System for Realizing the Triple Point of Mercury to Calibrate Industrial-Type Platinum Resistance Thermometers

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Abstract Most platinum resistance thermometers (PRTs) sent to CENAM for calibration are of the industrial type (IPRT). The cells used to calibrate both standard PRTs (SPRTs) and IPRTs form part of the national standard of temperature. In order to reduce their use, we built a set of fixed-point cells, furnaces, and baths to calibrate IPRTs using fixed points, including an apparatus and cells to reproduce the Hg triple point. To realize the triple point of mercury (TP-Hg), an apparatus that operates from room temperature to −45 °C using a CENAM-constructed heat pipe was designed and built. With the heat pipe, it is unnecessary to use a recirculation bath to provide a temperature-controlled environment, the temperature gradient is reduced, and the system is more efficient because its thermal mass is reduced. In this way, it is possible to reproduce the TP-Hg for long periods of time to facilitate IPRT calibration, using cells of smaller size than is conventional and without using expensive liquid baths. The system was tested with cells having 400 g and 800 g of mercury, and a reproducibility of about 0.1 mK was obtained.

1 Introduction

At CENAM, calibrations of platinum resistance thermometers (PRTs) are currently carried out with cells that are part of the national temperature standard of México. The electrical resistance of the industrial-type PRT (IPRT) as a function of temperature is well described by the same ITS-90 equations used for standard PRTs (i.e., SPRTs)

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[1], but most IPRTs do not have the reproducibility of an SPRT. Often, IPRTs have dimensions that make its calibration difficult (they are too short), and the thermal contact between the IPRT and the fixed-point cells is poor. To improve that situation, we established a system of fixed points (cells, furnaces, and associated apparatus) with accuracy similar to the national standard, but with dimensions smaller than CENAM's SPRT reference cells. In this work, we describe the design of the apparatus, the experiments, and the results that were obtained for the triple-point-of-mercury reproduction.

2 Realization of the Triple Point of Mercury

If an IPRT is calibrated using fixed points, due care should be paid to the experimental realization because some problems may arise. For example, in the case of mercury, we found that heat leaks and gradients may lead to errors of the order of 0.01 °C, which is too large compared with CENAM's typical uncertainty for SPRTs of 0.5 mK (k=2) [2].

There are several methods to prepare the triple point of mercury (TP-Hg), all of them having as their goal the generation of a solid phase in contact with a liquid phase at the corresponding vapor pressure. This is commonly achieved by using controlled-temperature liquid baths with a working range down to at least −45 °C [3]. In this case, the sample is submerged in the liquid bath to keep the whole sample frozen; afterwards, the temperature is controlled close to the TP-Hg temperature value and a liquid phase is induced by inserting a "warm" rod into the thermometer well of the fixed-point cell. Even though this method is simple, it is well known that temperature gradients and heat leaks are the main problems that must be overcome.

On the other hand, simple experiments have been reported [4,5] for open cells and very simple experimental conditions (using slim cells) where the sample is frozen when placed in a mixture of "dry ice" (CO_2) and alcohol, and afterwards the cell is placed in a Styrofoam pouch to let the melt proceed naturally. More stringent experimental conditions are required to use adiabatic calorimetric techniques to reproduce the TP-Hg [5]. By comparing these two methods, we found that the reproducibility of the first one is as good as the second, but the former may be repeated several times in one hour while the adiabatic technique takes at least half a day.

We developed a system to realize the TP-Hg using a technique similar to that used for other metal fixed points using the heat-pipe technique.

3 Apparatus

An apparatus to prepare and maintain the triple-point condition was designed and built. It has a closed-cycle cooling system (Fig. 1), a heat pipe, and a temperature controller. The closed-cycle cooling system has a 1/4 HP compressor loaded with 70 g of the refrigerant dichlorodifluoromethane (R12) and can reach a temperature of −45 °C.

3.1 Heat Pipe

A low-temperature heat pipe made of copper was designed and built at CENAM. The dimensions of the heat pipe are 40 mm OD, 26 mm ID, and the depth of the well is
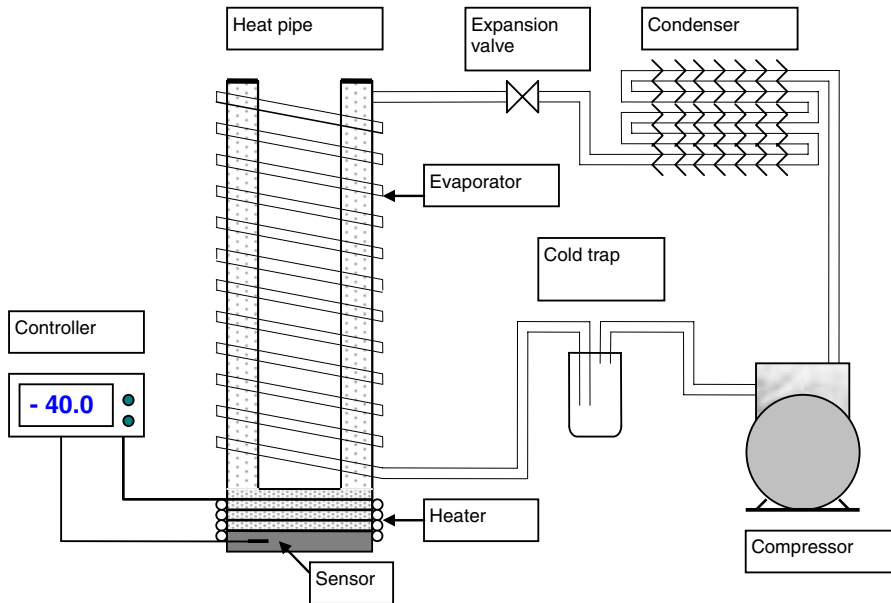
Fig. 1 Diagram of the heat-pipe-based apparatus to realize the Hg triple point

26 cm. The working fluid is R502 (chlorodifluoromethane and chloropentafluoroe-thane mixture). This fluid was selected because its boiling point is −45 °C, and its vapor pressure at −39 °C is 480 hPa, which is suitable for efficient operation as a heat-pipe working fluid. It has a vapor pressure of 1.1 MPa at room temperature, which is a reasonable pressure to handle safely under regular laboratory conditions. By trial and error, we found that the heat pipe should be loaded with 30 g of R502 to a liquid level of about 10 mm at −40 °C in order to obtain a uniform temperature profile.

3.2 Temperature Control

The temperature control of the heat pipe is accomplished with the chiller (evaporator) of the cooling system as the cooling source while an electrical heater of 30 W, wound on the heat-pipe base (1 cm), provides controlled heating. The electrical heating is determined by a proportional-integral-derivative (PID) controller with a resolution of 0.1 °C. This controller uses an IPRT (Pt100) placed at the heat-pipe base (Fig. 1) as the sensing element. With these elements, a stability of ±0.03 °C was obtained.

4 Cells

At CENAM, Hg cells to calibrate SPRTs at the TP-Hg are of the design shown in Fig. 2a, and contain approximately 2.4 kg of mercury. These cells require a medium with a good thermal profile to maintain phase equilibrium. This requirement is more demanding when the dimensions of the cells are reduced. For example, the TP-Hg
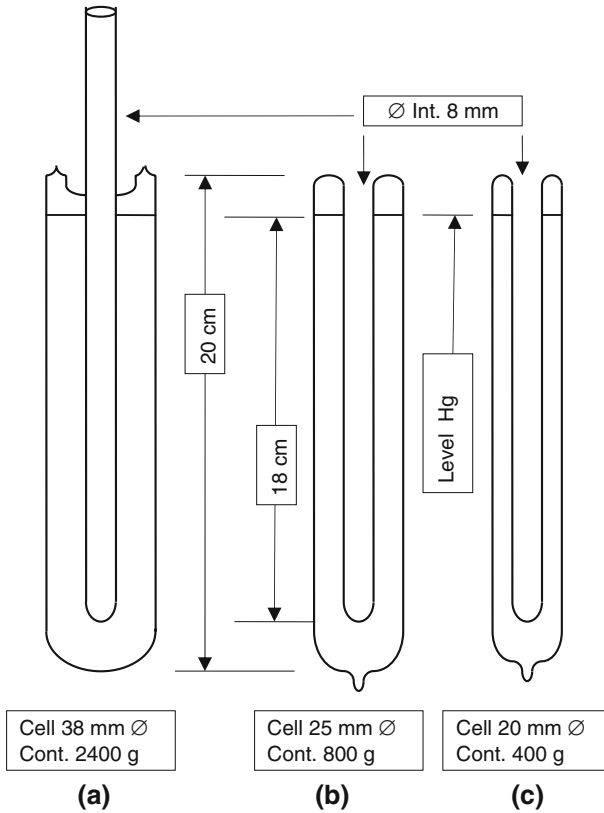
Fig. 2 Mercury cells constructed at CENAM from borosilicate glass: (**a**) shows dimensions of a regular cell used for SPRTs at CENAM and (**b**) and (**c**) show dimensions of cells built and reported in this work for IPRT calibration

may be realized under adiabatic conditions [5–7] with small quantities of mercury, but that method has other practical problems.

For the calibration of IPRTs, three cells were manufactured from borosilicate glass. They are all 20 cm long, and one is 25 mm in diameter (Hg07-3; Fig. 2b); the other two cells are 20 mm in diameter (Hg07-1 and Hg07-2; Fig. 2c). All of them have a thermometer of well length that allows 18 cm of immersion measured from the bottom of the well to the liquid level. The cells were washed with acetone, then with nitric acid, and rinsed with distilled water. Afterwards, the cells were heated with an air gun while being vacuum pumped to dry them.

The filling of the cells was realized under vacuum [8]. A flexible Teflon hose was used to connect the cell to a mercury container (Fig. 3). A cold trap was placed between the cell and the vacuum pump. Once a vacuum was established, the mercury container was slowly tilted to fill the cell to the desired level. Then, the cell was sealed while it was kept under vacuum. The approximate mass of mercury in the cells of 25 mm and 20 mm diameter is 800 g and 400 g, respectively.
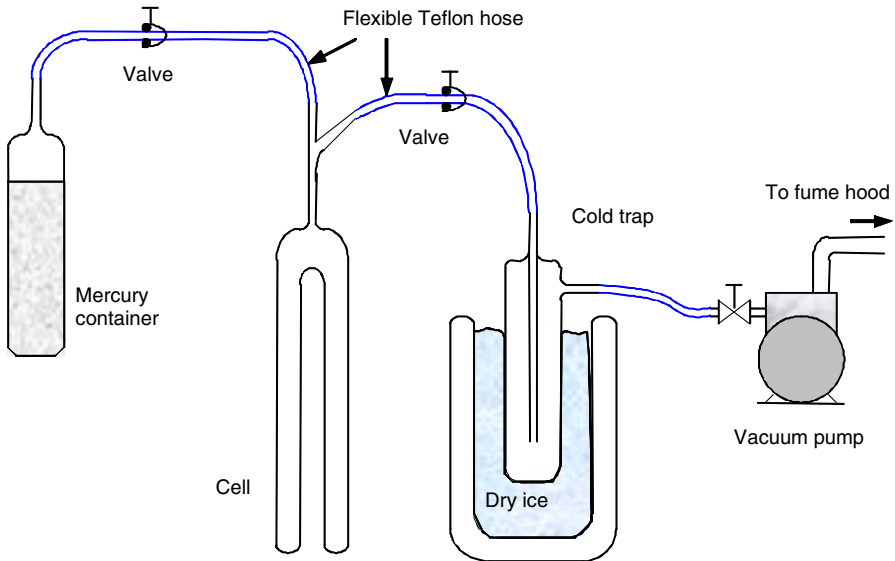
Fig. 3 System used to fill mercury cells

The mercury used to fill cell Hg07-1 is commercial triple-distilled, and that to fill cells Hg07-2 and Hg07-3 has a specified purity of 99.9999 %. No further purity test was done.
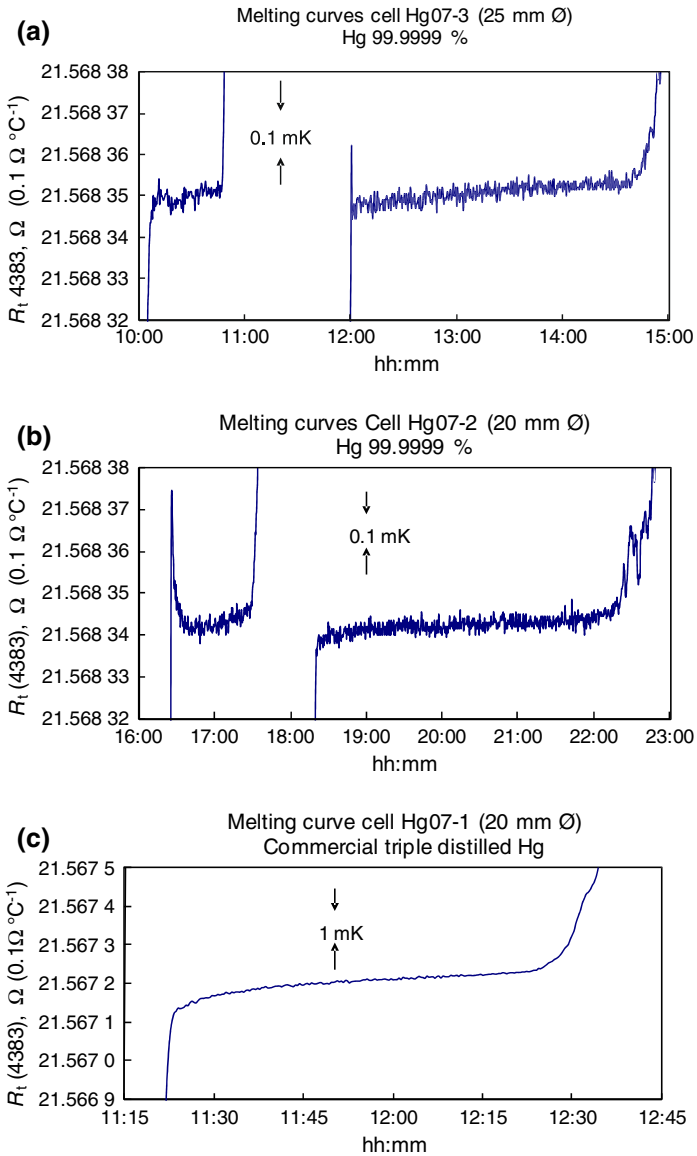
5 Experimental

5.1 Reproduction of the Triple Point of Mercury for IPRT Calibration

To realize the TP-Hg, the cell is placed in the cavity of the heat pipe, with a copper cell holder that has an auxiliary electric heater of 50 W wound uniformly on its wall. After installing the cell, the heat pipe is filled with alcohol to a level about 1 or 2 cm below its top edge; in this way, the cell is completely submerged in alcohol. The cell is then cooled to freeze it completely by allowing the cooling system to work to its maximum capacity and without temperature control. During the cooling process, a SPRT is placed in the cell to observe the solidification process.

Once the sample is completely frozen, the temperature set point is set about 0.2 °C above the Hg melting point. Once that temperature is reached, the auxiliary heater wound on the cell holder is turned on for 30 s. Finally, a room-temperature copper rod (6.3 mm diameter) is inserted into the thermometer well for 30 s to induce a film of liquid mercury around the thermometer well.

5.2 Heating-Rate Test

To test the influence of the heating rate on the value of the triple point, several melting curves were obtained with cells Hg07-2 and Hg07-3 (Fig. 4a, b) by fixing the

(a)

Melting curves cell Hg07-3 (25 mm Ø)
Hg 99.9999 %

(b)

Melting curves Cell Hg07-2 (20 mm Ø)
Hg 99.9999 %

(c)

Melting curve cell Hg07-1 (20 mm Ø)
Commercial triple distilled Hg

Fig. 4 Melting curves of mercury cells for different melting times

temperature control value above the TP-Hg value. The melting ranges are practically the same (of the order of 0.05 mK) for the different melting times (ranging from 20 min to 4 h) for both sizes of cells (25 mm and 20 mm diameter). This is an indication that the heating rate does not influence the TP-Hg temperature value.

The melting curve of cell Hg07-1, filled with triple-distilled mercury (Fig. 4c), deviates about 11 mK with respect to cells Hg07-2 and Hg07-3, and it has a melting
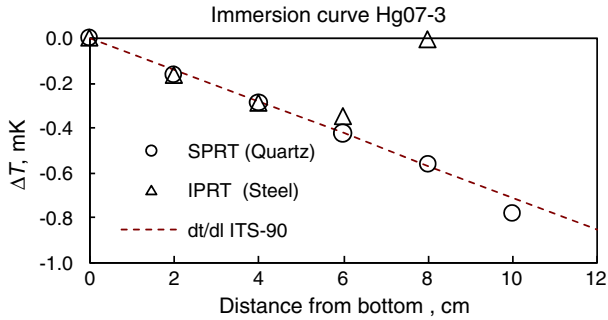
Fig. 5 Thermal immersion profile for insertion into the thermometer well of cell Hg07-3. The type A uncertainty ($k = 2$) is approximately indicated in the figure by the size of the symbols

range of 0.5 mK, i.e., about 10 times larger than the value observed with cells having 6N-purity Hg. The observed shift (of the temperature value) and the melting range are more likely due to the presence of impurities. If the temperature value is corrected and the observed melting range is considered in the uncertainty budget, this cell may be used with an uncertainty of the order of 1 mK, which is adequate for the calibration of IPRTs.

5.3 Immersion Test

The immersion test was realized in cell Hg07-3. The thermal profile in the thermometer well was measured with a quartz-sheathed SPRT (7 mm diameter) and with a stainless-steel-sheathed IPRT (6.3 mm diameter).

The results shown in Fig. 5 were obtained after applying the self-heating correction (readings corrected to 0 mA). In this graph, the results are compared with the corresponding value given in the text that defines the International temperature Scale of 1990 (ITS-90) [9]. The thermal profile obtained with the SPRT was as expected up to 10 cm from the bottom, and the profile obtained with the IPRT was as expected up to 6 cm. These results are understandable because the IPRT has greater heat leakage through its stem than a quartz-sheathed SPRT. Since the sensing zone of an IPRT is often located within 4 cm from the tip of the sheath, the profile obtained indicates that the cell is adequate for the calibration of an IPRT.

5.4 Comparison with Reference Cell

Comparison of the TP-Hg temperature of cells Hg07-2 and Hg07-3 (filled with 99.9999 % Hg) was carried out against one reference cell of CENAM (Hg002) that belongs to the national standard. This cell has a diameter of 38 mm, and it was prepared in a bath designed and manufactured at CENAM [10]. The comparison was realized with two SPRTs (one quartz sheathed and the other Inconel sheathed); both of them were measured with an ASL F18 resistance bridge with a resolution of 0.01 ppm (0.01 mK). The measured difference was (0.12 ± 0.05) mK ($k = 1$) for cell Hg07-2

and (0.13 ± 0.07) mK $(k = 1)$ for cell Hg07-3. The quoted uncertainty is of type A, and represents simply the dispersion of the temperature readings.

6 Conclusions

The TP-Hg may be reproduced easily using the system described here with an uncertainty adequate for accurate calibration of IPRTs. In fact, we found that this system provides a better thermal environment for the reproduction of the TP-Hg even for regular size cells. Thus, we are planning to replace the bath system used to maintain the triple-point condition of the cells belonging to the national standard with a heat-pipe system similar to the one described here.

Once the system is tuned, plateaux may last up to 4 h (with the set point 0.2 °C above the melting point), which provides enough time to calibrate several IPRTs in a single run. Moreover, this system does not require special skills from the operating personnel, unlike other methods. Thus, the system described here represents a sensible choice for the calibration of IPRTs at the TP-Hg for both national institutes and calibration laboratories.

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