

THE MELTING POINT OF TIN

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Abstract

The benefits of using the melting point of tin (MPT) rather than its freezing point as a temperature fixed point are discussed. A procedure for the realization of the MPT with high accuracy was developed. An improved procedure for inducing the freeze by using outside-gas-flow cooling is also described. The calibration data obtained from the MPT are compared with that from the freezing point of tin. Thirteen SPRTs were calibrated on eighteen pairs of freezing curves and melting curves. The average difference between the melting point and freezing point was found to be -0.33 mK. The MPT can, therefore, be used to calibrate SPRTs instead of the freezing point of tin in the situations where an expanded uncertainty ($k=2$) of about 1.5 mK or larger is acceptable, which satisfies most requirements for SPRT calibrations.

Introduction

The freezing point of tin is one of the defining fixed points of the International Temperature Scale of 1990 (ITS-90) and is broadly used to calibrate standard platinum resistance thermometers (SPRTs). Because of its large amount of supercooling, the realization of the freezing point of tin is much more difficult and inefficient than the freezing point of zinc or other freezing points. Tin melting point is generally considered to be less accurate than its freezing point. But, it is much more easily realized and it provides a very long melting plateau which permits more than one SPRT to be calibrated in a single melting curve.

Melting curves of high-purity tin (99.9999+%) measured in the laboratory show that a large portion of each melting curve is extremely flat and the so-called 90% melting ranges were well within 1 mK. We investigated the reproducibility and accuracy of the tin melting point as an alternative calibration point for SPRTs rather than the freezing point of tin.

Fixed Point Furnace and Tin Point Cell

In order to obtain a long and flat freezing curve or melting curve with a high-purity sample, it is extremely important to provide a temperature envelopment that is uniform, stable and controlled. A new three-zone furnace was designed and developed for this purpose (Fig. 1). The main furnace heater was wound over the entire furnace core. The upper and lower zone heaters were wound only on the top and bottom ends of the core. These zone heaters assist in bringing the core into temperature uniformity across its entire length. Three separate temperature controllers were used for the three zones. The top and bottom zones are slaved to the center zone and offsets due to the thermocouple sensors can be adjusted by changes in the controller set values. The vertical temperature distribution profile of the furnace can then be adjusted by means of the top and bottom controller set values. A few examples of temperature distribution profiles at different set values are shown in Fig. 2 and Table 1. It is not difficult to obtain a temperature uniformity of 0.01°C in a region of 7 inches (178 mm).

There is a RS-232 interface in the main heater controller allowing it to be connected to a personal computer to create an automatic calibration system. Another 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 the recalescence during the start of a freezing curve.

A sealed tin point cell was used throughout the work. The design of the cell has been described in detail previously ^[1].

Table 1 Vertical temperature distributions at different top and bottom set values.

	Set Values				
	53	52	51	51	51
Top	53	52	51	51	51
Bottom	61	58	56	55	54
Height (inches)	Temperature difference from the bottom, Δt (°C)				
0 (0 mm)	0	0	0	0	0
2 (51 mm)	-0.0384	-0.0172	-0.0126	-0.0027	0.0066
4 (102 mm)	-0.0548	-0.0276	-0.0274	-0.0063	0.0133
6 (152 mm)	-0.0317	-0.0171	-0.0309	-0.0030	0.0209
7 (178 mm)	0.0033	0.0005	-0.0292	-0.0001	0.0275
Maximum difference in the region	0.0581	0.0281	0.0309	0.0063	0.0275

Realization of the Freezing Point and Melting Point of Tin

Because of a large amount of supercooling when high purity tin freezes, it is necessary to use a special process to induce the freeze. The classic method is to extract the crucible of tin into the throat of the furnace or out of the furnace and to hold the crucible in the cooler environment until recalescence occurs. ^[2,3] The crucible is then immediately lowered into the furnace, which will still be close to the freezing temperature. A very flat freezing plateau

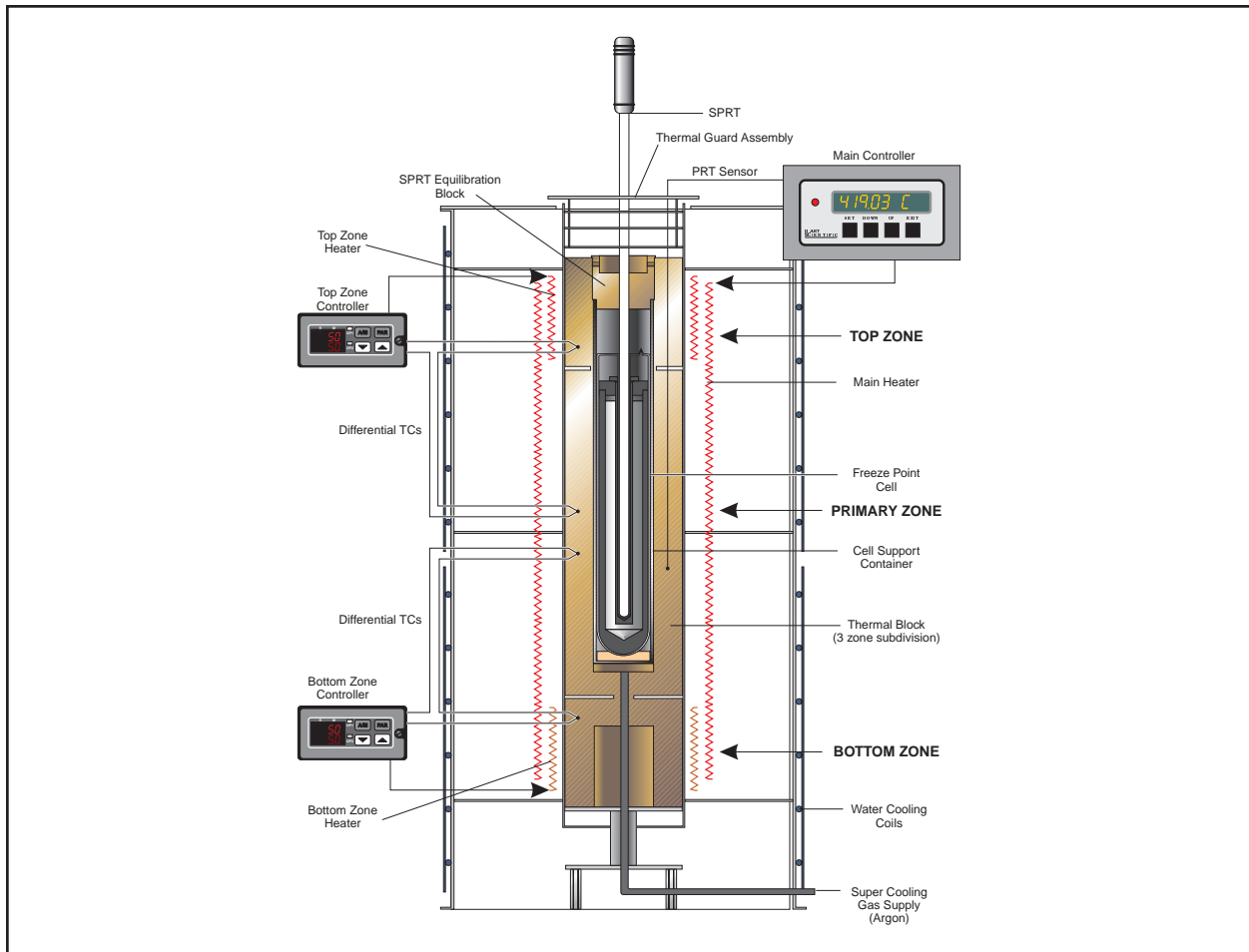


Figure 1 Fixed Point Furnace

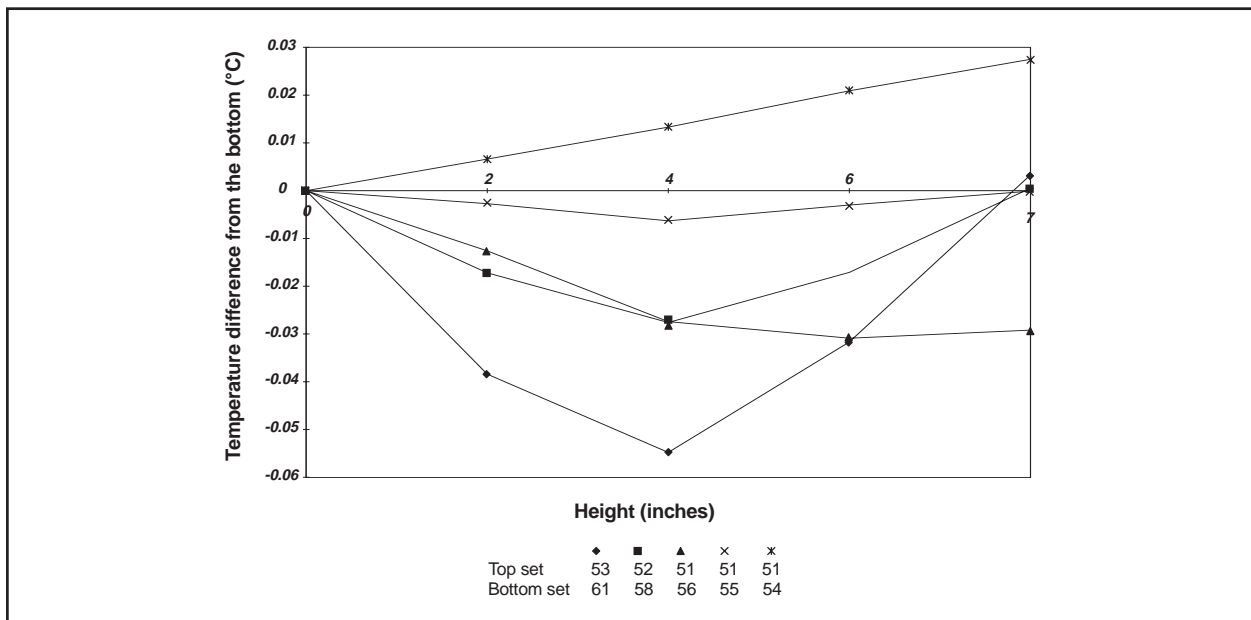


Figure 2 Temperature distribution profiles at different set values.

and a highly reproducible freezing point could be obtained in this way. However, it is difficult to operate, especially when using a sealed tin cell instead of the more traditional crucible holder design.

Our experiments yield a more convenient procedure for introducing freeze. First, we raised the temperature of the furnace about 10°C higher than the freezing point. After all metal was completely melted, we set the furnace to a stable temperature about 2°C higher than the freezing point and left it over night. The next morning, we programmed the furnace temperature to decrease at a rate of 0.2°C per minute and then we monitored the tin sample temperature using an SPRT inserted in the cell. When the tin sample temperature reached the freezing point, cold air was 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 was formed at the outer walls of the crucible. As soon as recalescence started, we shut off the cold air and kept the furnace at a stable temperature of 1°C below the freezing point. Then we took the SPRT we used to monitor the furnace temperature out of the furnace and inserted 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 was inserted into the furnace and into the tin cell. In this way a very flat freezing curve was usually obtained.

A typical freezing curve is shown in Fig. 3. The reproducibility of the freezing point of tin in the laboratory is 0.2 mK and the expanded uncertainty ($k=2$) is 0.9 mK^[1].

The following instructions lead to the realization of the melting point of tin. Keep the furnace temperature at 1°C below the melting point over night. The next morning increase the furnace temperature to 6°C above the freezing point at a rate of 0.5°C per minute. When the temperature of the tin sample, indicated by a monitor SPRT, stops rising, move the monitor SPRT from the furnace and insert a quartz rod pre-heated to 280°C into the tin cell for one minute to melt a thin film of tin around the thermometer well. Then a pre-heated

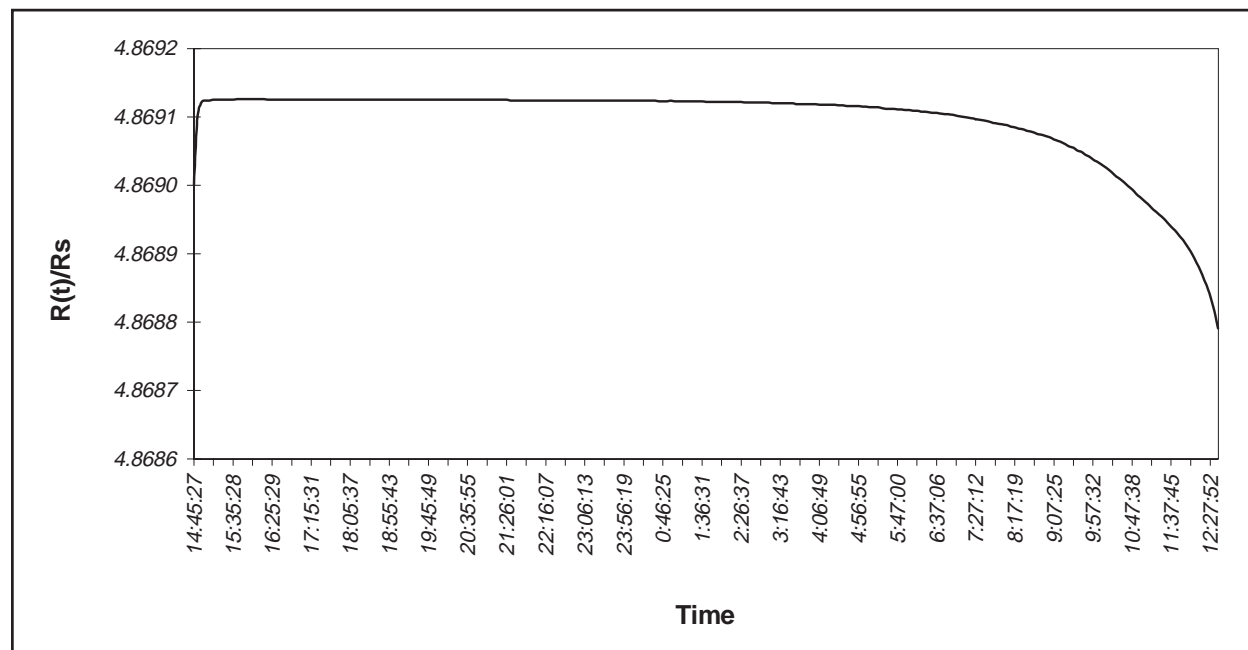


Figure 3 A typical freezing curve of tin.

SPRT to be calibrated is inserted into the tin cell and the furnace temperature is kept stable at a temperature of 1°C above the melting point. A very flat melting curve, which usually lasts longer than 24 hours, can be obtained in this way. A typical melting curve is shown in Fig. 4. It is possible that ten or more SPRTs can be calibrated on a single melting curve. The realization of the melting point of tin is much easier and more efficient than the freezing point.

An automatic direct-current-comparator resistance bridge Model 6675 was used to measure resistance of SPRTs. The expanded uncertainty for measurement of the ratio of two resistances is less than 0.2 ppm. The bridge was connected to a personal computer through an IEEE-488 interface to constitute an automatic measurement system. The software was written using C-language. All data acquisition was controlled by the computer and most of the calculations, such as self-heating correction of SPRTs and static head correction, were performed automatically by the computer as well.

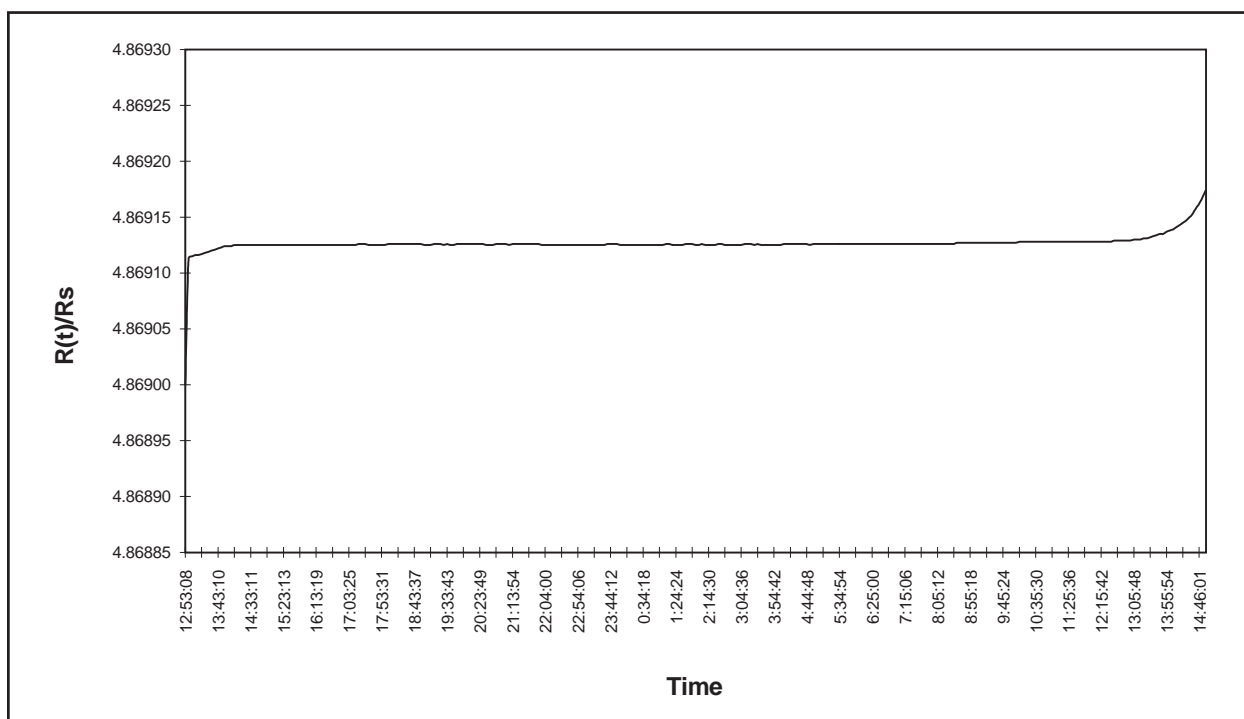


Figure 4 A typical melting curve of tin.

Comparison between the Melting Point and Freezing Point

It is routine practice to calibrate an SPRT both at the freezing point and at the melting point of tin in the laboratory. Much of the data have been accumulated to allow us to analyze the difference between the melting point and the freezing point of tin. Eighteen groups of calibration results of thirteen SPRTs are listed in Table 2. The average difference between the melting point and the freezing point of tin was found to be -0.33 mK with a standard deviation of 0.51 mK, which can be ignored for most SPRT calibrations. Some early data in Table 2 were obtained without inner melting at the beginning of the melting curve, and the melting point calibration results are a little lower than that from the freezing point. Recently the results obtained by using an inner melting technique yield a much better

Table 2 Comparison between the Melting Point and Freezing Point of Tin.

SPRT S/N	Melting Point		Freezing Point		W(Sn)
	Date	W(Sn)	Date	W(Sn)	
1001	2/21/95	1.89267607	2/22/95	1.89267744	-1.37E-6
1016	10/13/95	1.89280507	10/11/95	1.89280807	-3.00E-6
1016	10/18/95	1.89280544	10/19/95	1.89280744	-2.00E-6
1016	11/01/95	1.89280664	10/31/95	1.89280961	-2.97E-6
1018	10/18/95	1.89280565	10/19/95	1.89280463	1.02E-6
1018	11/01/95	1.89280431	10/31/95	1.89280568	-1.37E-6
1021	5/30/95	1.89280743	5/31/95	1.89280951	-2.08E-6
1022	5/30/95	1.89280803	5/31/95	1.89280850	-0.47E-6
1024	5/30/95	1.89280270	5/31/95	1.89280145	1.25E-6
1029	10/13/95	1.89269816	10/11/95	1.89270032	-2.16E-6
1029	10/18/95	1.89269802	10/19/95	1.89270064	-2.62E-6
1029	11/01/95	1.89270084	10/31/95	1.89270113	-0.29E-6
4175	5/30/95	1.89257489	5/29/95	1.89257284	2.05E-6
92017	1/17/95	1.89264625	1/16/95	1.89264705	-0.80E-6
92172	2/21/95	1.89237752	5/29/95	1.89237991	-2.39E-6
92221	1/17/95	1.89275779	1/16/95	1.89275818	-0.39E-6
92222	1/12/95	1.89273827	2/22/95	1.89274006	-1.79E-6
RS94X-12	5/30/95	1.89263898	5/29/95	1.89264133	-2.35E-6
Average					-1.207E-6 (0.33 mK)

agreement between the melting point and freezing point of tin. The investigation is still in progress and a better result will be obtained in the near future..

Conclusions

The following conclusions can be obtained from the work:

1. The melting point of tin realized in the way described in this paper can be used to calibrate SPRTs rather than using the freezing point of tin. Except for the situations where the highest accuracy is required, such as in some national laboratories, the melting point of tin is an excellent choice for SPRT calibrations.
2. Using the melting point of tin provides many benefits as compared to using freezing point of tin. The melting point of tin is easier to achieve, requires less training and makes calibration work more efficiently.

References

1. Xumo Li et al, "Realization of ITS-90 from 273.15 K through 1234.93 K: one company's Approach", Measurement Science Conference 1996
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