MINI METAL-CASED FIXED-POINT CELLS

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ABSTRACT

Mini metal-cased fixed-point cells have been developed for the triple point of water (TPW), the melting point of gallium (MPG), and the freezing point of indium (FPI). The outer case is made from stainless steel. An inner vessel, used for the MPG and FPI, is made of virgin PTFE. The design of the new cells is described in detail.

Realization methods were investigated for each of these newly designed fixed-point cells. Data was obtained from melting and freezing the cells. These cells were compared with traditional fixed-point cells. The differences between the new small cells and traditional size cells were well within 3 mK for the MPG and the FPI. The differences of the newly manufactured TPW cell and a traditional TPW cell were within 0.5 mK, but this difference was found to increase with time. This degradation is addressed.

The stainless steel–cased cells are much less fragile than Pyrex and quartz glass, so the new cell design fits many applications where more durability is desirable such as in ocean vessels or mobile labs, where traditional fixed-point cells are easily broken or damaged.

1. INTRODUCTION

Traditional fixed-point cells and related equipment are used for realizing the International Temperature Scale (ITS) or for calibrating primary temperature standards such as standard platinum resistance thermometers (SPRTs). Fixed-point cells provide very high accuracy and do not require reference thermometers for calibrations. These cells and related equipment, however, have very poor productivity and are difficult to operate for secondary or industrial calibrations.

A few years ago, we developed smaller fixed-point cells and maintenance apparatus [1,2] that are convenient for secondary and industrial calibrations. Their benefits include improved accuracy, reliability, efficiency, ease of operation, and cost. These cells were fabricated using fused silica or Pyrex glass as their envelopes. While excellent materials for primary laboratory applications, fused silica and Pyrex glass are too fragile for industrial applications. Under a contract from NIST we developed a series of metal-cased fixed-point cells for these applications. We began with the triple point of water (TPW), the melting point of gallium (MPG), and freezing point of indium (FPI), because they are used close to room temperature. Here we report the results of this development.

2. METAL-CASED FIXED-POINT CELLS

304 stainless steel (SS) was chosen as the case material because we thought it would not contaminate the pure substance in the cell. It turned out that SS may be not good for TPW cells as we will discuss later. An inner vessel, used for the MPG and FPI, is made of virgin PTFE. It separates the high-purity gallium (or indium) from the SS to avoid contamination (Fig. 1). The total length of each cell is 127 mm (5”), so it can be used in dry-wells, Micro-Baths, and furnaces. Immersion depth is about 100 mm for the TPW and about 75 mm for the MPG and the FPI. Because of the relatively short immersion depth, a close fit between the probe and the reentrant well of the cell is important. The diameter of many PRT probes in North America is 6.35 mm (1/4”) while the diameter of many popular metal sheath SPRTs is 5.56 mm (Rosemount 162CE and Hart 5699). Therefore, two inner diameter (ID)

sizes of reentrant wells were used for these probes—6.64 mm for 6.35 mm probes and 5.84 mm for 5.56 mm probes.

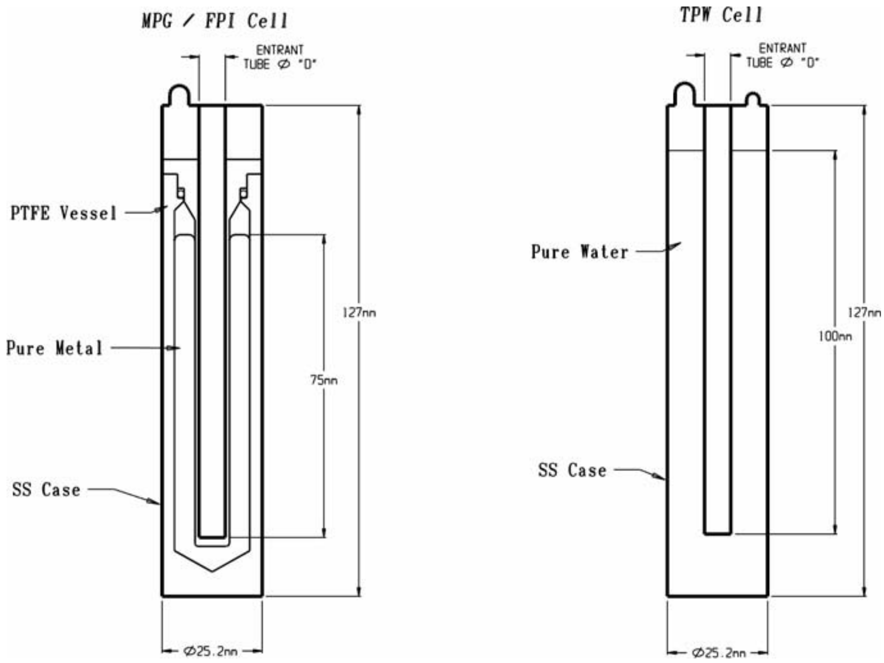

Fig. 1: Mini metal-cased fixed-point cells

Gallium with a purity of 99.99999+% and indium with a purity of 99.9999+% were used to fill the cells. High purity water with resistivity higher than 17.8 MΩ·cm was double distilled into the TPW cell. Thoroughly cleaning all parts is extremely important. The SS parts were cleaned using the following procedure:

1. Clean the parts with acetone in an ultrasonic washer for twenty minutes.
2. Flush the parts with acetone and dry them.
3. Soak the parts in a special acid solution for about 15 minutes.
4. Rinse the parts with pure water.
5. Flush the parts with high-purity steam for many hours.
6. Dry thoroughly with clean dry air or argon.

The PTFE parts were cleaned using the following procedure:

1. Soak and brush the parts with a brush and a detergent solution.
2. Clean the parts with a detergent solution in an ultrasonic washer for twenty minutes.
3. Rinse the parts with pure water.
4. Soak the parts in aqua regia overnight
5. Rinse the parts with pure water.
7. Flush the parts with high-purity steam for many hours.
8. Dry thoroughly with clean dry air or argon.

The gallium and indium were first sealed into their PTFE vessels using a specially made O-ring in a pure argon (99.999%) atmosphere at a pressure close to 101,325 Pa at the respective melting temperatures of the metals. The assembled PTFE vessel was then encased in a SS cylinder. A SS top, including the reentrant well, was joined to the cylinder using argon-arc welding. The SS case was then connected to a vacuum system and pumped for a few hours. During the pumping period, the cell was purged with high purity argon several times. Finally, it was filled with 99.999% pure argon and sealed at almost the same pressure as that in the PTFE vessel.

3. REALIZATION OF FIXED POINTS

Realization of these fixed points using the mini metal-cased fixed-point cells is very simple. Many varied apparatus can be used with these cells, including Micro-Baths, dry-wells, and small, portable furnaces. A few examples are shown in Fig. 2 and Fig. 3.

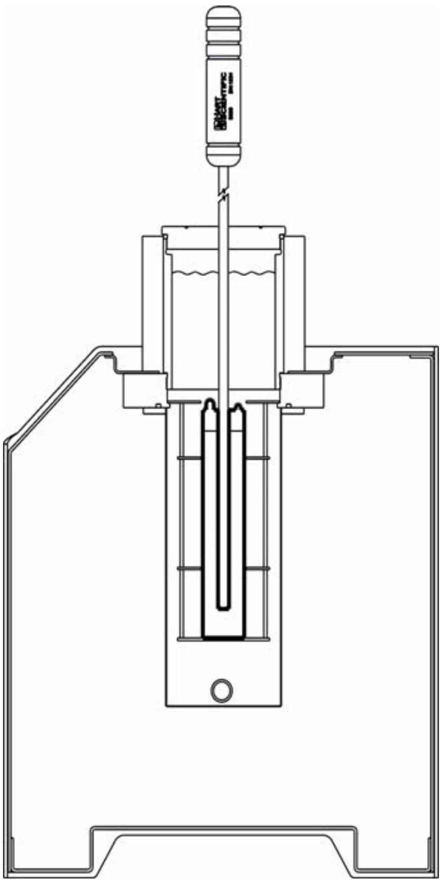

Fig. 2: A TPW cell in a Micro-Bath

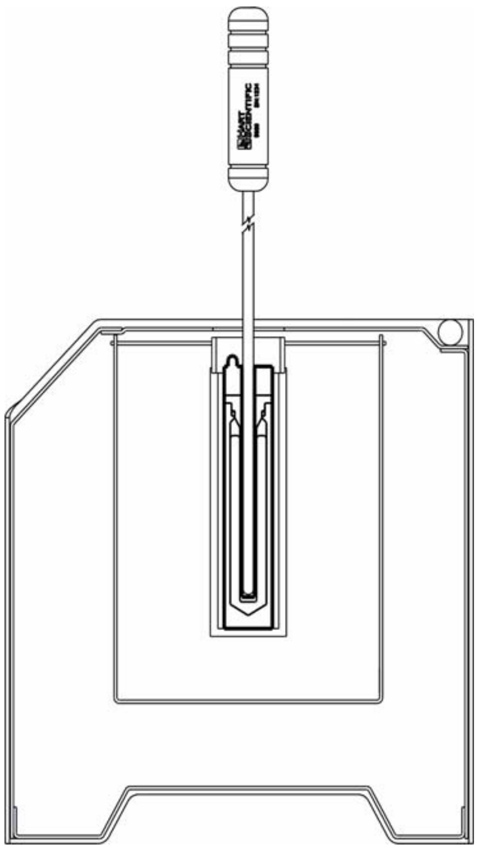

Fig. 3: A MPG cell in a dry-well

Realization of the TPW with the new mini metal-cased cells is quite simple. Cool the cell to about –4°C for a few minutes in a bath or a dry-well. Remove the cell from the apparatus and give the cell a shake. The water in the cell (supercooled at a temperature of –4°C) immediately begins to freeze. Fine-needle crystals (dendrites) of ice appear uniformly throughout the cell and approximately 5% of the water freezes within a few seconds. Return the cell into the apparatus and maintain the apparatus temperature close to 0°C.

An alternative method for freezing the cell is as follows. Pre-cool the cell to approximately 0°C. Add a few drops of liquid nitrogen into the reentrant well of the cell. Sequentially insert two metal rods pre-cooled to the liquid nitrogen temperature into the well and leave each rod in the cell for two minutes. An equilibrium temperature curve recorded in this way for a newly manufactured cell (#31004, SS) is shown in Fig.4. An SPRT was measured in a traditional TPW cell (#1022) before the curve started and at about the 29th hour of the curve. The temperature differences between cell #1022 and the new mini cell #31004 were well within 0.5 mK. One year later, however, we repeated the measurements and found the differences between them had become much larger (> 2 mK). Hydrogen generation in the cell might cause the problem when water is in contact directly with SS for a long time [3,4].

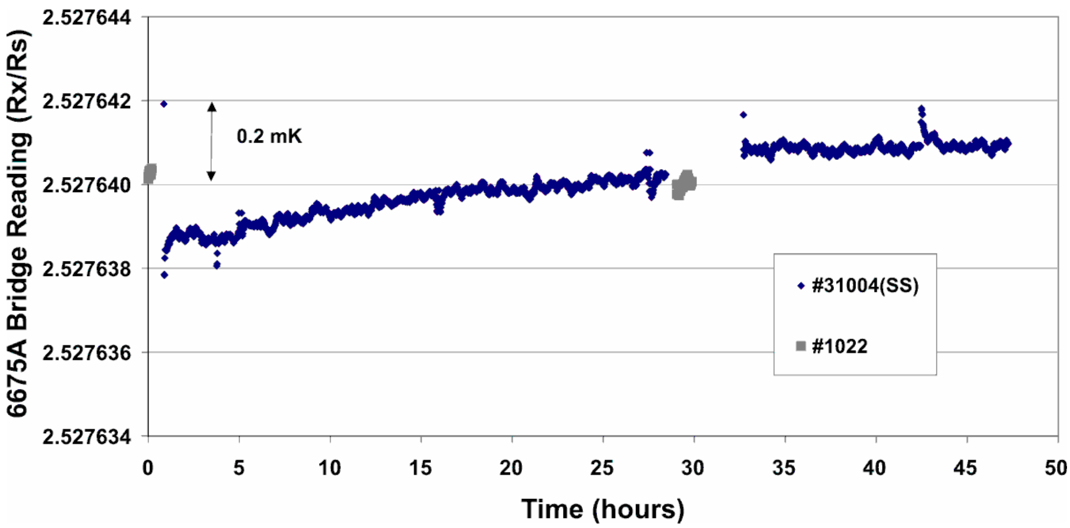

Fig. 4: Data from a new mini TPW cell compared with a traditional TPW cell

Realization of the MPG is as follows. Make sure that all gallium is frozen before starting. Maintain the Micro-Bath or dry-well at 0.5°C below the melting point (MP) for at least 30 minutes. Raise the temperature to 0.5°C above the MP at a rate of 0.2°C per minute and maintain the apparatus at this temperature for five minutes. Then decrease the temperature to 0.1°C above the MP at a rate of 0.2°C per minute and maintain the apparatus at this temperature. A typical melting curve obtained in a dry-well is shown in Fig. 5. SPRT #1111 and a Model 1590 Super-Thermometer were used for the measurement. Before the measurements, SPRT #1111 was calibrated at the MPG in a traditional MPG cell with an expanded uncertainty of 0.08 mK. The expanded uncertainty of the Model 1590 is 1 ppm for resistance measurements, which is equivalent to 0.25 mK of temperature uncertainty. The melting curve lasted for 25 hours and 10 minutes. The average measured value on the melting curve was 29.76499°C ±0.0006°C. The difference between the ITS-90 assigned value and the measured average value was +0.39 mK. The difference was much smaller than our goal (10 mK) and the estimated expanded uncertainty (2.2 mK, k=2).

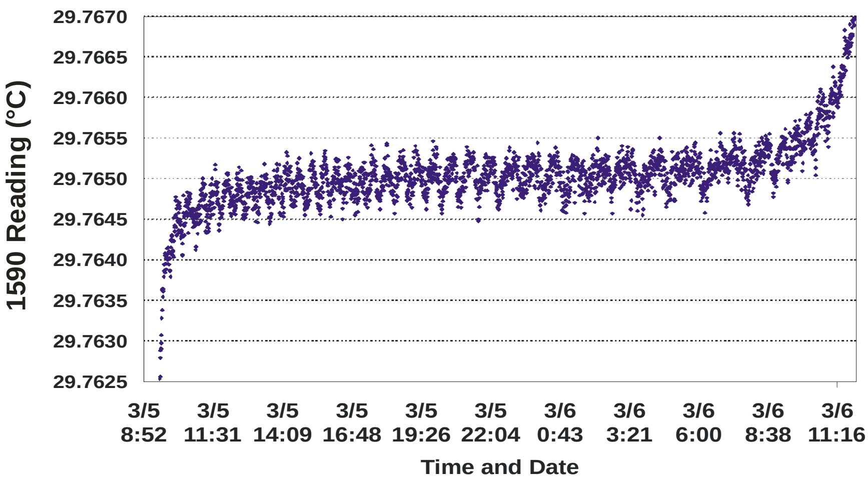

Fig. 5: A typical melting curve of gallium using a mini SS case gallium cell in a dry well

The FPI can be realized in two ways—melting or freezing. Realization of a melting curve is almost the same as for the MPG. The freezing curve can be obtained using the follow procedure. When all of the indium is melted, maintain the apparatus at a temperature of about 0.5°C above the MP for at least 30 minutes. The apparatus temperature is then decreased to about 2°C below the MP at a rate of 0.2°C per minute. (Monitor the temperature by using an SPRT inserted into the cell.) As soon as the temperature stops decreasing and begins to rise, give the cell a light shake and set the apparatus at a temperature about 0.1°C below the MP. A typical melting curve and freezing curve is shown in Fig. 6 and Fig.7.

A new mini indium cell (#34003) was compared with a traditional indium cell (#5004). The comparison lasted for two days. Three SPRTs and a 0.2-ppm automatic bridge were used for the comparison. Two freezing curves were realized on Cell #5004. One freezing curve and one melting curve were realized on mini cell #34003. Fig. 8 shows the results obtained using SPRT #1111. The differences between the new mini cell and the traditional cell were well within ±3 mK. The melting values on the mini cell were a little higher than that of the traditional cell, and the freezing values were a little lower. Since the temperature of the surroundings was a little higher during the melt and a little lower during a freeze, the differences are thought to originate mainly from conductivity along the SPRT stem.

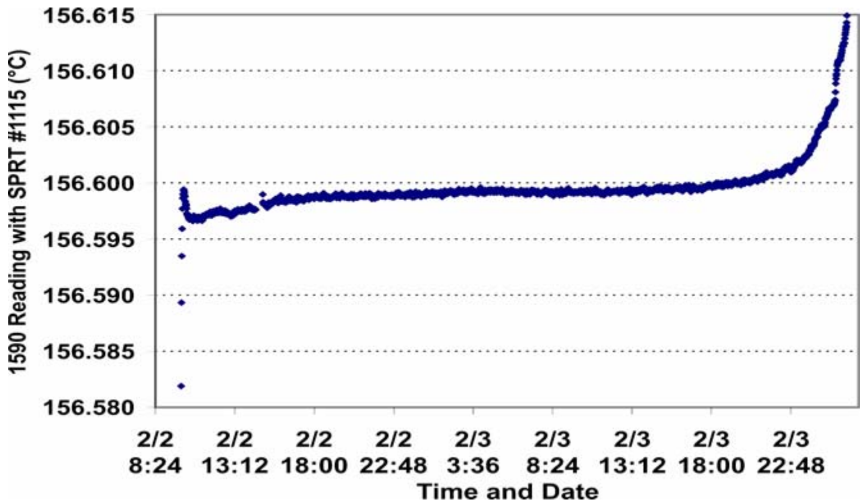

Fig. 6: A typical melting curve indium using a mini indium

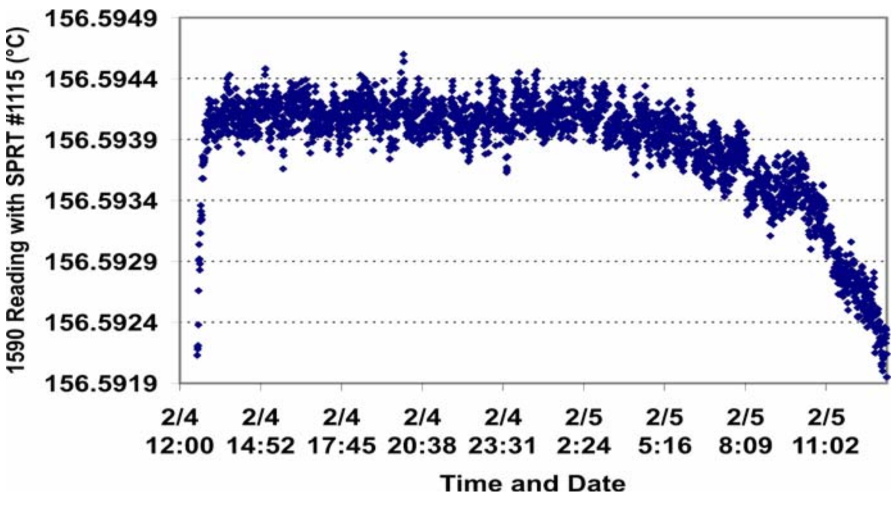

Fig. 7: A typical freezing curve of indium using a mini indium cell

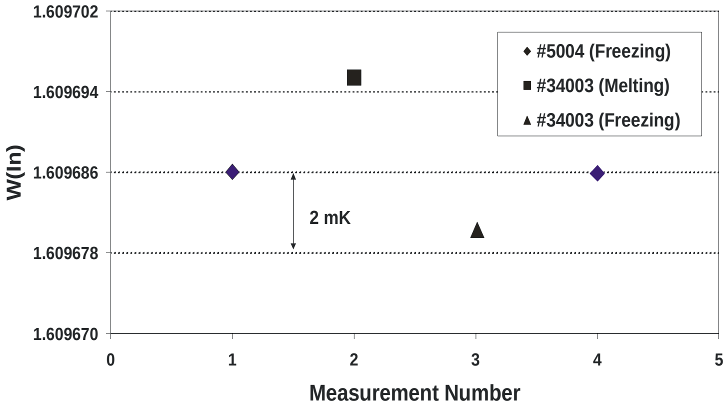

Fig. 8: A direct comparison between mini indium cell #34003 and traditional indium cell #5004

The uncertainty components of the new mini metal-cased cells are listed in Table 1.

Table 1: Estimated uncertainty

Source of uncertainty	Value of uncertainty component (1 σ in mK)	
	MPG	FPI
Reproducibility (A)	0.4	0.6
Conductivity	1.0	1.6
Impurity in the sample	0.1	0.5
From pressure difference	0.1	0.1
Combined	1.1	1.8

4. CONCLUSIONS AND DISCUSSION

The new mini metal-cased cells for MPG and FPI provide much improved uncertainty for secondary and industrial calibrations. The sturdy metal-cased cell can be used in many industrial and field applications, especially in tough environments. Other advantages include better reliability, long-term stability, and ease of use.

The primary error source is from stem conductivity. If we increase the immersion depth from 75 mm to 100 mm or more, the uncertainty can be further improved.

SS is unsuitable as a TPW case material and we will try other materials. Oxygen-free cooper may be better material for TPW cells.

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