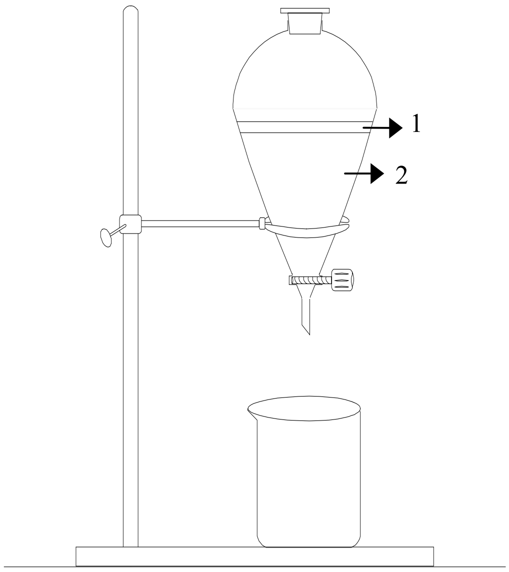

FIGURE 1. – Set-up for mercury purification, where: 1 – acid plus impurities, 2 – mercury sample.

PROCEDURE FOR MANUFACTURE OF THE MERCURY CELLS

Four mercury cell enclosures were manufactured using borosilicate glass, 190 mm long and 34 mm external diameter. The thermometric wells are 180 mm long, with 8 mm internal diameter and three cells have protruding thermometric wells (serving as an extension) 200 mm long (model 2). All cells have two glass tubes in their external top zone. These tubes are used to evacuate the air and to fill the cells with mercury.

Figure 2 shows the set-up used to make a mercury triple–point cell, without a tube extension for thermometric well (model 1). After that cell, glass funnel and rubber tubes have been cleaned with ultrasonic sound waves (84 kHz) and washed with distilled water and sulphuric-nitric acid solution, the set-up was prepared.

The mercury cell was manufactured following the sequence below:

1. Pour the purified mercury into the borosilicate glass funnel (with valve);
2. close the funnel with the glass stopper;
3. connect the glass funnel and the cell through the rubber tube;
4. fix the cell and the funnel (with two claws) in vertical position;
5. connect the cell and the trap formed by two glass cells immersed in liquid nitrogen;
6. fill the dewar trap with liquid nitrogen — when the mercury vapour passes through it the temperature of liquid nitrogen (−196°C) freezes the mercury;
7. connect the high vacuum system and the trap with another rubber tube to purge the air inside the cell using a vacuum pump (with ±3 mbar vacuum);
8. fill the cell with purified mercury, opening the funnel valve slowly (step by step until the air leaves completely the mercury);
9. finish the mercury filling operation when the level of mercury reaches approximately 1 cm below the top;
10. cut and to weld the two filling glass tubes, sealing the cell.

This procedure lasted approximately 1 hour (welding, air purging, mercury filling and cell sealing).

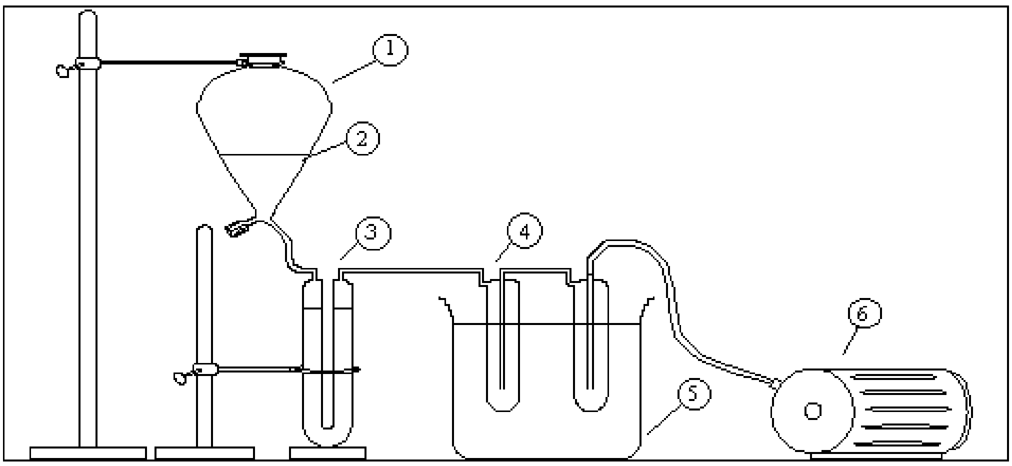

FIGURE 2. – Set-up for filling of the mercury triple–point cell.
1- Glass funnel 2- Mercury 3- Cell 4- Trap 5- Dewar vase with N_2 liquid 6- Vacuum pump

MEASUREMENT EQUIPMENT, CELLS AND FACILITIES

A model F18 AC Bridge from Automatic System Laboratory was used to perform the measurements, in conjunction with a standard resistor from H.Tinsley (100 Ω s/n 236063) immersed in a controlled oil bath (Guildline model 9732 VT). During the measurements the oil temperature in the bath was kept at 20.00 °C ± 0.01 °C.

The comparisons between four HG TP cells and the Inmetro mercury reference cell (manufactured by Isotech, s/n M036) were performed with a 25 Ω SPRT Hart model 5681 s/n 1251.

For the Inmetro cell, the Hg TP was realized in a Isotech cryostat (specially designed to work with the Inmetro cell). The other four mercury cells (see Figure 3) were frozen in a Lauda cryostat and kept in a metallic box thermally insulated with expanded polystyrene.

FIGURE 3 – Mercury triple point cell manufactured by Inmetro and Visomes (INM_VIS_03).

The mercury test cells are INM_VIS_01, INM_VIS_02, INM_VIS_03 (these cells were manufactured by Inmetro and Visomes Comercial Metrológica Ltda.) and VIS_Hg_01 (this cell was manufactured by Visomes Comercial Metrológica Ltda.).

The data acquisition between the AC bridge and the personal computer was done through software written in the Visual Basic language, developed at the Thermal Division of Inmetro.

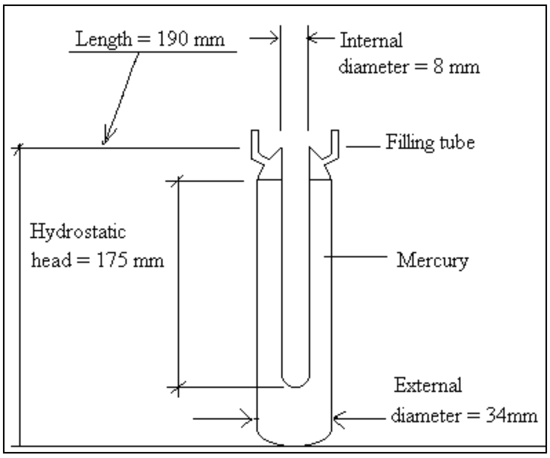

FIGURE 4. Dimensions of the mercury triple point cell manufactured by Inmetro and Visomes (INM_VIS_01).

MERCURY CELLS QUALIFICATION METHODOLOGY

1. The mercury triple point was realized using the Inmetro reference cell (normally in a melting mode) — the temperature set-point in the Isotech cryostat was initially set at –41°C. When the mercury was totally frozen, the controller was adjusted to –38°C, until the beginning of melting process — the SPRT was used to monitor this process. During the plateau, the set-point was adjusted to –38.5°C;
2. The test mercury cell was kept in the Lauda cryostat in the temperature range between –50°C to –60°C. When the mercury was totally frozen, the cell was removed from the cryostat;
3. The test mercury cell was kept in a thermally insulated metallic box which contained some alcohol to improve the thermal contact;
4. The SPRT was inserted in the thermometric well, which was filled with alcohol, to measure the mercury triple point of the test cell — in the melting mode;
5. Before the melting plateau was finished, the SPRT was returned to the Inmetro mercury reference cell to check the resistance values of the SPRT in the reference cell (see Figure 5);

NOTE: All resistance values were corrected for hydrostatic head and self heating effects with the measurements performed with 1 mA and 1.414 mA, to determine the zero power resistance values.

Figure 5 (below) shows graphically a direct comparison between the Inmetro mercury reference cell (Isotech M036) and the Visomes mercury cell (Vis_Hg_01) realized on April 09th 2002. In the reference curve, are the measured data from the Inmetro cell, and in the central curve are the measured data from the Visomes cell.

As mentioned above, the realization of the melting point of the Visomes cell was performed during the Hg TP of Inmetro cell, in the following sequence: Inmetro cell – Visomes cell – Inmetro cell. When the melting curve of the Visomes cell was finished, the SPRT was returned to Inmetro reference cell to check the reference values.

Both melting curves show measurements with 1 mA and 1.414 mA over four hours.

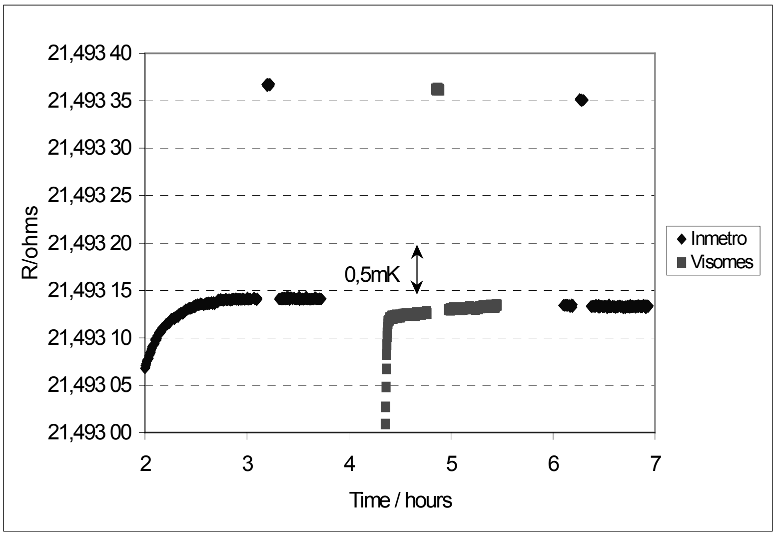

FIGURE 5. Direct comparison between the Inmetro Hg TP reference cell and the Visomes Hg TP cell. The temperature of the Visomes cell was 0.15 mK lower than the Inmetro cell (after self-heating and hydrostatic head corrections).

RESULTS

The direct comparisons between Hg TP test cells and the Inmetro Hg TP cell were performed during three days or more. Table 1 contains the comparison results between four test mercury cells and the Inmetro reference cell.

TABLE 1. Hg TP cells comparison results

Date	Manufacturer of cell	Testing cell	T.test.cell – T.ref.cell /mK
Nov. 2001	Inmetro and Visomes	Inm_Vis_01	–0.09 ± 0.73
Dec. 2001	Inmetro and Visomes	Inm_Vis_02	0.15 ± 0.73
Dec. 2001	Inmetro and Visomes	Inm_Vis_03	0.25 ± 0.73
April 2002	Visomes	Vis _Hg_01	–0.19 ± 0.74

Expanded uncertainties were calculated with k =2

Although R_{WTP} (measured resistance at the water triple point) was measured each day after the comparison, to check the SPRT stability, the temperature differences between cells depend only on the $R_{HG\ TP}$ differences.

All resistance measurements were corrected for self-heating and hydrostatic head effects (all mercury cells have approximately the same depth of immersion = 175 mm).

UNCERTAINTY EVALUATION

The main component of the Inmetro uncertainty budget for the Hg TP cells is the cell uncertainty (or uncertainty due to the purity of cell). Inmetro evaluates this uncertainty through intercomparisons of cells involving Inmetro and other NMIs.

Inmetro performed three comparisons using this same mercury triple point reference cell (Isotech cell s/n M036): Inmetro x CENAM (Mexico) –1997 [4], Inmetro x NRC (Canada) – 2000 [5] and Inmetro x PTB (Germany) – 2001 [6]. The temperature differences between the cells are given in table 2 below:

TABLE 2 Results from bilateral comparisons for mercury triple point cell: Temperature difference between Inmetro and CENAM, Inmetro and NRC and Inmetro and PTB. Uncertainties are given for *k* = 2.

T **(Inmetro) – *T*** **(PTB) / mK**	***T*** **(Inmetro) – *T*** **(CENAM) / mK**	***T*** **(Inmetro) – *T*** **(NRC) / mK**
-0.06 ± 0.81	- 0.19 ± 0.18	- 0.4 ± 0.6

TABLE 3 - Measurement uncertainties of Inmetro for the HG TP cell comparison. All values are in millikelvins.

Fixed-point	**Hg**
Type B uncertainty components	
1. Uncertainty of reference cell	0.35
2. Hydrostatic head -- Ref. Cell	0.015
3. Heat-flux -- Ref. Cell	0.058
4. Self-heating -- Ref. Cell	0.004
5. Hydrostatic head -- Test. Cell	0.015
6. Heat-flux -- Test. Cell	0.058
7. Self-heating -- Test. Cell	0.004
8. Measurement system stability	0.021
9. Standard resistor	0.036
10. Cells difference	0.036
Type B combined	0.364
Type A uncertainty for Refer.cell	3.9E-2
Type A uncertainty for the Test cell	2.1E-2
Combined uncertainty	0.364
Expanded uncertainty, *k* = 2	0.73

CONCLUSIONS

In this paper, the manufacturing procedure for four mercury triple-points cells was described and results were given for the comparison of these cells against the Inmetro mercury reference cell (Isotech cell with 99.999 % of purity). Two these cells (INM_Vis_03 and Vis_Hg_01) were made with mercury of certified purity issued by Labsint Ltd and two other (INM_Vis_01 and INM_Vis_02) cells with mercury that was purified, beginning with a mercury sample of 99.3 % purity.

Although the purity of mercury in the test cells has not been evaluated through chemical analysis by Inmetro or another accurate procedure by Inmetro, the results show that the temperature differences 0.25 mK (maximum mean value) and –0.19 mK (minimum) between the test cells and the Inmetro reference cell agree with the results of three previous mercury cell comparisons between Inmetro, NRC, CENAM and PTB (covered for expanded uncertainty of ±0.74 mK, *k*=2). With these results we can continue to use these cells as working-standard cells to perform resistance thermometer calibration within our best measurement capabilities while continuing to investigate them in order to verify any deviation coming from chemical impurities inside them.

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