

NIST REALIZATION OF THE GALLIUM TRIPLE POINT

Gregory F. Strouse
National Institute of Standards and Technology
Gaithersburg, Maryland

ABSTRACT

The gallium triple point (302.9166 K) instead of the gallium melting point (302.9146 K) is used at NIST in the realization of the International Temperature Scale of 1990 (ITS-90). Four different sources of gallium with purities of at least 99.999 995 wt. % were compared at NIST over the last eight years. One of these four sources was a 30 kg lot designated for use as a Standard Reference Material[®]. Three different fixed-point cell designs were used to fabricate twelve cells from these sources. Different methods of preparation of the gallium triple point were investigated to determine the optimum realization method and to determine if different methods affect the realization temperature of the triple point. Pressure and immersion characteristics were tested to check the agreement with the ITS-90 assigned values for the effect of pressure and hydrostatic head. Comparison of the twelve cells with the previous NIST reference gallium triple-point cell (Ga-1) containing 99.999 99+ wt. % pure gallium shows that the triple-point temperatures of the twelve cells are about 0.03 mK hotter than that of Ga-1. Additionally, repeated measurements of the twelve gallium triple-point cells give a reproducibility that is equivalent to that of a similar group of water triple-point cells. The uncertainty ($k = 2$) assigned to the current NIST reference gallium triple-point cells is the same as that assigned to the NIST reference water triple-point cells, i.e. 0.04 mK. This paper presents the fixed-point cells' designs, fabrication method, realization technique and the uncertainty of the NIST-realized gallium triple-point temperature.

1. INTRODUCTION

The National Institute of Standards and Technology (NIST) uses the gallium triple point (302.9166 K) instead of the gallium melting point (302.9146 K) in the realization and dissemination of the International Temperature Scale of 1990 (ITS-90) [1]. A pressure correction of -2.011 mK per 101.325 kPa is applied for the temperature difference between a triple-point and a melting-point realization [2]. Inherently, a triple-point realization provides results that are more reproducible than a melting-point realization due to the fact that a triple-point realization is not dependent on pressure and is less subject to contamination.

Over the last eight years, four different lots of high-purity gallium (≥ 99.999 995 wt. % pure) and three different cell designs were used to fabricate twelve gallium fixed-point cells. Nine of the twelve cells were sealed with a valve at the top of each cell and can be realized as either a triple point or melting point of gallium. The nine cells that are sealed with a valve are under vacuum during the realization of a triple point. Additionally, the valve allows for verification of the assigned pressure effect on the realized temperature. The other three cells were permanently sealed during the realization of the gallium triple point. This paper gives the direct comparison results of these twelve cells relative to the original NIST reference gallium triple-point cell (Ga-1) containing 99.999 99+ wt. % pure gallium, the effects of different methods of realization, and the uncertainty assigned to the NIST gallium triple-point temperature.

2. GALLIUM FIXED-POINT CELLS

Table 1 gives the fixed-point cell serial number, metal source, lot number, purity, cell design, and the immersion depth for a standard platinum resistance thermometer (SPRT) for the Ga-1 cell [2, 3] and the twelve subsequent cells. Three of the twelve cells contain Standard Reference Material[®] (SRM) 1751 gallium [4]. SRM 1751 consists of 150 argon-filled plastic bottles each containing 200 g of gallium that are part of a 30 kg lot.

The assembly of a gallium fixed-point cell was performed in an argon-filled glove box. The crucible and its cap were machined from virgin PTFE. The crucible was designed with five ribs spaced 54 mm apart to provide structural integrity during the 3.1% expansion on solidification of the gallium and to minimize thermal contact with the outer envelope. Similarly, the crucible rests on a Nylon ring inside the outer envelope to thermally isolate the bottom of the crucible from the outer envelope. The re-entrant well (glass or Nylon) passes through the PTFE cap in the top of the PTFE crucible. After assembly of the cell, the 1 kg sample of gallium was solidified prior to removal from the glove box. A detailed description of the cells is given in references [2-4].

Table 1. The fixed-point cell designation, metal source, lot number, purity, cell types, and the immersion depth for a standard platinum resistance thermometer (SPRT) for the various gallium triple-point cells.

Ga cell s/n	metal source	mfg. lot no.	purity wt. %	cell type*	immersion depth, cm	special notes
Ga-1	Allusuisse [†]	F171/252	79+	NTNV	13	1989-1992 reference
Ga 921	Rhône-Poulenc	9117563	795	NTNV	18	1992-1994 reference
Ga 943	Johnson Matthey	L22C25	795	GTGV	18	
Ga 944	Johnson Matthey	L22C25	795	GTGV	18	1994-1998 reference
Ga 961	Rhône-Poulenc	9619363	795	GTNV	18	
Ga 962	Rhône-Poulenc	9619363	795	GTNV	18	
Ga 963	Rhône-Poulenc	9619363	795	GTGS	18	
Ga 964	Rhône-Poulenc	9619363	795	GTGS	18	
Ga 965	Rhône-Poulenc	9619363	795	GTNV	18	
Ga 971	Rhône-Poulenc	9619463	795	GTGS	18	
Ga 981	Rhodia-Chime	9800763	795	GTGV	18	SRM 1751, present reference
Ga 982	Rhodia-Chime	9800763	795	GTGV	18	SRM 1751
Ga 983	Rhodia-Chime	9800763	795	GTGV	18	SRM 1751

* NNTV = Nylon outer envelope, PTFE crucible, Nylon re-entrant well and valved

GTGV = borosilicate glass outer envelope, PTFE crucible, borosilicate glass re-entrant well and valved

GTNV = borosilicate glass outer envelope, PTFE crucible, Nylon re-entrant well and valved

GTGS = borosilicate glass outer envelope, PTFE crucible, borosilicate glass re-entrant well and sealed

[†] Certain commercial sources identified in this paper does not imply endorsement by NIST

2.1. Type I cell: NNTV

The NNTV cell with a Nylon outer envelope, PTFE crucible, Nylon re-entrant well and valve is the original design used at NIST [2, 3]. The Nylon outer envelope and a single Nylon piece comprised of a re-entrant well and top were screwed together and sealed with epoxy. A Nylon pumping tube was screwed into the cap (and then epoxied) and sealed with a valve. The inner diameter of the re-entrant well of the original reference cell (Ga-1) is 8 mm and that for cell Ga 921 is 13 mm. The larger diameter re-entrant well was designed to accommodate a special 12.5 mm outer diameter capsule SPRT holder.

2.2. Type II cell: GTGV and GTGS

The GTGV and GTGS designed cells with a borosilicate glass outer envelope, PTFE crucible, borosilicate glass re-entrant well and valve/sealed are of the type normally used at NIST [4, 5]. The borosilicate outer envelope and a single borosilicate glass piece comprised of a re-entrant well and top are fused together on completion of the cell. A borosilicate pumping tube is part of the top. The inner diameter of the re-entrant well is 8 mm with an outer diameter of 11 mm. The pumping tube is either sealed with a valve or flame sealed during a realization of the triple point. The sealed cell design is used as a transfer cell for comparison with other laboratories.

2.3. Type III cell: GTNV

The GTNV cell^{††} with a borosilicate glass outer envelope, PTFE crucible, Nylon re-entrant well and valve was designed as a more robust transfer cell that can be shipped with less concern of breakage. The borosilicate outer envelope is sealed with an O-ring compression fitting to a single Nylon piece used for the re-entrant well, header and pumping tube. The inner diameter of the re-entrant well is 8 mm and the outer diameter is 11 mm. The valve is normally closed during a realization of the triple point of gallium.

3. TRIPLE-POINT REALIZATION AND MEASUREMENTS

NIST has three maintenance furnaces for realizing the fixed point of gallium. Each of the furnaces consists of a closed-bottom cylindrical-tube aluminum core with a non-inductively, single-layer, bifilarly wound heater on the outside of the core. The furnaces are designed to provide about a 1 mm annular space between the gallium cell and the inner wall of the aluminum core. The aluminum core is filled with mineral oil to improve thermal contact between the cell and the furnace core. One of the three furnaces which operates at 313.15 K \pm 0.01 K is

used for the preparation of the outer liquid-solid interface. In this furnace, the triple-point plateau will last approximately 13 hours. The other two furnaces operate at a temperature of $303.05\text{ K} \pm 0.01\text{ K}$. In these two furnaces, the triple-point plateau will last at least 6 months. An immersion heater operating at a temperature of 313.15 K is used to establish the inner liquid-solid interface. During preparation of the triple-point plateau and during subsequent measurements, the thermometer well is completely filled with mineral oil to improve thermal contact of the immersion heater and of the SPRT, and to improve the immersion characteristics of the SPRT.

3.1 Triple-point realization techniques

Multiple methods of realizing the triple point of gallium were investigated. Two of the three methods were studied only for the purpose of determining the effect on the realized triple-point temperature. The third method is the technique that is normally used at NIST in the realization of the triple point of gallium. Additionally, the effect on the triple-point temperature as a function of how the gallium was frozen was studied.

The first step in preparing the gallium cell for a triple-point realization involved attaching the cell designed with a valve to an oil-free diaphragm and turbo-molecular pumping system, and then evacuating the cell overnight. During preparation of the cell and realization of the triple point, the cell was pumped continuously. The cell design that is sealed for use as a triple point requires no additional evacuation.

The second step is to insure that the gallium metal is in the solid state. An investigation into different freezing techniques was conducted. The three methods of freezing the gallium were 1) freezing from the outside inward, 2) freezing from the inside outward, and 3) from the inside and outside simultaneously. For the first method, the cell was placed in a glass beaker that extends over the length of the cell, then the beaker was filled with crushed dry ice. In approximately three hours, the gallium in the cell was frozen. The second method involved using an immersion cooler [6]. The immersion cooler was placed into the re-entrant well of the cell to freeze the gallium from the inside outward. The immersion cooler can cool the cell down to a temperature of about 229 K . Approximately, five hours was required to solidify the gallium using this second method. The third method was the combination of the first two and required about 90 min to solidify the gallium metal. Since the gallium is $\geq 99.999\ 995\text{ wt. \%}$ pure, the observed effect on the realized triple-point temperature, for the three methods, differed by no more than the reproducibility of measurement system of 0.01 mK . The first method is the technique normally used at NIST to solidify the gallium prior to realization of the triple point.

The third step involved the creation of the liquid-solid interface(s) in order to achieve the triple point of gallium. Three methods were tried for realizing the triple point. In the first method, the cell was placed in the 313.15 K furnace to establish the outer liquid-solid interface with no inner liquid-solid interface. In the second method, the cell was placed in the 313.15 K furnace to establish the outer liquid-solid interface and an immersion heater (operating at 313.15 K) was placed into the re-entrant well for 20 min to establish a partial inner liquid-solid interface. In the third method, the cell was placed in the 313.15 K furnace to establish the outer liquid-solid interface and an immersion heater (operating at 313.15 K) was placed into the re-entrant well for 45 min to establish a complete inner liquid-solid interface. This third method is the technique normally used at NIST to realize the triple point of gallium.

3.2. Pressure and hydrostatic-head effect

The confirmation of the pressure effect between the triple point and melting point of gallium was performed on the cells of the different types. First the cell was measured at the triple-point pressure, then measurements of the cell were made at different pressures up to 106.7 kPa , and finally the cell was re-evacuated for a second measurement at the triple point. Twenty minutes were allowed for the SPRT to re-equilibrate after changing the pressure in the cell before making the next set of measurements. Approximately, one hour was required to re-evacuate the cell to the triple-point pressure for the last measurement. A Bayard-Alpert pressure gauge in the vacuum system was used to determine the base pressure during the triple-point realization. A Bourdon tube gauge with an uncertainty of 0.13 kPa was used to determine the pressure at the other pressures.

Proper immersion of the SPRT was verified by determining if the SPRT could track the assigned hydrostatic-head effect of gallium. This was tested by measuring the SPRT starting 10 cm from the bottom of the thermometer well, then inserting the SPRT in 2 cm steps until 4 cm from the bottom, at which time the SPRT was then inserted in 1 cm steps until the bottom of the thermometer well was reached. Before measuring the SPRT at each step, twenty minutes were allowed for the SPRT to re-equilibrate after changing the immersion depth. The immersion depth of the SPRT was calculated from the sensor midpoint to the height of the metal column during the triple-point realization with about 20 % of the metal melted.

3.3. Direct comparison with the reference cell

In order to confirm the quality of a cell, direct comparison measurements were performed by simultaneously realizing the triple point in the melting mode for both cells. This was obtained by realizing simultaneous triple points for the two cells in the two 303.05 K furnaces and making three sets of alternate measurements, at equal time intervals, on their plateaus, using an SPRT. This ensured that the comparison measurements on the two cells were made at approximately the same liquid-solid ratio of the metal samples. Corrections were made for any differences in hydrostatic-head effects in each cell. Each cell was measured using an SPRT three times during the direct comparison and this procedure was repeated for a total of three independent triple-point realizations.

3.4. Instrumentation and measurement techniques

The measurement equipment used for the testing of the cells included a commercially-available ac resistance ratio bridge operating at a frequency of 30 Hz, a thermostatically-controlled ($262.15\text{ K} \pm 10\text{ mK}$) ac/dc reference resistor and an SPRT. A detailed description of the measurement system is found in reference [7]. Measurements of the triple-point plateaus were made with an excitation current of 1.0 mA. Measurements of the pressure effect, hydrostatic-head effect and the direct comparisons were made with two excitation currents of 1.0 mA and 1.414 mA for extrapolation to 0 mA. The 1 mA reading was repeated after the 1.414 mA reading to insure that the SPRT was at thermal equilibrium. The two 1 mA readings were required to repeat to within the equivalent of 0.01 mK for the measurements to be valid. Following each experimental measurement set at the triple point of gallium, the SPRT was measured at the triple point of water.

4. RESULTS

4.1 Triple-point realization

Figure 1 shows the effects of the three methods used for the realization of the triple point of gallium. The effect of no inner liquid-solid interface (first method) on the triple-point realization is evident in the behavior and the apparent large melting range of about 1 mK (first 70 % of the plateau) before reaching a relatively stable plateau. The effect of a partially formed inner liquid-solid interface (second method) on the triple-point realization gives a non-reproducible curve with large scatter ($\pm 0.02\text{ mK}$) in the data. The properly realized triple point with a completely formed inner liquid-solid interface (third method) gives by far the most reproducible and stable results. As expected, the third method, which is the method normally used at NIST [7], yields a plateau that is reproducible to within the capabilities of the measurement system (0.01 mK) for over 90 % of the melt duration.

4.2. Pressure and hydrostatic-head effect

Based on the results shown in figure 2, a pressure effect on the realized temperature of the gallium fixed point is calculated to be $-2.01\text{ mK per }101.325\text{ kPa}$. Previously published results give a pressure effect on the realized temperature of the gallium fixed point of $-2.011\text{ mK per }101.325\text{ kPa}$ [2, 3] and the ITS-90 assigns a pressure effect of $-2\text{ mK per }101.325\text{ kPa}$ [1].

Figure 3 shows the immersion characteristics of the SPRT used in the measurements in the three cell types. The SPRT is capable of measuring the ITS-90 assigned hydrostatic-head effect (-1.2 mK/m) [1] over at least the bottommost 8 cm. A minimum of 3 cm is required for the SPRT to be considered properly immersed and for the measured temperature not to be influenced by stem-conduction loss.

4.3. Direct comparison relative to original reference cell

Table 2 gives the results of the direct comparison measurements of the twelve cells relative to the original reference cell (Ga-1). The twelve cells are, on average, about 0.03 mK hotter than the Ga-1 cell. A cell that is "hotter" usually has fewer impurities, since impurities in these samples will usually decrease the triple-point temperature. The small difference in the realized triple-point temperature between the twelve cells and the Ga-1 cell is comparable to the difference in the purity of the gallium samples. The spread in the realized triple-point temperature of the twelve cells is 0.02 mK with a standard deviation of 7 μK .

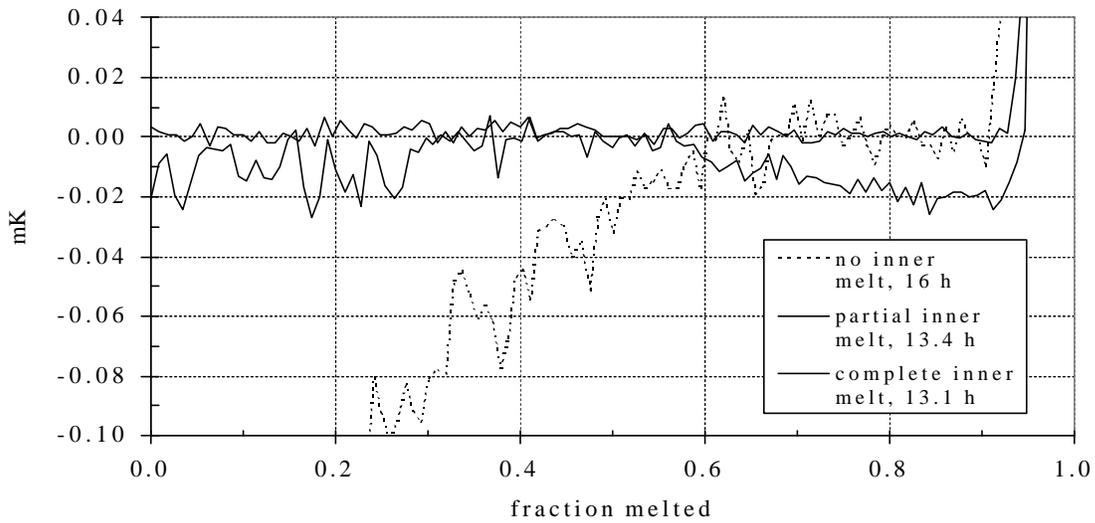


Figure 1. Gallium triple-point realizations in the melting mode for the three different methods of realization.

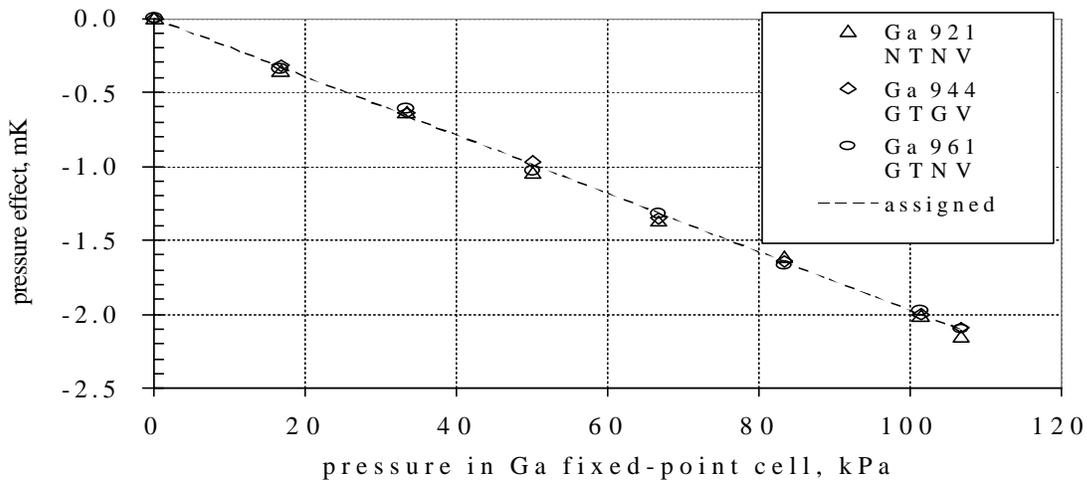


Figure 2. Pressure effect on realized temperature of gallium fixed point.

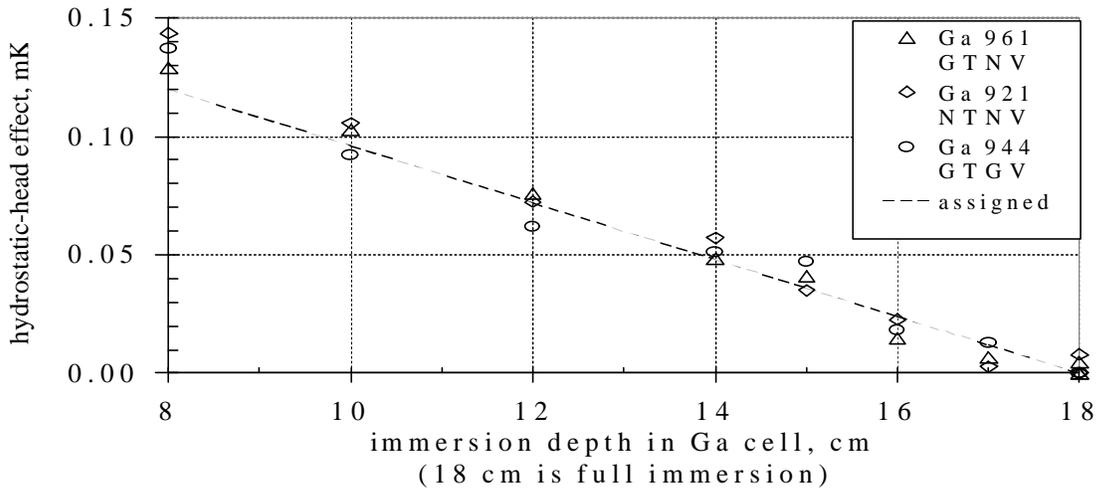


Figure 3. Immersion profile of an SPRT in the three cell types with respect to the assigned value of the hydrostatic head effect.

Table 2. Direct comparison results of twelve gallium triple point cells relative to original reference cell Ga-1.

Ga cell s/n	DC* ΔT mK	Ga cell s/n	DC* ΔT mK	Ga cell s/n	DC* ΔT mK
Ga 921	0.02	Ga 962	0.02	Ga 971	0.03
Ga 943	0.04	Ga 963	0.03	Ga 981	0.04
Ga 944	0.03	Ga 964	0.04	Ga 982	0.02
Ga 961	0.03	Ga 965	0.03	Ga 983	0.03

*DC = direct comparison (Ga 9XX – Ga-1)

5. UNCERTAINTY

For the twelve triple point of gallium cells the uncertainties of realization are calculated using the following components [8]. The Type A standard uncertainty of 12 μK is the standard deviation of $W(t_{90})$ values of repeated measurements on 87 triple-point realizations with the Ga 943 cell using an SPRT. The Type B standard uncertainty from the six known contributions was 18 μK . The Type B contributions are 1) chemical impurities, 2) exact immersion depth of the SPRT, 3) adequacy of immersion of the thermometer to eliminate thermometer stem conduction, 4) SPRT self-heating, 5) gas pressure and 6) the direct comparisons (worst case), with values of 4 μK , 2 μK , 1 μK , 12 μK , 0 μK , and 12 μK , respectively. The assigned expanded uncertainty ($k = 2$) for the twelve cells is 0.04 mK. The small differences in the realized triple-point temperatures among the twelve cells does not contribute significantly to the overall assigned expanded uncertainty ($k = 2$) of 0.04 mK.

6. CONCLUSION

The realized triple-point temperature in the twelve cells is independent of the cell design. The formation of a complete inner liquid-solid interface is critical for the realization of a triple-point plateau that is flat to within the capabilities of the measurement system. The twelve triple point of gallium cells gave results (realized triple-point temperature differences, reproducibility, and stability) that are equivalent to that of a similar group of water triple-point cells. The uncertainty ($k = 2$) assigned to the current NIST reference gallium triple-point cells is the same as that assigned to the NIST reference water triple-point cells, i.e. 0.04 mK.

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- †† The author acknowledges the help from B.W. Mangum and W.C. Ausherman in the design of the GTNV cell.
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