A New Stainless Steel-Cased Gallium Cell and its Automatic Maintenance Apparatus

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Abstract. A new stainless steel-cased gallium cell has been developed. The new cell design, including an open cell version, is described. A new cell was compared against a NIST-certified gallium cell, and the difference between them was well within 0.1 mK. Multiple cells of the new design were intercompared with each other, with differences well within 0.1 mK. A new automatic maintenance apparatus has been developed for simplifying the operation. A melting plateau as long as seven days is easy to obtain using the new apparatus. The expanded uncertainty (k=2) was estimated to be about 0.2 mK for the whole system.

INTRODUCTION

The melting point of gallium (GA MP), 29.7646°C, is one of the defining fixed points of the International Temperature Scale of 1990 (ITS-90). Its temperature is in the range of room temperature, making it a very useful calibration point in biological engineering, life science, pharmaceuticals, environmental and oceanographic studies, and many other fields. More and more labs are using or will use the GA MP. Classic designs of GA MP cells and apparatus work very well in many national labs [1-4], where vacuum and argon filling systems are usually available. Such systems might not be available for many other users. Permanently sealed Pyrex-Teflon cells are much easier to use for most users [5]. Such sealed cells can provide an expanded uncertainty (k=2) of about 0.1 mK with superb long-term stability. While being an excellent material for standard lab applications, Pyrex glass is too fragile for many other users; so a stronger material, such as stainless steel (SS), is more desirable as the outer case material for many users. The difficulty is how to avoid the possible contamination of the high-purity gallium from the case material. It is the goal of our research to eliminate such contamination in order to obtain the same uncertainty as the Pyrex-Teflon cell. The new cell design is mainly for the calibration of standard platinum resistance thermometers (SPRTs) and other high-accuracy thermometers.

Realizing the GA MP is not a complicated procedure for many national labs. The gallium sample is frozen completely before starting a melting curve. Because of a large amount of supercooling and a volume expansion of about 3.1% when high-purity gallium freezes, the freezing should start from the bottom of the cell upward; otherwise the volume expansion of gallium during freezing might break the cell. Good vertical temperature uniformity (±0.02°C or better) around the cell during a melting curve is also required. Many users could benefit from a maintenance apparatus for the GA MP that is fully automated, including freezing of the gallium sample, so we started to develop such an apparatus two years ago. Our goal was for the apparatus to be easy to use, even for technicians in industrial labs. Also, we wanted the uncertainty to be close to that of the classic apparatus of many national laboratories.

THE NEW GALLIUM CELL

In order to eliminate the possible contamination from SS, a double sealing technique is used. The new GA MP cell consists of a SS outer case with a thin-wall SS thermometer well and a Teflon crucible containing the high-purity gallium with a nylon lid and

well (Fig. 1). The immersion depth from the bottom of the reentrant well to the upper surface of the sample is 168 mm. The purity of the gallium used to fill the cell is higher than 99.99999 % (by weight). A typical impurity analysis provided by Johnson Matthey is shown in Table 1. The total impurities of the gallium sample are 13 ppb by weight. Before the cells were assembled, all of the parts used were thoroughly cleaned. Teflon crucibles were soaked overnight in aqua regia, thoroughly rinse with de-ionized water (DI water), and then with high-purity water (resistivity > 17.8 MΩ·cm). Subsequently, the Teflon crucibles were flushed with pure water steam for about 100 hours and then dried in vacuum. Nylon parts were washed in a detergent solution, rinsed thoroughly with high-purity water and then with double-distilled water, and vacuum dried. The gallium samples were melted into the Teflon crucible in a glove box containing a dry, pure argon atmosphere. Then the nylon lid with the reentrant well was joined into the Teflon crucible by using a special epoxy. The surface of Teflon does not normally permit bonding, so a special treatment was used to change the molecular structure of the Teflon surface before the bonding. There is a port on the nylon lid so the Teflon crucible assembly can be connected to a high-vacuum system and pumped down to a pressure as low as 10^{-5} Pa to ensure a good vacuum sealing between the Teflon crucible and the nylon lid. The crucible assembly was pumped for at least 100 hours. During this period, the crucible assembly was repeatedly purged with 99.999 % pure argon, and the gallium sample was completely melted and then completely frozen. Finally, during a melting plateau, the crucible assembly was filled with pure argon and sealed permanently at a pressure close to 101.325 kPa. The actual pressure was recorded so that a correction could be made for the phase equilibrium temperature to adjust for the pressure difference from the standard atmosphere.

The permanently sealed crucible assembly was inserted into the SS outer case, and the SS cap with the reentrant well was arc-welded to the SS outer case. A special cooling jacket was used during welding to avoid damage to the crucible assembly from overheating. The welded SS case was connected to the same high-vacuum system and pumped according to a similar procedure for the crucible assembly. The SS outer case was sealed at almost the same argon pressure during a melting plateau. The gallium was first sealed into the Teflon crucible assembly as a precaution to avoid any contamination of the gallium from the SS outer case. Since Teflon and nylon can be permeable to gases and moisture [2-6], the sealed SS outer case protects the crucible assembly by maintaining a pure argon atmosphere at the same pressure as that inside the crucible assembly.

TABLE 1. **Impurities present in the gallium sample (Lot# F20K24).**

Impurity	**Concentration** (ppb, wt)
Al	4.0
Cr	1.0
Cu	5.0
Fe	1.0
Si	2.0

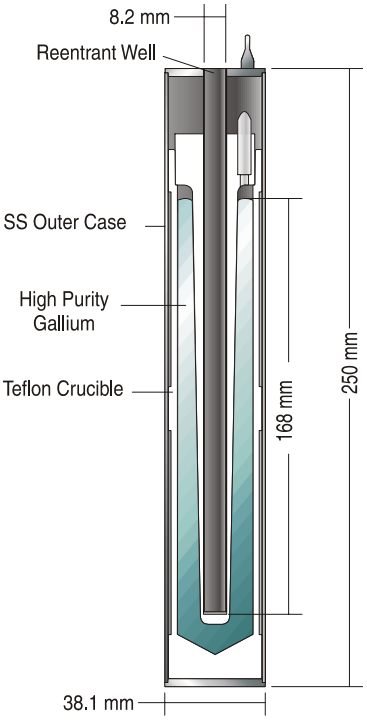

FIGURE 1. Schematic diagram of the new GA MP cell.

An open-cell version contains an open port on the top of the Teflon crucible assembly. A vacuum valve and a SS tube are attached to the top of the SS case (Fig. 2). The cell can then be pumped and filled with pure argon at any time. It can be used not only for the GA MP, but also for the triple point of gallium.

FIGURE 2. An open version gallium cell.

AUTOMATIC GALLIUM MAINTENANCE APPARATUS

Current dry-well maintenance apparatus for gallium cells are capable of achieving melt plateaus lasting about 24 hours. While these devices are much less expensive and easier to use than controlled liquid baths, they fall short of the melting plateau length achieved by a bath. In order for a dry-well apparatus to approach the performance of a bath, its temperature accuracy and stability must meet strict requirements. The initial design requirements set for the apparatus are listed in Table 2. During freezing a large temperature gradient is required, so that the gallium starts freezing from the bottom upward.

TABLE 2. The initial design requirements set for the apparatus.

Set point accuracy	± 0.05 °C
Temperature stability in the block	± 0.02 °C per day
Temperature gradient during a melting plateau	< 0.03 °C/150 mm
Temperature gradient during freezing	> 10 °C/150 mm

Initially, different designs were tried. The first designs used a blanket resistance heater wrapped around a tube that held the cell. Insulation was then placed around the heater and tube, and the heater was then controlled by regulating a DC current through it. Several problems became apparent from this design. Irregularities in the blanket heater caused irregularities in the temperature distribution along the cell. A blanket heater surrounded by insulation cannot dissipate any excess heat, especially being so close to ambient temperature. If the temperature controller overshoots slightly as it approaches the desired temperature, the additional heat is trapped and then transferred into the cell. The controller then stops all current flow to the heaters until the whole assembly cools down enough to start controlling again. This can lead to stability errors. This design also needed a way to refreeze the cell from the bottom. Peltier modules were mounted to the bottom of the block to achieve the large 10°C temperature difference required over the length of the block and cell.

The need for both cooling and heating directed us to incorporate only Peltier devices instead of a resistive heater. A rectangular aluminum block was used to hold the cell and allowed the Peltier modules to be placed on the outer flat sides. The Peltier devices remove or add heat from the block into the heat sinks. The additional Peltier modules and heat sink on the bottom of the block were now not needed, thus reducing the complexity. The new construction of the apparatus is shown in Fig 3.

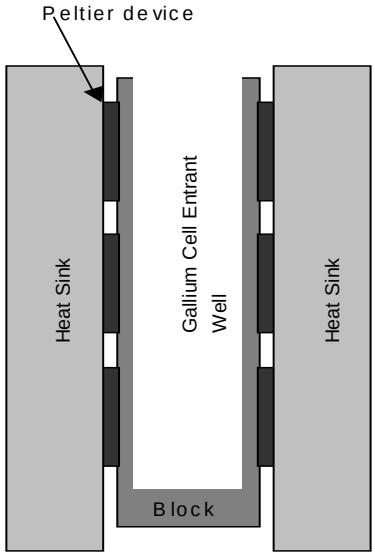

FIGURE 3. Cutaway view of the maintenance apparatus

The aluminum block can quickly transfer heat either in or out, as necessary. It also equalizes the temperature from the Peltier modules uniformly over the entire block, which helps reduce temperature gradients. One drawback of using the aluminum block and a SS cell is the possibility of galvanic corrosion. To reduce this problem, the aluminum block was

nickel-plated. Aluminum heat sinks are attached to each outer side of the Peltier modules for transfer of heat in or out. A fan moves air from the bottom of the unit and then out of the top to direct heat in and out of the heat sinks. Each level of Peltier modules can be controlled independently to provide the 10 °C temperature difference needed for refreezing the cell. The Peltier devices are controlled in sets at the different levels along the sides of the block (bottom, middle, and top). A PRT sensor is located in the block to provide feedback to the controller.

Foam insulation is placed around the block and Peltier devices, and up to the inside surface of the heat sink. This provides isolation from ambient changes that could affect stability and accuracy. Additional isolation was obtained by having the cell sit deep in the well and using foam insulators on top of the cell. The insulators have a center hole to allow probes to enter the well of the cell.

Temperature accuracy is obtained by calibrating the RTD and controller together as a unit. For calibrations of the apparatus, a dummy aluminum cylinder is used to simulate the cell. The reference probe is then inserted into the dummy cell. Calibrations are performed close to the gallium melting point temperature. This allows the apparatus to maintain the cell at 29.86 °C—or near the actual melt temperature during the melt plateau.

Automation of the gallium melt-freeze cycle was obtained by programming the microprocessor to simulate the manual operation in many national laboratories.

When freezing the gallium cell, certain precautions needed to be observed. The freeze gradient must be monitored to ensure the cell is being frozen from the bottom up. At least two sensors would be needed, one at both ends of the block. This approach would add additional circuitry and a sensor. As an alternative, we used the controller to monitor the power being used in the Peltier modules and compare the readings against measured power levels in a normal freeze. If the power levels are out of bounds, an alarm is sounded to allow the user to remove the cell and freeze it manually.

Power outages during a freeze could cause the apparatus to start up in a mode where the cell would be frozen with no gradient. To solve this, non-volatile memory was used to remember what state the unit was in when the power went out.

Our goal was to make the automatic mode as simple as possible. All the necessary temperature set-points and times are preset to standard values. In the manual mode, menus are available within the controller to change times and set-point temperatures for each of the stages of the melt-freeze cycle. This allows the user some freedom to experiment and adapt the cycle to specific needs.

TEST AND RESULTS

The new gallium cell and maintenance apparatus were first tested separately and then as a complete system.

A new SS cell (#43002) was compared against our reference gallium cell (#7010) in a bath. The bath temperature was set at 0.05 °C above the melting point. The melting curves of the two cells started at almost the same time. An 8 W heater in the reentrant well of each cell was turned on for four minutes at the beginning of the melting curve. The reference cell is an old, permanently sealed Pyrex-Teflon cell, which was originally certified by NIST (the difference between it and the NIST reference cell [Ga 98-1] was within 0.06 mK [7]). A standard platinum resistance thermometer (SPRT, #61064) and an ASL F18 bridge were used in the comparison. The resistance measurements were made at 1 mA, at 1.414 mA, and then again at 1 mA each time. This allowed the measurement results to be extrapolated to the values corresponding to zero power. Three sets of data were taken. The comparison results are shown in Fig. 4. The measured mean difference between the two cells was within 0.01 mK with a standard deviation of 0.03 mK.

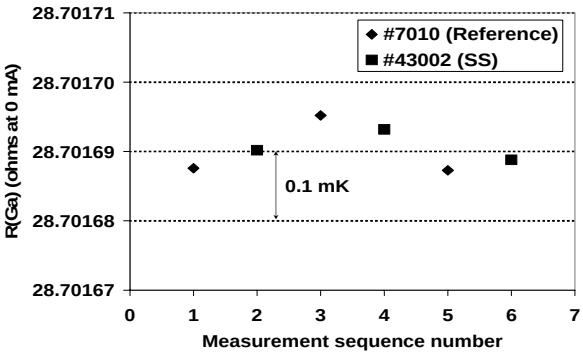

FIGURE 4. A direct comparison of a new SS cell #43002 with Hart reference gallium cell #7010.

The vertical temperature gradient in the maintenance apparatus was tested, and the results are

shown in Fig. 5. The maximum temperature differences within 150 mm were well within 0.03°C.

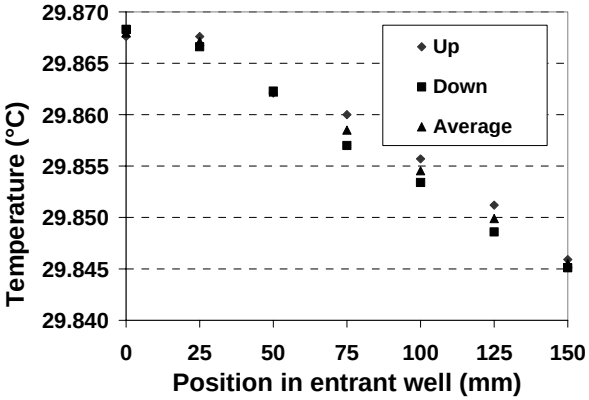

FIGURE 5. Vertical gradients inside the maintenance apparatus.

A typical melting curve obtained using cell #43002 in the automatic maintenance apparatus is shown in Fig. 6. The melting curve lasted for more than seven days. The changes in temperature during 90 % of the melting plateau were within about 0.1 mK. An immersion check was made during a melting plateau (Fig. 7). The measured values tracked the hydrostatic pressure effect very well in a range of 20 mm from the full immersion.

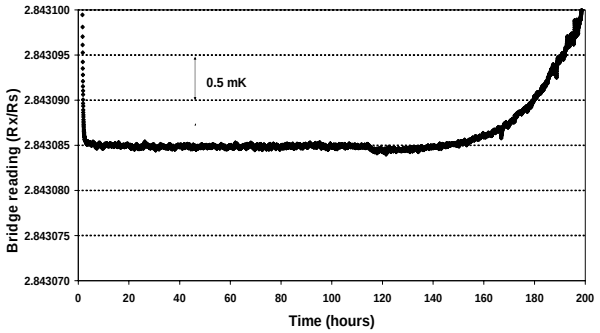

FIGURE 6. A typical melting curve using the new automatic maintenance apparatus

Four new SS cells maintained by the new automatic maintenance apparatus were compared with a Pyrex-Teflon cell (#03030), which was placed in a bath at a temperature of 0.05 °C above the melting point. SPRT #1018 and the F18 Bridge were used for the comparison. All five of the cells started their melting curves at almost the same time. An 8 W heater in the reentrant well of each cell was turned on for four minutes at the beginning of the melting curve. The comparison started at about the 40th hour (the third morning) from the beginning of the melting curves. The measurements started in cell #03030 and were

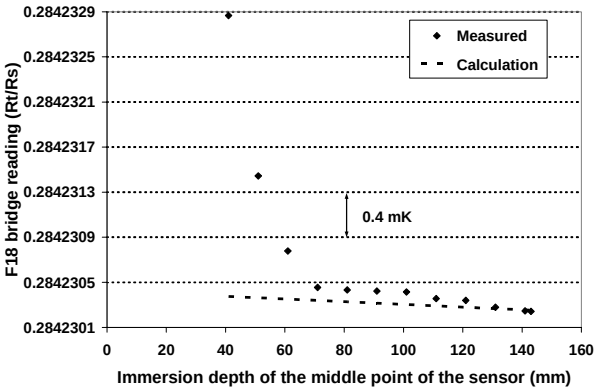

FIGURE 7. An immersion profile in the reentrant well during a melting curve.

then taken in each of the four SS cells successively. The resistance at the GA MP [R(Ga)] corresponding to zero power was calculated from the data for each cell. The measurements were repeated in the opposite sequence, i.e. from the last cell in the first run to cell #03030. The mean values of the two runs for each cell are listed in Table 3. The differences between the four cells and cell #03030 were within 0.03 mK, and the maximum difference among the five cells was within 0.05 mK. The difference between cell #03030 and the reference cell #7010 was found to be well within 0.1 mK in a previous measurement.

Cell #43002 was sealed in June 2000. The cell was used in a series of comparisons with many other cells subsequently sealed in the past one and one-half years. All of the differences between cell #43002 and the other cells were within 0.1 mK.

TABLE 3. A comparison among five gallium cells

S/N of the cell	R(Ga) (Ω)	Δt (mK)
#03030	28.5363613	0.00
#43010 (SS)	28.5363596	–0.017
#43011 (SS)	28.5363639	+0.026
#43012 (SS)	25.5363591	–0.022
#43013 (SS)	25.5363596	–0.017

RESULTS AND DISCUSSION

The uncertainty components for the GA MP realized by using the new permanently sealed SS gallium cell with its automatic maintenance apparatus are listed in Table 4. The uncertainty associated with the calibration of the cell from the national standard is not included here. The estimated expanded uncertainty (k=2) is 0.11 mK for the cell itself, and 0.20 mK for the whole system. The new apparatus is much easier to use compared to the classic apparatus. The new apparatus and the cell provide common users an easy way to realize the GA MP with an uncertainty level that was generally only obtained in national labs in the past. The stability of the new SS cell has been observed to be within 0.1 mK during a period of eighteen months. The longer-term stability may need further investigation, especially for the open version cell.

TABLE 4. Uncertainty budget.

Source of uncertainty	Uncertainty (mK)	Component
	Cell only	System
Resistance reading (A)	0.022	0.022
Repeatability of thermal state (A)	0.035	0.075
Total A	0.041	0.078
Impurities (B)	0.014	0.014
Hydrostatic correction (B)	0.012	0.012
Pressure correction (B)	0.010	0.010
Immersion (B)	0.010	0.050
SPRT self-heating (B)	0.020	0.020
Propagated TPW (B)	0.010	0.010
Bridge non-linearity (B)	0.011	0.011
Total B	0.034	0.060
Total standard uncertainty	0.053	0.098
Expanded uncertainty (k=2)	0.11	0.20

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