The Development of a Primary Laboratory for the Calibration of Standard Platinum Resistance Thermometers

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Abstract. Henry Troemner LLC has assembled a temperature calibration laboratory for the calibration of standard platinum resistance thermometers (SPRTs). Calibrations are performed using thermometric fixed points to realize the International Temperature Scale of 1990 over the range 83.8058 K to 933.473 K. These realizations offer the chance to discuss realization techniques necessary to maintain reproducibility and stability of the fixed-points.

INTRODUCTION

The Henry Troemner LLC (Troemner) Primary Platinum Resistance Thermometer (PPRT) Calibration Laboratory provides calibrations based on the International Temperature Scale of 1990 (ITS-90) [1] to government owned facilities, industry and secondary calibration laboratories.

Troemner was founded over 160 years ago by Henry Troemner. The company started as a manufacturer of scales and weights. Today, Troemner, an ISO 9001 company, still is a market leader in the manufacture of precision weights. Troemner certifies weights to the highest tolerance standards of the ASTM and OIML, with the mass calibration laboratories being accredited to ISO 17025 by the United Kingdom Accreditation Service (UKAS) and the National Voluntary Accreditation Program (NVLAP), which is sponsored by the National Institute of Standards and Technology (NIST). Troemner also has a pipette calibration laboratory accredited by NVLAP.

The PPRT calibrates Standard Platinum Resistance Thermometers (SPRTs) by realizing the fixed-points covering the range 83.8058 K to 933.473 K except at the argon triple point where a comparison is made at the boiling point of liquid nitrogen (77.356 K). The PPRT laboratory utilizes a computer and software to automate and speed the collection of data.

COMPONENTS

The PPRT laboratory is a new space within the Troemner facility. Special precautions have been made during the construction of the laboratory to reduce the effects of electrical noise, radio frequencies and other potential interference problems.

The measuring device is an Automatic Systems Laboratories (ASL) model F18 A/C resistance ratio bridge. The NIST has calibrated the bridge and calculated the linearity using a Hamon network. This linearity check is complimented by comparing measured ratios of several calibrated reference resistors of different value to the expected value of the same resistors. To check the repeatability of the bridge, readings from a 25 Ω resistor compared to a 100 Ω resistor have been taken over several days.

All the reference resistors are AC/DC type A and are calibrated biannually. The resistors are maintained in a temperature-controlled oil bath. The stability of the bath is ±0.01 K and is monitored with a calibrated thermistor. This, coupled with the temperature coefficient of the resistors, equates to reference resistor stability of ±0.01 ppm when using a 100 Ω reference resistor and a typical 25 Ω SPRT.

FIXED-POINTS AND REALIZATION

All the thermometric fixed points realized in the Troemner PPRT are the sealed type. This choice is logical for a privately operating laboratory by reducing the amount of apparatus needed to realize the fixed points. The fixed points of gallium, indium, tin, zinc and aluminum are sealed at the manufacturer at one atmosphere to reduce pressure effects. During the manufacturing of the triple points of water (TPW) and mercury (TPHg) the area above the material's surface is evacuated and the cell is sealed, leaving only vapor, allowing the cell to be realized as a triple point.

All of the reference thermometric fixed-point cells have undergone intercomparison at the NIST. The cells are on a four-year intercomparison interval with the NIST. This term will be shortened if the measurements from a monitoring thermometer indicate a change in the reproducibility of the plateau.

The aluminum freezing-point (FP) cell is the sealed type. The cell is cleaned thoroughly to be free from acids and oils to protect the silica glass shell against devitrification. The cell is placed in an Inconel tube, which is closed on one end. A ceramic disk cushions the cell at the bottom, and several ceramic disks are placed on the top of the cell with Inconel washers in between them to act as heat shunts. The entire assembly is then placed in the furnace. The furnace is an Isothech model 875, which is a unique design using air to fluidize alumina powder, which is sealed in a chamber to eliminate the loss of alumina into the laboratory. This design keeps vertical gradients below 50 mK, ensuring the cell does not freeze from the top down. An SPRT is used to monitor the cell during the heating, melting and super-cool. The monitoring SPRT is preheated in an auxiliary furnace taking care to ramp the temperature from 725 K to 936 K over a two hour time period. The aluminum freezing point is achieved by first heating the ingot 5 K above the freezing point. The furnace temperature is then set 0.5 K to 1 K lower than the freeze-point, thus super-cooling the ingot. When the point of recalesence is observed through the monitoring SPRT and the bridge, the SPRT is removed from the cell and inserted into an auxiliary furnace set 3 K above the freezing-point temperature. To set the inner freeze, three clean, ambient-temperature silica rods are inserted in the reentrant well in succession, each for three minutes. This is commonly termed the "double freeze" method, leaving a frozen mantle around the reentrant well and a frozen layer against the outer wall of the crucible.

Any SPRTs that are removed from the aluminum freezing point are inserted into a separate furnace set at 933 K. They are then cooled at a constant rate from 933 K to 700 K over a three-hour period before they are removed to ambient temperature. This protects the thermometer from lattice defects caused by quenching.

The freezing point of zinc assembly is similar to the aluminum cell. The Isotech model 875 is also the furnace used to realize the zinc freezing point. Figure 1 shows the vertical temperature nonuniformity of the 875 with the zinc cell to be 35 mK. The zinc cell is heated 5 K above the freeze temperature for at least eight hours to ensure the ingot is entirely melted. The double freeze method is used to realize the fixed point. The zinc will super-cool 0.1 K below its freezing point. Silica rods are also used to set the inner freeze. SPRTs are preheated before being inserted in the zinc point, but they may be removed and cooled directly to ambient conditions.

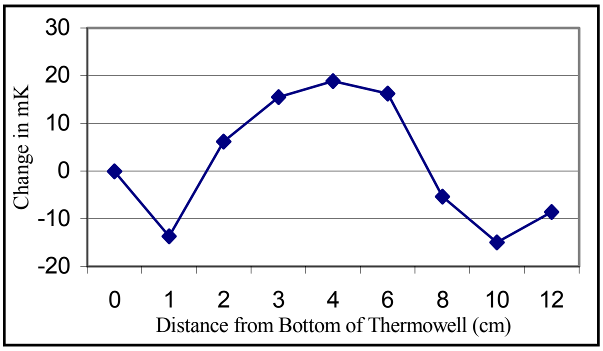

FIGURE 1. Vertical temperature profile of Zn cell in fluidized sand bath furnace, versus distance from the bottom of the re-entrant well.

The tin freezing-point cell assembly consists of the cell being placed in an Inconel basket with a cushion at the bottom and a centering ring at the top, both made of Teflon. The assembly is placed in an Isotech model 915 bath filled with silicone oil. The assembly is suspended deep enough in the oil to keep vertical temperature nonuniformity below 10 mK. The bath is heated to 5 K above the tin freezing point and held there until the ingot is completely melted. The bath temperature is set to 0.5 K below the freezing point, and the entire is assembly is removed from the bath. This method is practiced because tin supercools approximately 25 K below the freeze point. When the monitoring SPRT indicates recalesence, the assembly is replaced in the bath. The monitoring SPRT is removed and two ambient temperature silica rods are inserted in succession for three minutes each. This sets the double freeze.

The freezing point of indium assembly is similar to the tin assembly. The indium assembly is not removed from the bath for super-cooling. Instead, the bath temperature is set 1 K below the freezing point. Upon recalesence the furnace temperature is raised once again to 0.5 K below the freeze point and two silica rods are inserted for four minutes each to set the inner freeze.

The melting point of gallium is maintained in an Isotech gallium apparatus. This apparatus has a timer, which is set to automatically freeze the gallium during the night and then begin a melt sequence to provide a gallium melting point lasting 20 hours. This automatic function allows the gallium melting point to be ready for use for all of a normal working day. The gallium is contained in a Teflon crucible.

The triple point of water (TPW) cell is maintained in an Isotech model 803 bath. This bath can hold up to three TPW cells at one time and utilizes a magnetic stirring mechanism. The TPW realization procedure is well document [2]. It is an essential point in all calculations of thermometers calibrated on the ITS-90.

The triple point of mercury consists of a stainless steel crucible filled with mercury. Air in the cell is evacuated, leaving only mercury vapor. It is advantageous to use stainless steel as it is robust and reduces the risk of accidents resulting in the release of mercury into the environment. The cell is placed in a similar apparatus to the tin and indium fixed-point cells. The triple point is realized by placing the assembly in an Isotech model 915 bath filled with ethanol. A chiller is used in conjunction with the 915 to cool the ethanol. The bath temperature is set 8 K below the triple point. The cell is left overnight at that temperature. The bath temperature is then set 0.5 K above the triple point. The monitoring SPRT indicates the point of nucleation, and the SPRT is removed and inserted into a pre-chill guide tube in the bath. Three ambient-temperature brass rods are inserted in succession into the reentrant well for three minutes over 30 minutes to set the inner melt. Having the liquidous inner and outer melts along with the frozen mercury and the mercury vapor in the cell results in the triple point.

The triple point of argon is not used in the Troemner PPRT Laboratory at present time. A comparison at the boiling point of liquid nitrogen is performed in its place. A NIST-calibrated SPRT is used as the reference in this comparison. The apparatus consists of a stainless-steel dewar with an insulated lid. A copper equalizing block is used to maximize temperature stability. A nitrogen-gas system stirs the liquid nitrogen to maximize uniformity.

CALIBRATION PROCEDURES

In order to calibrate SPRTs on the ITS-90 there are three basic steps: annealing, fixed-point measurements and calculations.

All SPRTs to be calibrated are first measured at the TPW. They are then annealed to remove mechanical strains in the platinum wire caused by shipping, general use and misuse. All SPRTs are first cleaned to remove oils and acids. All SPRTs are annealed for four hours at 725 K to 750 K. SPRTs that are used up to and below the zinc point are then removed to ambient to cool. SPRTs that are to be used to 933 K are then heated to 945 K with a ramp function that ensures the time it takes to raise the SPRT from 750 K to 945 K is more than two hours. The SPRT is held at 945 K for two and half-hours, then the annealing furnace temperature is set to 750 K. A ramp function is used to ensure this cooling process takes more than three hours. The SPRT is then removed to ambient conditions. The thermometer is measured at the TPW again, and if the TPW values before and after the anneal are not within 0.75 mK the annealing process is repeated and continued until the thermometer is stable, or deemed unsuitable for calibration. Studies have been conducted by the NIST to determine the optimum time required for annealing and thermal treatment of SPRTs [3].

All SPRTs have their insulation resistance checked at ambient conditions and at the highest temperature during the annealing process. These are compared to manufacturer’s specifications and standards set by committees, such as ASTM.

If the SPRT is to be used above the TPW, the next measurement is made at the fixed point of the upper limit of the range of the SPRT. The successive measurement sequence for a SPRT to be calibrated from the TPW to the freezing point of aluminum would be: TPW, FPAl, TPW, Zn, TPW, Sn, TPW. If the SPRT is to be calibrated below the TPW, the next measurements would be at TPHg, TPW, comparison at the boiling point of liquid nitrogen, TPW.

Corrections must be made to ensure the SPRT was measured at the ITS-90 assigned fixed-point temperature. At the Troemner PPRT Laboratory corrections are made for hydrostatic head and external self-heating. No correction is made for pressure because all of the cells were sealed at one atmosphere when they were manufactured. The hydrostatic head effect is calculated by knowing the distance from the bottom of the re-entrant well to the top of the column of liquid and the distance from the tip of the SPRT to the mid-point of the sensing element. The difference in these distances is the amount of hydrostatic head. Troemner has chosen to rely on the information provided from the manufacturer regarding the hydrostatic head measurement of each cell, save TPW, which is easily seen and measured with a rule. One could X-ray a cell to obtain a better hydrostatic head measurement, but the fact that our cells have been intercompared at the NIST ensures the manufacturer's data is within uncertainties Troemner desires. The hydrostatic head correction is converted to ohms and added to the measured resistance of the SPRT. The external self-heating correction, if any, is also added. The Troemner PPRT Laboratory has adopted the NIST external self-heating error of an SPRT with 1 mA current applied to be 0.1 mK in a fixed-point cell. By measuring at two currents and extrapolating to zero power, the external self-heating errors can be eliminated. The formula for the extrapolation is shown in equation (1) where R_0 is the resistance at zero power, R_1 is the resistance at the lower current i_1, and R_2 is the resistance at the higher current i_2.

$$R_0 = R_1 - i_1^2\left[\frac{(R_2 - R_1)}{(i_2^2 - i_1^2)}\right] \tag{1}$$

All measurements are taken via an IEEE interface between the ASL model F18 bridge with a scanner and a personal computer. The ASL model F18 computer software enables the user to select the reference resistor and scanner channel to be measured. All the reference resistors are Tinsley AC/DC type A and are maintained in a temperature-controlled oil bath at 296.15 K ± 10 mK. The reference resistors are calibrated at regular intervals by the NIST. To ensure there is no drift in the value of the reference resistance, the temperature of the reference resistor is checked at the beginning and end of the day.

Measurements are only taken when thermal equilibrium has been achieved. A series of measurements is taken at the fixed point and the data is analyzed to ensure thermal equilibrium. Once equilibrium is proved, measurements are taken and a final average of this data is used in the calibration calculations for the SPRT being calibrated. Each SPRT being calibrated is also measured with a minimum of two currents to extrapolate to zero power. A monitoring SPRT is used prior to each set of test thermometer measurements at a fixed point to ensure the fixed point is on its plateau. Typically, up to four SPRTs can be measured at each fixed point followed by a repeat measurement with the monitoring SPRT to prove the fixed point remained on the plateau for the entire calibration time. The difference in the two measurements of the monitoring SPRT indicates the total change of temperature during the measurements. If the difference in temperature of the monitoring SPRT at the aluminum, zinc and tin freeze points exceeds 0.5 mK, or 0.25 mK at the indium freeze point, or 0.1 mK for the gallium melting point, or 0.15 mK for the mercury triple point, the calibration is repeated. These limits are set based on repeated monitoring of the realizations.

The data from the measurements at the fixed points can now be utilized to calculate the $W(T_{90})$ values, where $W(T_{90})=R(T_{90})/R(273.16\ \mathrm{K})$. This equation is the basis for calculating the coefficients of the deviation functions of the ITS-90. The Troemner PPRT Laboratory has adopted the NIST notations for the sub-ranges of the ITS-90 [4].

The ASL computer software validates the SPRT calibration data to ensure the SPRT meets the specifications of the ITS-90 relative to W(Ga) and/or W(Hg).

All SPRTs are checked over the course of their calibrations for changes in resistance at the TPW. If these deviations over the range 83.8 K to 933.4 K with a 25 Ω SPRT are more than 0.8 mK for silica sheathed SPRTs or more than 1.0 mK for metal-sheathed SPRTs, the SPRT may be rejected. Special attention is paid to the TPW readings before and after the freezing point of zinc. A temperature change larger than 0.4 mK at zinc usually indicates insufficient annealing time or large mechanical strains. If this is the case, it may be possible to anneal the SPRT for a longer period at 750 K and re-calibrate the SPRT in an attempt to reduce the change.

Although sometimes redundant, the SPRT is measured at all fixed points in its range. These extra measurements are sometimes necessary to ensure that the SPRT meets the specifications of the ITS-90 relative to W(Ga) and/or W(Hg). These measurements also serve as a good check to compare measured $W(T_{90})$ with expected values of $W(T_{90})$.

UNCERTAINTIES

In developing the uncertainty budget at each fixed point, Troemner follows the NIST publication Technical Note 1297, *Guidelines for Evaluating and*

Expressing the Uncertainty of NIST Measurement Results [6].

The uncertainty of an SPRT calibration, in the most basic sense, is dependent upon the reproducibility and the stability of the fixed points. There are many things which can effect the reproducibility of the fixed-point realizations, including the measuring system, which comprises the reference resistor, bridge, scanner and wiring, and the stability and drift of the check SPRTs. The level of impurities in the fixed point also plays a major role in the uncertainty budget.

The major components in the uncertainty budget are listed in Table1. The bridge repeatability component was determined by repeated measurements of a 25 Ω standard resistor compared to the 100 Ω reference resistor over a 72 h period. The bridge non-linearity component was derived from having the bridge calibrated at the NIST using a Hamon network. Phase transition repeatability is determined by realizing the fixed point and comparing the monitoring thermometer measurements to previous realizations. Currently Troemner is still conducting some of these measurements. Quadrature effects have been determined by examining the difference between short and long wiring paths at a single frequency. Temperatures were simulated using resistors of different value held in an oil bath. The reference-resistor resistance component is established by knowing the temperature coefficient of the reference resistor and the resistor temperature. The temperature coefficient is known from manufacturer specifications and the resistor temperature was measured over time. It is important to note that if two different reference resistors are used during a calibration, the uncertainty of the value for the resistor must also be combined in this component. Tromener has set the impurity and gas pressure of each fixed-point cell as one component in the uncertainty analysis based on the NIST intercomparisons. The NIST has provided a report stating the average difference from the NIST reference cell from nine measurements, which were taken from three separate realizations. The NIST has accounted for hydrostatic head differences between the Troemner cell and the NIST reference cell. The uncertainty of the NIST reference cell used in the intercomparison is included in this component as well. Hydrostatic head measurements are quantified as a separate component. Distances from the tip of a thermometer to the center of its sensor differ, forcing this component to change with almost every thermometer. In order to convert the distance from the measurement to a temperature, the distance measurement of head is multiplied by the hydrostatic effect for the specific cell. SPRT external self-heating is estimated from manufacturer's specifications, if none are available 0.1 mK/mA^2 is used. Heat flux is also considered as a separate component. To determine the amount of heat flux the SPRT is measured over the bottom most 3 cm of the fixed point cell. The SPRT must track the hydrostatic head effect over this distance. The deviation from the assigned hydrostatic head effect is calculated as this component. The slope of the plateau must be considered as well. The uncertainty is determined by analyzing the difference in resistance value from the beginning and end of the plateau using the data measured from the monitoring thermometer. This sets the limits for allowable change during the calibration. Isotopic variations of the TPW cell is considered and has been incorporated in the TPW cell uncertainty component as the cell has been intercompared at the NIST. Propagation of the TPW uncertainty is a separate component and is determined by using the reference function $W_r(T)$ of the SPRT.

TABLE 1. Major uncertainty components (shown with values for H_2O and the Hg fixed point).

Component	H_2O	Hg
Type Type A (in mK)		
Bridge Repeatability	0.020	0.020
Bridge Non-linearity	0.046	0.046
Phase Transition Reproducibility	0.030	0.100
Total Type A	0.059	0.112
Type B (in mK)		
Quadrature Effects	0.010	0.030
Reference Resistor Resistance	0.010	0.010
Cell Certification by NIST	0.070	0.310
Hydrostatic Head Effect	0.005	0.012
External Self-heating	0.010	0.010
Heat Flux	0.007	0.007
Slope of Plateau	0.000	0.000
Propagated TPW	0.000	0.073
Isotopic Variations	0.020	0.000
Total Type B	0.043	0.185
Total Type A and B combined	0.073	0.216
$U(k=2)$	**0.146**	**0.433**

METROLOGY CONTROLS

Periodic checks of all instruments in the calibration chain are performed to ensure repeatability and proof of drift or the lack of drift. Control charts are kept for each monitoring SPRT at each fixed point. These control charts show the phase transition repeatability of the fixed-point realizations. Figure 2 shows the repeatability of the control SPRT of the TP of Hg cell. It is important to note that the drift of these monitoring SPRT's is also kept as a control chart. This is possible by measuring each monitoring SPRT at the TPW before and after each time it is used at a fixed point and analyzing this data in a separate chart.

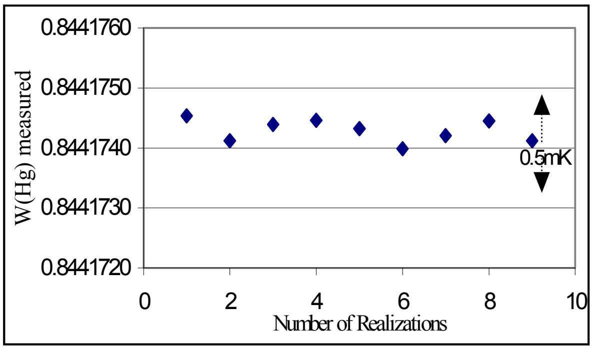

FIGURE 2. Control chart for an SPRT at the TP of Hg over 10 realizations in terms of *W*(Hg).

Calibrated reference resistors of three different values are used in a three-way complement check every three months [5]. This ensures resistance ratio bridge accuracy and linearity. In addition to these three-way complement checks, daily measurements of a 25 Ω resistor against the 100 Ω reference resistor ensure bridge repeatability. This procedure is also performed quarterly taking measurements over a 48 hour period. These measurements provide a repeatability control chart for the resistance ratio bridge. Figure 3 shows one of these repeatability charts. All the reference resistors are calibrated at the NIST every 6 months.

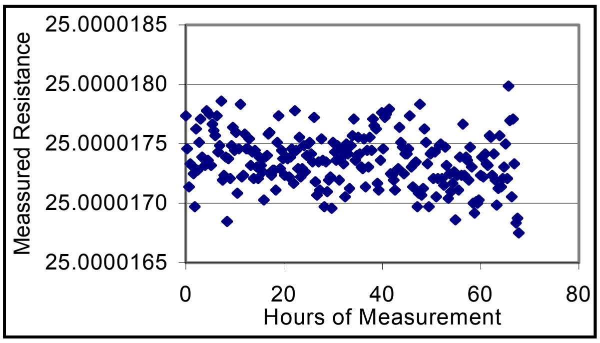

FIGURE 3. Measurements of a 25 Ω resistor versus a 100 Ω reference resistor shown as resistance measured over time (72 hours). Each point is the average of 36 readings. F18 bridge settings: 30 Hz, 1 mA, 0.1 Hz bandwidth.

Each time a fixed point is realized, a monitoring thermometer is used to indicate when the plateau has been achieved. Each fixed point has a dedicated monitoring thermometer. All the measurements for each fixed point are plotted in terms of *W* in a chart. This chart is used to analyze the reproducibility of the fixed point. The chart can be use to indicate a problem with any particular realization and to ensure there is no drift in the fixed point. Each monitoring SPRT also has a control chart of each measurement at the TPW. This is useful to analyze drift in the monitoring SPRT.

FUTURE PLANS

Foremost, finishing the collection of data for the realization repeatability on all the fixed-point cells will be completed. This will include heat flux testing at each fixed point as well as testing for errors caused by self-heating. Future plans also include participating in the NIST Measurement Assurance Program (MAP). Troemner also is seeking accreditation by NVLAP.

Future plans also include procuring dedicated furnaces for each of the fixed points currently in use at the Troemner PPRT Laboratory. Further, the addition of the argon triple point will provide a fixed-point calibration to 83.8058 K. A second resistance ratio bridge equal to the ASL F18 will improve throughput as well as provide a means of intercomparing measurements.

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