Realization of the Triple Point of Water in Metallic Sealed Cells at the LNE-INM/CNAM: A Progress Report

F. Sparasci · L. Pitre · Y. Hermier

Abstract   A miniature metallic cell for the water triple point (TPW, temperature 273.16 K) was developed for capsule-type thermometer calibrations for realizations with adiabatic calorimetry techniques. The LNE-INM/Cnam previously developed a copper cell for the water triple point and the techniques for cleaning, filling, and sealing. On the basis of previous work, a new copper cell prototype for the TPW was developed and filled at the LNE-INM/Cnam. Measurements were performed using an appropriate calorimeter and a comparison block containing several thermometers. Preliminary results show a scatter of the temperatures measured at the phase transition of the order of 0.2 mK when measurements are repeated over a short-term period (1 month). A positive drift in the phase transition temperature of about $30\,\mu\mathrm{K} \cdot \mathrm{month}^{-1}$ was observed over several months. Studies are in progress to improve the cell, to reduce the reproducibility uncertainty to less than 0.1 mK and to have a phase transition with better temporal stability.

Keywords   Adiabatic calorimetry · Metallic cell · Thermometer calibration · Triple point · Water

1 Introduction

The typical large glass cells used to realize the water triple point are unsuitable to measurements under adiabatic conditions, i.e., by supplying controlled heat pulses to melt the sample, as is usually the case for the low-temperature triple points of the International Temperature Scale of 1990 (ITS-90). Measurements are therefore

F. Sparasci (✉) · L. Pitre · Y. Hermier
Institut National de Métrologie LNE-INM/Cnam, 61 rue du Landy,
93210 La Plaine Saint Denis, France
e-mail: fernando.sparasci@cnam.fr

performed at an unknown fraction F of melted ice, with an unknown distribution of impurities between the liquid and solid phases. Consequently, it is not possible to determine the temperature at the liquidus point, as the melting process cannot be adequately controlled. The only exception is the experiment performed by Méndez-Lango to evaluate the impurity content in the triple-point-of-water cells by performing complete solidification of the sample [1].

A metallic miniature sealed cell for the TPW (temperature 273.16 K), inserted in a suitable adiabatic calorimeter, could be used to perform adiabatic realizations of the water triple point. The aim is to obtain an overall uncertainty, in the calibration of thermometers at the TPW, of the order of some tens of microkelvin.

At the Institut National de Métrologie (INM), a metallic cell made of copper was used to realize the TPW 20 years ago [2,3], and the techniques to clean, fill, and seal the cell were developed at that time. The reproducibility of the melting plateau was studied over 2 years. No significant differences were observed between the metallic cell and the classical glass cell, and no changes were observed in the phase transition temperature of the metallic cell during that time, at the level of 0.1 mK [4]. The original cell design allowed the calibration of a single capsule-type thermometer during one run, and was assembled with cryogenic fixed-point cells (H_2, Ne, O_2, Ar) in a multi-cell configuration so that all the fixed points could be realized in the same run. As the production was discontinued after this first study, there has been no design evolution—in particular, it would be advantageous to calibrate several thermometers in a single run by incorporating a copper block and to realize it separately from the cryogenic fixed points. Furthermore, no studies are available of the phase-transition-temperature stability over several years.

Hence, the studies performed in the past have been resumed to realize a new copper cell for the water triple point. The geometry of the cell was modified to have the possibility to calibrate up to eight capsule-type thermometers in a single run. The cleaning and filling techniques were also adapted to the new cell design. A suitable adiabatic calorimeter was developed, and measurements were performed to test the reproducibility of the phase transition and its temporal stability.

2 Metallic Cell for the Water Triple Point

2.1 Choice of Materials

Several materials were previously tested for miniature TPW cells. With stainless steel, nickel, and brass, the water became contaminated over time, and the temperature of the phase transition changed with time because of the increasing concentration of impurities dissolved in the water.

Tests were also performed with glass but, since its thermal conductivity is poor, the recovery time τ after a heat pulse on the plateau is of the order of several hours. Hence, glass was not considered a suitable material, as τ is required to be of the order of several tens of minutes for adiabatic plateau realizations.

Platinum was studied by NMIJ [5]; it has high thermal conductivity and does not contaminate the water. However, it is expensive, and welding and sealing are difficult.

Copper has high thermal conductivity, but oxidization due to interaction with water, with consequent water contamination, has to be taken into account. Previous studies proved that a copper oxide layer, separating the non-oxidized copper from the water, prevents the water from becoming contaminated. Hence, a water cell with a copper wall that is oxidized before performing the final filling and sealing can remain stable with time. Another advantage of copper is that the cell can be sealed using the same techniques developed for cryogenic cells [6,7].

As a consequence, copper was chosen to realize cells for the water triple point.

2.2 Cell Design

The main criterion for the design of the cell is the ease of cleaning and filling. The cell is equipped with three filling tubes of length 100 mm and diameter 2 mm. This allows cleaning of the cell with a continuous water flow to remove the impurities and develop the oxide layer inside the cell. One of the three tubes can be used for leak tests.

The inner chamber is cylindrical (height: 8 mm and diameter: 40 mm) with a heat exchanger at the bottom to increase the heat exchange surface area. Two threaded connectors are placed on the top and at the bottom of the outer part of the cell to aid in assembling the cell to a copper block that holds the thermometers within the cryostat. The total mass of the assembly is 618 (12) g.[1]

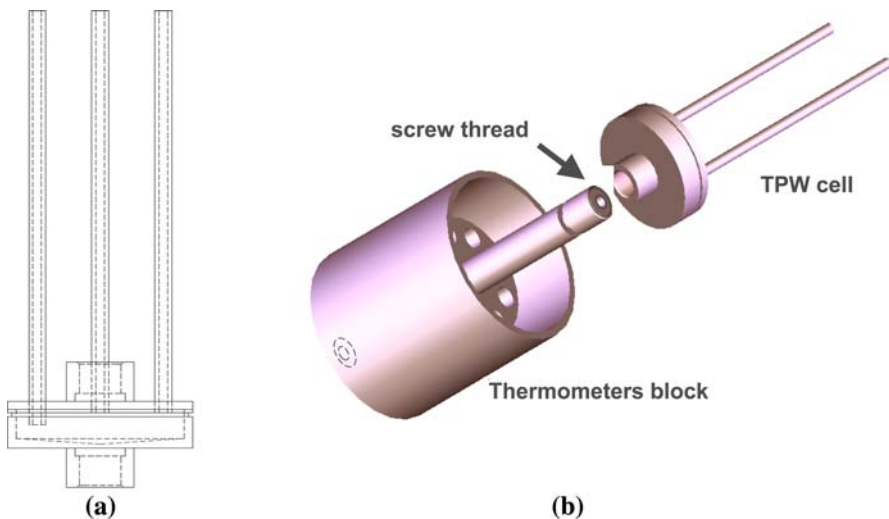The design of the cell and the thermometer block are given in Fig. 1.

Fig. 1 (**a**) Design of the water-triple-point cell and (**b**) the cell and the thermometer block (CAD realization, A. Richard)

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[1] All the uncertainty values in this text are reported for a coverage factor $k = 1$, unless otherwise specified in the text.

2.3 Filling Procedure

Impurities are removed by flushing the cell with a continuous water flow. Doubly distilled water is used for cleaning. The cell is directly connected to the still to ensure a flow of freshly produced water. This reduces contamination of water by atmospheric gases, particularly the dissolution of carbon dioxide—one of the atmospheric gases with the highest absorption coefficient. Contamination due to storage of water in a tank is also avoided.

The cleaning process lasts up to 2 weeks. According to previous studies performed at INM, this should be enough to develop a suitable oxide layer on the inner wall of the cell. The presence of the oxide layer has not been visually confirmed, as it would require opening the cell.

Sealing has to be performed so that only liquid water and water vapor are contained inside the cell. The procedure followed for cell filling and sealing is briefly described here. The cell is completely filled with water, and then it is heated slightly below the water boiling point to increase the vapor pressure of the water. Vapors inside the cell are evacuated via the filling tubes; this avoids external air entering the cell. A check for residual gas inside the cell has not been performed on the first cell prototype. A specific procedure for degassing and a residual gas check should be established when filling new cells. The mass of the cell is monitored during the process of evaporation, and the cell is sealed—the filling tubes are pinched off—when the remaining mass of water inside the cell is less than 1.5 g. It is then possible to calculate the amount of heat needed for the phase transition. Since the latent heat of fusion is $334 \, \text{J} \cdot \text{g}^{-1}$, between 330 J and 500 J has to be supplied during the plateau realization for a cell containing between 1 g and 1.5 g of water.
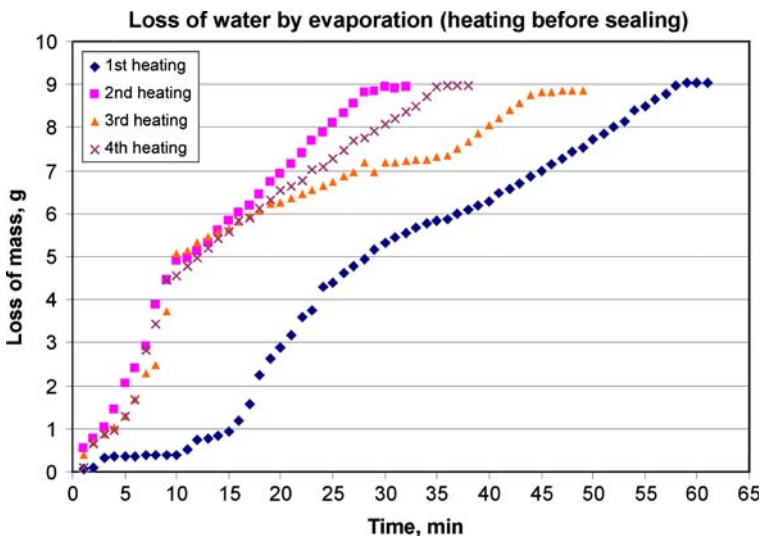

Fig. 2 Loss of mass of the cell due to evaporation of water under controlled heating prior to sealing

Fig. 3 (**a**) Water-triple-point cell, (**b**) block for capsule type thermometers, and (**c**) calorimeter

The graph in Fig. 2 represents the tests performed to observe the loss of mass with time as the cell is heated prior to sealing. The differences are mainly due to adjustments of the heat source. The maximum water content of the cell corresponds to about 9 g of water. The cell can be sealed after about 30 min of heating, so as to have about 1.5 g of water inside. Figure 3a is a photograph of the cell.

2.4 Adiabatic Calorimeter

The calorimeter consists of a stainless-steel container, within which the cell and the block holding the thermometers are installed, that provides thermal isolation from the surroundings by means of a high vacuum ($<5 \times 10^{-4}$ Pa). A heater of about 160 Ω, to supply heat pulses during the plateau, is glued onto the cell and all the wires are thermally anchored to the container. A radiation shield is mounted in the upper part of the calorimeter, to reduce the radiation coming from the vacuum pumping tube.
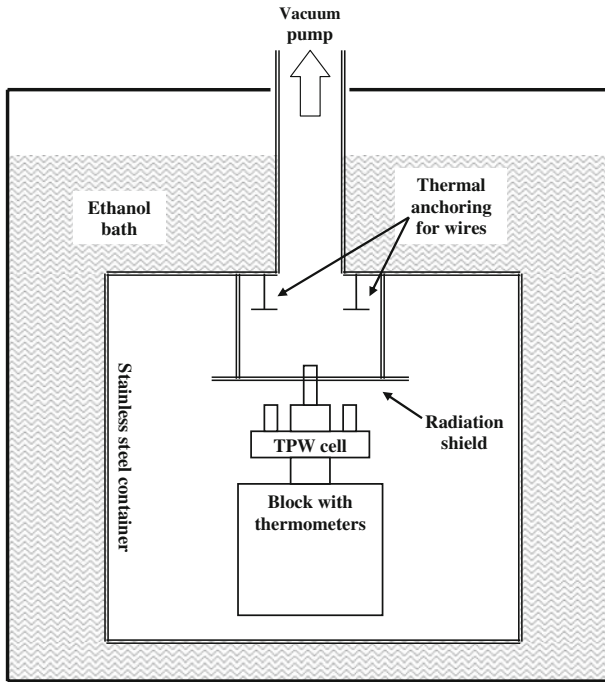
Fig. 4 Schematic of the calorimeter (not to scale)

The calorimeter is inserted in a temperature-controlled ethanol bath (Fluke, Model 7381) regulated at a few tens of millikelvin below the triple-point-of-water tempera-ture during the plateau. The temperature of the bath is regulated before each run, so as to minimize the temperature drift of the cell induced by the parasitic heat flows. The temperature stability of the bath is $\pm 0.005°C$ (2σ), and the uniformity is $\pm 0.007°C$ (manufacturer's data).

Considering the stability and uniformity of the bath and the thermal isolation given by the high vacuum, we decided not to install a temperature-controlled radiation shield around the cell in this preliminary measurement campaign. More accurate triple-point-realizations will require the use of an adiabatic shield.

A schematic of the calorimeter is given in Fig. 4.

3 Measurements

Measurements were performed over a period of 3 months following the filling of the cell. One platinum thermometer was used as a reference, Tinsley B296, and its resistance was measured at each melted fraction F after each heat pulse. The other thermometers were measured at about $F = 50\%$. Measurements were carried out using either an Automatic Systems Laboratories Model F18 resistance bridge or a Measurements International Model 6010T resistance bridge. The same Tinsley 25 Ω

Table 1 Summary of measurements of the heat of melting for the metallic water-triple-point cell

Plateau No.	Duration (h)	Number of pulses	Total heat of pulses (J)	Total heat from thermometers (J)	Total heat of melting (J)
1	83	24	132.2	12.5	144.7
2	80	24	137.8	7.5	145.3
3	52	25	138.7	4.9	143.6

reference resistor was used with both bridges to minimize the uncertainty contributions coming from the resistance transfer standards.

3.1 Melting Heat Determination

Data from three melting plateaux realized with adiabatic calorimetry techniques are used to determine the heat of melting, and Table 1 lists the values found. The average value of 144.5 (2.5) J, much below the expected value ($1.5\,\text{g} \times 334\,\text{J} \cdot \text{g}^{-1} = 501\,\text{J}$), corresponds to a quantity of water inside the cell of the order of 0.43 (0.01) g. This discrepancy may be due to the way in which the cell is sealed. The temperature of the upper part of the filling tubes from which vapor is evacuated during heating is lower than the temperature of the cell body, and this leads to condensation. As the tops of the filling tubes are cut when they are pinched off, we surmise that most of the water is not sealed in the cell (verification through weighing was not performed at the moment of sealing). The remaining water is, however, sufficient to realize the triple point and to stabilize the temperature of the cell and that of the thermometer block.

3.2 Recovery Time Evaluation

The recovery time t_r for thermal re-equilibration of the cell following a heat pulse was determined after each heat pulse. Let us consider ΔT, the temperature difference between the maximum temperature after a heat pulse $T_{\max}$ and the equilibrium temperature T_{equil}; that is, $\Delta T = T_{\max} - T_{\text{equil}}$. The recovery time has been determined as the time interval during which the temperature decreases from $T_{\max}$ to $T_{\text{equil}} + 0.05\Delta T$, i.e., the time necessary to recover 95% of ΔT.

Figure 5 shows the recovery times as a function of the melted fraction F. Values for three plateaux are reported (the same as used for the melting heat determination). As a first approximation, we can consider t_r independent of F and, hence, constant. The average of the points represented in Fig. 5 gives a rough estimate of the mean recovery time, $t_r = 1140\,\text{s}$, with a deviation of 15%.

3.3 Short-Term Reproducibility of the Triple Point: Preliminary Evaluation

The three plateau realizations mentioned in the previous paragraphs have been used to evaluate the short-term reproducibility of the phase transition. In fact, they were
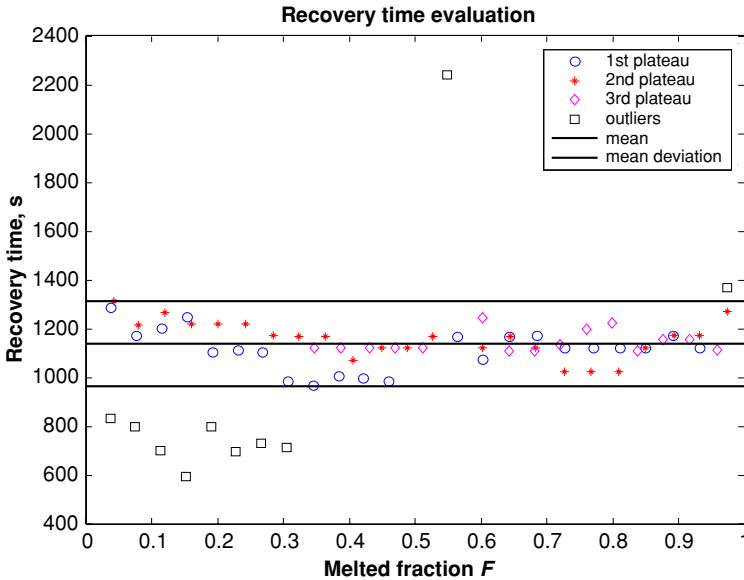
Fig. 5 Evaluation of the recovery time for different F values. Measurements performed on three plateaux

performed during three consecutive weeks (in February 2007), 2 months after the filling. Figure 6 shows the results obtained with four different platinum thermometers. All the measurements are performed at $F = 50\%$. For each thermometer, the temperature differences are calculated with respect to the average of the measurements performed with it. The uncertainty bars indicate the uncertainty contributions arising from electrical noise and the self-heating correction. The temperatures of the different plateau realizations are contained within an interval of 0.15 mK. This variability is roughly the same for each thermometer. A more complete analysis of the uncertainties has not been carried out due to the limited number of plateau realizations available. The possible reasons for such variability in the measurements include incorrect temperature set points of the ethanol bath, room temperature instability, and electromagnetic perturbations (with a consequent effect on the resistance bridges). Further plateau realizations need to be performed to investigate these aspects. The use of a temperature-regulated thermal shield covering the cell will presumably improve the adiabaticity of the calorimeter by reducing radiation effects and, hence, the dispersion of the measured temperatures.

3.4 Preliminary Tests of Temporal Stability

The three plateaux of February 2007 have been compared with a previous one—performed 2 months before at the time of the filling in December 2006—and two other subsequent plateaux carried out in September 2007, to make a preliminary evaluation of the temporal stability of the cell. Thermometers Tinsley B132 (25 Ω at 0°C) and a
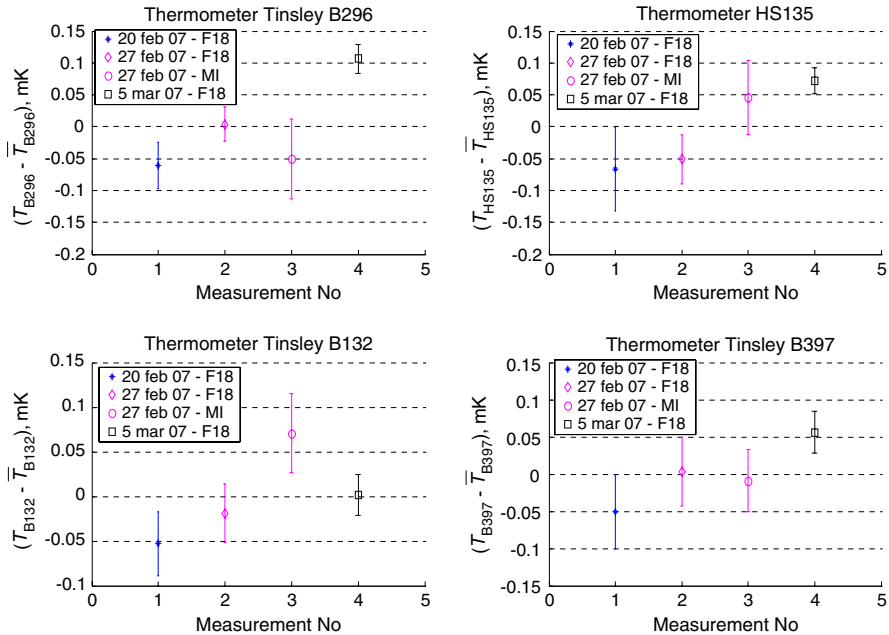
Fig. 6 Evaluation of short-term reproducibility of the water triple point. Measurements were performed with four platinum thermometers. $\bar{T}$ is the average of the values measured with the thermometer

miniature PRT-5V from VNIIFTRI (101 Ω at 0°C)[2], Serial Number 533, were used. They were calibrated at the triple point of water in a typical large glass cell, to determine the temperature difference between the metallic cell phase transition and the conventionally realized TPW. The results are shown in Fig. 7, where the evolution in time of the temperature difference between the metallic and glass cells is represented. A linear fit has been calculated by a weighted least-squares method, using weights proportional to the variances of each experimental point. The variances, corresponding to the uncertainty bars in Fig. 7, take into account the uncertainty contribution related to electrical perturbations, the uncertainty of the self-heating determinations, and the uncertainty related to the thermometer calibration at the TPW. Details of the uncertainty budget are reported in Table 2. Figure 7 shows an increase of the phase-transition temperature of the metallic cell with time, with a positive drift of 0.035 (0.009) mK · month^{-1}.

Several hypotheses have been formulated to explain such a positive temperature drift, concerning in particular the quality of the water (presence of impurities from distillation, contamination from the copper walls, possible leaks, etc.) and possible effects coming from the measurement system (stability of thermometers and reference resistors, bridge linearity, etc.). Investigations are being performed to quantify these possible effects. A plausible explanation cannot be provided at the moment.

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[2] PRT-5V thermometers have been used by VNIIFTRI in the key comparison CCT-K2.1. We considered they are sufficiently stable to perform the stability tests on the phase-transition temperature.

Table 2 Uncertainty budget in determining the temperature difference between the metallic and glass TPW cells

Uncertainty components ($k = 1$)	Values (mK)
Electrical perturbations[a]	0.037
Self-heating correction	0.059
Thermometer calibration at TPW[b]	0.202

[a] Including electrical noise and variations in the reference resistor value due to the thermal bath
[b] Contribution of the reference resistor calibration is included here; the same reference resistor is used for both measurements
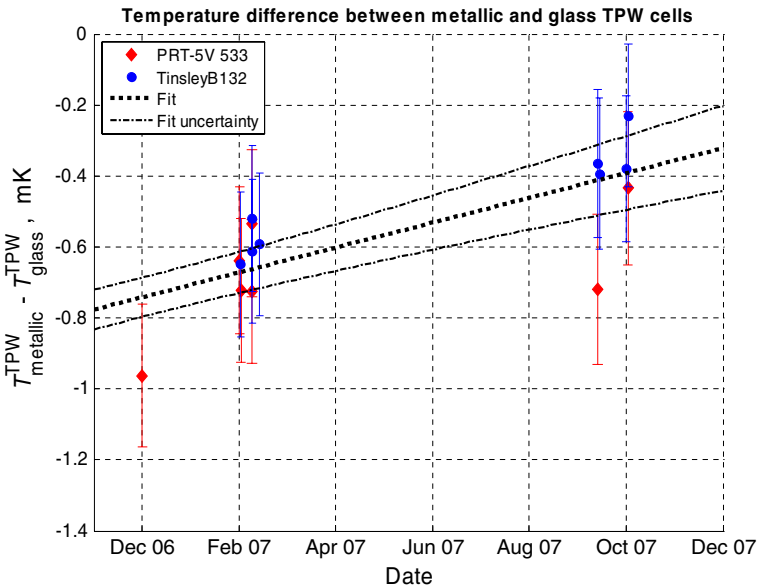

Fig. 7 Temperature evolution of the metallic cell phase transition. Values are referred to the glass cell TPW temperature

4 Conclusions

The characteristics of a new prototype metallic cell for the water triple point, realized at the LNE-INM/Cnam, have been discussed and preliminary results of some tests have been presented. The preliminary short-term repeatability is below 0.2 mK, but the cell shows a temperature drift with time. The results are very encouraging, but further studies are needed to improve the reproducibility and the stability of the phase transition. In addition, improvements to the adiabatic calorimeter and the overall measuring system are required to properly check the characteristics of the cell.

Changes to the filling procedure are under study to realize new prototypes and to study their characteristics. Comparisons among different prototypes and with a classic glass water triple point will be carried out as well.

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