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New Approach in Filling of Fixed-Point Cells: Case Study of the Melting Point of Gallium

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Abstract The typical way of constructing fixed-point cells is very well described in the literature. The crucible is loaded with shot, or any other shape of pure metal, inside an argon-filled glove box. Then, the crucible is carefully slid into a fused-silica tube that is closed at the top with an appropriate cap. After that, the cell is removed from the argon glove box and melted inside a furnace while under vacuum or filled with an inert gas like argon. Since the metal comes as shot, or in some other shape such as rods of various sizes, and takes more volume than the melted material, it is necessary to repeat the procedure until a sufficient amount of material is introduced into the crucible. With such a procedure, there is the possibility of introducing additional impurities into the pure metal with each cycle of melting the material and putting it back into the glove box to fill the cell. Our new approach includes the use of a special, so-called dry-box system, which is well known in chemistry. The atmosphere inside the dry box contains less than 20 ppm of water and less than 3 ppm of oxygen. Also, the size of the dry box allows it to contain a furnace for melting materials, not only for gallium but for higher-temperature materials as well. With such an approach, the cell and all its parts (pure metal, graphite, fused-silica tube, and cap) are constantly inside the controlled atmosphere, even while melting the material and filling the crucible. With such a method, the possibility of contaminating the cell during the filling process is minimized.

Keywords Dry box · Fixed-point filling · Gallium melting point

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1 Introduction

The International Temperature Scale of 1990 (ITS-90) was designed by the Consultative Committee for Thermometry so that temperature values obtained with it would deviate from thermodynamic temperature by less than the uncertainties of the latter at the time the ITS-90 was adopted. ITS-90 replaced the International Practical Temperature Scale of 1968 (IPTS-68), the Amended Edition of 1975 (IPTS-68 (75)), and the 1976 Provisional 0.5–30 K Temperature Scale (EPT-76) [1].

Temperatures on the ITS-90 are defined in terms of phase-transition temperatures of pure substances (defining fixed points), interpolating instruments, and equations that relate the measured properties of the instruments to the ITS-90. These states are explained in detail in the ITS-90 definition and supplementary information [1,2].

Since the purity of the metals used for fixed-point cells is generally at least 99.9999%, ensuring a low concentration of impurities is crucial in realizing the proper temperature of the fixed point [3]. Prior to assembling fixed-point cells, metal samples are analyzed and the content of impurities is determined. However, additional impurities can be introduced when assembling fixed-point cells and in the process of using them. This can change the temperature of the fixed point. Four different methods of analysis (mole fraction sum of impurity components, freezing curve, direct comparison, and 1/F realization curve) can be used to both estimate and crosscheck the value used for the impurity uncertainty component [3,4]. In order to decrease the possibility of introducing additional impurities, a new method of filling fixed points is suggested. This method includes the use of a dry box, whose size allows all the parts of the fixed-point cell to be kept inside the dry box during the whole process of assembling the cell. With such a method, the potential contamination that may occur during the filling process is minimized.

2 Description Of Dry Box

The purpose of the dry-box system, together with a glove box, is to maintain a pure inert gas (argon) atmosphere inside a hermetically sealed enclosure. Materials that are sensitive to moisture and/or oxygen are handled by using the attached gloves or additional specially designed handling systems. The material transfer takes place by means of special antechambers without influencing the glove box atmosphere. A schematic of our dry-box system is presented in Fig. 1 [5]. The inside of the dry-box system has the following dimensions: height of 900 mm, depth of 1,200 mm, and length of 1,800 mm. This enables us to put inside all the necessary components for the construction of a fixed-point cell, including a special furnace, if needed.

The dry-box system consists of the glove box, antechamber, vacuum pump, and gas purification system. The programmable logic controller (PLC) controls an automatic regenerable H_2O/O_2 purifier, monitors the water and oxygen concentrations with appropriate sensors, monitors and regulates the over-pressure inside the glove box, monitors temperature inside the box, and controls the vacuum pump and optional water cooling of the dry box. The glove box is a vacuum-tight stainless steel working space with a number of gloves. The antechamber is used to transfer the fixed-point cell

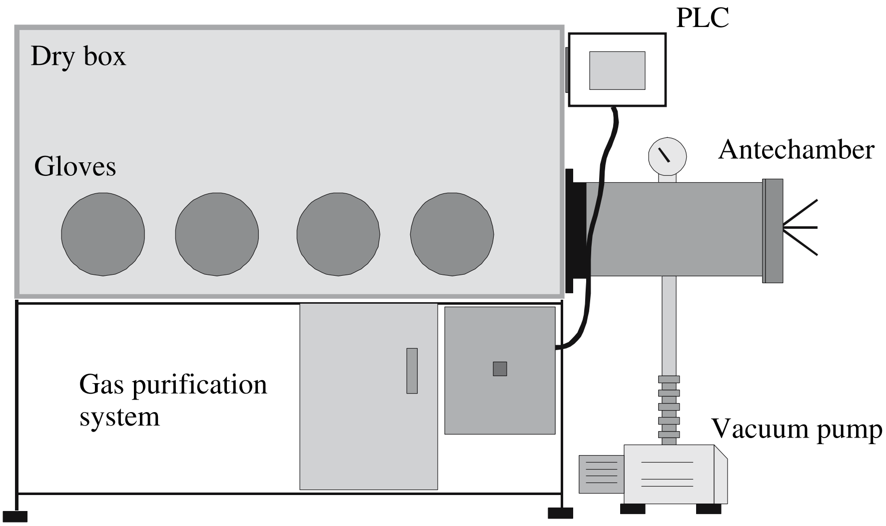

Fig. 1 Dry box used for assembling the gallium melting-point cell

components to the inside of the glove box. The vacuum pump is an essential device for the operation of the system. It is used to evacuate the system, evacuate the antechamber, reduce the box pressure, and for the final cleaning of the purifiers at the end of the regeneration cycle. The gas purification system is operated in accordance with the principles of circulation. The gas continuously circulates between the glove box and the gas purification system. The gas is purified to a level of <1 ppm with respect to moisture and oxygen, depending on the purifiers used. The PLC unit controls and monitors the circulation process. The inlets and outlets of the circulation tubes are protected by aerosol exhaust filters. The filters supply a particle-free atmosphere and separate the box from the purifier(s) and tubes. The purifier unit consists of an oxygen part (chemical binding to polydisperse copper) and a moisture part (adsorption in a microporous molecular sieve). The dry-box system is also capable of regulating pressure within 2 kPa of atmospheric pressure. The size of the dry box enables us to completely assemble a fixed-point cell inside the controlled atmosphere, including the melting of materials up to 700°C in a special furnace.

3 Gallium Melting-Point Cell

In order to test this new approach, we have decided to make a batch of gallium melting-point cells as a case study. So-called virgin polytetrafluoroethylene (PTFE) was used as the basis for the enclosure and thermometer well. In order to decrease the possibility of any leakage of the cell, the container was constructed of only two parts, as shown in Fig. 2. We have used aluminum tubes inside and outside; with this design, the radial heat transfer from the surrounding furnace has increased compared to designs using other materials, such as glass. The dimensions are 30 cm length, 3.5 cm width, and 20 cm immersion depth.

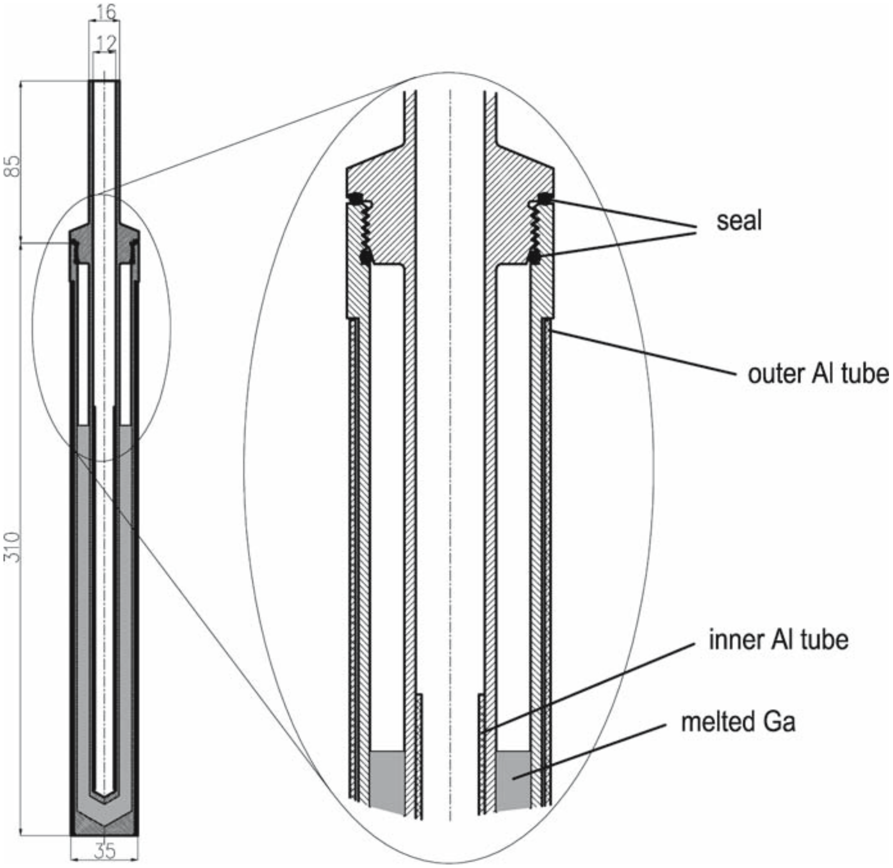

Fig. 2 Melting-point-of-gallium cell (all dimensions are in mm)

The gallium used for the filling exceeded 7N purity. It was provided with a chemical analysis carried out using inductively coupled plasma mass spectrometry (ICPMS). The main impurities detected were silver ($<0.005\,\mu g\cdot g^{-1}$), aluminum ($0.005\,\mu g\cdot g^{-1}$), copper ($<0.002\,\mu g\cdot g^{-1}$), iron ($0.005\,\mu g\cdot g^{-1}$), magnesium ($0.005\,\mu g\cdot g^{-1}$), lead ($0.004\,\mu g\cdot g^{-1}$), tin ($<0.005\,\mu g\cdot g^{-1}$), zinc ($0.006\,\mu g\cdot g^{-1}$), manganese ($0.003\,\mu g\cdot g^{-1}$), and silicon ($<0.05\,\mu g\cdot g^{-1}$). The gallium rods were purchased from a Chinese manufacturer, Guangzhou Youyuan Metals & Chemicals Co., Ltd. The repeated analysis by ICPMS showed no significant difference from the initial analysis of the material. Also, no isotopes, other than gallium isotopes, were found in the sample. Further analysis is planned using glow discharge mass spectrometry in order to perform detailed analysis of the material as well as to crosscheck the methods [6].

The effect of impurities on the melting temperature of gallium can be found in the literature [7,8]. Also, problems with the sealing of the cell, the purity of the inert gas, and impurities remaining on the PTFE enclosure have been reported by others [9–11].

Prior to filling the PTFE enclosure, it was cleaned in three stages. The first stage included dry cleaning with oil-free compressed air and cleaning with a mild detergent, to remove any residue from the machining process. The next step included cleaning with alcohol and rinsing with distilled water. The last step was ultrasonic cleaning with distilled water. After a thorough cleaning, all the parts were put inside the dry box through the antechamber. The metal was melted inside the controlled atmosphere of the dry box by placing the plastic bottle from the supplier that contained the gallium on top of a small heater, and then it was poured into the PTFE enclosure. In the next stage, the part with the thermometer well was fixed in place and the cell was sealed with two O-rings (Fig. 2). In such a way, a new melting-point-of-gallium cell was built.

4 Gallium Melting-Point Cell Realization and Measurements

Our reference cell is an 8-year-old commercial cell containing 7N-purity material that was provided with a chemical analysis. It has been thoroughly characterized through a number of realizations and intercomparisons [12,13]. The value of our reference gallium cell from the EUROMET.T-K3 [12] comparison is 0.16 mK above the weighted mean of the comparison. This value was confirmed in a bilateral comparison with PTB [13].

MIRS/FE-LMK has two means to realize the melting point of gallium. The first is a commercial furnace, made for our current reference cell, and the second is a specially adapted water bath, within which we can realize up to four melting-point cells of gallium simultaneously. This enables us to see if there are any additional influences on the melting point of gallium as well as to directly compare our reference cell to our newly constructed batch of cells.

Our standard procedure was followed to realize the melting point of gallium. The gallium cell was slowly heated to 29.5°C and left at that temperature for at least one hour. After that, the temperature of the bath was increased to 30.8°C for 15 min. After 5 min at 30.8°C, a special electric heater to initiate the inner melt was introduced into the thermometer well for 10 min [10]. After that, the bath temperature was set to 29.9°C, and within 30 min, the cell was at the melting-point temperature.

For the measurements, an ASL F900 AC automatic resistance bridge connected to a reference resistor in an oil bath stable to within 3 mK over one month was used. The standard platinum thermometer used for the measurements was a quartz-sheathed Hart Scientific Type 5681. After five realizations of the melting point carried out in accordance with the above described procedure, the measured difference between the commercial reference cell and the new cells was $-40\,\mu\text{K}$ (the new cells had a higher temperature), with a standard uncertainty of the comparison of $25\,\mu\text{K}$. The standard uncertainty of the comparison consists of repeatability, reproducibility, the hydrostatic head of the transfer and reference cells, uncertainty due to the self-heating effect, and uncertainty due to the perturbing heat exchange. The detailed uncertainty budget is presented in Table 1. The measurements of the hydrostatic-head effect in the new cell are compared to the theoretical prediction in Fig. 3. Typical melting curves of gallium for the old and a new cell are presented in Fig. 4. The differences among the three newly made melting-point-of-gallium cells is $25\,\mu\text{K}$, which is consistent with the literature [10].

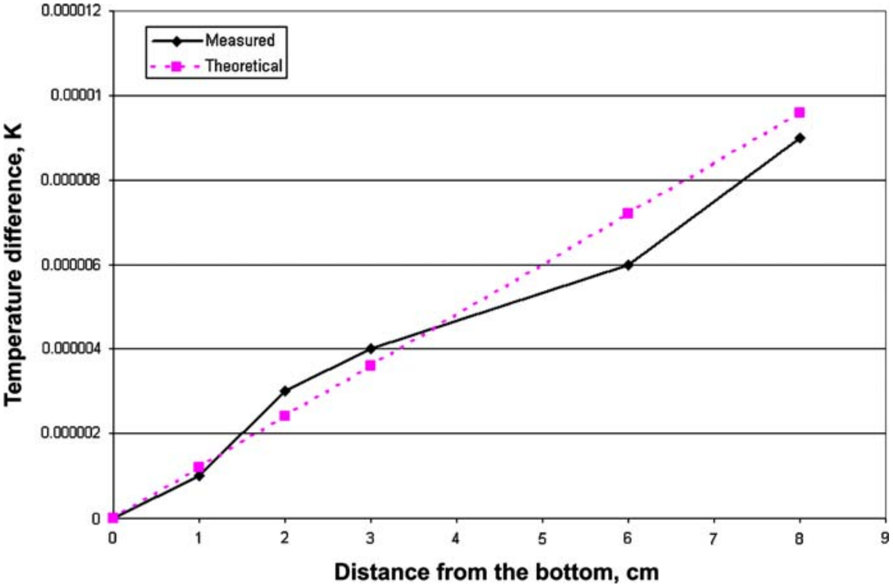

Fig. 3 Hydrostatic-head measurements in the new cell

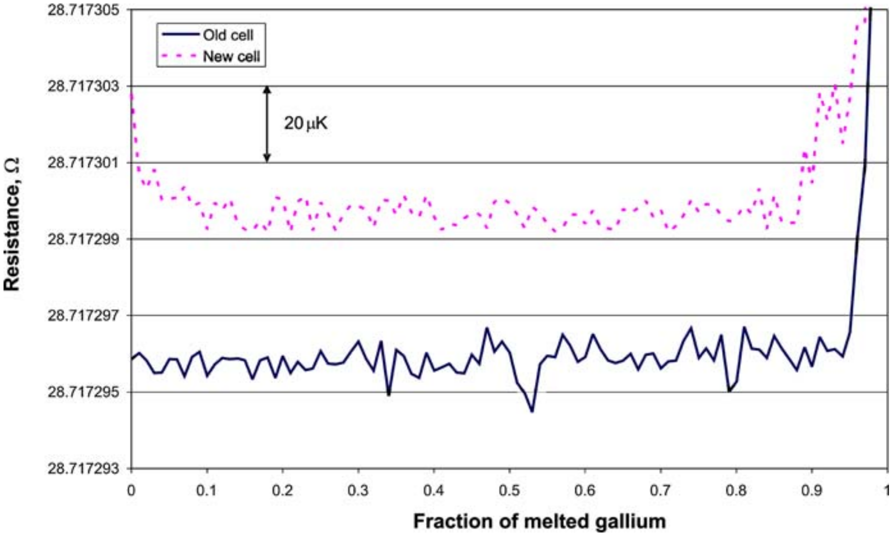

Fig. 4 Typical melting curves for the old and a new cell

5 Conclusions

A batch of three gallium melting-point cells was constructed using a new approach to fill the cells. In order not to contaminate the cells, a dry box was used for the complete process of melting the materials and filling the cell. Comparison with our laboratory

Table 1 Uncertainty budget for the comparison of the reference cell with the new cell

Uncertainty source	Contribution in μK ($k = 1$)
Repeatability	8
Reproducibility	10
Hydrostatic head of reference cell	7
Hydrostatic head of new cell	7
Uncertainty due to the self-heating effect	12
Perturbing heat exchanges	14
Total standard uncertainty	25

reference cell has shown that the newly constructed cell has a melting point 40 μK above the reference cell.

After these promising results, further investigations will include the construction of a batch of zinc fixed-point cells and other fixed-point cells as well.

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