Int J Thermophys (2008) 29:836–843
DOI 10.1007/s10765-008-0417-x

Method for Compensating Heat Flux Errors in Mini-TPW Cell Measurements

M. Heinonen · E. Isosaari

Abstract Small triple-point-of-water cells (mini-TPW) are used in laboratories to monitor the stability of PRTs. Compared with a standard TPW cell, heat flow in the thermometer well usually disturbs the apparent equilibrium temperature to a larger extent in a mini-TPW cell due to its smaller dimensions. In this paper, the heat flow effect is studied on the basis of experimental data. Special attention is paid to the thermal conduction along a thin thermometer probe and to the self-heating of the probe. A new method for compensating the error due to the heat flow is presented. It is shown that the compensated results are in good agreement with results obtained with standard TPW cells. The determined differences were well within the estimated expanded uncertainty of 2 mK ($k = 2$). The heat flow effect was studied experimentally by controlling the temperature of the upper part of a PRT inserted in a mini-TPW cell. Also, the effect of different fillings of the measurement well of the cell was studied. Without the compensation, thin metal-sheathed PRTs (1.6 and 2.2 mm) indicated 3 to 9 mK differences between mini-TPW and standard TPW cells.

Keywords Mini-TPW · Thermal conduction · Triple point of water

1 Introduction

Small triple-point-of-water cells (mini-TPW) are used in laboratories to monitor the stability of PRTs. The use of dry-well block calibrators as maintenance baths has made the use of the cells fairly easy. However, when measuring thin metal-sheathed PRTs in a mini-TPW, the results may differ from a calibration with a standard TPW cell by several millikelvin. We have demonstrated differences of 3 to 9 mK with PRTs of 1.6

M. Heinonen (✉) · E. Isosaari
Centre for Metrology and Accreditation (MIKES), P.O. Box 9, Tekniikantie 1, 02150 Espoo, Finland
e-mail: martti.heinonen@mikes.fi

and 2.2 mm diameter, respectively. Because the PRT resistances in our mini-TPW cell were higher than those in the standard TPW cell, it was assumed that the differences were mainly due to heat conduction along the probe.

In the work reported in this paper, a simple method to compensate the thermometer readout error caused by heat flow is presented. Also, heat flow between a PRT and a mini-TPW cell is analyzed. Experiments with two thin metal-sheathed PRTs form the basis for the analysis. We were also looking to confirm the origin of the observed differences in the measurement results with different types of TPW cells.

Characterization of mini-TPW cells of the type studied in this work have been reported in [1,2]. Heat conduction and self-heating of SPRTs in standard TPW cells have been analyzed by several researchers (see, for example, [3–5]). The scope, however, has been different from the work reported in this paper because the design of standard TPW cells and SPRTs has been optimized and standardized for ITS-90 realization.

2 Experiments

2.1 Description of Equipment

The mini-TPW cell investigated in this work was a Hart Model 5901B-G. The cell was located in a Hart 9210 maintenance apparatus as shown in Fig. 1. Measurements were made using two metal-sheathed Pt-100 thermometers. The length and the diameter of the first one (‘Pt6’) are 250 and 2.2 mm, respectively. The length and the diameter of the sensing element are 8 and 1.5 mm, respectively. For the other thermometer (‘Plamic’), the dimensions are 200 and 1.6 mm for the sensor tube, and for the sensing

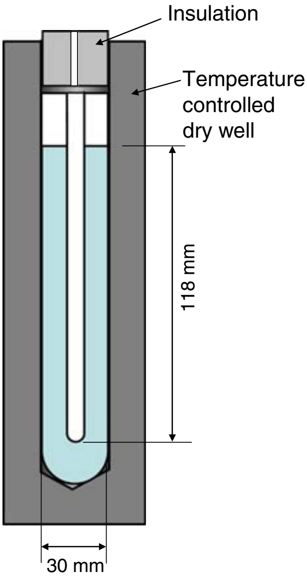
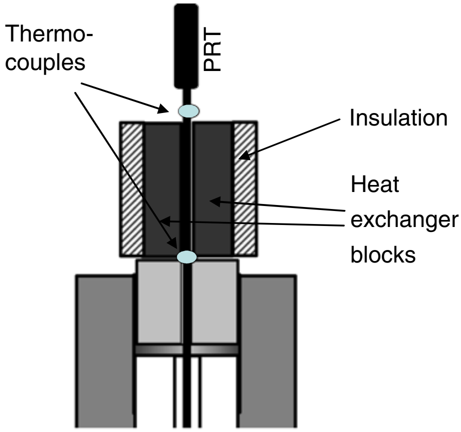


Fig. 1 Drawing of the mini-TPW cell in the maintenance apparatus

Fig. 2 Setup for measuring the heat conduction effect



element, 10 and 1.2 mm. An ASL F700B resistance bridge was used to measure the resistance of the PRTs in the mini-TPW cell. An ASL F18 resistance bridge was used in the comparison of the mini-TPW cell to the standard TPW cells Jarrett JA-11-2043 (‘Jarrett’), Hart 5901A-G (‘Hart’), and F. Glas-Wertheim TP 12/14-50-440S (‘203’).

The uncertainty of the temperature measurement consists of the uncertainty of the resistance measurement, the instability of the sensor during the measurements, and the repeatability of the results. The uncertainty of the resistance measurement in turn consists of the standard deviation of the resistance ratio, the non-ideality of the bridge, and the uncertainty of the standard resistor. The combined expanded uncertainty ($k = 2$) was estimated to be 1.5 mK. In the comparison measurements with the standard TPW cells, the estimated uncertainty ($k = 2$) was 1.0 mK.

Small heat-exchanger blocks were used for measuring the effect of heat conduction. The temperature of liquid passing through the blocks was controlled by a thermostatted bath. Type K thermocouples were used to measure the temperature along the PRT above the top cover of the TPW maintenance apparatus. Figure 2 shows the setup.

2.2 TPW Realization with the Mini-cell

In this work, the triple point of water was realized in the mini-TPW cell as follows. The cell was first cooled to −4.5°C. Then, the cell containing supercooled water was removed from the maintenance apparatus and shaken. Once it was obvious that the nucleation and growth of ice had occurred, the cell was inserted back into the maintenance apparatus and the temperature of the apparatus was adjusted to 0.01°C. After reaching stable thermal conditions in the apparatus, the cell was again removed from the apparatus. To force the ice mantle in the cell to flow freely, the outer surface of the cell was slightly heated by hand and a thermometer at room temperature was inserted into the well for approximately one minute. The tests showed that slightly longer or shorter heating times had no influence on the results.

A small amount of ethanol was in the well of the apparatus to improve the thermal contact between the cell and the well. Ethanol was also in the thermometer well of the cell, enabling better thermal contact between the cell and a PRT inserted into the cell. As described later, measurements were also carried out with a totally dry thermometer well and with a water–ethanol mixture in the well.

In all measurements, it was assured by observation that a freely floating ice mantle covered the whole thermometer well below the level of the water. Before inserting a thermometer into the thermometer well, the thermometer was always pre-cooled to about 0°C.

2.3 Heat Conduction Measurements

The setup shown in Fig. 2 was used to investigate the heat conduction effect with Pt6. Due to the smaller thermometer length of Plamic, some measurements were made with horizontally oriented heat-exchanger blocks. Measurements were made by decreasing the temperature of the blocks from +22 to +2°C in steps. The PRT resistance was measured continuously during the exercise. Also, the stem temperature of the PRT was monitored by the thermocouples shown in Fig. 2. The results obtained with Pt6 and Plamic are shown in Figs. 3 and 4. Temperature values were calculated using the latest calibration results for both thermometers. Pt6 shows an effect equivalent to about 0.01°C whereas Plamic seems to be insensitive to the ambient temperature.

2.4 Comparison of the Mini-TPW Cell to the Standard TPW Cells

To compare the mini-TPW cell to standard TPW cells, the maintenance apparatus was located close to the maintenance bath of the standard cells. The cells were measured with both PRTs. Each measurement was carried out with both 1 and $\sqrt{2}$ mA measurement currents to determine the self-heating.

By comparing the results obtained with the measurement current of 1 mA, we can identify a difference of 9 mK for Pt6 and 1 to 3 mK for Plamic (see Fig. 5). The situation

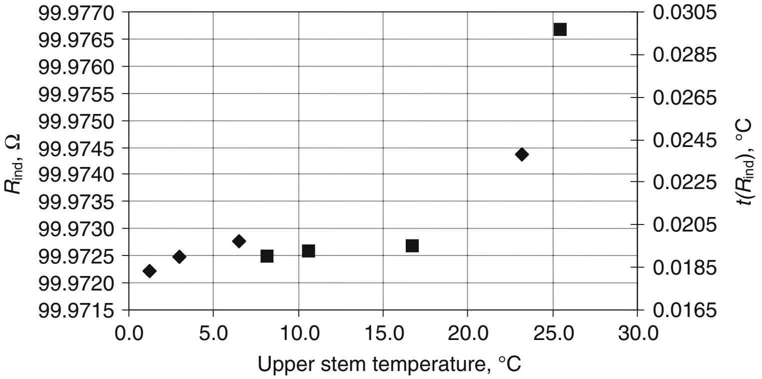


Fig. 3 Results of two sets of heat conduction measurement with Pt6

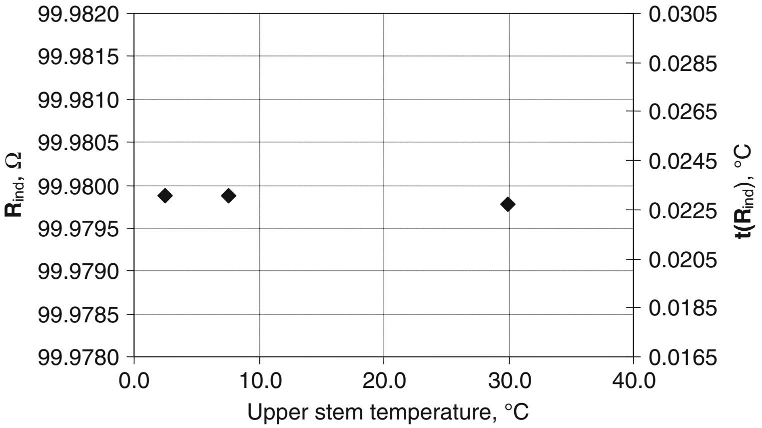


Fig. 4 Results of heat conduction measurement with Plamic

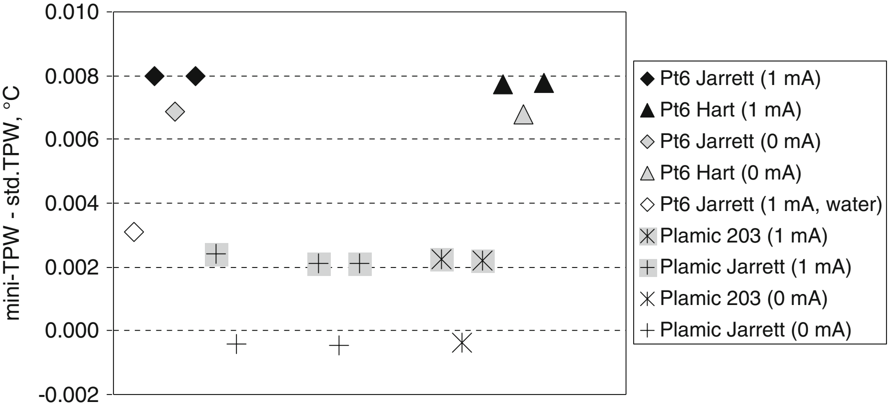


Fig. 5 Difference between the mini-TPW and standard TPW cells. During these measurements, the filling liquid in the well of the standard cell was distilled water. In the mini-TPW cell, the filling liquid was ethanol, except in one of the measurements where the filling liquid was water, as indicated in the figure

changes, however, after applying the self-heating correction. It can be easily shown that the error (δ_{sf}) can be calculated as

$$\delta_{\mathrm{sh}} = t_{\mathrm{ind0}} - t_{\mathrm{ind1}} = (2t_{\mathrm{ind1}} - t_{\mathrm{ind2}}) - t_{\mathrm{ind1}} = t_{\mathrm{ind1}} - t_{\mathrm{ind2}} \tag{1}$$

where t_{ind0}, t_{ind1}, and t_{ind2} are the temperature values obtained from the resistance measurements with currents of (0, 1, and $\sqrt{}2$) mA, respectively (see, e.g., [5]). As shown in Fig. 5, the difference between the mini-cell and the standard cell is less than 1 mK when using Plamic, i.e., the result is within the measurement uncertainty. Pt6 shows a difference of 7 mK between the mini-cell and the standard cell. These results agree well with the results of the heat conduction experiments.

It was concluded that the discrepancy in the Pt6 results with 1 mA was mainly due to the different filling liquids in the thermometer wells. This is also supported by the results from measurements with water in the mini-TPW thermometer well. As shown in Fig. 5, the difference between the cells is significantly smaller in this case. This is discussed further in the next section.

The hydrostatic pressure correction is smaller in the mini-TPW than in the standard TPW cells due to the smaller immersion depth. The difference is about 0.1 mK as calculated according to [3]. This is negligible compared with the measured differences and associated uncertainties.

3 Compensation Method

3.1 Description of the Compensation Method

Heat transfer in the thermometer well of the mini-TPW cell is induced by thermal conduction along the thermometer and walls of the well, self-heating of the thermometer, evaporation of ethanol, condensation of water vapor, thermal radiation, and chemical reaction between water and ethanol. The effects of evaporation and chemical reaction can be avoided by replacing the ethanol in the well with pre-cooled water when the cell is in the triple-point state. The better thermal conductivity of water should also decrease the effect of heat flow on the thermometer indication. Water is, however, impractical in everyday use because the thermometer well cannot be filled with water when cooling the cell to the supercooled state. Using water would not be consistent with the basic idea of an easy stability-checking method. A water–ethanol mixture can be a compromise but the exothermic reaction from the mixing of water and alcohol must then be considered.

According to our results, the thermal radiation effect is negligible in this setup when compared to other uncertainty sources. The combined effect of the other heat-transfer mechanisms was studied by analyzing the results obtained when the thermometer well was empty and filled to the cell water level with ethanol and distilled water.

Let us first consider the case where the thermometer well is filled with water. In this case, only heat conduction and self-heating affect the measurement result (The effect of evaporating water from the well is minimized by enclosing the thermometer within the cover of the maintenance apparatus). If we ignore the vertical thermal flow in the water, the heat flux between the thermometer and the wall of the thermometer well is independent of the liquid and the distance between the thermometer and the wall. These factors affect, however, the temperature difference between the thermometer and the wall because of different thermal resistances. The effect can be maximized by comparing measurements with water filling to measurements with air filling because the thermal conductivity of air is significantly smaller than in water (or ethanol). We can write

$$k_{\mathrm{w}}(T_{\mathrm{sw}} - T_0) \approx k_{\mathrm{a}}(T_{\mathrm{sa}} - T_0) \tag{2}$$

where k_{a} and k_{w} are the thermal conductivity of air and water, respectively. T_0, T_{sw}, and T_{sa} are the temperatures of the well wall and the thermometer in water and air, respectively. By re-arranging Eq. 2, we can derive an equation that can be used to

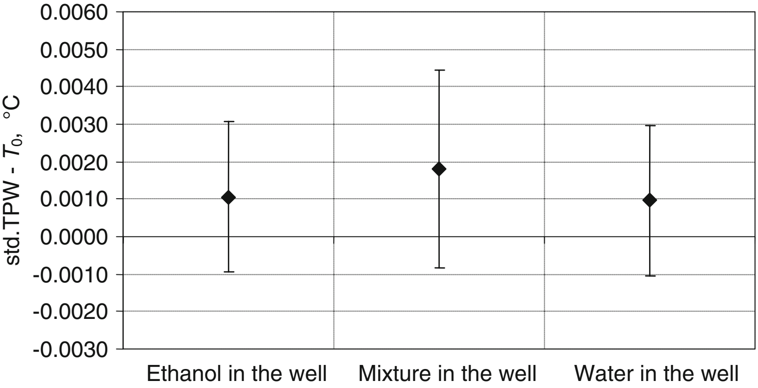


Fig. 6 Difference between the standard TPW cell results and T_0 values calculated with Eq. 3. The T_0 calculations were carried out for the cases where the mini-TPW thermometer well was filled with ethanol, ethanol/water mixture, and water. The error bars show the uncertainties ($k = 2$) estimated for the differences

estimate experimentally the cell temperature,

$$T_0 = \frac{k_w T_{sw} - k_a T_{sa}}{k_w - k_a} \tag{3}$$

This equation can also be used in the case with ethanol in the thermometer well if 'w' is replaced with 'e,' referring to ethanol. In this case, however, all the heat transfer mechanisms affect the temperature. If we compare T_0 values obtained from the measurements with ethanol and water, we can estimate the error due to heat conduction.

3.2 Applying the Method

Measurements were only made with Pt6 because the results shown above indicate that the heat transfer effect is largest with this thermometer. Pt6 in the empty thermometer well showed a 0.09°C higher temperature than with water filling. Calculations were made using the following heat conduction data: $k_w = 0.55574\,\mathrm{W \cdot m^{-1} \cdot K^{-1}}$, $k_e = 0.18508\,\mathrm{W \cdot m^{-1} \cdot K^{-1}}$, and $k_a = 0.02444\,\mathrm{W \cdot m^{-1} \cdot K^{-1}}$. These data were obtained from the Liquid Thermal Conductivity Calculator and the Gas Property Calculator [6].

In Fig. 6, the calculated T_0 results are compared with the results measured in standard TPW cells. The error bars in the figure show the uncertainties ($k = 2$) estimated from the temperature measurement uncertainty, the uncertainty of the heat conduction values, and the repeatability of the results. The results show that T_0 predicts well the measurement result obtained with a standard TPW cell.

The good agreement between T_0 and the standard TPW cell result indicates that the combined heat flow effect due to heat transfer mechanisms other than self-heating in the thermometer cannot be omitted when using ethanol in the thermometer well. However, well within the uncertainty, there seems to be a small difference between

T_0 and the standard TPW cell result. This is probably due to the direct contact of the sensor tip with the mini-TPW cell wall.

4 Conclusions and Discussion

It was shown in this work that it is not always easy to get reliable results when using a small TPW cell with thin PRTs. If an accuracy better than 0.01°C is needed, liquid is needed in the thermometer well to improve the thermal contact between the thermometer and the cell. On the other hand, water is not practical in use and ethanol has a smaller thermal conductivity than water. With ethanol, errors of 9 mK were demonstrated.

The heat conduction experiments show that the errors were mostly due to heat conduction and self-heating in the thermometer. The errors are highly affected by the dimensions of the PRTs. Also, the filling liquid in the TPW well affects the error. The smaller the gap between the sensor and the TPW well wall and the better the thermal conductivity of the liquid, the smaller is the error. On the other hand, heat conduction along the PRT is larger with a larger PRT diameter and thicker sheath, inducing a larger error in the measurement results. With a fused-silica sheath, the heat conduction error is significantly smaller than with a stainless steel sheath due to its smaller thermal conductivity.

A new method for compensating the heat conduction along the sheath was successfully developed in this work. With this method, measurement results obtained with small-diameter PRTs in mini-TPW cells can be corrected. The consistency of compensated results with results obtained with standard TPW cells was demonstrated at an uncertainty level of 2 mK.

Because the heat conduction error is mainly due to geometrical parameters and the properties of the filling liquid, it is sufficient to carry out experiments for the compensation only once, or at least infrequently.

References

1. X. Li, M. Hirst, in *Proceedings of TEMPMEKO '99, 7th International Symposium on Temperature and Thermal Measurements in Industry and Science*, ed. by J.F. Dubbeldam, M.J. de Groot (Edauw Johannissen bv, Delft, 1999), pp. 75–79
2. M. Zhao, R. Walker, *Cal Lab*, Jan/Feb/March 2006, pp. 25–29
3. *Supplementary Information for the International Temperature Scale of 1990*, BIPM (1990)
4. M. Stock, S. Solve, D. del Campo, V. Chimenti, E. Méndez-Lango, H. Liedberg, P.P.M. Steur, P. Marcarino, R. Dematteis, E. Filipe, I. Lobo, K.H. Kang, K.S. Gam, Y.-G. Kim, E. Renaot, G. Bonnier, M. Valin, R. White, T.D. Dransfield, Y. Duan, Y. Xiaoke, G. Strouse, M. Ballico, D. Sukkar, M. Arai, A. Mans, M. de Groot, O. Kerkhof, R. Rusby, J. Gray, D. Head, K. Hill, E. Tegeler, U. Noatsch, S. Duris, H.Y. Kho, S. Ugur, A. Pokhodun, S.F. Gerasimov, Metrologia. **43**, Tech. Suppl. 03001 (2006)
5. J.V. Nicholas, D.R. White, *Traceable Temperatures: An Introduction to Temperature Measurement and Calibration*, 2nd edn. (Wiley, New York, 2002)
6. Cambridge University Press, www.fluidmech.net