Comparison Between Melting and Freezing Points of Indium and Zinc

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Abstract: In the interest of improving convenience and plateau duration, the use of melting points instead of freezing points for temperature fixed points in temperature calibration is considered. The question is whether adequately low uncertainties can be achieved with melting plateaus. Experimental research was carried out to compare the melting and freezing points of indium and zinc by using the inter-comparison method with standard platinum resistance thermometers (SPRTs). The influence of the furnace maintenance temperature on the performance of melting plateaus of indium and zinc was investigated and discussed. Differences in results between the melting points and the freezing points are shown. Uncertainty budget analysis of the melting points is presented. The experimental results show that because of the small differences between the freezing points and melting points using the optimal methods of realization, it is possible to replace the freezing point with the melting point in the calibration of SPRTs in secondary-level laboratories.

1. Introduction

In the International Temperature Scale of 1990 (ITS-90), the freezing plateau is used for most defining metal fixed points because it provides the best stability and reproducibility of temperature. But operation and realization of freezing plateaus is more difficult than that of melting plateaus, primarily because of supercooling and induction of nucleation during the realization of the freezing plateau. Realization of the melting plateau avoids these problems, and the duration of the melting plateau can be longer than that of the freezing plateau. But the temperature uncertainty of the melting plateau is higher than that of the freezing plateau. The performance of the melting plateau is influenced by the prior freezing history. As a consequence, melting plateaus are not used in ITS-90 for most metal fixed points. In this paper, comparisons of the melting plateaus and the freezing plateaus of indium and zinc were carried out. Factors that influence the quality of the melting plateaus were studied, and the temperature uncertainties of the melting and freezing plateaus of indium and zinc are evaluated. The possibility of using the melting plateau instead of the freezing plateau to calibrate standard platinum resistance thermometers (SPRTs) in secondary-level laboratories is discussed.

2. Experimental Methods and Results

In this study, one classic quartz shell indium cell (Fluke Hart Scientific model: 5904)[1] and one classic quartz shell zinc cell (Fluke Hart Scientific model: 5906) were used to realize the melting and freezing points. The metal purities of both cells are over 99.9999%. The diameter is 34 mm, and the height is 215 mm for both metal ingots. A three-zone freeze-point furnace (Fluke Hart Scientific model 9114) was used in the experiment to maintain the fixed point cells. Three standard platinum resistance thermometers (SPRTs, Fluke Hart Scientific models 5681 and 5683) were used to measure melting plateaus and freezing plateaus. A resistance bridge (Measurements International DC current comparator model 6010T, accuracy ± 0.05 ppm) was used to measure the resistances of the SPRTs. A Tinsley 10 ohm AC/DC standard resistor was used with the bridge. A triple point of water cell (Fluke Hart Scientific model 5901) with a maintenance bath (Fluke Hart Scientific model 7312) provided the temperature comparison standard.

In order to get long and stable melting and freezing plateaus, the furnace temperature gradient must be adjusted carefully. In this study, the largest difference between the top and the bottom of the furnace's working zone (the area for holding fixed point cell) was 0.03 °C at a temperature of 160 °C, and 0.07 °C at 425 °C.

2.1 Indium Melting and Freezing Plateaus

Extensive studies have been carried out by McLaren [1,2], McLaren and Murdock [3,4] to test freezing points of high purity metals as precision temperature standards. In those studies, the melting points were examined following different types of freezing with and without overnight anneals near the solidus temperature. They found that the shape of the melting curves was strongly influenced by segregation of impurities due to coring on freezing. Li and Hirst [5] studied the influence of the inner freeze on the performance of the melting plateaus. Their results showed that the technique of slow freezing and inner freeze was very useful in improving the quality of the melting plateaus. Therefore, in this study, the procedure used for realizing the melting plateau of the indium cell was similar to Li and Hirst's method [5]. On the first day of the experiment, the furnace temperature was set to about 1.0 °C below the melting point and maintained overnight in order to "anneal" the metal. On the second day, the furnace temperature was raised to 4.0 °C above the melting point at a scan rate of 0.1 °C/min. A quartz rod was pre-heated to about 5 °C above the melting point. As soon as melting started, the pre-heated quartz rod was inserted into the re-entrant well for two minutes. Then the monitoring SPRT was inserted back into the re-entrant well, and the furnace temperature was lowered to 0.4 °C above the melting point at a scan rate of 0.1 °C/min. According to Li and Hirst's results, the temperature at the beginning of the melting curve is often 0.1 mK to 0.5 mK lower than the eventual stable value. It usually takes two to three hours to reach the stable value. In this study, three SPRTs were used sequentially to measure the melting plateau two hours after melting began. After testing, the triple point of water values of the three SPRTs were tested to check their stability.

[1] Certain commercial equipment, instruments, or materials are identified in this paper in order to adequately describe the experimental procedure. Such identification does not imply recommendation or endorsement by the author or NCSL International, nor does it imply that the materials or equipment identified are the only or best available for the purpose.

After measurements of the melting plateau were completed, the furnace temperature was raised to 2 °C above the freezing point in preparation for testing the freezing plateau the next day. The technique used for realizing the freezing plateau can be found in the reference [6]. After the induction of nucleation, the furnace maintenance temperature was lowered to 0.4 °C below the freezing point. The measurement of the freezing plateau started one hour later after induction of nucleation. The same three SPRTs were used in the same way to measure the freezing plateau as during the melting plateau test. After testing, the furnace temperature was reduced to 1.0 °C below the freezing point for the next round of measurements of the melting plateau. This procedure was repeated four times, alternately measuring the melting plateau and the freezing plateau.

Figure 1 shows one complete melting plateau and one freezing plateau of the indium cell. Again, the furnace temperature was held 0.4 °C above or below the melting or freezing point. The data shows that the stable temperatures of both plateaus are very close. The duration of melting plateau is about 25 hours, longer than that of the freezing plateau, which is about 18 hours before dropping 2 mK.

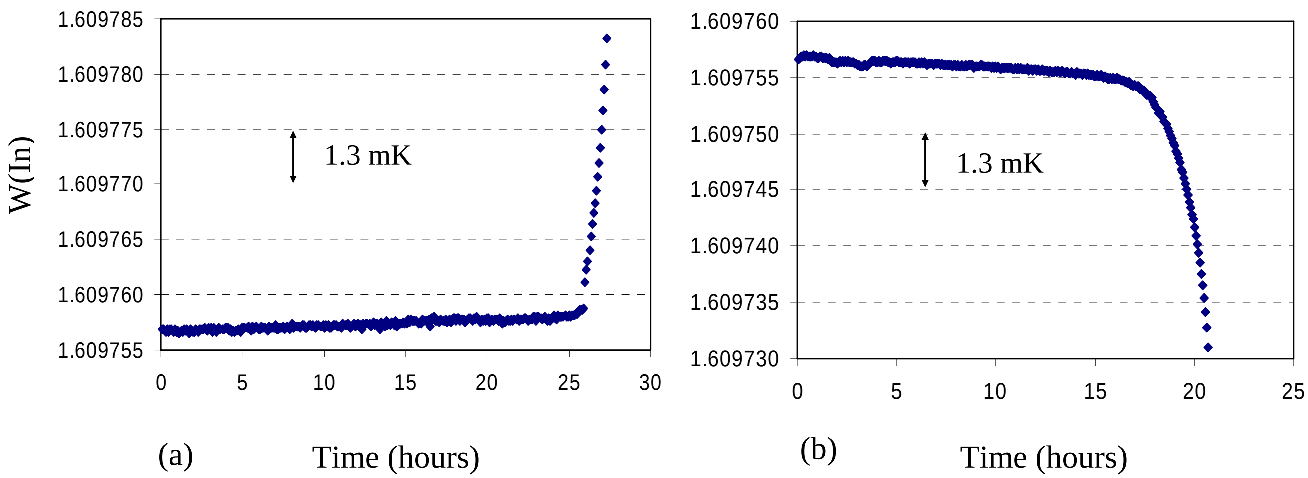

Figure 1. The melting plateau (a) and freezing plateau (b) of the indium cell.

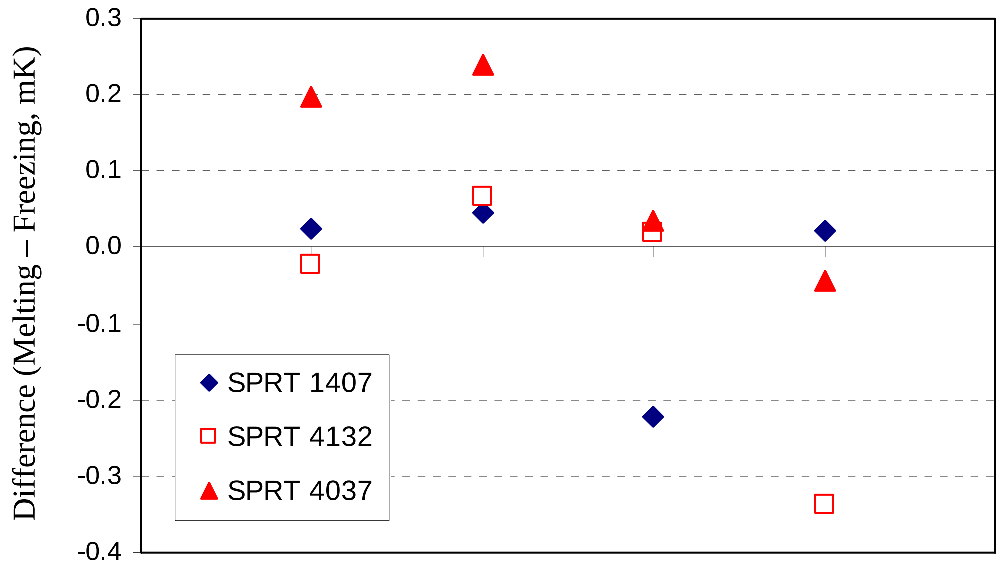

Figure 2. Comparison of the melting plateau and the freezing plateau of the indium cell.

Figure 2 shows comparison results of four groups of measurements of the melting plateau and the freezing plateau of the indium cell. For each group of measurements, three SPRTs were used in the same sequence. It can be seen that the largest difference among the four groups is 0.33 mK, and the smallest difference is 0.02 mK. Coincidentally, the average difference is only 0.0027 mK. This shows that the melting plateau of the indium cell is almost as accurate as that of the freezing plateau, if proper techniques are used.

2.2 Zinc Melting and Freezing Plateaus

The procedures for realizing the melting and freezing plateaus of the zinc cell were similar to that of the indium cell. Again, three SPRTs were used in the tests. For the melting plateau, two hours elapsed after melting started before measuring began, and one hour for the freezing plateau. The furnace maintenance temperature was set to 0.4 °C above the theoretical melting point for the melting plateau, and 0.4 °C below for the freezing plateau. Four groups of plateau measurements were collected.

Figure 3 shows melting and freezing plateaus observed with the zinc cell. The duration of the melting plateau is about 25 hours. The duration of the freezing plateau is about 40 hours, much longer than that of the melting plateau. Comparison between the two shows that the freezing plateau is more stable than the melting plateau. The temperature increases about 1.4 mK during the first 20 hours of the melting plateau, but only drops about 0.2 mK in the fist 20 hours of the freezing plateau.

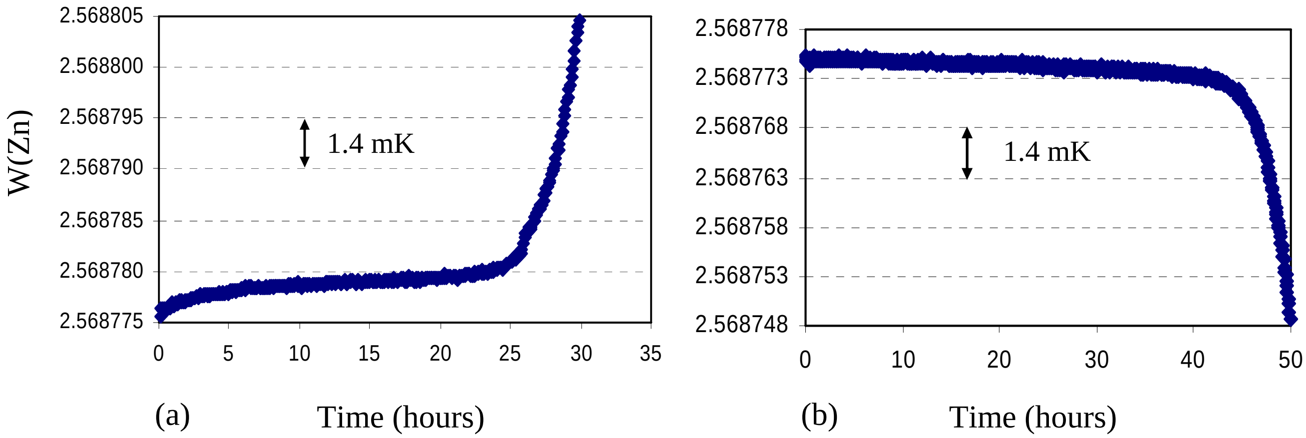

Figure 3. The melting plateau (a) and the freezing plateau (b) of the zinc cell.

Figure 4 compares the melting and freezing temperatures of the zinc cell. The largest difference is 0.85 mK, and the smallest is 0.40 mK. The average difference is 0.59 mK. The differences are much larger than those seen with the indium cell, and they are always positive. This should be expected considering the large positive slope of the zinc melting curve seen in Fig. 3. The difference between the melting and freezing temperatures is smaller near the beginning of the plateaus but increases as time goes on. It appears that for high temperature defining fixed point metals the freezing plateau is much more stable and reproducible than the melting plateau.

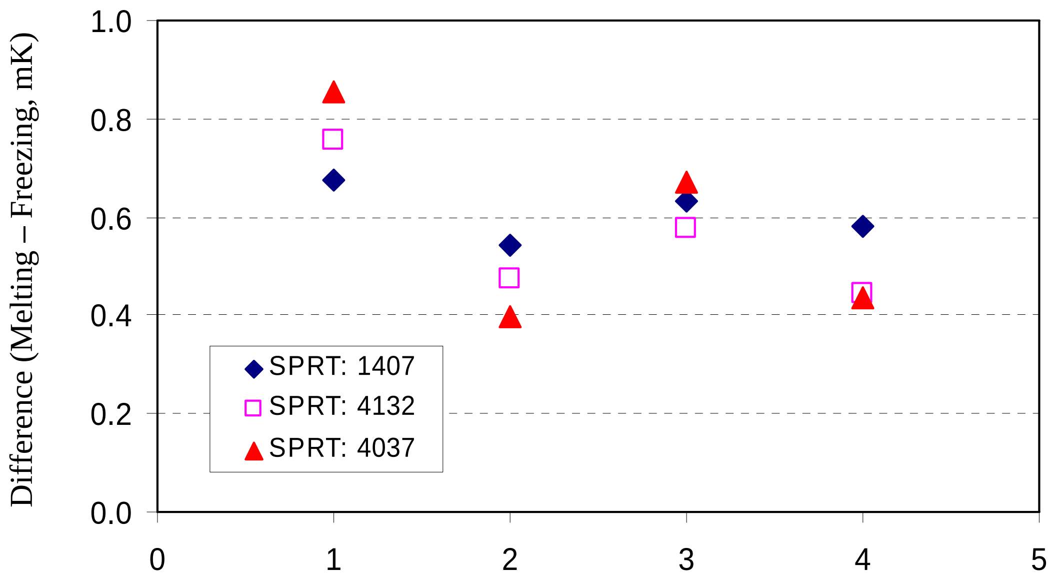

Figure 4. Comparison of the melting plateau and the freezing plateau of the zinc cell.

2.3 Influence of Furnace Maintenance Temperature

In the interest of optimizing the melting plateaus of indium and zinc, the influence of the furnace maintenance temperature on the quality of the plateau was investigated. In the experiment, four different furnace maintenance temperatures were tested. Figure 5 shows melting plateaus of indium with the various temperature settings (above the theoretical melting temperature). It can be seen that the melting plateau duration decreases significantly as the furnace maintenance temperature is increased. The plateau duration drops from 25 hours to 10 hours with the furnace maintenance temperature increasing from 0.4 °C to 1.0 °C. The melting plateau duration is less than five hours at a maintenance temperature of 2.0 °C. The experimental results show that the furnace maintenance temperature should be set close to the theoretical melting point in order to a get a long melting plateau. Other techniques, such as the inner melting procedure, should also be used to ensure a stable melting plateau.

Figure 6 shows melting plateaus of zinc at four different furnace maintenance temperature settings. The plateau duration of zinc also decreases significantly as the furnace maintenance temperature is increased. The plateau duration is about 25 hours at the furnace maintenance temperature of 0.4 °C, but drops to about 10 hours at the temperature of 2.0 °C.

3. Uncertainty Estimation

The estimated uncertainties of the melting plateaus and the freezing plateaus of indium and zinc are listed in Table 1. The purities of both indium and zinc are higher than 99.9999%. Heat flux was estimated from difference between the measured immersion characteristics and the predicted immersion profile. The

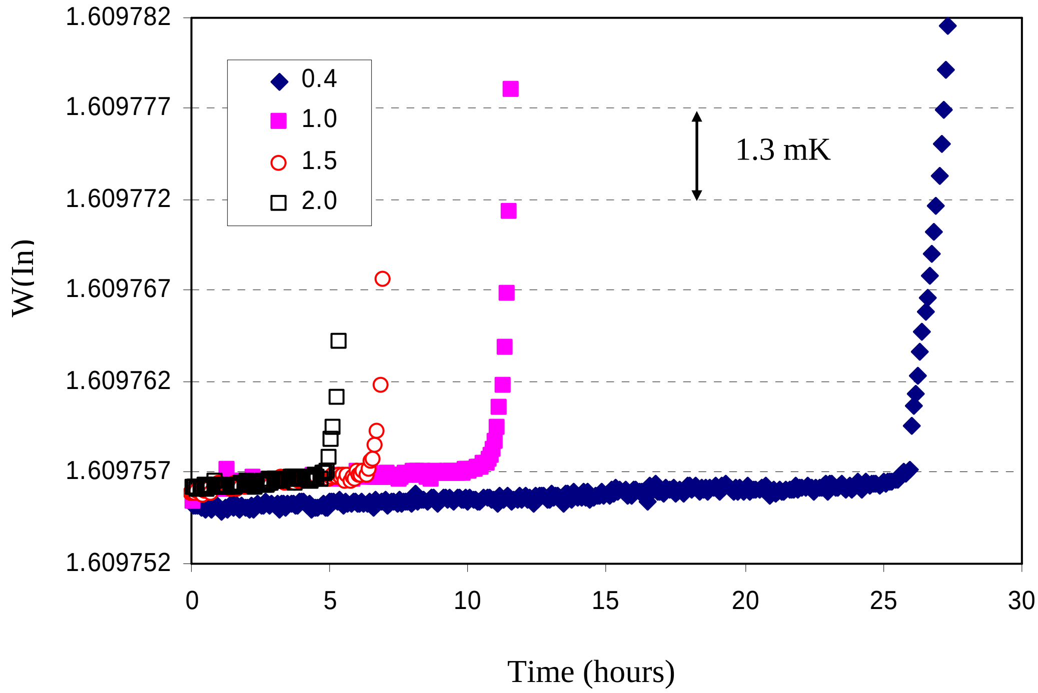

Figure 5. Melting plateaus of indium at four different furnace maintenance temperatures: 0.4, 1.0, 1.5, and 2.0 °C, respectively.

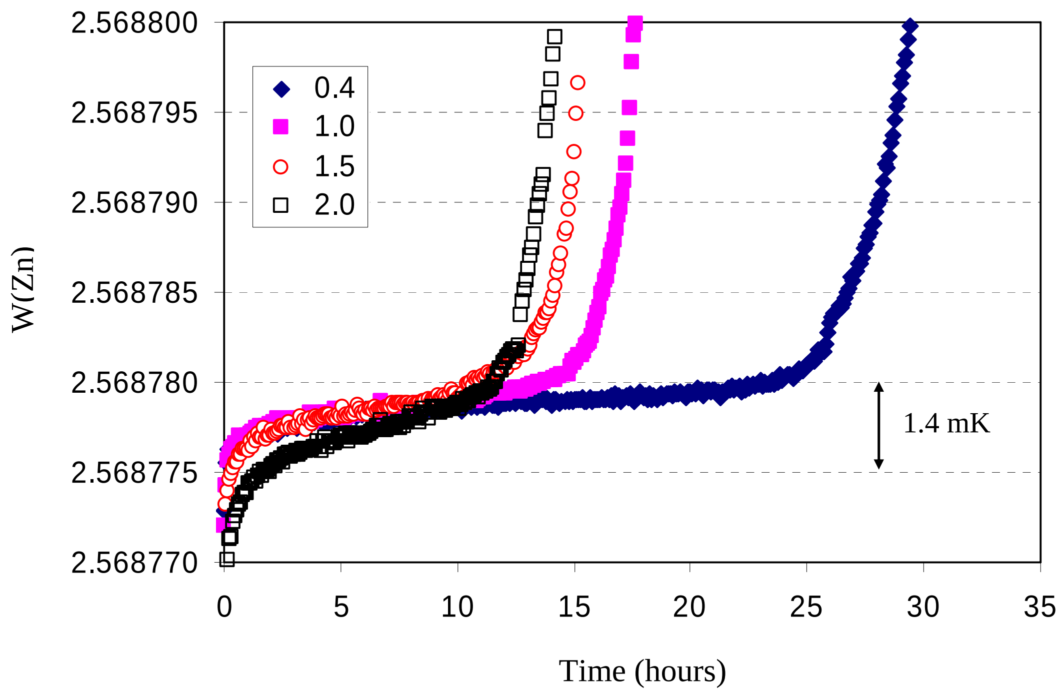

Figure 6. Melting plateaus of zinc at four different furnace maintenance temperatures: 0.4, 1.0, 1.5, and 2.0 °C, respectively.

estimated uncertainties (k = 2) are 0.75 mK for the freezing plateau of indium, and 1.11 mK for the melting plateau of indium. The uncertainties of the freezing plateau and melting plateau of indium are close. If the purity of indium can be improved to 99.99999%, the uncertainties of both the freezing plateau and the melting plateau can be improved to 0.42 mK and 0.92 mK respectively. The uncertainty of the freezing plateau of zinc is 0.84 mK, but it is 1.61 mK for the melting plateau.

Given the experimental results (melting plateau duration and stability) and the uncertainty estimations for indium and zinc, although the melting plateaus of both indium and zinc are not as stable as their freezing plateaus, it appears they could be used for the calibration of SPRTs in secondary-level laboratories.

Table 1. Estimated uncertainties of the melting and freezing plateaus of indium and zinc.

Source of Uncertainty	Indium (mK)		Zinc (mK)	
	Freezing	Melting	Freezing	Melting
Resistance reading (A)	0.034	0.034	0.059	0.059
Reproducibility (A)	0.180	0.450	0.300	0.750
Total Type A	0.183	0.451	0.306	0.752
Impurities (B)	0.320	0.320	0.270	0.270
Hydrostatic correction (B)	0.022	0.022	0.027	0.027
Pressure correction (B)	0.007	0.007	0.009	0.009
Immersion (B)	0.011	0.011	0.011	0.011
SPRT self heating (B)	0.030	0.030	0.030	0.030
Propagated from TPW (B)	0.050	0.050	0.080	0.080
Bridge non-linearity (B)	0.025	0.025	0.025	0.025
Total Type B	0.327	0.327	0.286	0.286
Total Standard Uncertainty	0.374	0.557	0.419	0.805
Expanded Uncertainty (k = 2)	0.749	1.114	0.838	1.610

4. Conclusions

The experiment results comparing the melting and freezing plateaus of indium and zinc show that the duration and stability of the melting plateau of indium is close to that of the freezing plateau. With zinc, the quality of the melting plateau was worse compared to the freezing plateau. The differences in temperature were up to 0.33 mK for indium and 0.85 mK for zinc. The estimated uncertainties of the freezing plateau and the melting plateau are 0.75 mK and 1.11 mK respectively for indium, and 0.84 mK and 1.61 mK for zinc. Both the experiment and uncertainty estimation results show that although the melting plateaus of both indium and zinc are not as stable as the freezing plateaus, they should be good enough for the calibration of SPRTs in secondary-level laboratories while offering greater convenience.

5. References

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