Study of the reliability and accuracy of thermistors for temperature measurements using transportable mercury triple point cells

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The triple point of high purity mercury filled in small sealed cells of borosilicate glass has been determined by using calibrated thermistors. The aim of the work is to check the accuracy of temperature measurement by using thermistors below zero degree Celsius. Two small sealed cells were used. The first was filled with mercury purified at the thermometry laboratory of the National Institute for Standard (NIS) by chemical treatment followed by triple distillation (NIS sample). The second cell was filled with mercury of purity 99.9999% obtained from the National Institute for Standards and Technology (NIST), USA (NIST sample). The values obtained for the triple point of mercury are: $-38.833 \pm 6.4 \times 10^{-3}$°C and $-38.834 \pm 6.4 \times 10^{-3}$°C for the NIS and NIST samples, respectively. These two values are in good agreement with each other and reproduce well the value adopted by the International Temperature Scale of 1990 (ITS-90) for the triple point of mercury, which is $-38.8344$°C. The results obtained indicate that the method of purification used in the present work is suitable to obtain mercury of purity better than 99.999%. It indicates also that thermistors can be used for precise temperature measurement below zero degree Celsius.

The use of small sensors such as thermistors has grown rapidly over the two decades and thermistors are now used in a wide variety of applications, e.g., in medical instrumentations, research laboratories, and in various biomedical applications. In spite of their wide use, they have not been adequately characterized with regard to their stability while being maintained at a fixed temperature or to their stability upon thermal cycling. In order to improve this situation, especially in regard to their use in accurate measurements, the present study was undertaken.

Urgent need was also felt for a mercury triple point cell to serve for the calibration of small sensors used for measuring temperatures between the sublimation point of solid carbon dioxide ($-78.5$°C) and the triple point of water ($0.01$°C). The accurate measurement of temperature in this range is of great importance, especially in cooling units and refrigeration.

For the realization of the mercury triple point a small transportable borosilicate-glass cell has been designed, constructed and filled at NIS with a pure sample of mercury.

To check the purity of our sample and the reliability of thermistors for temperature measurements in this range, a similar cell designed, constructed and filled at NIS with a standard sample of mercury supplied from NIST, USA, with a purity of 99.9999% was investigated.

Experimental Procedure

The mercury used in the (NIS) sample is a commercial one that has been chemically cleaned using nitric acid and sodium hydroxide to remove metallic impurities. Then it was distilled under atmospheric air to oxidize the metal impurities. This was followed by distillation under vacuum. The triple point cell used was made of borosilicate glass; it is shown in Fig. 1. The two entrance tubes b and c were required for steam cleaning of the cell. Before the cell with high purity mercury, it was cleaned with chromic acid followed by steam cleaning until a continuous film of water was formed on the inner walls of the cell. After cleaning, the cell was dried in an oven and then filled with high purity mercury. About 0.63 kg of mercury was found to be sufficient for filling the cell which was then sealed under vacuum. To check the purity of the NIS sample, and also to test the reliability and accuracy of thermistors for temperature measurements, another triple point cell filled with a standard reference mercury sample obtained from NIST, USA (NIST sample), of purity 99.9999% was prepared in the same way as the NIS cell.

Temperature measurement—The thermistor used for temperature measurements was of the bead type, sealed in a glass envelope, with an external diameter of about 2 mm and resistance of about 10 kΩ at room temperature increasing to about 20 kΩ at the triple point of mercury.
itself was about 4 mK at -38°C. This was improved to 0.5 mK by the copper block of about 7 cm diameter and 20.0 cm length. The block has four holes which serve as thermistor and thermometer wells. Around the copper block a heater was wound to adjust and control the block temperature at the required value. A styrofoam shield surrounded the entire copper block to provide insulation so that the temperature variations of the alcohol bath would not affect the thermal stability of the block.

Measurement of the triple point of mercury

The melting procedure was used for the realization of the triple point of mercury. Since the mercury samples were very pure, the triple points obtained by freezing or melting should yield nearly the same temperature values. The impurity segregation during freezing should be relatively small, so that the temperatures observed during melting were expected to be quite close to those obtained during the freezing experiments.

In preparation for the melting point experiment, the mercury had been frozen as rapidly as possible by immersing the cell in the alcohol bath previously described. The bath temperature was kept at several degrees lower than the freezing point of mercury. In borosilicate glass cells the mercury was completely frozen within 20-30 min after the end of the supercool, which was about 6°C below the freezing temperature of mercury. When the freezing was complete the alcohol bath temperature was readjusted as close to the melting point as possible, such that the melting duration lasted for about 3 h. During measurements of the cell temperature, ethyl alcohol was used in the thermometer well to enhance heat transfer.

After the frozen mercury reached a steady state as observed by a thermocouple immersed in the thermometer well, a warm rod was introduced into the thermometer well to just start melting the mercury. After sufficient warming, a thin film of melted mercury was formed around the thermometer well during measurement. The triple point was observed with the thermistor which was inserted in the thermometer well. The depth of immersion of the thermistor in the mercury cell was not less than the 10 cm which was required to eliminate the influence of the thermal conduction along the thermistor’s wires. The measurement of the thermistor’s resistance was taken each two minutes until the mercury cell temperature increased at least 0.5 K above the melting value. The alcohol bath temperature was adjusted to give a melting plateau of about 3 h. This gives one to two hours of stable conditions between the start of melting and the temperature rise which occurs in the later part of the melting curve.
Results and Discussion

Table 1 gives the data obtained for the triple point of mercury from 6 runs using the cell filled with mercury purified in our laboratory by the technique previously mentioned and for the triple point from 4 runs with the NIST sample results are also given in Table 1 for comparison. To correct the triple point temperature for hydrostatic pressure we have used the value adopted by ITS-90 which is $7.1 \times 10^{-3}$ K m$^{-1}$. In the present case the correction is $-0.0012^\circ$C. Hence, the corrected values are $-38.8337 \pm 6.4 \times 10^{-3}$ and $-38.8340 \pm 6.4 \times 10^{-3}$°C for the NIS and NIST samples, respectively.

In calculating the total uncertainty of the mercury triple point we have considered three sources of this uncertainty which are: a systematic uncertainty of approximately $\pm 1$ mK relative to ITS-90 owing to the calibration of the standard platinum resistance thermometer, and the uncertainty in calibrating the thermistor, which is about $\pm 5$ mK. The third source of uncertainty rises from the scatter in the sample melting plateaus. As an estimate of the scatter we used the standard deviation expressed in the form of 95% confidence limit which is about $\pm 0.38$ mK to calculate the triple point temperature given in Table 1. Because the three uncertainties are normally unrelated we added them to obtain an estimate of the uncertainty in the mercury triple point on ITS-90 which is $\pm 0.0064^\circ$C.

During measurements the temperature gradient along the well of the thermometer was studied. At the beginning of the freezing experiment, the thermistor was placed at the bottom of the thermometer well, and subsequent measurements were made as the thermistor was withdrawn in increments of about 1 cm. It was found that the temperature was stable till a height of 5 cm which indicates the absence of temperature gradient along the thermometer well.

![Table 1 - The results for the triple point of mercury for NIS and NIST samples on ITS-90](image)

Fig. 2 shows the effect of the temperature gradient between the bath and the cell during melting of mercury on the duration of the melting plateau as well as on the mercury melting temperature. From these curves it is clear that the melting plateau extends from 2 to 4 h when the bath temperature varies from $-38.0$ to $-38.2^\circ$C. The average triple point temperatures for both curves are $-38.8333$ and $-38.8337^\circ$C. This indicates that the variation of the bath temperature has no influence on the plateau of the melting curves, within the limits of the instruments resolution (i.e. $0.0005^\circ$C) other than to change the duration of the melts.

Melting curves of the two samples are shown in Fig. 3. From these curves it can be observed that, the difference in the mean values of the plateau is $7 \times 10^{-4}$ which is in the order of the measurement uncertainty. This means that the purity of both samples is nearly the same.

The two values obtained for the triple point of mercury are in good agreement with each other and reproduces well the value adopted by the International Temperature Scale of 1990 (ITS-90) for the triple point of mercury which is $-38.8344^\circ$C.

In our laboratory previous work on the triple point of mercury using a platinum resistance thermometer had been carried out. The obtained result when recalculated on ITS-90 was found to be...
\[ -38.8312 \pm 0.0003^\circ\text{C} \] which agrees with the obtained value in the present work to within the uncertainty of the present measurements.

**Conclusion**

There are two main conclusions from this study. The first is that thermistors are reliable and accurate for temperature measurements below zero degree Celsius and do not need frequent calibration. The second is that the purification technique described is good enough to obtain high purity mercury suitable for a standard reference material in thermometry.

**References**