

NIST implementation and realization of the ITS-90 over the range 83 K to 1235 K: reproducibility, stability, and uncertainties

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ABSTRACT

The National Institute of Standards and Technology is using thermometric fixed points to realize the International Temperature Scale of 1990 (ITS-90) and disseminate the temperature scale through the calibrations of standard platinum resistance thermometers over the range of 83.8058 K to 1234.93 K. This work involved the optimization of experimental techniques and measurement procedures to reduce uncertainty in the data. The realization of the scale allows for an in-depth investigation of reproducibility and stability of the fixed points used to define the various temperature subranges of the ITS-90. Additionally, propagation of errors associated with the ITS-90 is discussed.

SUBJECT INDEX: International Temperature Scale of 1990 (ITS-90), Fixed points, Platinum resistance thermometers and Thermometry

INTRODUCTION

This paper documents how the National Institute of Standards and Technology (NIST) has implemented and realizes the International Temperature Scale of 1990 (ITS-90) (1) over the range of 83 K to 1235 K. NIST is responsible for maintaining and disseminating the ITS-90 within the United States of America. The ITS-90 is the official international temperature scale adopted by the Comité International des Poids et Mesures in September 1989 and which came into effect on 1 January 1990. It supersedes the International Practical Temperature Scale of 1968, Amended Edition of 1975 [IPTS-68(75)] (2) and the 1976 Provisional 0.5 K to 30 K Temperature Scale (EPT-76) (3). The NIST Platinum Resistance Thermometry (PRT) Laboratory realizes all of the ITS-90 fixed points from 83.8058 K (argon triple point) through 1234.93 K (silver freezing point). The cadmium freezing point (594.219 K) is not a defining point on the ITS-90, but a cell for realizing it has been added as a check point for the calibration of thermometers up to and above the freezing point of zinc and in the study of non-uniqueness of the ITS-90. A fixed-point cell for realizing the freezing point of gold is also used in high-temperature studies.

The PRT laboratory has achieved a high level of automation in the calibration of standard platinum resistance thermometers (SPRTs) and high-temperature SPRTs (HTSPRTs) through the use of computer assistance. This automation has enabled the PRT Laboratory to increase the number of thermometers calibrated while maintaining a high level of required accuracy. Additionally, this automation has allowed more time for research on the new scale. With more fixed points and temperature subranges than were available with the IPTS-68(75), the ITS-90 has greater flexibility in its realization. This implementation of the ITS-90 enables NIST to conduct a long-term study of the reproducibilities and stabilities associated with the new defining fixed points. Some results of that study will be presented. The investigation has led to the optimization of experimental techniques and measurement procedures to reduce the errors in the NIST realization of the ITS-90. The addition of two automatic ac bridges under computer control has eliminated human error in that aspect of the measurement process. Also, the propagation errors associated with the various temperature subranges and their fixed points will be discussed.

REALIZATION PROCEDURES

The calibration of SPRTs in accordance with the ITS-90 requires the use of thermometric fixed points. The fixed points over the range of 83.8 K to 1235 K that are realized in the NIST PRT laboratory are listed in Table I. The furnaces, refrigerators and the fixed-point cells (except for the triple point of water (TPW) (273.16 K) cells and the accompanying maintenance bath) were all constructed at NIST. Table I shows the NIST-realized thermometric fixed points, purity of material, quantity of material and furnace type. A description of each thermometric fixed point and the techniques used for the realization of each defining fixed point for optimum performance is as follows.

TABLE I: NIST Thermometric Fixed-Points

Thermometric Fixed Point		Purity of Material, %	Quantity	Immersion Depth, cm	Furnace/Refrigerator Type
Ar	TP	99.9999	15 mol	10.9	dewar
Hg	TP	99.999999	2.3 kg	17.0	styrofoam
H ₂ O	TP	99.99999	500 cm ³	31.5	maintenance bath
Ga	TP	99.99999	0.9 kg	13.0	single-zone
In	FP	99.9999 ⁺	1.5 kg	19.0	three-zone
Sn	FP	99.9999 ⁺	1.0 kg	18.0	three-zone
Cd	FP	99.9999 ⁺	1.7 kg	18.0	three-zone
Zn	FP	99.9999 ⁺	1.0 kg	18.0	three-zone
Al	FP	99.9999 ⁺	0.4 kg	16.7	sodium heat pipe
Ag	FP	99.9999 ⁺	1.5 kg	13.3	sodium heat pipe

There exists a dedicated furnace or bath for each of the fixed-point cells listed in Table I. These furnaces and baths, constructed at NIST, were designed specifically to yield optimal performance from each fixed point. The furnaces used for In (429.7485 K), Sn (505.078 K), Cd and Zn (692.677 K) have three heater zones (top, middle and bottom) with the top and bottom acting as guard zones. The use of these guard zones yields a uniform temperature environment over the length of the fixed-point crucible with axial gradients not exceeding 5 mK. The deep immersion of the fixed-point cell in the furnace also provides a tempering zone (28 cm) for the SPRT. This tempering zone helps prevent the thermometer from "sensing" the outside environment. All four of the three-zone furnaces are interchangeable so that the direct comparison of several fixed points (Zn, Cd, Sn or In) is possible. The sodium heat-pipe furnaces used for the high-temperature fixed points (Al (933.473 K), Ag (1234.93 K) and Au (1337.33 K)) are also interchangeable and may be used for direct comparison of fixed-point cells used in the range 933 K to 1337 K. The heat pipe is used to provide an isothermal environment over the length of the fixed-point crucibles. Additionally, the length of the heat pipe (45.7 cm) provides a uniform tempering zone for the SPRT or HTSPRT. The heater windings of all of the furnaces are dc-powered to prevent an ac effect associated with the higher currents used to drive the heaters at temperatures above 933 K. The control systems of each type of furnace are interchangeable and use programmable proportional, integral, derivative (PID) controllers with control thermocouples for the setting of the furnace temperature. These control systems are designed to hold a furnace at the set temperature to within 10 mK during operation. The use of these specially designed and constructed furnaces and baths eliminates concern over their influence on the reproducibility of the realization of a fixed point.

The silver freezing-point cell was constructed with 1500 g of 99.9999% pure metal contained within a graphite crucible with a graphite cap and reentrant well. The cap is designed to allow the reentrant well to float freely upwards and downwards. This movement of the well is caused by the buoyant force of the metal as it freezes and melts. Without such movement the pressure from the freezing silver would cause the cell to lose its integrity. The graphite assembly is inserted into a high-purity

silica-glass envelope with a high-purity, silica-glass reentrant well inserted into the graphite well. The silica-glass well must be frosted on the outside to prevent "light-piping". Next, the silica-glass assembly is filled with purified argon at a pressure of one atmosphere (atm) (101325 Pa) at the freezing point and sealed. It is important to remove absorbed oxygen from the silver as it will depress the realized freezing-point temperature. The completed cell is inserted into a 61 cm long Inconel protecting tube with suitable radiation shields and a thermometer guide tube. The furnace used for temperature fixed points above the zinc freezing point is a sealed sodium heat-pipe with a range of 773 K to 1373 K. The radial gradients do not exceed 5 mK and the axial gradient over the length of the graphite crucible do not exceed 10 mK.

The silver freezing point is achieved by melting and heating the ingot of metal, heating to 5 K above the freezing point, cooling and then monitoring the supercool with a thermometer. The furnace temperature should be set 0.5 K to 1 K below the Ag freezing point during the supercool and the subsequent rise of the temperature to the freezing plateau. Recalescence will occur when the supercool is approximately 0.1 K to 0.2 K below the freezing point. At the beginning of recalescence, the thermometer is removed to an auxiliary furnace operating at approximately 5 K above the freezing-point temperature. A clean, cool silica-glass rod is then inserted into and withdrawn from the reentrant well of the fixed-point cell at one-minute intervals over a period of three minutes. Finally, the "hot" thermometer is reinserted into the fixed-point cell for measurement. The successive insertions of a silica-glass rod and "hot" thermometer will insure a solid mantle of silver on the outside of the graphite reentrant well as well as on the inside of the graphite crucible. This "double freeze" technique produces a reproducible freezing point of silver.

The realization of the freezing point of silver requires special attention in the handling of the cell and the HTSPRT under investigation. The cell and the thermometer must be completely free of oils and acids or the silica glass will devitrify at this elevated temperature. The thermometer should be handled only when wearing with clean polyethylene gloves. The silica-glass sheath should be cleaned with isopropyl alcohol to remove any possible contaminants before its exposure to temperatures above 723 K. The thermometer is heated in an auxiliary furnace, ramped from about 773 K to 1243 K over two hours and then placed into the reentrant well of the silver freezing-point cell. The thermometer in the auxiliary furnace is protected by a closed-end 61 cm tube of platinum, with 0.13 mm thick walls, from metal ions that may diffuse through the silica-glass sheath and degrade the purity of the Pt resistor at this temperature. This Pt tube is located between two high-purity silica-glass test tubes to protect the Pt from damage. When measurements are completed, the HTSPRT is removed from the silver freezing-point cell and reinserted in the auxiliary furnace which is at a temperature of about 1243 K. The auxiliary furnace is held at 1243 K for 30 minutes and then cooled at a constant rate to 773 K over a period of four hours. This method safeguards the thermometer from thermal shock and quenching-in of lattice defects, all of which would cause an increase in the measured resistance at the TPW.

The aluminum freezing-point cell has a design similar to that of the silver cell. The graphite well is allowed the same vertical movement as that of the silver cell. The graphite crucible contains 358 g of 99.9999% pure metal in a silica-glass envelope with a pumping tube connected to a vacuum system that allows the removal of the inert gas (argon) and replacement of it with purified argon. The open cell insures that the freezing point is achieved at one atmosphere and allows studies of pressure effects on the freezing-point temperature. The "double freeze" method used to realize the aluminum freezing point is the same as that of silver with the recalescence occurring at approximately 0.4 K below the freezing point temperature. The temperature of the furnace should be at least 1 K below the freezing-point temperature to achieve a supercool and recalescence. Also, the silica-glass rod technique is used to insure the presence of a mantle of solid metal on the graphite reentrant well. The furnace also uses a sodium-filled heat pipe to generate a uniform temperature environment.

When handling the aluminum cell, the precautions outlined previously for the silver cell should be followed. Also, the same handling procedures for SPRTs as were used at 1235 K must be followed. The thermometer, however, should be heated in the auxiliary furnace to a temperature of only 943 K before placement into the aluminum freezing-point cell. A three-hour cooling time from 943 K to 773 K is used for all types of thermometers (0.25 Ω to 25.5 Ω) before removing them to room temperature. It is important to remember that aluminum is highly reactive in a molten state and will react with oxygen, water, silica glass, and most

of the materials used in furnace construction. When the freezing-point cell is not in use, the furnace should be kept about 5 K below the melting point of aluminum to minimize the possibility of catastrophic reactions with the cell's surrounding environment if the graphite crucible were to lose its integrity.

Within their respective freezing-point cells, the metals (Zn, Cd and Sn) are in identical graphite crucible assemblies which have been inserted in borosilicate test tubes and which are open at the top for insertion of a thermometer through a modified silicone-rubber gas seal and a 3 mm diameter tube used for the introduction of helium gas (4). The purity of the metal used in the construction of these freezing-point cells is 99.9999+%. The metal sample of a given cell is kept in a molten state at about 5 K above the melting point for a minimum of eight hours to insure that the ingot has completely melted. Zinc and cadmium will supercool to temperatures no lower than 0.1 K below their respective freezing temperatures. High-purity tin will supercool to approximately 25 K below the freezing point and for this reason the recalescence is achieved outside the furnace. When the SPRT in the tin cell has cooled to the freezing-point temperature, the tin cell with the monitoring thermometer is removed from the furnace until the beginning of recalescence is achieved. For all three cells (Zn, Cd and Sn), once the nucleation of the freeze has started the SPRT is removed and two cool silica-glass rods are inserted for five minutes each into the reentrant well to create a solid mantle on the graphite reentrant well and insure a "double freeze". The "cool" thermometer is then reinserted into the cell and one hour is allowed for the cell and thermometer to come into thermal equilibrium before measurements are made. A furnace temperature 0.75 K below the fixed-point temperature is used during the time of the freezing plateau. This yields a total freezing time of at least 16 hours. The furnace type used to realize the freezing points of Zn, Cd and Sn is of a three-zone heater arrangement with the top and bottom zones acting as guard zones to provide an axial gradient of no more than 5 mK over the length of the graphite crucible.

The indium freezing-point cell uses a polytetrafluoroethylene (Teflon) crucible in a stainless-steel enclosure with 1500 g of 99.9999+% pure metal. The nucleation of the freeze occurs at approximately 1 K below the freezing-point temperature and may be performed inside the furnace. Insertion of two cool glass rods for three minutes each and reinsertion of the "cool" SPRT will cause a solid uniform mantle on the reentrant well. The temperature of the furnace is maintained at about 0.5 K below the fixed-point temperature with a typical freezing plateau of 22 hours.

Instead of the melting point of gallium, the triple point is used at the NIST. The triple point yields greater reproducibility than that of the melting point. The all-Teflon crucible and nylon container continuously pumped to achieve triple-point conditions. Pressure corrections (-2.011 mK/atm) (5) must be taken into account when assigning a value to the realized temperature. The Teflon crucible containing 900 g of 99.99999% pure metal allows for the 3.1% expansion of gallium upon solidification. The gallium cell with a solid ingot of metal is inserted into a preparation furnace operating at about 313 K. Additionally, an immersion heater, also at about 313 K, is inserted into the reentrant well which is filled with a light mineral oil to insure proper thermal conductance between the cell and the immersion heater. The above procedure is conducted over a period of 35 minutes, producing a "double melt" which isolates the thermometer completely from the outside environment. After the 35 minutes, the immersion heater is removed and the cell is placed inside another furnace operating at 302.9 K. Oil is used during normal measurement of the SPRT to insure good thermal contact. The gallium triple point may be maintained for periods longer than one month.

The TPW cell is the only commercially purchased fixed-point cell used in the PRT laboratory. The borosilicate-glass cell containing 400 to 500 cm³ of water, water vapor and ice, all of high purity and naturally-occurring isotopic abundance, is used for the realization of the triple point of water. This is the one defining fixed point that is common to the ITS-90 and the Kelvin Thermodynamic Temperature Scale and is assigned the same temperature for both scales. Preparation of a triple point of water has been described elsewhere (6). This triple point is the reference point for SPRTs and HTSPRTs and its use is necessary in the mathematical calculations of the ITS-90. Also, TPW measurements are vital to tracking the stability of a given thermometer.

The triple-point-of-mercury cell consists of 2300 g of 99.999999% pure metal in an all-stainless-steel (304) crucible (4). The use of a stainless-steel crucible prevents the hazard of accidental loss of cell integrity. This steel crucible is sealed under triple-point conditions, then placed in another stainless-steel enclosure that is evacuated to isolate the cell from the outside environment. In use, the assembly is placed in a large, low-

density-styrofoam container instead of a refrigeration unit. The triple point is prepared by freezing the mercury sample with an immersion cooler (heat pump driven by dry ice and ethyl alcohol) inserted into the reentrant well; the latter is filled with alcohol to provide thermal conductance and the prevention of ice formation in the reentrant well which would influence the realized temperature. After the sample is frozen, warm copper rods are inserted into the well (to induce a melt around the reentrant well) until the SPRT measures the steady-state condition of the triple point. The lack of a maintenance refrigerator causes the mercury on the inside of the stainless-steel crucible to begin melting. Using this "double melt" technique, the duration of the triple point approaches 12 to 14 hours.

The argon triple-point apparatus (7) at NIST allows for the simultaneous calibration of six or seven long-stem and seven or six capsule SPRTs. The argon cell, containing about 15 moles of 99.9999% pure gas, is in an adiabatic condition during operation and may be maintained as long as sufficient quantities of liquid nitrogen are available for refrigeration. The triple point is realized by condensing argon into its crucible and then freezing the sample. This frozen sample is then heated by the introduction of a specific amount of heat to initiate melting. When all three phases (gas, solid and liquid) are present, using the above method, the cell is sealed and controlled adiabatically.

CALIBRATION PROCEDURES

The fixed points and the methods of their realizations described above are used in the calibration of SPRTs on the ITS-90. There are three steps in the procedures for calibration of SPRTs: annealing, fixed-point measurements, and calculations.

First, the thermometer that is to be calibrated is annealed to remove mechanical strains that have occurred during general use and shipping. An SPRT used up to the zinc point is subjected to a temperature of about 723 K to 753 K for 4 hours before calibration. Thermometers used up to the aluminum point are thoroughly cleaned and heated from 773 K to 943 K over 1 hour, held at 943 K for 1.5 hours, cooled to 773 K over 3 hours, and then removed to ambient conditions for final cooling. Metal-sheath thermometers are tested for insulation resistance during their annealing. HTSPRTs that are used to the silver freezing point are measured at the triple point of water for a baseline measurement, cleaned with alcohol, heated to 1243 K over 2 hours, held at 1243 K for 1 hour, cooled to 773 K over 4 hours, and then removed to ambient conditions for final cooling. Studies have been conducted in the PRT laboratory to determine the optimum time required for the annealing and thermal treatment of SPRTs and HTSPRTs (8).

Second, after the annealing procedure is completed, the SPRT used up to the aluminum freezing point and down to the argon triple point is calibrated by making successive measurements in the sequence TPW, Al, TPW, Zn, TPW, Cd, TPW, Sn, TPW, Hg (234.3156 K), TPW, Ar, and TPW fixed points. The measurements are performed by utilizing a semi-automated system which is controlled by a computer. The two automatic ac bridges, reference resistors, digital multimeters, thermometer port connections and computer are all connected via IEEE-488 connections through scanners. The scanners are controlled by macro commands issued by the data-acquisition program used to run the computer. The macro commands allow the program to connect the thermometer to the resistance bridges, as well as change the reference resistor (100 Ω for a 25.5 Ω SPRT, 10 Ω for a 2.5 Ω HTSPRT and 1 Ω for a 0.25 Ω HTSPRT) for the bridge requiring an external reference resistor. The reference resistors in use are considered to be ac/dc-type resistors at low frequencies. A thermostatically-controlled oil bath (298.15 K) holds several reference resistors of each value (1, 10 and 100 Ω) that are calibrated on a four-month cycle and intercompared daily to ensure proper maintenance of the ohm. The temperature of the reference-resistor bath is monitored by the data-acquisition program through the use of a calibrated thermistor. The frequency used in the commercially available bridge is 30 Hz, with excitation currents of 1 and 2 mA for 25.5 Ω , 5 and 7.07 mA for 2.5 Ω , and 10 and 14.14 mA for 0.25 Ω thermometers. One of the NIST Cutkosky (9) bridges operates at a frequency of either 15 Hz or 30 Hz, with a maximum resistance reading of 32 Ω for HTSPRTs, and the other bridge operates at 30 Hz, with a maximum resistance reading of 112 Ω for SPRTs. The resolution of the commercially available bridge is 0.5 $\mu\Omega$ for a 100 Ω reference resistor, 0.05 $\mu\Omega$ for a 10 Ω reference resistor and 0.005 $\mu\Omega$ for a 1 Ω reference resistor. The resolution of the Cutkosky bridge is 1 $\mu\Omega$ for the 112 Ω model and 0.1 $\mu\Omega$ for the 32 Ω model.

This configuration allows the measurement of the SPRT with two (potentially up to eight) different resistance bridges at multiple currents (for extrapolation to 0 mA). Calibration of an SPRT with two resistance bridges acts as a check that the measurement system is performing properly. All of the computer-accessible bridge functions may be controlled with the macro commands. Also, the program is designed to monitor the drift of the thermometer and will accept data only when the thermometer is in thermal equilibrium. This is determined by calculating the slope of the readings and converting $\mu\Omega/\text{min}$ to mK/min. The multimeter is used to verify the excitation current used by the resistance bridges and identify the thermometer under test by its port connector. The connector attached to the SPRT throughout the calibration process has an additional identification resistor that allows the program to determine which SPRT is being measured. Also, by the unique range of values of measured resistance at a fixed point, the data-acquisition system can determine which fixed point is being used for that measurement. All data taken are subsequently logged to a data file for later analysis.

Typically, calibrations of SPRTs at a fixed point are conducted in batches of five thermometers. A check thermometer is used to measure the beginning of the plateau of the appropriate fixed point, then the batch of five thermometers under test are measured successively, and finally the check thermometer is reinserted into the fixed point (e.g. Check 1, SPRT 1, SPRT 2, SPRT 3, SPRT 4, SPRT 5 and Check 2) for a final measurement at the plateau and a check for changes in its temperature. This closing of the loop indicates the total change of temperature for the duration of measurements. If the total change in temperature from the first check measurement to the second check measurement (Check 2 - Check 1) exceeds 1.0 mK for Ag; 0.5 mK for Al, Zn, Cd and Sn; 0.2 mK for In; 0.1 mK for Hg; and 0.05 mK for Ga and Ar, all of the thermometers are remeasured the following day. The total number of thermometers in a batch measured at the silver freezing point is one test HTSPRT plus two measurements (at the beginning and at the end) on the check thermometer; and at the aluminum freezing point two test SPRTs are measured plus two measurements on the check thermometer because of the time involved in the special thermal treatment given to those thermometers.

Third, data from measurements at the fixed points required for the subranges used in the calibration of a thermometer are used to calculate the $W(T_{90})$ [$W(T_{90}) = R(T_{90})/R(273.16 \text{ K})$] values used in the determination of the coefficients of the deviation functions of the ITS-90. The coefficients used in each temperature subrange have been assigned subscripts to avoid confusion when SPRTs have been calibrated over more than one subrange (10). This is not part of the official scale but has been in use at NIST beginning 1 January 1990. Table II shows the temperature subranges available, fixed points required, and the coefficients of the relevant deviation functions with their appropriate subscripts. The computer program written to solve for the deviation-function coefficients is also designed to check its calculations by using the calculated coefficients and the original data in the appropriate deviation function. The program validates the calibration data in accordance with the specifications of the ITS-90 relative to $W(\text{Ga})$ or $W(\text{Hg})$, and $W(\text{Ag})$ when applicable.

TABLE II: Temperature Subranges of the ITS-90 for which calibrations are offered at NIST

Temperature Subrange	Fixed Points Required	Coefficients
83.8058 K to 273.16 K	Ar, Hg, TPW	a_4, b_4
234.3156 K to 302.9146 K	Hg, TPW, Ga	a_5, b_5
273.15 K to 302.9146 K	Ga, TPW	a_{11}
273.15 K to 492.7485 K	In, TPW	a_{10}
273.15 K to 505.078 K	Sn, In, TPW	a_9, b_9
273.15 K to 692.677 K	Zn, Sn, TPW	a_8, b_8
273.15 K to 933.473 K	Al, Zn, Sn, TPW	a_7, b_7, c_7
273.15 K to 1234.93 K	Ag, Al, Zn, Sn, TPW	a_6, b_6, c_6, d
25.5 Ω SPRT from 83.8058 K to 692.677 K, mica-type coil support		
2.5 Ω SPRT from 83.8058 K to 933.473 K, SiO_2 , ceramic-type support		
0.25 Ω SPRT for the subrange up to 1234.93 K, SiO_2 support		

The thermometers under test must pass official criteria of the ITS-90 as well as be stable at 273.16 K. The total allowable equivalent temperature change at the TPW during calibration over the range from 83.8 K to 934 K of a 25.5 Ω SPRT is 0.75 mK for the glass-sheath

thermometers and 1.0 mK for a metal-sheath thermometer. Thermometers calibrated from 273.15 K to 1235 K must meet the criterion that the change at the TPW must be no greater than the equivalent of 2.0 mK. If thermometers do not pass this test, they are annealed a second time and then calibrated a second time. Also, the change between the first TPW reading before the freezing point of zinc and the reading after measurements at the zinc freezing point should not be larger than the equivalent of 0.35 mK. A large change at this point of the calibration usually denotes large mechanical strains and insufficient annealing time, and the SPRT will be subjected to an overnight annealing at 723 K before recalibration.

As a check on the calibration of an SPRT, the thermometer is also measured at the redundant fixed point(s) within the temperature subrange. This extra measurement establishes the validity of the calibration by comparing the measured $W(T_{90})$ at the redundant fixed point with the $W(T_{90})$ calculated from the calibration. This difference may be expressed in terms of temperature.

It is important that all possible corrections be made to the ITS-90 assigned temperature of each fixed-point used in the calibration of an SPRT. These include corrections for hydrostatic head (HH), pressure and external self-heating (ESH). The hydrostatic-head correction is always added to the assigned value for the fixed point. It is calculated by determining the depth of immersion of an SPRT in the fixed-point cell and multiplying it by the hydrostatic-pressure correction. This immersion depth is the distance from the mid-point of the thermometer sensor to the top of the column of liquid. The pressure correction is also added to the assigned value; it is determined from the pressure of the inert gas in the fixed-point cell multiplied by the pressure correction for that fixed point. Melting points and freezing points have assigned values for a pressure of one atmosphere. The external self-heating correction also should be applied. The value used at NIST for a 1 mA current in an SPRT in a fixed-point cell either making a close fit or containing a bushing is 0.1 mK. Zero-power data are used to eliminate error from self-heating. Measurements at two currents may be used to determine the 0 mA values using equation 1 for the extrapolation. R_0 is the resistance at zero power dissipation, R_1 is the resistance at the current i_1 , and R_2 is the resistance at the higher current i_2 .

$$R_0 = R_1 - i_1^2 \frac{(R_2 - R_1)}{(i_2^2 - i_1^2)} \quad (1)$$

The above corrections are made to the assigned temperature values of the measured fixed points and then these are used in the calculation of the coefficients of the appropriate deviation functions. The other important correction is made to the measured resistance value for the SPRT at the triple point of water. Because of the hydrostatic head and any external self-heating effects at the triple point of water, the SPRT is not measured at a temperature of exactly 273.16 K. The ITS-90 equations, however, are defined by using $W(T_{90})$ which requires the resistance value at 273.16 K in the denominator of the resistance ratio, as shown in equation 2:

$$W(T_{90}) = \frac{R(T_{90})}{R(273.16 \text{ K})} \quad (2)$$

$R(T_{90})$ is the measured resistance at T_{90} and $R(273.16 \text{ K})$ is the calculated resistance for that SPRT at the triple point of water. By using equation 3, $R(273.16 \text{ K})$ may be calculated from the measured resistance at the triple point of water.

$$R(273.16 \text{ K}) = \frac{R(T_{90})}{W(T_{90})} \quad (3)$$

The $W(T_{90})$ is calculated from the appropriate ITS-90 reference function. The difference between the slope (dR/dT_{90}) of a real thermometer and the slope of the reference function at the triple point of water is negligible as the reference functions are based on real thermometers. These corrections should be applied to the assigned

values of the defining fixed points before determining the coefficients of the deviation function for the SPRT being calibrated.

RESULTS

The uncertainties associated with a calibration of an SPRT are based on the stability and reproducibility of the defining fixed points used. The total uncertainty that is assigned to a defining fixed point is based on the level of impurity for the material and the reproducibility of a check SPRT. The utilization of check thermometers allows a study of fixed-point reproducibility to be performed over a long time period.

These long-term check-thermometer data also yield results related to what is possible for thermometer stability. The check SPRT is measured only at its defining fixed point and at the TPW to determine the resistance ratio $W(T_{90})$. Table III gives the uncertainties (1σ) associated with each fixed point relative to each check thermometer and the total uncertainty associated with that fixed point. Typically, the first reading of the check SPRT during a calibration is made at the peak of the freezing curve or minimum of the melting curve. Figures 1 (Al), 2 (Sn), 3 (Ga) and 4 (Ar) display the control charts for the check thermometers and the appropriate fixed points over the past 20 months. The solid triangles represent data obtained with a commercially-available ac resistance bridge and the open circles represent those obtained with a NIST-designed-and-manufactured ac resistance bridge. Both measuring devices have an operating frequency of 30 Hz. In most cases, the difference between the two ac resistance bridges does not exceed the equivalent of 0.2 mK

TABLE III: NIST Fixed-Point Uncertainties

Thermometric Fixed Point	Check SPRT Random (1σ), mK	Total Random+Systematic (1σ), mK
Ar TP	0.07	0.1
Hg TP	0.09	0.1
H ₂ O TP	0.05	0.1
Ga TP	0.03	0.1
In FP	0.14	0.7
Sn FP	0.14	1.0
Cd FP	0.22	1.0
Zn FP	0.24	1.0
Al FP	0.26	1.0
Ag FP	0.64	2.0

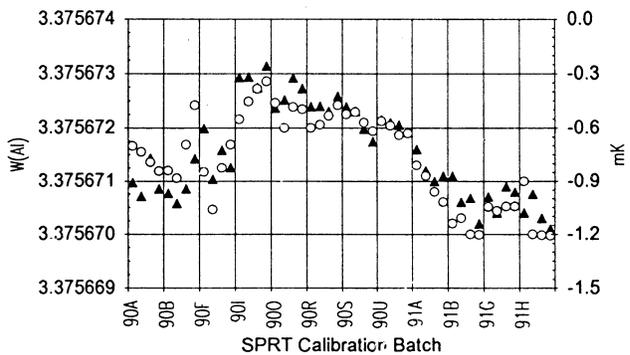


Figure 1. Control chart for check SPRT at the aluminum freezing point over 20 months. The solid triangles are for a commercially available 30 Hz ac resistance bridge and the open circles are for a NIST-designed 30 Hz ac resistance bridge.

The aluminum freezing point of the ITS-90 is a new defining fixed point. Several manufacturers produce 25.5 Ω SPRTs capable of use up to 934 K. The extended temperature range of the SPRT as a defining standard for the ITS-90 illustrates reliable one of these thermometers can be at these temperatures over time. In Figure 1, the 25.5 Ω check thermometer values of $W(T_{90})$ for the aluminum freezing point has a standard deviation of ± 0.26 mK for either ac resistance bridge. The thermometer data show what effect the elevated temperature may have

on the reproducibility of an SPRT. The instability of the thermometer is evident in the behavior exhibited in the figure. Part of the instability of this new check SPRT is caused from the "aging" that a new thermometer of this manufacturer typically undergoes. Even with this inherent instability, the random uncertainty at aluminum is small relative to the total uncertainty of ± 1.0 mK.

Monitoring of the freezing point of tin has been retained in changing from the IPTS-68(75) to the ITS-90, and it continues to be a very reproducible fixed point. Figure 2 shows the measured $W(T_{90})$ values for the tin check SPRT over a 20 month time period with a standard deviation of ± 0.14 mK. The check thermometer is not exposed to extreme temperatures and shows only a gradual change in its data. The random uncertainty of this SPRT is much smaller than the total uncertainty of ± 1.0 mK assigned to the freezing point of tin.

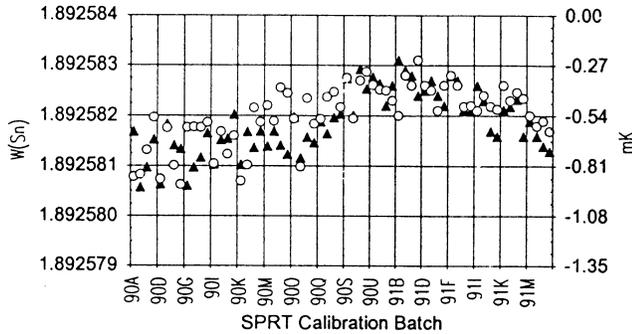


Figure 2. Control chart for check SPRT at the tin freezing point over 20 months. The solid triangles are for a commercially available 30 Hz ac resistance bridge and the open circles are for a NIST-designed 30 Hz ac resistance bridge.

Figure 3 shows the measured $W(T_{90})$ values for our triple-point-of-gallium check SPRT having a standard deviation of ± 0.03 mK, with a total assigned uncertainty of ± 0.1 mK. While the gallium point is not crucial for most temperature subranges, the $W(\text{Ga})$ value is one of the ITS-90 criteria for determining if a thermometer may be used as a defining standard of the scale. It is important that the fixed points used to establish thermometer suitability be of the highest purity and reproducibility. The control chart for gallium clearly displays the required stability and reproducibility that are associated with a triple point. All NIST-calibrated SPRTs are measured at the gallium point to determine if their $W(302.9146 \text{ K})$ values meet the required ITS-90 criterion.

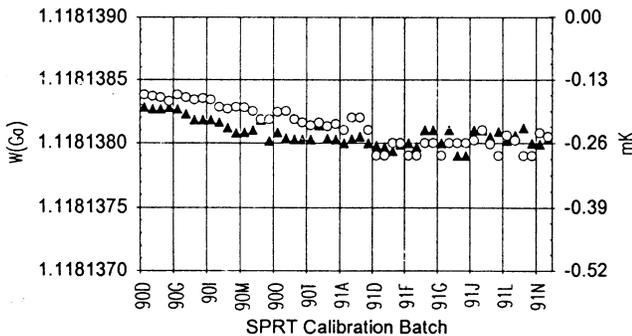


Figure 3. Control chart for check SPRT at the gallium triple point over 20 months. The solid triangles are for a commercially available 30 Hz ac resistance bridge and the open circles are for a NIST-designed 30 Hz ac resistance bridge.

The argon triple point, which was an optional calibration point on the IPTS-68(75) and is now a defining point on the ITS-90, is considerably more reproducible than that of the oxygen condensation point of the IPTS-68(75). The high purity of available gas and the decreased uncertainties associated with a triple point make the argon fixed point a large improvement over the oxygen condensation point. The data, shown

in Figure 4, from the check SPRT have a standard deviation of ± 0.07 mK with the total uncertainty being ± 0.1 mK. The graph shows a decrease in scatter with time, associated with the learning curve in using the rather complex apparatus utilized in the realization of the argon-triple-point temperature. The obvious decrease in the difference between bridges is attributed to a realignment of the NIST-constructed bridge between test-thermometer calibration batches.

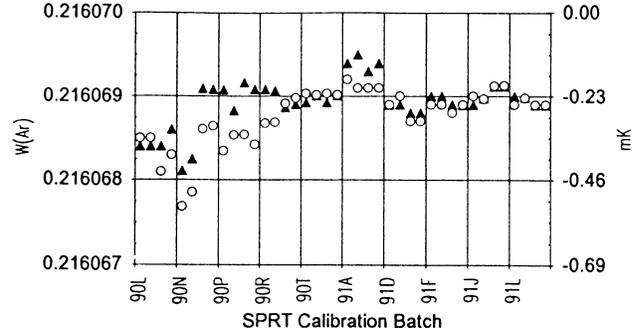


Figure 4. Control chart for check SPRT at the argon triple point over 20 months. The solid triangles are for a commercially available 30 Hz ac resistance bridge and the open circles are for a NIST-designed 30 Hz ac resistance bridge.

The aluminum, tin, gallium and argon control charts are representative of all those for the high-purity fixed points used at NIST for the maintenance of the ITS-90. Table III lists the total uncertainties that NIST assigns to its defining fixed points. The highly-reproducible fixed points of Ar, Hg, TPW and Ga have random uncertainties that are still high relative to their total uncertainty, but the limitations of the measurement equipment hampers the ability of the check SPRT to yield an even smaller random uncertainty. The total uncertainties assigned to each fixed point may be used to determine how an error propagates throughout each temperature subrange for each defining fixed point.

An assessment of total uncertainty for an SPRT calibration is important in the determination of the user's total uncertainty in his use of the thermometer. The total calibration error for each temperature subrange is determined from the propagated error from each defining fixed point. Table IV lists the total calibration uncertainty associated with each temperature subrange for a calibrated SPRT. The total error propagated from each defining fixed point is calculated for each subrange by assuming the error of that fixed point with no error at the other fixed points, and determining mathematically how that error propagates. The propagated error is determined by inducing an error in the fixed point by the desired amount and keeping the other fixed points without error and then recalculating the coefficients of the deviation function. Using the difference between the two deviation functions for a given T_{90} and the first derivative of the deviation function, the difference in terms of temperature may be easily determined. The total error for a given T_{90} is determined from the root-sum-square (RSS) error arising from the various components from all of the fixed points in the calibration. Figures 5 and 6 show the error propagation curves for the subranges 83.8058 K to 273.16 K and 273.15 K to 933.473 K. The propagated error for each fixed point used in the calibration is shown, with the TPW error being that incurred by the user, not an error in the NIST calibration. The thick line represents the total RSS error for that subrange using the uncertainty associated with the NIST fixed points.

TABLE IV: NIST Total Calibration Uncertainties

Temperature Subrange	Total Uncertainty (RSS), mK
83.8058 K to 273.16 K	0.19
234.3156 K to 302.9146 K	0.10
273.15 K to 302.9146 K	0.10
273.15 K to 492.7485 K	0.70
273.15 K to 505.078 K	1.00
273.15 K to 692.677 K	1.01
273.15 K to 933.473 K	1.18
273.15 K to 1234.93 K	2.00

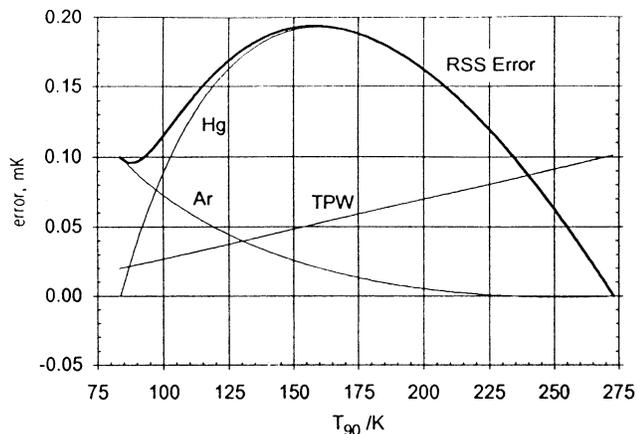


Figure 5. Propagation-of-error curve for the temperature subrange 83.8058 K to 273.16 K. The propagated error for each fixed point is shown, with the TPW error that being incurred by the user. The thick line represents the total RSS error for that subrange based on the uncertainty of the NIST thermometric fixed points.

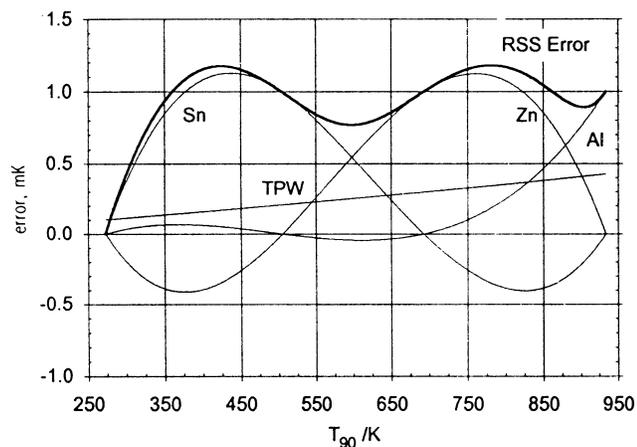


Figure 6. Propagation-of-error curve for the temperature subrange 273.15 K to 933.473 K. The propagated error for each fixed point is shown, with the TPW error being that incurred by the user. The thick line represents the total RSS error for that subrange based on the uncertainties of the NIST thermometric fixed points.

CONCLUSIONS

Through the use of high-quality thermometric fixed points, NIST realizes the ITS-90 over the range from the argon triple point (83.8058 K) to the silver freezing point (1234.83 K). The use of control charts verifies that all of the defining fixed points over this range are highly reproducible and have uncertainties that are acceptable for defining the ITS-90. The introduction of the ITS-90 resulted in an increase in the number of NIST-calibrated SPRTs by almost a factor of two. This increase has been manageable through the use of a semi-automated measurement system. The automation of the data acquisition at NIST has removed a large part of the human error in associated with platinum resistance thermometry. Constant checks on the calibration procedures and equipment ensure a reproducible realization of the ITS-90.

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- Certain commercial equipment, instruments or materials are identified in this paper in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the NIST, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.
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