The Comparison Between the Freezing Point and Melting Point of Tin

Xumo Li, Mike Hirst
Hart Scientific, Inc.
799 E Utah Valley Drive
American Fork, UT 84003-9775
Phone: 801.763.1600 Fax: 801.763.1010
Internet: http://www.hartscientific.com

The Comparison Between the Freezing Point and Melting Point of Tin

Xumo Li, Mike Hirst
Hart Scientific, Inc.

Abstract

Preliminary data from thirteen Standard Platinum Resistance Thermometers (SPRTs) on eighteen pair of freezing and melting curves of high-purity tin (better than 99.9999%) showed that the average calibration difference between the melting point and freezing point was within approximately 0.3 mK. Therefore, the melting point of tin (MPT) can be used to calibrate SPRTs instead of the freezing point of tin (FPT) for most situations.

Further investigation was made toward improvement of the reproducibility and accuracy of MPT in order to see if it is possible to use it instead of FPT as a defining fixed point for the International Temperature Scale as is the case with gallium. In order to acquire the highest accuracy from MPT, the following key points were found to be vital: the highest possible purity tin must be used; the temperature uniformity in the furnace should be better than 10 mK throughout a vertical distance of 180 mm; an inner melting technique must be used to create two liquid-solid interfaces in the crucible during the entire melting course; and in order to distribute all remaining impurities uniformly, the tin should be maintained overnight at a temperature of 1°C below the melting point. Two SPRTs were calibrated in this way at the MPT and the FPT alternately. The average differences between the melting point and the freezing point were well within 0.1 mK for both SPRTs. It seems that the MPT, rather than the FPT, may be used as a defining fixed point of the International Temperature Scale.

Introduction

The FPT is one of the defining fixed points of the International Temperature Scale of 1990 (ITS-90) and is broadly used to calibrate SPRTs. Because of the large amount of supercooling, the realization of the FPT is much more difficult and inefficient than the freezing point of zinc or other freezing points. It was found that the MPT with a high-purity tin (better than 99.9999%) gives almost the same value as the FPT. Using the MPT provides many obvious benefits as compared to using the FPT. It is much easier to realize and requires less training. Also, it is very easy to obtain a very long melting plateau (usually longer than 24 hours) in which many SPRTs can be calibrated in a single melt. Considering that the melting point of gallium is accepted as one of the defining fixed points of the ITS-90, we must ask: Why can we not do the same for tin? So we decided to investigate the MPT further in order to improve its reproducibility and accuracy and to see if it is possible to use the MPT as a defining fixed point of the International Temperature Scale.

Preliminary Comparison Between MPT and FPT

The equipment and procedures used to realize the FPT and other fixed points in the range from 0°C through 961.78°C have been reported in detail elsewhere [1,2]. Here we will only give some of the main points. A three-zone furnace is used for the FPT and the MPT. The distinguishing feature of the furnace is that cold air can be introduced into the furnace from the bottom to flow upward around the fixed-point cell in order to provide sufficient cooling to initiate recalescence during the start of a freezing curve.

We usually maintain the furnace overnight at about 2°C higher than the freezing point. The next morning, we decrease the furnace temperature until the temperature indicated by an SPRT inserted in the cell is close to the freezing point. Then cold air is introduced into the furnace from the bottom allowing it to flow upward around the fixed-point cell to induce the freeze. A solid shell of tin of approximately uniform thickness is formed at the outer walls of the crucible. As soon as recalescence starts, we shut off the cold air and keep the furnace at a stable temperature of 1°C below the freezing point. Then we take the monitor SPRT out of the furnace and insert a cold quartz rod into the tin cell for one minute to form a thin mantle of solid tin around the thermometer well. After that, the SPRT to be calibrated is inserted into the tin cell.

The procedure for realizing the MPT is very simple. We maintain the furnace at about 1°C below the melting point overnight. The next morning we raise the furnace temperature to about 6°C higher than the melting point. As soon as the melting starts, we set the furnace at a stable temperature 1°C higher than the melting point. A very long and flat melting plateau is usually obtained in this way. Ten or more SPRTs can be calibrated in a single melting plateau.

In order to compare the MPT with the FPT we have calibrated SPRTs both at the MPT and the FPT in our laboratory since the beginning of 1995. Much of the data has been accumulated and analyzed. The preliminary comparison results have been published [3]. The average difference between the melting point and the freezing point of tin from eighteen groups of calibration results of thirteen SPRTs was –0.33 mK with a standard deviation of 0.51 mK. It is clear that the MPT can be used for most SPRT calibrations where an expanded uncertainty (k=2) of about 1.5 mK or larger is acceptable.

Improvement of the Melting Point of Tin

It was found in our research that the following four factors have great influence on the reproducibility and accuracy of the MPT. The first is the purity of tin used. The higher the purity of tin, the better reproducibility and accuracy obtained. 99.99992% of tin is the highest purity we can get right now. Generally speaking, the purer the material used, the easier it can be contaminated. So it is equally important to maintain the purity during the entire life of the tin cell. The sealed cell design and technique seem to be effective at maintaining the integrity of the metal [1,2]. The total impurity in the graphite which comprises the crucible is less than 3 PPM. The crucible and other graphite parts used were subjected to a high-temperature, high-vacuum treatment just before loading the tin sample. Melting the tin into the crucible and assembling the cell were performed in a high vacuum or high-purity argon atmosphere. The assembled graphite crucible, with the high-purity tin, was then enclosed in a quartz cell and connected to a high vacuum system. The cell was pumped to high vacuum at a temperature slightly higher than the freezing point of tin for several days. During this period the cell was purged with high purity argon repeatedly. Finally, the cell was filled to 1 atmosphere at the melting point with 99.999% pure argon and permanently sealed.

Second, an inner melting technique was found to significantly improve the melting curve. It was observed during the preliminary comparison that the value at the beginning of the melting

curves was often a little lower (0.1 mK – 0.5 mK) than the eventual point of stability which is very near the freezing value. It would usually take 2 – 3 hours to attain this point of stability. That explains why some of the data for the MPT during our preliminary comparison was lower than the data for the FPT, since we usually started to calibrate SPRTs in about thirty minutes after melting started, which we now recognize as too soon. Two liquid-solid interfaces during a melting plateau are helpful as is true during a freezing curve [4]. In order to obtain the second liquid-solid interface, take the monitor thermometer out of the cell as soon as the melting starts and insert a quartz rod pre-heated to 280°C into the tin cell for two minutes. In this way a second, very thin, liquid-solid interface is formed around the thermometer well. Then take the quartz rod out and put the SPRT to be calibrated into the furnace and start the measurement after about forty minutes. The SPRT should be heated to a temperature very close to the melting point before inserting it into the furnace. The procedure described here provides a flatter melting curve (especially at the beginning of the curve) and much more reproducible calibration results.

Third, we can improve the temperature uniformity in the furnace. Only a very uniform temperature distribution around the tin sample will create a uniform liquid-solid interface. There are three heaters in the furnace. The main furnace heater was wound over the entire furnace core. The upper and lower heaters were wound only on the top and bottom ends of the core. Three separate temperature controllers were used for the three zones. The maximum temperature difference throughout a 180 mm distance from the bottom of the central well upward was about 0.06°C during the preliminary comparison. By carefully adjusting the set-point values of the top and bottom controllers, we can obtain a uniform vertical temperature distribution profile with a maximum temperature difference of 0.007°C (Figure 1).

Fourth, we "anneal" the tin sample at a temperature 1°C below the melting point overnight before taking a melting curve. This treatment will distribute impurities in the tin more uniformly and will further improve the melting curve.

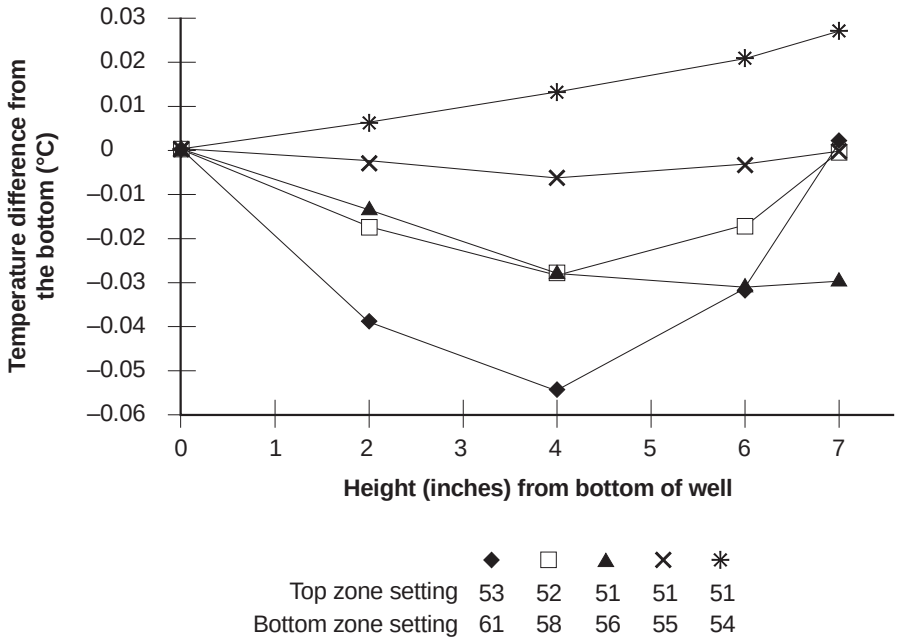

Figure 1. *Temperature distribution profiles in the furnace at different top and bottom zone set values.*

Accurate Comparison Between the MPT and the FPT

Using the new procedure for the MPT, we made a second set of comparisons between the MPT and the FPT. Two SPRTs were used for the comparison. They were calibrated at the FPT and the MPT alternately until eight calibration results were obtained for each thermometer—four from the FPT and four from the MPT. The main results obtained in the comparison are shown in Table 1 and Table 2.

Table 1. Comparison between data of MPT and FPT, SPRT S/N: 1031

	W (Sn)		Difference	
Date	FPT	MPT	ΔW	Δt
12/27/1995	1.89269766			
12/28/1995		1.89269862		
12/29/1995	1.89269931			
1/2/1996		1.89269907		
1/31/1996	1.89269892			
2/1/1996		1.89269850		
2/2/1996	1.89269890			
2/5/1996		1.89269840		
Average	1.892698698	1.892698648	0.000000050	0.01 mK
S. D. (W)	0.000000717	0.000000296		
S. D. (t)	0.19 mK	0.08 mK		

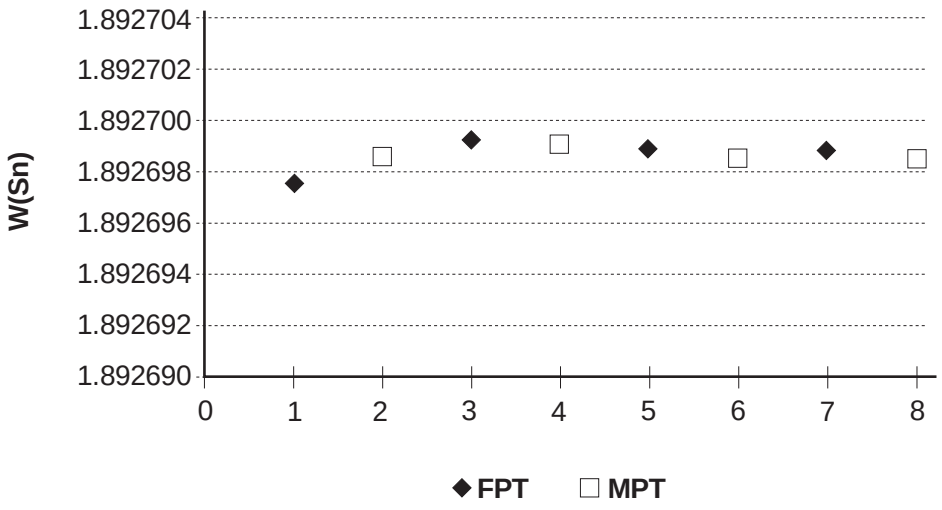

Figure 2. *Comparison between the MPT and the FPT, SPRT S/N:1031*

Table 2. Comparison between data of the MPT and the FPT, SPRT S/N: 1037

	W (Sn)		Difference	
Date	FPT	MPT	ΔW	Δt
12/27/1995	1.89264430			
12/28/1995		1.89264502		
12/29/1995	1.89264684			
1/2/1996		1.89264565		
1/31/1996	1.89264534			
2/1/1996		1.89264568		
2/2/1996	1.89264616			
2/5/1996		1.89264640		
Average	1.892645660	1.892645688	–0.000000028	–0.01 mK
S. D. (W)	0.000001095	0.000000564		
S. D. (t)	0.29 mK	0.15 mK		

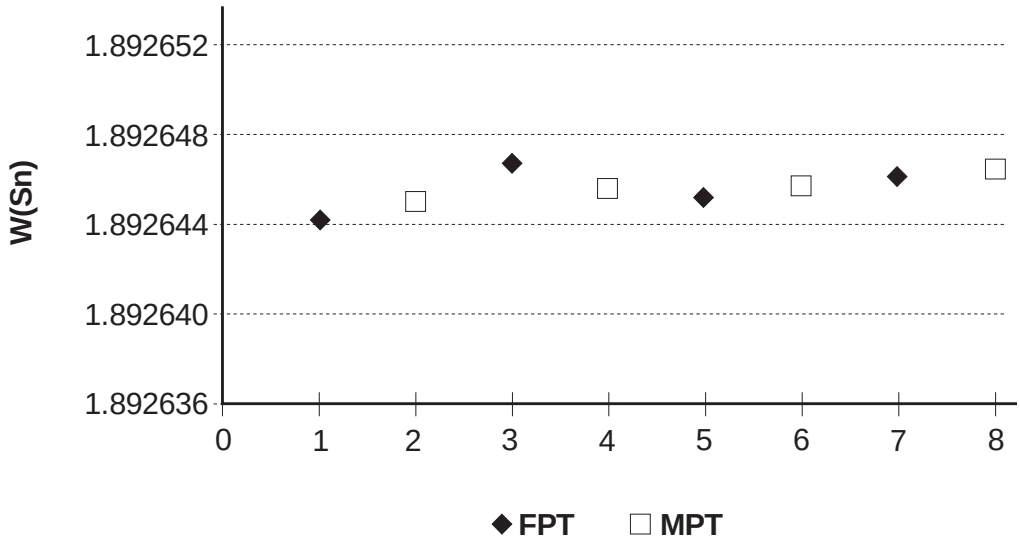

Figure 3. *Comparison between the MPT and the FPT, SPRT S/N: 1037*

The combined standard deviation calculated from all eight data points for SPRT S/N 1031 was 0.14 mK and for SPRT S/N 1037, 0.22 mK. The average values and standard deviations for the MPT, FPT and combined data are compared in Figure 4 and Figure 5. The differences between the MPT and the FPT average values were extremely small, much smaller than the standard deviations. All the data appear to belong to the same normal distribution and no obvious systematic differences are found between the MPT and the FPT.

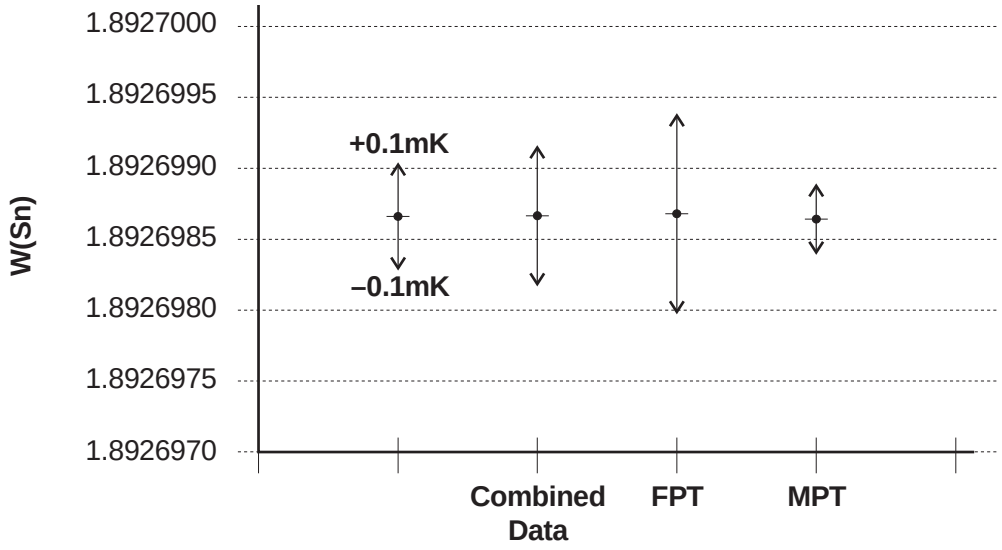

Figure 4. *Comparison of the absolute values and standard deviations among the MPT, FPT and combined data, SPRT S/N: 1031*

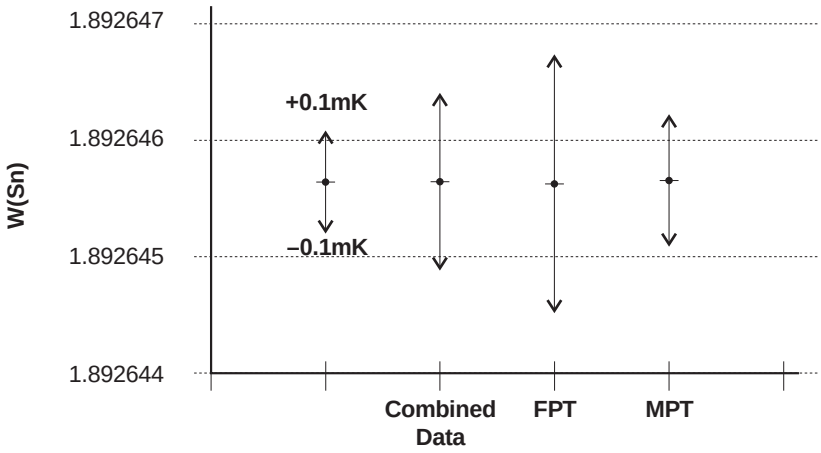

Figure 5. *Comparison of the absolute values and standard deviations among the MPT, FPT and combined data, SPRT S/N: 1037*

Conclusion and Suggestion

The MPT is at least as accurate as the FPT and there is no systematic error between the MPT and the FPT. The MPT has many advantages compared with the FPT as detailed in Table 3.

Table 3. Comparison between the MPT and the FPT with a purity of 99.9999%

	FPT	MPT
Reproducibility	Excellent Usually 0.1 mK to 0.2 mK	Excellent Usually 0.1 mK to 0.2 mK
Absolute value	Same as MPT	Same as FPT (The difference between MPT and FPT is within 0.1 mK)
Duration of plateau	Very long Usually 15 – 20 hours	Extremely long Usually longer than 24 hours
Efficiency	Poor 3 or 4 SPRTs can be calibrated on a single freezing plateau	Excellent 10 or more SPRTs can be calibrated on a single melting plateau
Degree of difficulty	Very difficult	Not difficult
Training required	Formal and extensive training is required	Brief training is adequate

It is strongly hoped that other laboratories repeat the tests described in this paper. If they obtain similar results, we suggest that the melting point of tin should replace the freezing point of tin as the defining fixed point in the upcoming amended edition of ITS-90.

Acknowledgments

The authors are grateful to Chris Juchau for meaningful advice and useful discussions and to Wayne Newland for help drawing figures and formatting the paper.

References

[1] Xumo Li et al, “The Comparison of the Freezing Point of Zinc”, 1995 NCSL Workshop & Symposium, p.747

[2] Xumo Li et al, “Realization of ITS-90 from 273.15 K through 1234.93 K: One Company’s Approach”, Measurement Science Conference 1996

[3] Xumo Li et al, “The Melting Point of Tin”, 1996 NCSL Workshop & Symposium, p.419

[4] Comite Consultatif de Thermometrie, Supplementary Information for the ITS-90, Bureau International des Poids et Mesures (BIPM), 1990