Realization of ITS-90 from 273.15 K through 1234.93 K: One Company's Approach

Xumo Li, Steve Iman, Mike Hirst, Mingjian Zhao
Hart Scientific, Inc.

Abstract

All of the fixed points of the International Temperature Scale of 1990 (ITS-90) in the range from 273.15 K to 1234.93 K have been realized in specially-designed, permanently-sealed cells. The purity of all of the metals used was 99.9999% or greater. Many improvements in design and techniques used were made in order to get the highest possible accuracy. Since it is important that all of the fixed points be traceable to NIST (National Institute of Standards and Technology), these fixed points were compared with NIST data by using two NIST-calibrated standard platinum resistance thermometers (SPRTs). The differences between the fixed point values and those measured at NIST were within 0.5 mK for the freezing points (FP) of tin and zinc, and within 1 mK for the FP of aluminum. The expanded uncertainties (coverage factor K=2) at the fixed points were 0.4 mK for the melting point (MP) of gallium, 1.0 mK for the FP of indium, tin, and of zinc, 4.0 mK for the FP of aluminum and 10 mK for the FP of silver. Two SPRTs were used to interpolate between the fixed points. A 25-ohm SPRT was used up to 933.473 K and a 0.25-ohm SPRT up to 1234.93 K.

Introduction

The International Temperature Scale of 1990 (ITS-90) became the official international temperature scale on January 1, 1990, superseding the International Practical Temperature Scale of 1968 (IPTS-68). During the last couple of years the efforts of our laboratory have been concentrated on establishing the new international temperature scale between 273.15 K and 1234.93 K. In order to realize all of the defining fixed points through this temperature range it was necessary to develop and manufacture high-quality furnaces and fixed-point cells including the triple point of water, the melting point of gallium, and the freezing points of indium, tin, zinc, aluminum, and silver. These fixed-point cells are of the sealed cell design to aid in the ease of use and convenience of intercomparison. In addition, two highly-stable SPRTs of the authors' design were calibrated by NIST and were used as the standard interpolation instruments in realizing the ITS-90 temperature scale.

Standard Platinum Resistance Thermometer

According to the ITS-90, the temperature between 13.8033 K and 961.78°C is defined by means of a platinum resistance thermometer calibrated at specified sets of defining fixed points. The uncertainties of the realization and dissemination of the ITS-90, therefore, depend closely on the stability of an SPRT. Special attention was paid in developing, testing and improving SPRTs. Three types of SPRTs have been developed and tested. The main specifications are shown in Table 1. The detailed test data are listed in Table 2 and Table 3.

A 25-ohm SPRT (S/N 92017) and a 0.25-ohm SPRT (S/N 92256) were calibrated by NIST and used throughout these tests to compare our fixed-point data with NIST. The data given in the NIST *Reports of Calibration* for these SPRTs are listed in Table 4. The resistance ratios W(t) at the exact

Table 1: Main specifications of three types of SPRTs.

Model	5681	5684	5685
Temperature Range	–189°C to 661°C	0°C to 1070°C†	0°C to 1070°C†
Nominal Resistance at T. P. Water	25Ω	0.25Ω	2.5Ω
Sensor Support	Quartz cross	Quartz strip with notches	Quartz cross
Diameter of Sensor Pt wire	0.07 mm	0.4 mm	0.2 mm
Protecting Sheath	Quartz Diameter: 7 mm Length: 520 mm	Quartz Diameter: 7 mm Length: 680 mm	Quartz Diameter: 7 mm Length: 680 mm
Typical stability of R_{tp}	1 mK/100h at 661°C	1 mK/100h at 1085°C	1 mK/100h at 1085°C

†The official maximum temperature of an SPRT as a defining interpolation instrument of the ITS-90 is 961.78°C, but these types of SPRTs were found to be stable up to at least 1070°C. The annealing temperature during the stability test was 1085°C. The lower temperature limit of these types of SPRTs can be as low as –189°C. In general, it is suggested that a 25-ohm SPRT be used in the range below 0°C.

Table 2: Results of stability tests with 2.5-ohm SPRTs.

R_{tp} (ohms)				Total Annealing time at 1085°C (hours)	Notes
S/N 2001	S/N 2002	S/N 2004	S/N 2006		
2.475910	2.463342	2.469168	2.458491	25	
2.475914	2.463354	2.469171	2.458499	50	
2.475905	2.463357	2.469168	2.458504	75	
2.475910	2.463355	2.469160	2.458514		After 1 thermal cycle†
2.475917	-	2.469162	2.458523		After 1 thermal cycle†

†Thermal cycle procedure: Put tested SPRT into a furnace at 962°C. Take the SPRT out of the furnace after twenty minutes and cool it in the air. Insert the SPRT into the furnace again, and after thirty minutes decrease the temperature of the furnace from 962°C to 480°C at a rate of 100°C per hour. Finally take the SPRT out of the furnace, cool it in the air and measure its R_{tp}.

temperatures of the freezing points of indium, tin, zinc, aluminum and silver were calculated by us

Table 3: Results of stability tests with 25-ohm SPRTs.

R_{tp} (ohms) S/N 1008	S/N 1009	S/N 1010	S/N 1013	Total Annealing time at 660°C (hours)	Notes
25.57653	25.70259	25.57474	25.53706	25	
25.57641	25.70255	25.57452	25.53702	50	
25.57639	25.70248	25.57450	25.53696	75	
25.57644	25.70247	25.57449	-	100	
25.57641	25.70256	25.57443	25.53962		After one thermal cycle†
25.57641	25.70258	25.57443	25.53942		After one thermal cycle†

†Thermal cycle procedure: Put a tested SPRT into a furnace at 660°C. Take the SPRT out of the furnace after twenty minutes and cool it in the air. Insert the SPRT into the furnace again, and after thirty minutes decrease the temperature of the furnace from 660°C to 480°C at a rate of 100°C per hour. Finally take the SPRT out of the furnace, cool it in the air and measure its R_{tp}.

according to the coefficients given in the NIST Reports. These calculated values are listed in Table 4 as well.

Defining Fixed Points

According to the ITS-90, the calibration of an SPRT from 273.16 K to 1234.93 K requires the use of defined fixed points. Actually, the fixed points are the most important part of the ITS-90. All of the

Table 4: The NIST calibration data of two SPRTs used for comparison.

SPRT S/N:	92017		92256	
NIST Test No:	253699		255156	
Date of Report	3 May 1994		13 April 1995	
	For zero-power	**For 1.0 mA**	**For zero-power**	**For 14.14 mA**
a_7 or a_6	–1.5526301E-04	–1.5988934E-04	3.6806657E-05	3.2513557E-05
b_7 or b_6	–1.5007187E-05	–1.7190604E-05	7.1081548E-05	6.1878236E-06
c_7 or c_6	2.2808655E-06	2.8945480E-06	–2.1652828E-06	–1.8774523E-06
d			5.1265611E-06	–2.6454136E-06
W(29.7646 °C)	1.11812035	1.11811977		
W(156.5985 °C)	1.60970212	1.60969863		
W(231.928 °C)	1.89264875	1.89264332	1.89283467	1.89283031
W(419.527 °C)	2.56864562	2.56863636	2.56898418	2.56897629
W(660.323 °C)	3.37558565	3.37557056	3.37610714	3.37609560
W(961.78 °C)			4.28654566	4.28652538

defining fixed points in this range were realized in specially-designed, permanently-sealed cells manufactured at Hart Scientific.

Fixed-Point Cell

The construction of all metal fixed-point cells is basically the same. Some of the materials used in construction are different, however. The particular metals used for each of the different type of cells are all 99.9999% pure or better. The gallium cell differs slightly in that a PTFE (Teflon) crucible is used instead of graphite. All cells are constructed using a quartz shell and reentrant well. Each cell is connected to a vacuum system after assembling. The cell is then evacuated at a selected temperature for more than 100 hours and during that period the cell is repeatedly purged with 99.999% pure argon. Once it has been determined that the cell is free from contaminants, it is filled with pure argon and sealed at a known atmospheric pressure exactly at the temperature of the fixed point.

The sealed cell solves most problems associated with open cell designs. Information on each cell is outlined in Table 5. The actual temperature of the sensor of an SPRT calibrated at a fixed point might be different from the value assigned to the fixed point by the ITS-90 because of small pressure differences.

Realization of the Fixed Points

Realization of a fixed point to a high level of accuracy requires a strict envelopment, the temperatures of which must be very uniform, stable and controlled. The equipment used to realize these fixed points is listed in Table 6. The three-zone furnace used for the freezing points of indium, tin, zinc and aluminum is shown in Figure 1 and the heat-pipe furnace for the freezing point of silver and aluminum is shown in Figure 2. A typical axial temperature distribution in the furnace at the freezing point of zinc is shown in Figure 3.

Table 5: Fixed point cell

Thermometric Fixed Point	Purity of Material, %	Quantity, kg	Immersion Depth, ‡cm
H_2O TP	†	0.76	23
Ga MP	99.99999	0.45	15
In FP	99.9999+	0.97	18
Sn FP	99.9999+	0.96	18
Zn FP	99.9999+	0.95	18
Al FP	99.9999+	0.35	18
Ag FP	99.9999+	1.35	18

†Water from a purification system, with a resistivity of about 18 megohm-cm, was distilled into the cell.

‡Immersion depth is calculated with the SPRT in its fully-immersed position in the cell. The distance from the midpoint of the sensor of the SPRT to the tip of the SPRT quartz sheath is about 1.5 cm. The actual distance from the upper surface of the metal to the bottom of the central well is 19.5 cm for the metal freezing points, and 16.5 cm for the melting point of gallium.

All resistance measurements were made using a Guildline DC automatic bridge, model 6675, S/N 60956. The resistance of the 25-ohm SPRT was measured using DC currents of 1 mA and 1.41 mA. The resistance of the 0.25-ohm SPRT was measured using DC currents of 14.14 mA and 20.0 mA. These currents allowed the measurement results to be extrapolated to values at zero power. The re-

Table 6: Equipment used for fixed points.		
Fixed point uniformity	**Equipment used**	**Temperature uniformity**
Triple point of water	Model 7012 bath	±0.001°C
Melting point of gallium	Model 7011 bath	±0.001°C
Freezing point of indium	Model 9114 furnace, three zones	±0.02°C
Freezing point of tin	Model 9114 furnace, three zones	±0.02°C
Freezing point of zinc	Model 9114 furnace, three zones	±0.02°C
Freezing point of aluminum	Model 9114 furnace, three zones	±0.03°C
Freezing point of silver	Model 9115 furnace, heat pipe	±0.05°C

sistance at the triple point of water was measured immediately after each measurement at the melting or freezing points described in this paper.

The triple point of water is the most important fixed point of the ITS-90. The stability of all SPRTs should be checked at the triple point of water periodically. According to the ITS-90, the temperatures are interpolated in terms of the ratio of the resistance at a temperature t (R_t) and the resistance at the triple point of water (R_{tp}) in the range from 13.8033 K to 961.78°C [1]. The measurement at the triple point of water, therefore, always follows a calibration at any other fixed point. In practical work, using resistance ratios instead of absolute resistance insures the greatest possible accuracy[2]. The triple point of water cell is comprised of a borosilicate glass shell, high purity water, ice and water vapor. Once frozen, the cell is maintained for approximately 3 months with regular use in a model 7012 constant-temperature bath.

The melting point of gallium (302.9146 K) is an important calibration point for biological, environmental, oceanographic, geological and energy research. The gallium cell as mentioned earlier has a Teflon crucible and an outer glass shell. The Teflon crucible allows for the 3.1% expansion of the gallium upon solidification. Two cells were used in the realization of the gallium point—serial numbers 01 and 02. The cells were first placed in a cooler below the melting point to insure that the gallium was completely solidified. They were then placed in a specially-designed fixture suited for a model 7011 constant-temperature bath. The temperature was raised to a temperature 1°C higher than the melting point for about 20 minutes to partially melt the gallium to form a liquid-solid interface. The cells were then maintained in the bath at a temperature reduced to 0.2°C higher than the melting point. This procedure usually resulted in the melting curve lasting for seven days or longer. A typical melting curve is shown in Figure 4. The melting point of gallium realized in this way was compared with NIST data through the NIST-calibrated SPRT S/N 92017. The comparison results are listed in Table 7. The temperature differences from NIST's were within 0.3 mK for both cells, and the difference between the two cells was within 0.1 mK.

All of the freezing points except tin were realized in a similar fashion. First, the temperature of the furnace was raised about 10°C higher than the freezing point. After the metal was completely melted, the furnace was set at a stable temperature 1 to 1.5°C higher than the freezing point and left overnight. The next morning, the furnace temperature was decreased slowly (0.1 to 0.15°C per minute). To monitor the metal sample temperature, a SPRT was inserted into the cell. The temperature of the metal sample decreased to a point lower than the freezing point before recalescence. The amount of this supercooling is different from metal to metal. Table 8 summarizes the amounts of

9114 Furnace Construction

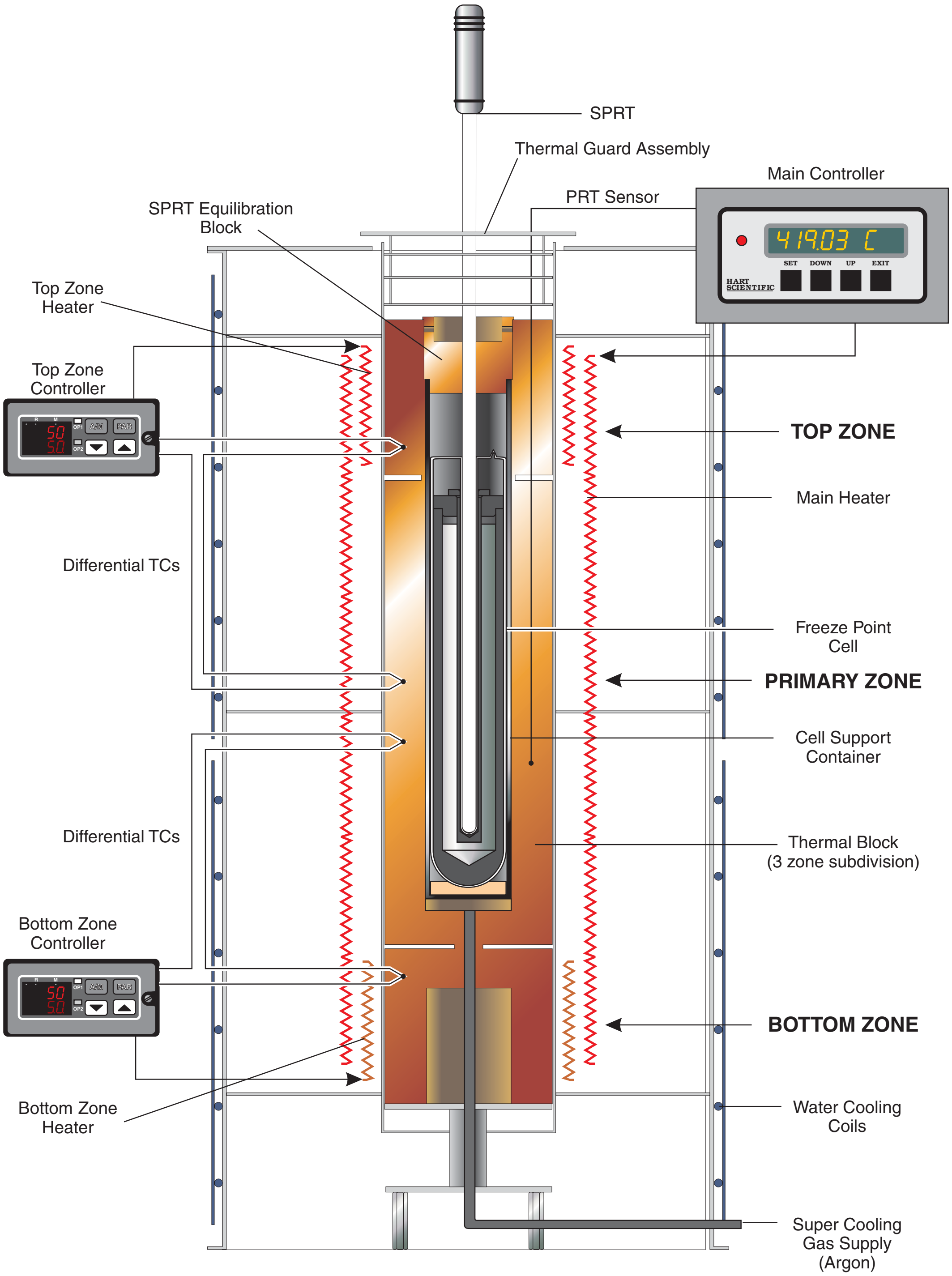

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Figure 1 *The three-zone fixed point furnace.*

9115 Furnace Construction

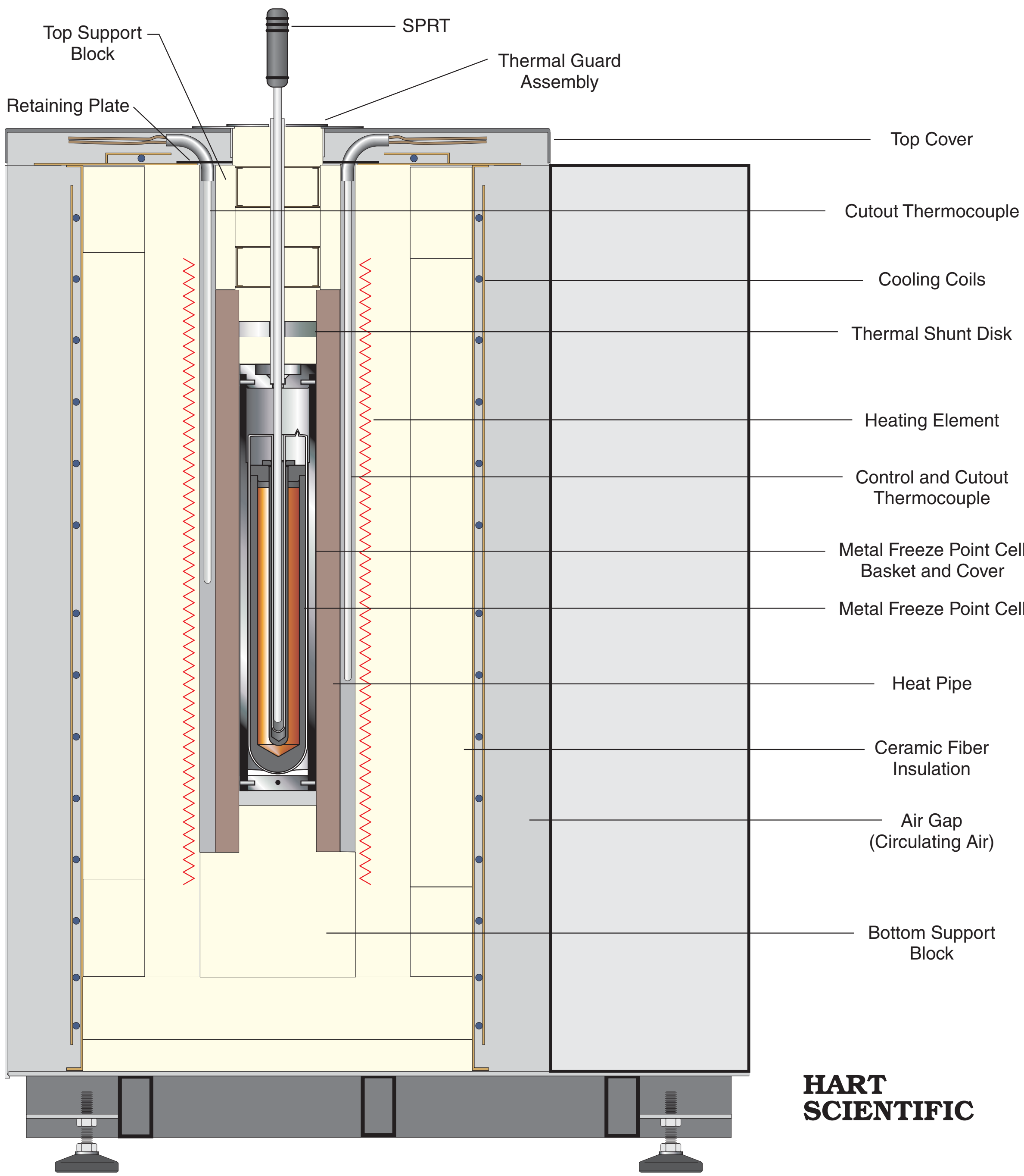

Figure 2 *The heat-pipe fixed point furnace.*

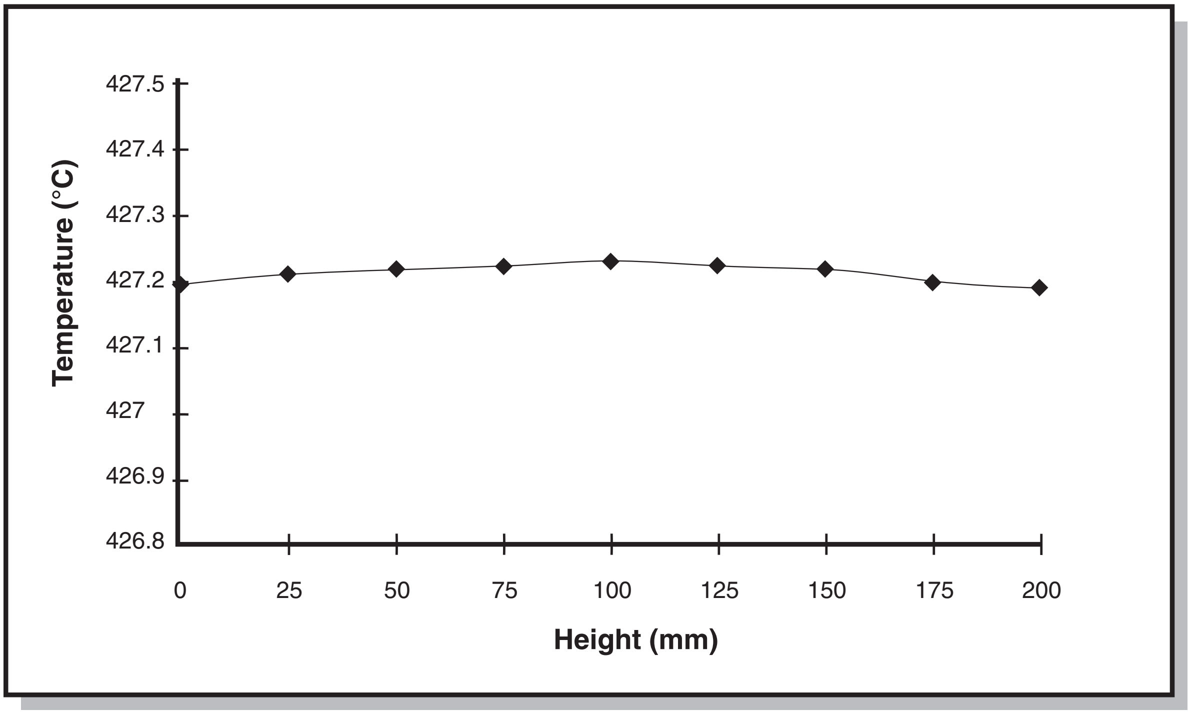

Figure 4   *Axial temperature distribution in the furnace near the freezing point of zinc.*

supercool observed in the laboratory. Immediately after recalescence the thermometer was removed from the furnace and a cold quartz tube was inserted into the fixed-point cell for one minute to initiate the freeze. At this point, the SPRT to be calibrated was introduced into the cell. Meanwhile, the furnace was kept at a stable temperature of 1°C below the freezing point. This procedure provides a very stable, long freezing plateau that typically lasts for more than ten hours. The changes in tem-

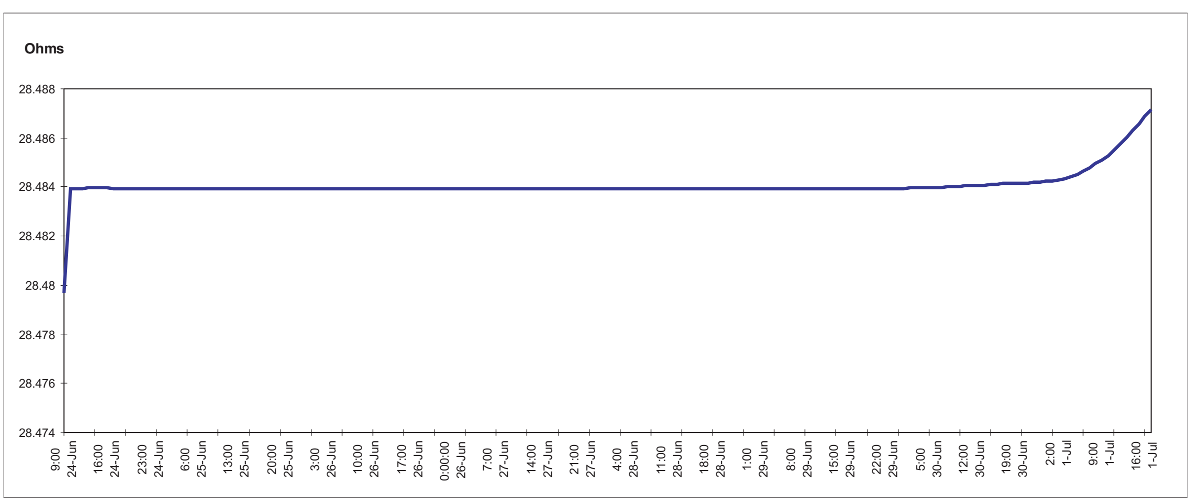

Figure 3   *A typical melting curve of gallium.*

Table 7: The comparison of the melting point of gallium (SPRT S/N: 92017)

Cell S/N	Calibration Results, W_{Ga}	NIST Data	Difference ΔW (10^{-6})	Difference Δt (mK)
Ga01	1.11812140	1.11812035	1.05	0.26
Ga02	1.11812132		0.97	0.25

Table 8: Supercool ranges for different freezing points observed in the laboratory.

Fixed point	Range of supercool (°C)
FP of indium	0.05 - 0.15
FP of tin	1.5 - 5.0
FP of zinc	0.01 - 0.03
FP of aluminum	0.5 - 1.0
FP of silver	1.0 - 1.8

perature during the first half of the plateau were usually within ±0.2 to 0.3 mK. A typical freezing curve is shown in Figure 5.

The procedure for the freezing point of tin is similar, with the following difference: when the temperature indicated by a thermometer immersed in the tin sample reached the freezing point, a cold gas current was forced upward around the outer surface of the cell until recalescence. Then the cold gas current was shut off. After recalescence the furnace was kept at a stable temperature of 1°C below the freezing point as with the other metals.

The freezing points realized in the laboratory were compared with NIST data through two NIST calibrated SPRTs S/N 92017 and S/N 92256. The comparison results are summarized in Table 9.

Uncertainty

The uncertainty of these measurements is expressed here in accordance with the new NIST policy[3]. The components of standard uncertainty are listed in Table 10. The reproducibility, an uncertainty of category A, is calculated from repeated calibration

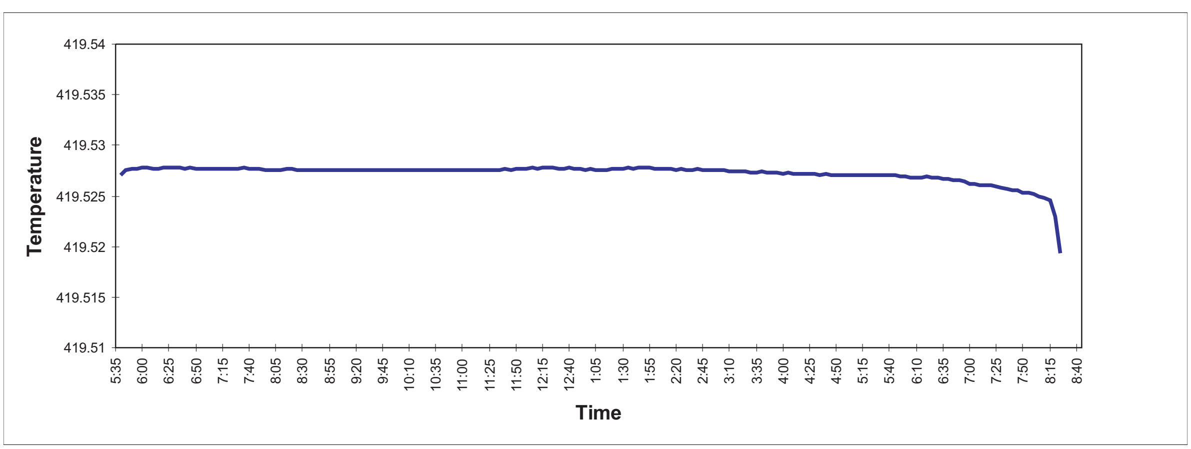

Figure 5 *A typical freezing curve of zinc.*

data of a SPRT at the fixed point. Another important source of uncertainty stemmed from impurities in the sample. The nominal purity of all pure metal samples used in the work was 99.9999+%. The expanded uncertainties (U) are obtained by multiplying the combined standard uncertainties (u_c) by a coverage factor (k). We used the same value k = 2 as NIST's new policy suggests.

Conclusions

The uncertainty for the freezing point of silver is better than 10 mK, for the freezing point of aluminum better than 4 mK, and for all of the other fixed points in the range, better than 1 mK. The comparison of the data obtained was well within the estimated expanded uncertainties. Therefore, this laboratory has established the ITS-90 in the range from 273.15 K to 1234.93 K, with traceability to NIST.

Table 9: Comparison of freezing points realized in the laboratory with NIST data.

Cell S/N	W(t) calibrated at the laboratory	NIST data†	Difference	
			ΔW (10^{-6})	Δt (mK)
In01	1.609697_{01}	1.60970212	–5.11	–1.34
In02	1.6096983_{0}		–3.82	–1.00
Sn01	1.89264802	1.89264875	–0.73	–0.20
Sn02	1.89264705		–1.70	–0.46
Zn01	2.56864470	2.56864562	–0.92	–0.26
Zn02	2.56864617		0.55	0.16
Al01	3.37558788	3.37558565	2.23	0.70
Al02	3.37558877		3.12	0.97
Al03	3.37558708		1.43	0.45
Ag01	4.28655863	4.28654566	12.97	4.57
Ag02	4.28655061		4.95	1.74

†NIST data was taken from Table 4. The NIST data for the freezing point of silver was that of SPRT S/N 92256 and others were of S/N 92017.

References

1. B.W. Mangum and G.T. Furukawa, "Guidelines for realizing the International Temperature Scale of 1990", NIST Technical Note 1265, (1990).

2. Xumo Li, "Producing the Highest Level of Accuracy from Standard Platinum Resistance Thermometers", Cal Lab, (July-August, 1995).

Source of uncertainty	Category A or B	Uncertainty (mK)					
		Ga	In	Sn	Zn	Al	Ag
Reproducibility	A	0.1	0.2	0.2	0.24	1.0	2.0
Impurity of sample	B	0.15	0.4	0.4	0.4	1.5	4.0
Non-linearity of the bridge	B	0.04	0.04	0.04	0.06	0.08	0.12
Stemmed from the t. p. water	B	0.04	0.07	0.08	0.11	0.16	0.23
Stemmed from the hydrostatic correction	B	0.01	0.03	0.02	0.03	0.02	0.05
Stemmed from the pressure correction	B	0.02	0.05	0.03	0.04	0.07	0.06
Combined uncertainty		0.19	0.46	0.46	0.49	1.81	4.48
Expanded uncertainty		0.38	0.92	0.92	0.98	3.62	8.96

Table 10: Estimated uncertainties in the fixed points.

3. Taylor, Barry N. and Kuyatt, Chris E., Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results, NIST Technical Note 1297, 1994 Edition.