COMPARISON BETWEEN MELTING AND FREEZING POINTS OF ALUMINUM AND SILVER

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Abstract – For metal fixed point cells, it will be convenient if the melting points can be used instead of the freezing points in calibration of standard platinum resistance thermometers (SPRTs) because of easier realization and longer plateau duration of melting plateaus. Experimental research was carried out to compare the melting and freezing points of aluminum and silver by using the inter-comparison method with SPRTs. The influence of the furnace maintenance temperature on the performance of melting and freezing plateaus were investigated and discussed. Differences in results between the melting points and the freezing points are shown. Uncertainty budget analysis of the melting points and freezing points is presented. The experimental results show that it is possible to replace the freezing point with the melting point of aluminum cell in the calibration of SPRTs in secondary-level laboratories if the optimal methods of realization of melting points are used.

1. INTRODUCTION

For most defined metal fixed points in the International Temperature Scale of 1990 (ITS-90), the freezing plateaus are used because of the best stability and reproducibility compared to their melting plateaus. Although the temperature uncertainty of the melting plateau is higher than that of the freezing plateau, but operation and realization of melting plateaus are easier than that of freezing 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. For freezing plateau, its performance is influenced by the purity of fixed point metal and current operation procedure, but not prior freezing and melting history. In contrast, 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 the prior research, the comparison between melting and freezing points of indium, tin, and zinc has been studied [1-2]. In this paper, comparisons of the melting plateaus and the freezing plateaus of aluminum and silver 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 aluminum and silver 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 aluminum cell (Fluke Hart Scientific model: 5907) and one classic quartz shell silver cell (Fluke Hart Scientific model: 5908) were used to realize the melting and freezing points. A three-zone freeze-point furnace (Fluke Hart Scientific model 9114) was used in the experiment to maintain aluminum cell, and a sodium heat pipe furnace (Fluke Hart Scientific model 9115) was used for silver cell. Four standard platinum resistance thermometers (SPRTs, 25 ohms, Fluke Hart Scientific models 5681 and 5683) were used to measure melting plateaus and freezing plateaus of aluminum. Four high temperature standard platinum resistance thermometers (HTSPRTs, 0.25 ohms, Fluke Hart Scientific model 5684) were used for silver cell testing. A resistance bridge MI-6010T (Measurements International DC current comparator model 6010T, accuracy ±0.05 ppm) was used for aluminum cell, and a resistance bridge 6675A (Guildline DC current comparator model 6675A, accuracy ±0.02 ppm) was used for silver cell. A Guildline AC/DC standard resistor 1.0 ohm was used for silver cell testing, and a Tinsley AC/DC standard resistors 10 ohm was used for aluminum cell testing. 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 temperature gradient of the furnace for maintaining aluminum cell must be adjusted carefully. In this study, the largest difference between the top and the bottom of the working zone was 0.08 °C at 665 °C for the furnace to maintain aluminum cell.

2.1 Comparison of melting and freezing plateaus of aluminum

The procedure used for realizing the melting plateau of the aluminum cell is similar to the previous method [1-2]. On the first day of the experiment, the furnace temperature was set at 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 raise to 4.0 °C above the melting point at a scan rate of 0.1 °C/min. According to previous research results, a thin liquid-solid interface around the re-entrant well can significantly improve the melting plateau [1, 3]. In this study, the inner melting technique was used during the realization of the melting plateaus. 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 – 0.5 mK lower than the eventual stable value. It usually takes two to three hours to reach the stable value. In this study, four SPRTs were used sequentially to measure the melting plateau two hours after melting began. After testing, the triple point of water values of the four SPRTs were tested to check their stability.

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 [4]. 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 two hours later after induction of nucleation. The same four 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 aluminum cell. The furnace temperature was held 0.4 °C above or below the melting or freezing point. It can be seen that the stable temperatures of both plateaus are very close. The duration of melting plateau is about 35 hours, but only 16 hours for the freezing plateau with 2 mK dropping.

Figure 2 shows comparison results of five groups of measurements of the melting plateau and the freezing plateau of the aluminum cell. For each group of measurements, four SPRTs were used in the same sequence. The figure shows that the largest difference among the five groups is 2.0 mK, and the smallest difference is 0.46 mK. The average difference is 1.26 mK. One possible reason for this difference is that the waiting time for testing melting plateau is not long enough. In this experiment, the waiting time is two hours. According to the later experimental results in this study, the waiting time should be at least four hours so that there is enough time for melting plateau of aluminum to reach the stable value.

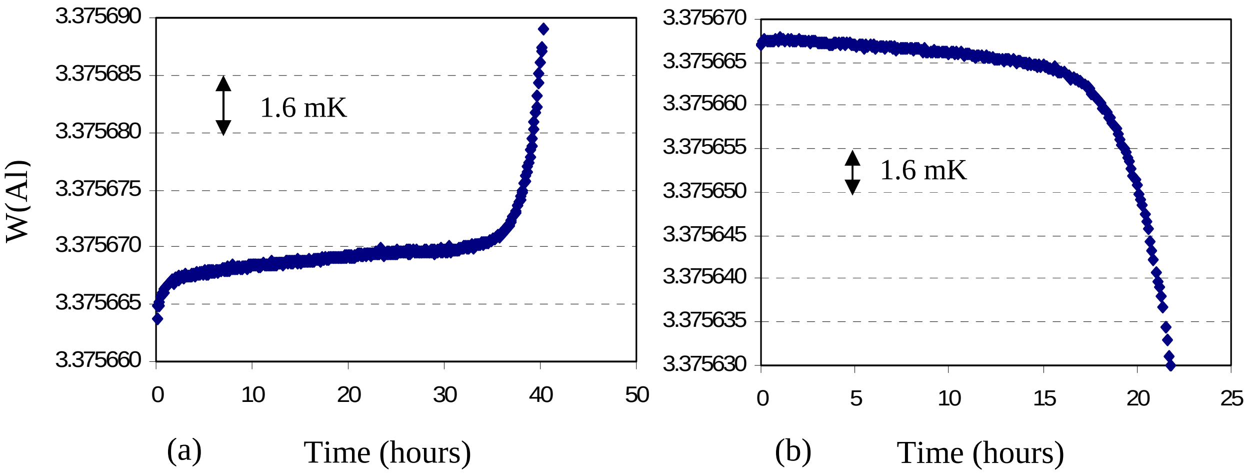


Figure 1. The melting plateau (a) and freezing plateau (b) of the aluminum cell.

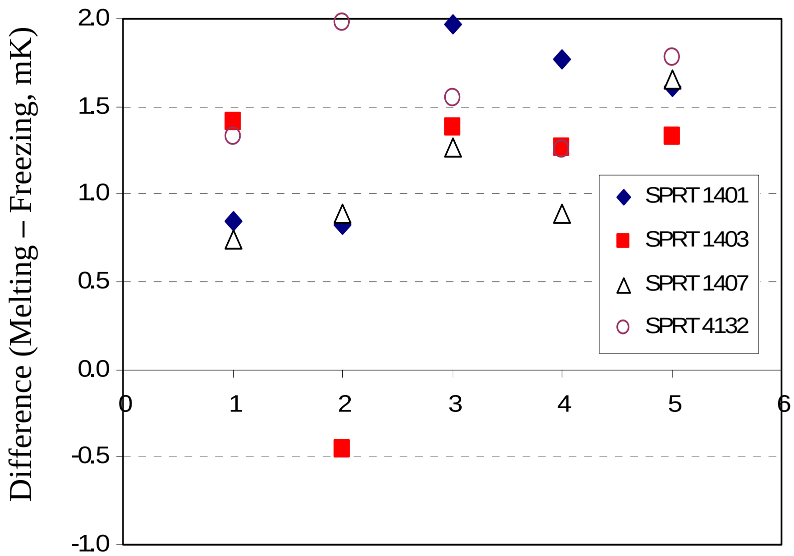


Figure 2. Comparison of the melting plateau and the freezing plateau of the aluminum cell.

2.2 Comparison of the melting and freezing plateaus of silver

Similar procedures as for the aluminum cell were used to realize the melting and freezing plateaus of the silver cell. Four HTSPRTs were used in the test. According to the trial experimental results in this study, the melting plateaus of silver did not reach stable valve until six to twelve hours later after melting started. In this study, the waiting time of six hours was used in testing the silver cell melting plateaus, and two hours for testing freezing plateaus. 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. Three groups of plateau measurements were collected.

Figure 3 shows melting and freezing plateaus observed with the silver cell. The duration of the melting plateau is about 25 hours, which is longer than the duration of the freezing plateau (15 hours). It can be seen that the freezing plateau is more stable than the melting plateau. The amplitude of the melting curve fluctuation can reach over 2.0 mK, but only 0.4 mK for the freezing plateau. It appears that for high temperature defining fixed point metals the freezing plateau is much more stable and reproducible than the melting plateau.

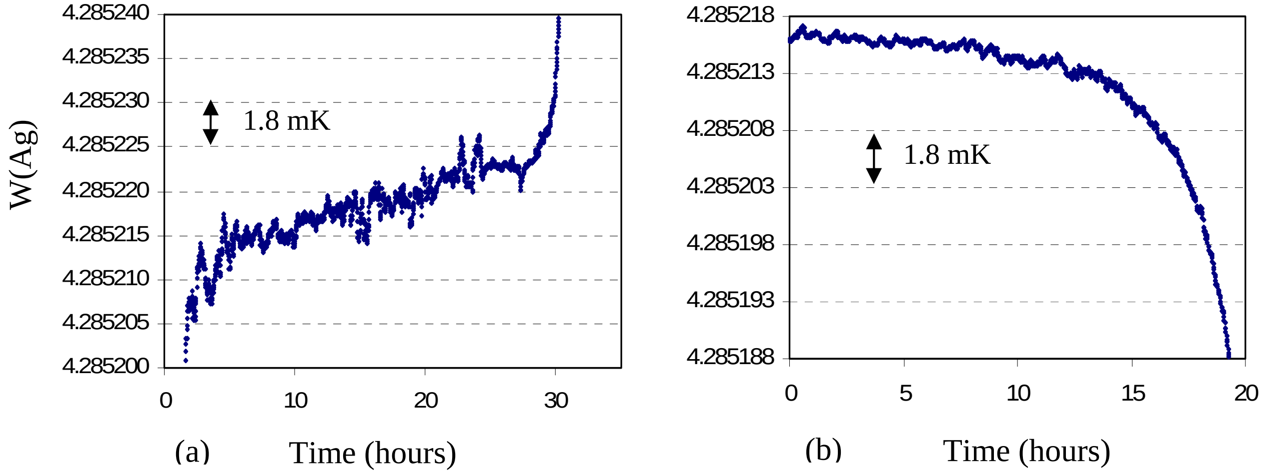


Figure 3. The melting plateau (a) and the freezing plateau (b) of the silver cell.

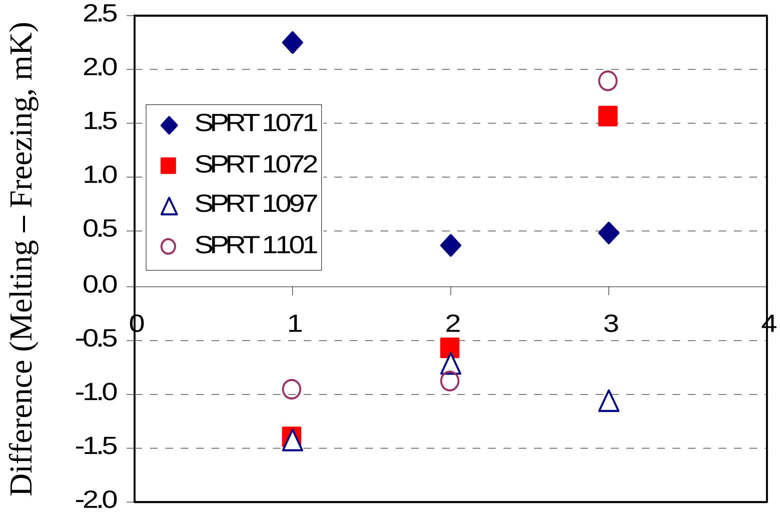


Figure 4. Comparison of the melting plateau and the freezing plateau of the silver cell.

Figure 4 compares the melting and freezing temperatures of the silver cell. The largest difference is 2.26 mK, and the smallest is 0.37 mK. The average difference is 0.042 mK. Because the melting plateau of the silver cell is not stable compared to the freezing plateau as seen in Figure 3, the length of the waiting time for testing melting plateau has a large influence on the comparison testing results. Figure 3 (a) shows that when testing melting plateau, it is better to wait over 10 hours before start the comparison testing in order to get suitable melting point values.

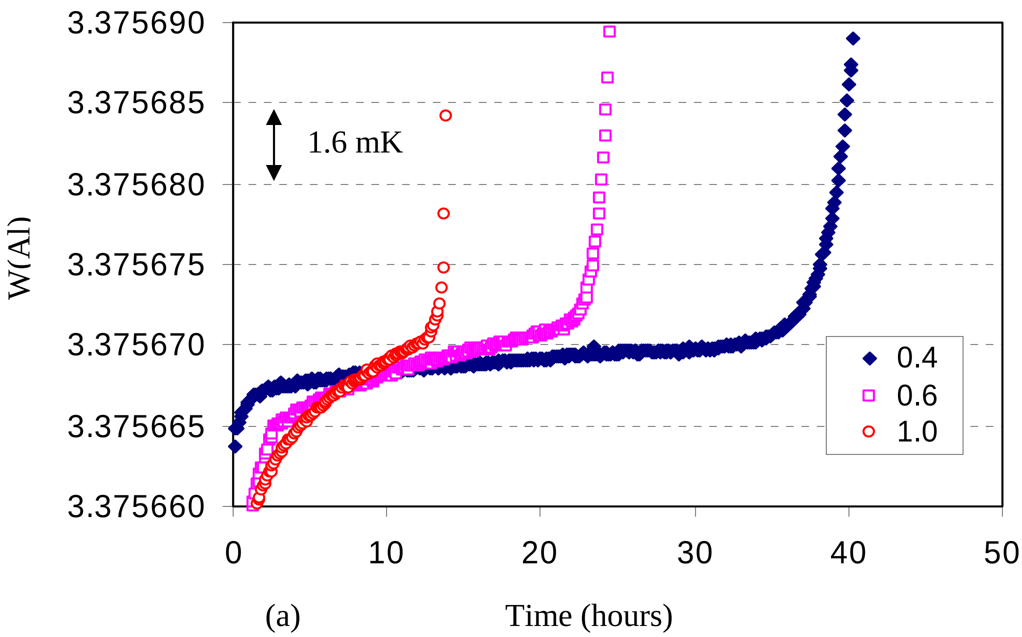
2.3 Influence of the furnace maintenance temperature on aluminum and silver

The furnace maintenance temperature has big influence on the performance and quality of the melting and freezing plateaus of aluminum and silver cells. In the experiment, three different furnace maintenance temperatures were tested. Figure 5 shows the melting plateaus (Figure 5(a)) and the freezing plateaus (Figure 5(b)) of aluminum with three temperature settings (above the theoretical melting temperature for melting plateau, and below the theoretical freezing temperature for freezing plateau). It can be seen that both the duration of the melting and the freezing plateaus decrease significantly as the furnace maintenance temperature is increased. The melting plateau duration drops from 35 hours to 15 hours, and the freezing plateau duration drops from 18 hours to 8 hours with the furnace maintenance temperature increasing from 0.4 °C to 1.0 °C. Figure 6 shows the melting plateaus (Figure 6(a)) and the freezing plateaus (Figure 6(b)) of silver at three furnace maintenance temperature settings. It shows that the duration of the melting plateaus drops from 20 hours to 8 hours, and drops from 15 hours to 8 hours for the freezing plateaus with the furnace maintenance temperature setting increasing from 0.4 °C to 1.0 °C.

Figure 5 and Figure 6 also show that the duration of the melting plateaus of both aluminum and silver are longer than that of their freezing plateaus at the same furnace maintenance temperature settings. For example, the duration of the melting plateau of aluminum is 35 hours at the temperature setting of 0.4 °C, but only 16 hours for the freezing plateau at the same temperature setting. The experimental results show that the furnace maintenance temperature should be set close to the theoretical melting or freezing point in order to a get a long melting or freezing plateau. According to our experiment experience, the temperature setting of 0.4 °C is suitable for aluminum, and 0.3 °C for silver.

3. UNCERTAINTY ESTIMATION

The estimated uncertainties of the melting plateaus and the freezing plateaus of aluminum and silver are listed in Table 1. The purities of both aluminum and silver are higher than 99.9999%.



(a)

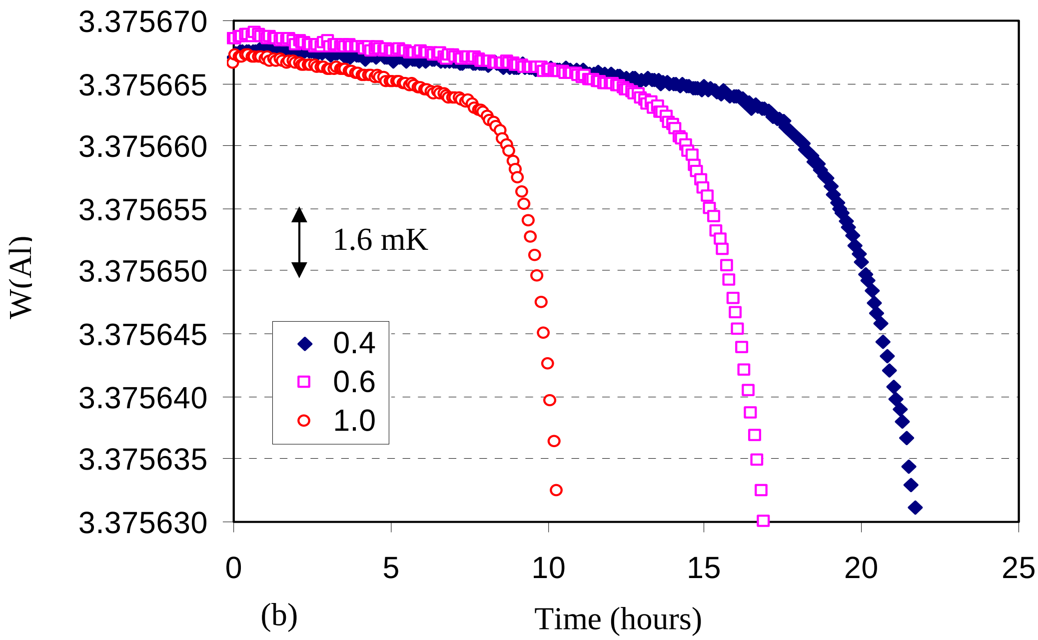
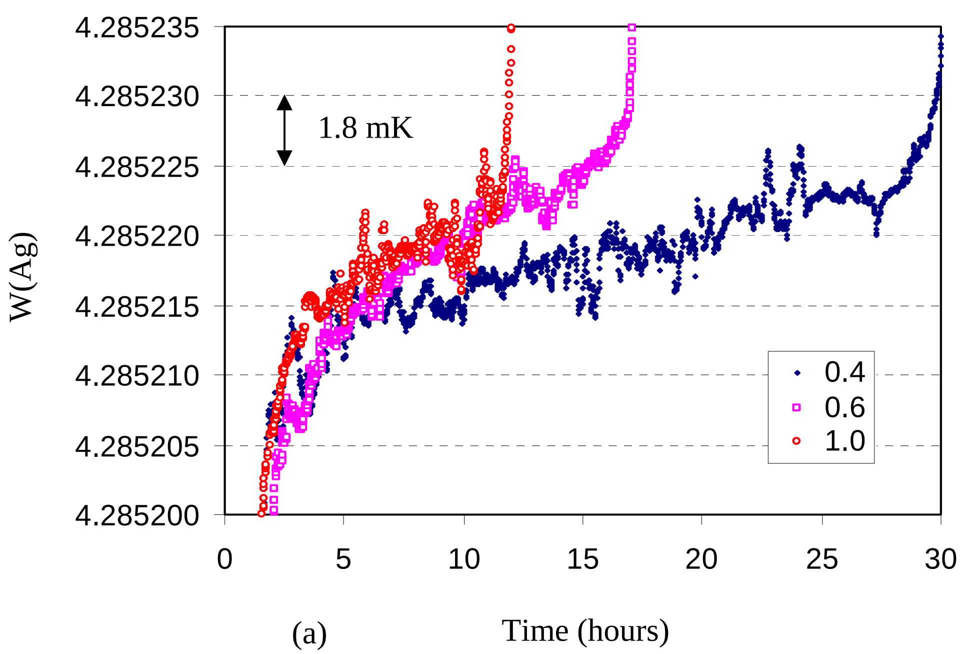


Figure 5. Melting and freezing plateaus of aluminum at three different furnace maintenance temperatures: 0.4, 0.6, and 1.0 °C, respectively.



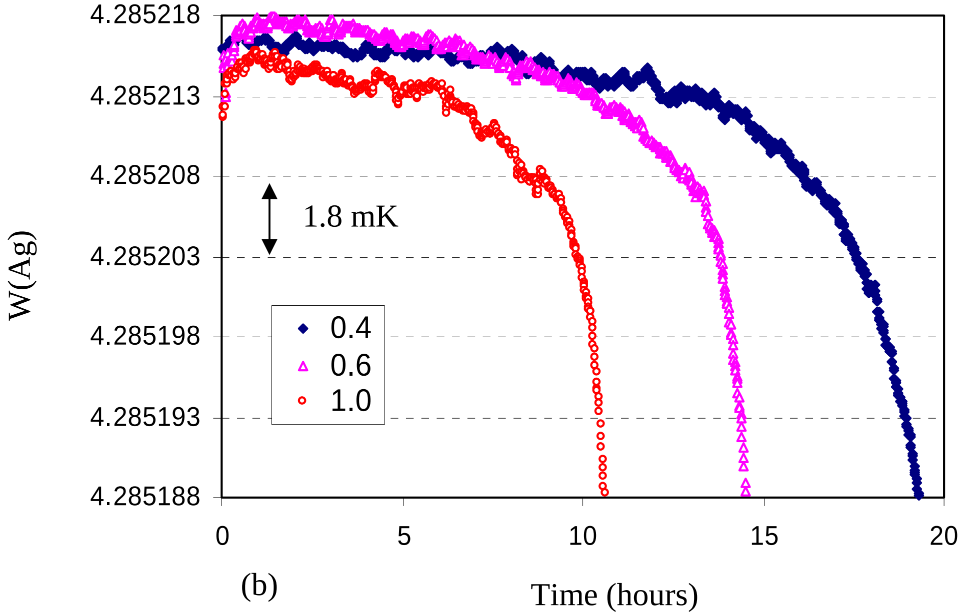


Figure 6. Melting and freezing plateaus of silver at three different furnace maintenance temperatures: 0.4, 0.6, and 1.0 °C, respectively.

The estimated uncertainties (k=2) are 1.036 mK for the freezing plateau of aluminum, and 1.84 mK for the melting plateau of aluminum. The uncertainty of the freezing plateau of silver is 2.044 mK, but drops to 2.996 mK for the melting plateau. If the purity of aluminum and silver can be improved to 99.99999%, the uncertainties of both the freezing and the melting plateaus can be improved to 0.80 mK and 1.72 mK for aluminum, and 1.22 mK and 2.50 mK for silver respectively.

Table 1. Estimated uncertainties of the melting and freezing plateaus of aluminum and silver.

	Aluminum (mK)		Silver (mK)	
Source of uncertainty	Freezing	Melting	Freezing	Melting
Resistance reading (A)	0.056	0.056	0.122	0.122
Reproducibility (A)	0.380	0.850	0.580	1.240
Total A	0.384	0.852	0.593	1.246
Impurities (B)	0.330	0.330	0.820	0.820
Hydrostatic correction (B)	0.006	0.006	0.022	0.022
Pressure correction (B)	0.005	0.005	0.004	0.004
Immersion (B)	0.016	0.016	0.025	0.025
SPRT self heating (B)	0.030	0.030	0.030	0.030
Propagated from TPW (B)	0.100	0.100	0.130	0.130
Bridge non-linearity (B)	0.025	0.025	0.025	0.025
Total B	0.347	0.347	0.832	0.832
Total standard uncertainty	0.518	0.920	1.022	1.498
Expanded uncertainty (k=2)	1.036	1.840	2.044	2.996

The experimental results (the melting plateau duration and stability) and the uncertainty estimations for aluminum show that although the melting plateau is not as stable as its freezing plateau, it could be used for the calibration of SPRTs in secondary-level laboratories. But because the silver melting plateau curve fluctuates with an amplitude of over 2.0 mK, it is not suitable to be used for calibration of SPRTs.

4. CONCLUSION

The experiment results comparing the melting and freezing plateaus of aluminum and silver show that the duration of the melting plateau of both aluminum and silver is longer than that of their freezing plateaus, but the stability of the melting plateaus is worse compared to their freezing plateaus. The differences in temperature were up to 2.0 mK for aluminum and 2.26 mK for silver. The estimated uncertainties of the freezing plateau and the melting plateau are 1.036 mK and 1.840 mK respectively for aluminum, and 2.044 mK and 2.996 mK for silver. Both the experiment and uncertainty estimation results show that although the melting plateau of aluminum is not as stable as the freezing plateau, it should be good enough for the calibration of SPRTs in secondary-level laboratories while offering greater convenience. But the melting plateau of silver is not suitable to be used to calibrate SPRTs because of its instability.

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