

NEW NIST MERCURY TRIPLE-POINT CELLS

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ABSTRACT

Six new Hg triple-point (TP) cells (234.3156 K) were manufactured in the NIST PRT Laboratory for use in the realization of the International Temperature Scale of 1990 (ITS-90). The fixed-point cells consisted of both glass and stainless steel designs with either an 8 mm or 12 mm inner diameter reentrant well. Triple-distilled Hg with nominal purities of 99.999 999 wt.% were used to fill the cells using a vacuum distillation filling process. The certification method of the new cells included measuring melting curve plateaus, direct comparisons with the PRT Laboratory reference Hg TP cell (Hg SS-1), and immersion profiling. The estimated amount of impurities leached out of the stainless steel crucible into the Hg sample of Hg SS-1 over 25 years was found to be 1 $\mu\text{g/g}$. This paper presents the fixed-point cell designs, fabrication method, results from the cell certification procedures, and the estimated uncertainty assigned to the Hg TP cells.

1. INTRODUCTION

The National Institute of Standards and Technology (NIST) Platinum Resistance Thermometry (PRT) Laboratory uses Hg triple-point (TP) cells (234.3156 K) for the International Temperature Scale of 1990 (ITS-90) calibration of Standard Platinum Resistance Thermometers (SPRTs) for those subranges that extend below 273.16 K [1]. The importance of using a Hg TP cell with low uncertainty becomes apparent when calculating the uncertainty propagation curves of the ITS-90 subranges that incorporate the Hg TP. For example, the uncertainty contribution from the Hg TP cell is magnified by a factor of 1.9 at 160 K for the Ar TP to H₂O TP subrange.

The fabrication of six new Hg TP cells is a continuation of work at NBS/NIST first pioneered by Furukawa in 1974 [2, 3]. Original work from 1974 to 1988 by Furukawa yielded 11 Hg TP cells from which the NIST Hg reference cells (Hg SS-1 and Hg DS-1) were selected in 1989 for use in the PRT Laboratory for the ITS-90 calibration of SPRTs. Five of the new Hg TP cells were made to replace Hg DS-1 (borosilicate crucible) for the calibration of capsule SPRTs. The sixth cell was made to accommodate long-stem SPRTs. As part of the continuing research on Hg TP cells, these new Hg TP cells were used to determine that the realized temperature of the Hg SS-1 cell changed due to about 1 $\mu\text{g/g}$ of impurities leaching out of the stainless steel crucible into the Hg sample over 25 years.

This paper gives information on the design and fabrication of the new Hg TP cells, the new maintenance system, the results from comparison with Hg SS-1, and the Hg TP cell uncertainties.

2. MERCURY SAMPLES

The Hg sample used for the filling of the Hg TP cells was obtained from the NIST Pressure and Vacuum Group. The commercially procured, triple-distilled Hg sample was further purified by vacuum distillation by the Pressure and Vacuum Group for use in Hg manometers. The nominally 99.999 999 wt. % pure Hg was supplied to the PRT Laboratory in two soda-lime glass bottles each containing about 13 kg of Hg. The as received density of the Hg sample was stated to be 13.545 808 g/cm^3 at 293.15 K and 0 Pa [2].

3. MERCURY TRIPLE-POINT CELLS AND FABRICATION

The two designs of the new Hg TP cells are similar to that used in the original NBS/NIST Hg TP cells. Detailed drawings of the designs that use either borosilicate glass or type 304 stainless steel for the crucible material are found in reference 2. A small modification made to the original designs used for Hg SS-1 and Hg DS-1 extends the immersion depth of the SPRT in the Hg sample by 2.5 cm (20.5 cm from inside bottom of reentrant well to Hg surface). The inner diameter (i.d.) of the thermometer reentrant wells is either 8 mm or 12 mm. The 8 mm i.d. design is used for the calibration of long-stem SPRTs and small diameter (<5.7 mm) capsule SPRTs. The 12 mm i.d. design is used for the calibration of large diameter capsule SPRTs (those with a glass to metal seal that extends outside metal sheath) that are placed in an 11 mm holder [2]. Additionally, the inner surface of the stainless-steel cells is electro-polished to minimize the possibility of contamination of the Hg over time.

The mass of Hg contained in the crucible of the borosilicate glass cell (12 mm i.d. reentrant well) is 3375 g, that of the stainless-steel cell (8 mm i.d. reentrant well.) is 2734 g, and that of the stainless-steel cell (12 mm i.d. reentrant well.) is 2575 g.

When filling the cell crucible with a Hg sample, there are two major advantages of using vacuum distillation over pouring. First is the further purification of the sample that occurs by leaving a small amount of Hg in the distillation flask at the end of the distillation process. This residual Hg contains the impurities left behind during the vacuum distillation process. The second is that no air is present in the filled, evacuated, and sealed cell.

The procedures involved in filling both the borosilicate glass and stainless steel cell crucibles with the Hg sample are essentially the same. Prior to filling a cell crucible with the Hg sample, the parts of the cell that come in contact with Hg must be thoroughly cleaned. The cell is soaked in undiluted nitric acid overnight, rinsed with copious amounts of distilled water, steam cleaned for five days (five liters of distilled water), air dried in an oven overnight at 100 °C, and then baked-out under high vacuum ($<1.3 \times 10^{-4}$ Pa) at 300 °C. After the cell is baked-out, the second fill tube (which is used for drainage during steam cleaning) is either sealed off by flame sealing (borosilicate glass) or by pinching and arc-weld cutting (stainless steel) while under vacuum. The mass of the empty cell is then determined.

Prior to filling the crucible with the Hg sample, the cell is attached to the distillation system, leak checked, and then baked-out (120 °C) under high vacuum (both the cell and the distillation system) for three days. A schematic of the distillation system is shown in reference 2. The distillation system and cell are then filled to an over pressure (103 kPa) of 99.9999 wt. % pure argon. While the distillation system and cell are being purged with argon, the pre-weighed Hg sample is transferred into the distillation flask. With the required amount of Hg in the distillation flask, the argon gas supply is shut off, the vacuum system (rotary vane and turbomolecular pumps) for the distillation system is started and the three cold traps are filled with liquid N₂. The cold traps prevent any possible Hg vapor from reaching the vacuum system. When the vacuum system reaches 1.3×10^{-4} Pa at the vacuum sensor, the bottom and top heaters surrounding the distillation flask are energized and the condenser cooling system is turned on. During the distillation process, the temperatures of both the bottom heater and the Hg vapor above the liquid sample in the still are monitored by thermocouples. The Hg sample in the distillation flask is kept at about 400 °C during the vacuum distillation filling process. The filling of the crucible with the Hg sample requires about five hours, after which the top and bottom distillation flask heaters are turned off and removed. While under vacuum and when the distillation system cools to near ambient, the first fill tube of the crucible is then sealed off either by flame sealing (borosilicate glass) or by pinching and arc-weld cutting (stainless steel).

Prior to inserting the filled and sealed Hg cell crucible in a stainless steel holder, the filled Hg crucible and the scrap fill tube (used in original empty cell weighing) are then weighed to determine the mass of Hg in the cell. From the mass and density of the Hg and the known volume of the crucible, a determination of the depth of immersion for an SPRT is calculated.

The two-piece stainless steel container used for the final assembly of the Hg TP cell is used with both the borosilicate glass and stainless steel crucibles. A dimensional drawing of the container is found in reference 2. The bottom section is a closed-bottomed stainless steel tube with a stainless steel o-ring grooved flange welded to the open end. The top section is a stainless steel flange with an o-ring compression seal for the thermometer well of the Hg cell and a valved vacuum port. Rings of PTFE between the bottom of the container and crucible as well as polyethylene insulation spacers above the crucible create an annular space between the Hg TP cell and the container. Realizing the Hg TP in the evacuated stainless steel container provides a thermal barrier against temperature fluctuations in the maintenance bath, reduces heat flux, and increases the duration of the Hg TP realization. The container also provides a safe method for storing and using the Hg TP crucibles made with borosilicate glass.

4. TESTING OF THE MERCURY TRIPLE-POINT CELLS

The computer-controlled measurement system used to test the quality of the new Hg TP cells consists of a 9½ digit ac resistance ratio bridge, a thermostated (298.15 K ± 8 mK) ac/dc 100 Ω reference resistor, a scanner, and two SPRTs. Details of this SPRT measurement system, located in the NIST PRT Laboratory, are found in reference 4. One of the SPRTs is the Hg check thermometer and the second is the spare Hg check thermometer. The pooled Type A standard uncertainty (realization to realization repeatability) for these two SPRTs in the NIST Hg reference cell is 0.04 mK (standard deviation of a single reading, $n = 90$).

A recently acquired (1998), commercially available maintenance bath is used to realize the Hg TP in the melting mode. The ethyl-alcohol filled maintenance bath accommodates two Hg TP cells and has a stability of better than ± 2 mK during use. The new maintenance bath is an improvement over the plastic foam container that was previously used [2] to maintain the Hg TP cell. Use of the new maintenance bath improves both the realization to realization repeatability (Type A uncertainty from check thermometers) by a factor of three (due to a reduction of heat flux) and increases the duration of the plateau by a factor of ten.

The testing of the new Hg cells includes tracing three realization plateaus of the TP in a melting mode, an immersion profile of an SPRT during realization, and three direct comparisons with the NIST reference Hg TP cell. The melting curve plateaus are used to estimate the amount of impurities in the Hg sample. The immersion profile of the SPRT is used to verify that the thermometer is measuring the inner liquid-solid interface and estimate the amount of heat flux. The direct comparison measurements of the cell under test with the reference cell determine the relative hotness between the two cells. An additional test is applied only to the stainless steel crucible to test for the presence of air. The sealed crucible is inverted to test for a Hg hammer sound (similar to that of a water hammer).

To realize the TP in a melting mode, the Hg TP cell is first placed in the maintenance bath which is then set at 226.15 K to freeze the Hg sample overnight. Second the maintenance bath is set to control at 234.55 K to bring the cell to a temperature hotter than the realization temperature and initiate the outer liquid-solid interface. Third, when the maintenance bath reaches the set point temperature, the inner solid-liquid interface of the Hg sample is induced by placing two copper rods alternatively in the ethyl alcohol filled thermometer well at three minute intervals over thirty minutes. Finally, the bath-chilled SPRT is placed in the thermometer well and thirty minutes are allowed to elapse for the SPRT and Hg sample to thermally equilibrate prior to measurement. The outer liquid-solid interface, which acts as a buffer from temperature fluctuations in the maintenance bath, slowly melts inward during the realization.

Plateau examples of the Hg TP in a melting mode realization for two of the new Hg TP cells (Hg GC1 and Hg SC1) and Hg SS-1 are given in Figure 1. The estimated average melting range (0 % to 100 % liquid) for the six cells is within the measurement scatter of ± 0.02 mK and determined by a linear fit (from the 10 % to 80 % fraction melted) to be 0.005 mK. Comparatively, the melting range for the Hg DS-1 cell is < 0.02 mK and 0.19 mK for the Hg SS-1 cell. At NIST, for the measurements of the

realization of a fixed-point cell to be acceptable for use in estimating the impurity concentration of the metal sample, the duration of the realization curve must be at least ten hours. A plateau duration of at least ten hours and two solid-liquid sample interfaces minimizes the influence that the maintenance system has on the slope of the realization plateau, thus making a slope in the plateau (10 % to 80 % fraction melted) primarily dependant on the impurity concentration of the metal sample.

Examples of an immersion profile of an SPRT in the Hg TP cell thermometer well during a melting mode realization for both the borosilicate glass and stainless steel cells are given in Figure 2. For the heat-flux interactions between a maintenance system, fixed-point cell and an SPRT to be acceptable at NIST, the SPRT must be able to track the hydrostatic head effect over at least the bottommost 3 cm during the fixed-point cell realization.

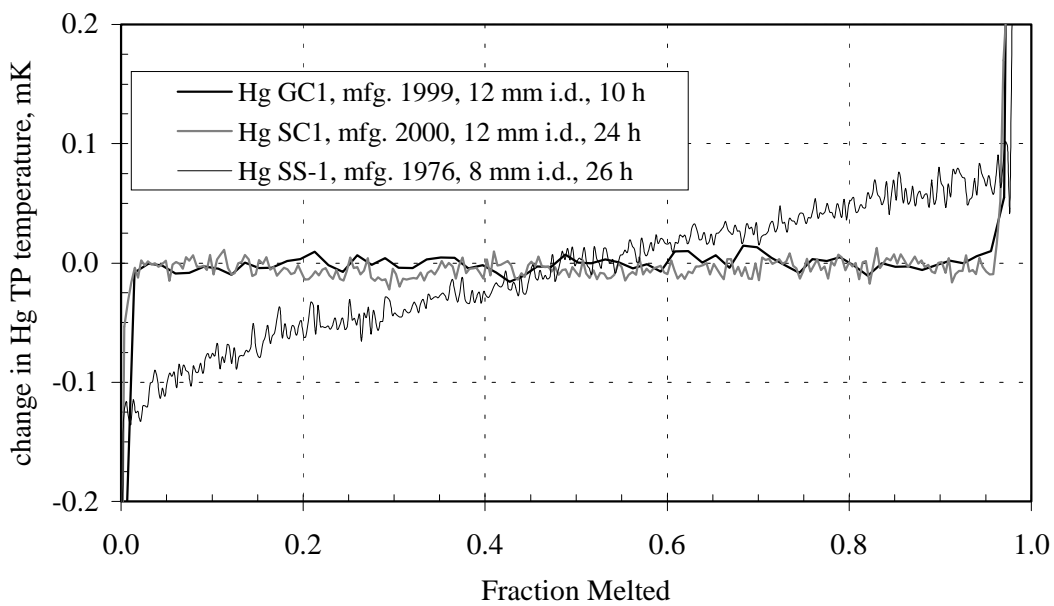


Figure 1: Plateau examples of a Hg TP in a melting mode realization for both the borosilicate glass (Hg GC1) and stainless steel (Hg SC1 and Hg SS-1) cells.

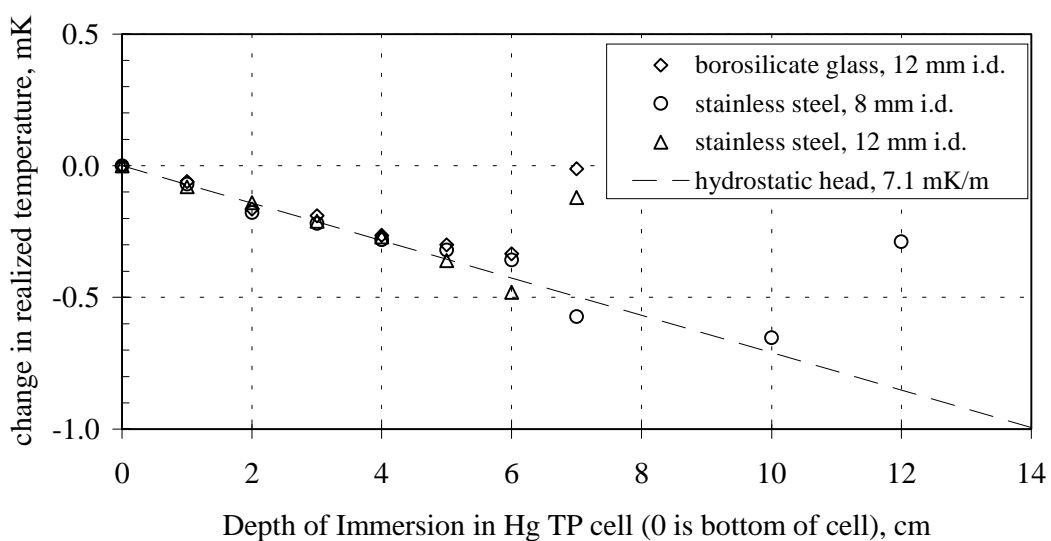


Figure 2: Examples of an immersion profile of an SPRT in the Hg TP cell thermometer well during a melting mode realization for both the borosilicate glass and stainless steel cells.

The direct comparison of the new cells with a reference cell is used to determine the relative hotness between the cells. During a direct comparison, both cells are realized in an identical manner in the maintenance system. An SPRT is alternately measured three times in each cell during the course of the direct comparison. The cells are then refrozen and directly compared in this manner two more times. Since the melting ranges of the Hg TP plateaus are small over the duration of measurements, all of the $W(T_{90})$ [$W(T_{90}) = R(T_{90})/R(273.16 \text{ K})$] values from the three direct comparisons are used to determine the relative hotness difference between the two cells. Since the direct comparisons of both Hg TP cells are made in the maintenance system simultaneously, the realized temperature difference between two cells (after corrections for differences in immersion) should be commensurate with the differences in impurity concentrations of the two samples. Any extraneous effect from air present in a sealed cell (+5.4 mK/101.3 kPa) or possible heat flux for cells of different designs can influence the realized fixed-point temperature. Cross checking the realized temperature differences from the direct comparisons with the estimation of impurities from the realization plateaus is used to estimate the magnitude of the extraneous effects.

5. UNCERTAINTIES

The uncertainty [U ($k = 2$)] assigned to the Hg TP cells is determined by adding in quadrature the Type A and Type B components. The Type A component is the pooled standard deviations of the direct comparison measurements and Hg TP check thermometers. The estimated Type B components are the chemical impurities of the fixed-point sample, results of the direct comparisons, SPRT self-heating correction, propagation of H₂O TP uncertainty, departure from thermal equilibrium (heat flux), ac bridge quadrature effects, reference resistor resistance, and bridge ratio measurement [5]. The U ($k = 2$) assigned to each of the Hg TP cells is given in Table 1.

6. RESULTS AND CONCLUSIONS

Table 1 gives the serial number of each tested Hg TP cell, the type of each cell, the results of the direct comparison with the reference cell (Hg SS-1) and the U ($k = 2$) assigned to each new cell. From the direct comparison measurements, the range in the realized Hg TP temperature differences of the six new Hg TP cells is 0.09 mK and on average the new cells are 0.20 mK hotter than Hg SS-1.

As evidenced from the direct comparison results of the six new Hg TP cells with the old reference Hg TP cell (Hg SS-1) given in Table 1, Hg SS-1 contains a less pure Hg sample. Since the source Hg for the old and the new cells is the same, the direct comparison results show that the estimated amount of impurities leached into the Hg sample of the Hg SS-1 cell from the stainless steel crucible are about 1 $\mu\text{g/g}$ over 25 years. As shown in Figure 1, the slopes of the melting curve plateaus verify that the Hg SS-1 cell contains a less pure Hg sample than that of the new Hg TP cells. Using Raoult's Law of dilute solutions and the slope of the melting curve plateaus, the estimated impurity concentration for the Hg SS-1 cell is 0.9₃ $\mu\text{g/g}$, 0.01 $\mu\text{g/g}$ for the Hg DS-1 cell, and 0.01 $\mu\text{g/g}$ on average for the six new Hg TP cells [7]. For Hg SS-1, the separately determined impurity concentrations that are estimated from the direct comparison and the melting curve plateaus are in close agreement.

In order to maintain a U ($k = 2$) of less than 0.2 mK on the Hg sample, the stainless steel reference Hg TP cell should be directly compared with a borosilicate glass crucible reference Hg TP cell and a realized melting curve plateau analyzed yearly. The reference Hg TP cell Hg SS-1 is now replaced with the reference Hg TP cell Hg SL1. The reference Hg TP cell Hg DS-1 is now replaced with the reference Hg TP cell Hg GC1. Future work will use the yearly collected direct comparison information to estimate the rate of contamination of the Hg sample in both Hg SS-1 and Hg SL1.

Table 1: List of the NIST Hg TP cells tested, type of each cell, inner diameter (i.d.) of thermometer well, the results of the direct comparison with the Hg SS-1 cell and the uncertainty assigned to each new cell.

Hg TP cell s/n	Type of cell and year manufactured	Cell X – Hg SS-1, mK	$U (k = 2)$, mK
Hg GC1	borosilicate glass, 12 mm i.d., 1999	0.24	0.12
Hg GC2	borosilicate glass, 12 mm i.d., 1999	0.23	0.12
Hg GC3	borosilicate glass, 12 mm i.d., 1999	0.16	0.15
Hg SC1	stainless steel, 12 mm i.d., 2000	0.18	0.14
Hg SC2	stainless steel, 12 mm i.d., 2000	0.15	0.16
Hg SL1	stainless steel, 8 mm i.d., 2000	0.23	0.12
Hg DS-1	borosilicate glass, 12 mm i.d., 1974	0.21	0.13
Hg SS-1	stainless steel, 8 mm i.d., 1976	–	0.25

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