

An Independent Quality Check Of Secondary Platinum Resistance Thermometer Calibrations Above 0 °C

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Abstract. Traditionally the use of least squares to evaluate the fit and consistency of a platinum resistance thermometer calibration requires the use of several redundant calibration points each of which adds time and expense to the calibration process. However the behavior of some secondary platinum resistance thermometers is sufficiently close to the ITS-90 reference function to allow a simplification to the deviation function, at least for the purpose of a quality check. By using the first order deviation function the number of degrees of freedom available for a least squares fit is increased and the linear correlation between PRT resistance ratios may be explicitly written in equation form.

INTRODUCTION

Traceability in temperature is provided over a significant portion of the temperature scale through platinum resistance thermometers. As stated in the definition of the ITS-90, “an acceptable platinum resistance thermometer must be made from pure, strain-free platinum, and it must satisfy” one of two specified resistance ratio relations. A platinum resistance thermometer (PRT) that does not satisfy all of these requirements cannot be called a Standard Platinum Resistance Thermometer (SPRT.) However SPRTs are very delicate instruments and there are many situations in which a more rugged design is appropriate. These rugged probes are often called secondary or industrial platinum resistance thermometers.

Secondary platinum resistance thermometer calibrations can be time consuming and expensive, especially as market forces favor lower uncertainties and laboratory accreditation adds additional layers to the process.

The quality check suggested in this paper strikes a balance between the competing requirements of cost and quality while improving the confidence of the metrologist in the uncertainties provided by his or another laboratory in the calibration of secondary platinum resistance thermometers.

LINEAR RELATIONSHIPS BETWEEN RESISTANCE RATIOS

The defining document of the ITS-90 also states that, “temperatures are determined in terms of the ratio of the resistance $R(T_{90})$ at a temperature T_{90} and the resistance $R(273.16K)$ at the triple point of water.” This ratio called $W(T_{90})$ has been found to be linearly correlated between temperature fixed points in Standard Platinum Resistance Thermometers. Like the resistance ratios of SPRTs, the $W(T_{90})$ values of secondary platinum resistance thermometers are linearly correlated in that they satisfy the relation:

$$W_{T_2} = mW_{T_1} + b. \quad (1)$$

The values ‘m’ and ‘b’ may be theoretically or empirically determined. Empirical determination involves performing a linear regression on data collected for many different thermometers. Theoretically it involves manipulating the available ITS-90 equations. Happily the results from both are consistent.

Once the linear regression is performed, a simple relationship appears.

$$m + b = 1 \quad (2)$$

Consequently (1) can be rewritten into the form:

$$W_{T2} - 1 = m(W_{T1} - 1) \quad (3)$$

This looks very much like the first order ITS-90 deviation function:

$$\Delta W_{T90} = a (W_{T90} - 1) \quad (4)$$

And since $W_{r, T90}$ represents the ITS-90 reference function at the temperature T_{90} we can also write:

$$\Delta W_{T90} = W_{T90} - W_{r, T90} \quad (5)$$

By using equations (4) and (5), equation (3) may be rewritten in terms of W_{T1} , $W_{r, T1}$, W_{T2} and $W_{r, T2}$. The resulting function gives a value for 'm' exclusively in terms of the reference function:

$$m = \frac{W_{r, T2} - 1}{W_{r, T1} - 1} \quad (6)$$

On the following plot the linear relationship between pairs of resistance ratios (W_{Sn} , W_{Zn}) for a number of thermometers is demonstrated. The plot of these thermometers satisfies equations (3) and (6).

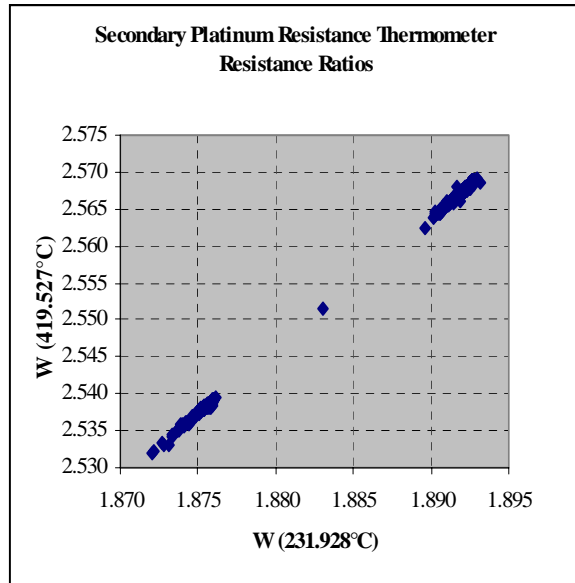


FIGURE 1. A plot of (W_{Sn} , W_{Zn}) for 1477 approximations of the ITS-90 using 1007 different Secondary Platinum Resistance Thermometers

Consistency Checks On PRT Calibrations

The linear correlation in PRT resistance ratios suggests equation (4) as a reasonable simplification to the ITS-90 deviation function for performing calibration quality checks. There are two main ways to use the simplified deviation function to check the consistency of calibration points above 0 °C. These are least squares and linear prediction.

Least Squares

A simplified deviation function is not necessary to perform least squares. However there is an advantage in the increased number of degrees of freedom. Since the simplified function reduces the number of coefficients by one or two it has the equivalent effect (for evaluation purposes) of increasing the number of calibration points, but without increasing the cost of the calibration. With more degrees of freedom the residuals become more useful and may give the metrologist more information about the quality of the calibration.

To apply least squares to the simplified deviation function, solve the following equation to obtain the ITS-90 coefficient expressed in equation (4):

$$a = \frac{\sum_i^N \Delta W_i (W_i - 1)}{\sum_i^N (W_i - 1)^2} \quad (7)$$

The residuals may then be calculated and converted into temperature by dividing by the sensitivity at each corresponding temperature.

$$R_{T90} = \frac{a(W_{T90} - 1) - (W_{T90} - W_{r, T90})}{\frac{dW_{T90}}{dT}} \quad (8)$$

In the situation where calibration points are not consistent, the residuals will indicate in terms of temperature how large the inconsistency is.

Linear Prediction

On the other hand, residuals for linear prediction are calculated using:

$$R_{LP} = \frac{\frac{W_{r,T2} - 1}{W_{r,T1} - 1} (W_{T1} - 1) - (W_{T2} - 1)}{\frac{dW_{T2}}{dT}} \quad (9)$$

Another, sometimes convenient, form of the equation for linear prediction residuals is:

$$R_{LP} = \frac{\frac{W_{r,T2} - 1}{W_{r,T1} - 1} \Delta W_{T1} - \Delta W_{T2}}{\frac{dW_{T2}}{dT}} \quad (10)$$

When $T1 < T2$, large residuals will result with small variations in $T1$. However, more realistic values for R are obtained when the condition $T1 > T2$ is met.

Whatever the method used, the general idea is to make logical deductions from the residuals to determine which calibration points least fit the model. For example, if the first order least squares residuals at Sn and In both have the same large magnitude and sign and the Zn point is also large in magnitude but opposite in sign then the Zn point should be double checked. With a larger number of data points, the decision making process is easier, however the

calibration also becomes more time consuming and expensive.

Empirical Data

The tables below were generated from data collected by measuring platinum resistance thermometers in mini fixed point cells using a Hart Scientific model 1590 digital thermometer readout. If a thermometer happened to be calibrated more than once, then only the most recent calibration data was admitted into the data set. Mean values were computed along with the standard deviation of the mean. The confidence interval chosen was 95% with the coverage factor computed using the Student's T for $N-1$ degrees of freedom.

Results for three popular models of secondary platinum resistance thermometers sold by Hart Scientific are presented in the tables below. The model 5628 has a range of $-200\text{ }^{\circ}\text{C}$ to $660\text{ }^{\circ}\text{C}$ and a nominal resistance at the triple point of water of 25

100 The model 5614 has a range of $-200\text{ }^{\circ}\text{C}$ to $420\text{ }^{\circ}\text{C}$ and a nominal resistance at the triple point of water of 100

TABLE 1. Average residuals from data fit to a first order deviation function using least squares.

Model Number	R_{In}	R_{Sn}	R_{Zn}	N
5628	$-0.7 \pm 0.3\text{ mK}$	$-0.7 \pm 0.2\text{ mK}$	$0.7 \pm 0.2\text{ mK}$	229
5626	$-2.4 \pm 0.2\text{ mK}$	$-1.8 \pm 0.1\text{ mK}$	$2.1 \pm 0.1\text{ mK}$	411
5614	$-6.6 \pm 1.6\text{ mK}$	$-8.1 \pm 2.1\text{ mK}$	$7.7 \pm 1.8\text{ mK}$	15

TABLE 2. Average residuals from data fit to a second order deviation function using least squares.

Model Number	R_{In}	R_{Sn}	R_{Zn}	N
5628	$-0.2 \pm 0.1\text{ mK}$	$0.2 \pm 0.1\text{ mK}$	$-0.1 \pm 0.0\text{ mK}$	229
5626	$-0.3 \pm 0.1\text{ mK}$	$0.3 \pm 0.1\text{ mK}$	$-0.1 \pm 0.0\text{ mK}$	411
5614	$1.1 \pm 0.9\text{ mK}$	$-1.1 \pm 0.9\text{ mK}$	$0.2 \pm 0.2\text{ mK}$	15

TABLE 3. Average residuals of data calculated using linear prediction.

Model Number	R_{In} (Calculated from W_{Sn})	R_{In} (Calculated from W_{Zn})	R_{Sn} (Calculated from W_{Zn})	N
5628	$-0.3 \pm 0.2\text{ mK}$	$-1.0 \pm 0.3\text{ mK}$	$-1.0 \pm 0.3\text{ mK}$	229
5626	$-1.2 \pm 0.1\text{ mK}$	$-3.0 \pm 0.2\text{ mK}$	$-3.2 \pm 0.2\text{ mK}$	411
5614	$-1.2 \pm 1.3\text{ mK}$	$-12.2 \pm 3.1\text{ mK}$	$-9.3 \pm 2.2\text{ mK}$	15

DISCUSSION

One trend in the results given in the tables is that model 5628 PRTs had the best fit in all of the schemes used, while the model 5614 was not fit as well by the linear models proposed. For all of the probe models the Sn (232.928 °C) and In (156.599 °C) temperature fixed points were the most consistent with each other. In the least squares data their residuals were nearly equal and opposite in magnitude from the Zn (419.527 °C) point.

Residuals calculated from linear prediction were larger than in any of the other schemes. Least squares used all of the available data to minimize the residuals. Linear prediction used only one resistance ratio at a temperature fixed point to calculate the resistance ratio at another temperature fixed point. W_{Zn} was most frequently the least consistent resistance ratio.

There are a number of possible factors that might have influenced the result at Zn. For example the designs of these thermometers are not strain-free and there may have been hysteresis with relaxation at the highest temperature (419.527 °C.) Yet these types of probes are not believed to exhibit hysteresis, generally speaking.

All three platinum resistance thermometer models have sufficient immersion in the mini fixed point cells. To verify this, PRTs long enough to be sufficiently immersed in large fixed point cells (length >18") were measured first in the large cells followed by measurements in the mini cells. Results were compared and found to differ by only a few tenths of a mK.

Model 5614 and 5626 PRTs have nominal resistances of 100 at the triple point of water compared to the 25 PRT (model 5628.) The 100

PRTs have the largest residuals from the first order least squares fit. This suggests that self heating may have contributed to the residuals.

Normally only the nominal current of 1 mA is used when calibrating secondary probes in our laboratory. The zero power was calculated on one 5614 and one 5626 in the mini fixed point cells in order to gain some insight into the self heating of the thermometers. The temperature differences between the zero power and 1 mA measurements increased slightly with increasing temperatures and were about 5 mK in all three cells for the 5626 and about 8 mK in all three cells for the 5614. The approximate contribution to the linear

prediction residual believed to be due to self heating is expressed in equation (11) and the resulting self heating contribution based on the previously mentioned measurements are listed in Table 4.

$$R_{SH}(T1, T2) = SH_{T1} \frac{W_{r,T2} - 1}{W_{r,T1} - 1} - SH_{T2} \quad (11)$$

TABLE 4. Self Heating Contribution to First Order Least Squares Residuals.

Residual	5614	5626
$R_{SH}(\text{Sn, In})$	-2 mK	-1 mK
$R_{SH}(\text{Zn, In})$	-5 mK	-2 mK
$R_{SH}(\text{Zn, Sn})$	- 4 mK	-2 mK

It is not clear from Table 4 that self heating alone will completely explain the residuals for the model 5614 PRTs. To illustrate, the self heating for the general population of probes would have to be nearly twice the previously measured values. However self heating effects do seem consistent with the residuals seen in the model 5626 PRTs.

Another influence quantity that may be responsible for the seemingly inconsistent value observed at Zn for the model 5614 PRTs is electrical leakage. Insulation resistance break down will be the most severe at high temperatures. All thermometers tested indicated at least 100 M of insulation resistance at 0°C, nevertheless lower insulation resistances at 420°C may have contributed to the results.

Finally, for some secondary platinum resistance thermometers a first order approximation may be limited in value above certain temperatures. For all models of PRT described here a first order approximation fits well up to 232 °C. On the other hand this approximation continues to be a good fit for the 5628 up through 660 °C.

CONCLUSION

The purpose of this paper has been to develop an independent quality check that gives additional support to claims of traceability by improving confidence in measurements made during the calibration of secondary platinum resistance thermometers. The method was to develop a model that made it possible to infer that a pair of resistance ratios may be inconsistent. The simplification to the deviation function used in this procedure was not intended to reduce the number of recommended calibration points;

on the contrary it becomes more powerful as the number of calibration points is increased. However it does make possible a check for consistency when a minimum of two calibration points are used.

In fact, an additional check of quality used in our laboratory includes taking more than the minimum number of temperature points to complete a calibration. One way of using the extra measurements is to least squares fit all of the available data to the ITS-90 deviation function. The function will not pass perfectly through each calibration point, and residuals are evaluated as an indication of the mathematical fit of the calibration. Additionally, when calibration points are properly spaced, the least squares method may have the benefit of averaging out some of the unusual behavior of secondary PRT's, as well as the added benefit of reducing the propagated uncertainties.

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