CALIBRATION AND ACCURACY OF SECONDARY STANDARD PRT'S TO THE ITS-90

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ABSTRACT

The Standard Platinum Resistance Thermometer (SPRT) portion of the ITS-90 was formulated for specific, very high quality PRT's. The accuracy of fit to the ITS-90 of these thermometers is well documented. In many cases, however, "secondary" grade thermometers are used when less accuracy can be accepted. The accuracy of fit to the ITS-90 that can be achieved with these thermometers is much less clear. Additionally, these thermometers are generally calibrated in comparison baths at temperatures which are likely to differ by some amount from the actual ITS-90 fixed points. This project was undertaken to study the behavior of these thermometers over the temperature range of 77.65 K to 693.15 K (-195.5 °C to 420 °C). It is composed of calibration as outlined in the ITS-90 with subsequent comparison calibration to SPRT's. Thermometers from several leading manufacturers are included. The data will be fitted to the mathematical formulae as specified in the ITS-90 and several alternative equations.

INTRODUCTION

Temperature has always been an important parameter in manufacturing, testing, and scientific endeavors. With each succeeding temperature scale, the ability to measure and disseminate temperature information has become more widely available and more precise. The introduction of the ITS-90 brought with it a much needed increase in the flexibility of the scale. The scale definition itself consists of defining fixed points, designated interpolation instruments, and specified mathematical formulae. The flexibility is due to the many subranges, overlapping ranges, and multiple definitions. The range of 13.8033 K to 1234.93 K will probably be the most used range of the ITS-90. The designated interpolating instrument for this range is the standard platinum resistance thermometer (SPRT). The reference functions and deviation functions which are specified for this range are straightforward and not difficult to use. Most primary and many secondary laboratories can benefit from the ITS-90 by having an SPRT directly calibrated at the appropriate fixed points by NIST or another primary facility. This

SPRT can in turn be used to calibrate other SPRT's by comparison methods or to calibrate other temperature reading devices.

When other SPRT's are calibrated against a reference SPRT by the comparison method, the process is again, very straightforward. First, comparison points are chosen which correspond very closely to the ITS-90 designated fixed points for the subrange(s) of interest. Second, measurements are made at all of the required temperatures. Third, corrections are applied for self heating, etc. Fourth, the functions are solved for the coefficients. Fifth, ITS-90 criteria compliance is checked. Finally, a Report of Calibration and/or an interpolation table is printed and the calibration is complete. Admittedly, this is a very simplified outline of SPRT calibration by comparison. The SPRT user can use either an interpolation table or a computer to convert measured resistance ratios (W's) to temperature values or, alternatively, a precision thermometer with the ITS-90 built in can be programmed with the SPRT coefficients and temperature can be read directly.

The mathematical formulae specified for the SPRT portion were developed around very high purity, essentially strain free platinum elements with calibrations at the fixed points specified. If the thermometer is a high quality SPRT, and it complies to the ITS-90[1], it can be assumed that it will fit the interpolation functions precisely. The propagation of errors at the calibration points to the points between has also been clearly shown[2]. Furthermore, much work has been done to demonstrate, with a high degree of confidence, the precision of the SPRT portion of the ITS-90 with its various subranges[3].

It can be concluded that, at the primary level, the ITS-90 is a precise, flexible temperature scale. It is relatively easy to implement and the mathematics are not complicated. The situation is not so clear at the secondary level. Since the reference and deviation functions were developed for SPRT's, it is not surprising that the fit achievable with secondary PRT's is less than optimum. Measurement errors larger than expected are being observed at intermediate temperatures. Also, in many cases, the range desired terminates at a temperature between two ITS-90 fixed point temperatures. Three questions present themselves:

1) What if the thermometer does not comply to the ITS-90 with respect to purity and/or mounting?
2) What if calibration is desired over a temperature range which is not one of the ITS-90 subranges?
3) Since there is no "standard" for secondary grade thermometers, how does the resistance vs. temperature relationship differ from one manufacturer to another?

If the ITS-90 does not fit these secondary grade thermometers well, it may be beneficial to apply alternative equations which fit them more precisely. If so, what form should the equation(s) take or, alternatively, which of the traditional equations should be used? Additionally, how many calibration points should be used and over what temperature range? It may be beneficial to employ different equations or different fitting schemes for the different temperature ranges. Finally, since many thermometer users employ digital thermometers in their measurement systems, it would be desirable to use an equation which is built in to the thermometer's firmware or to introduce an equation which is sufficiently universal to warrant firmware revisions.

This project was undertaken to investigate these issues. A total of 14 thermometers from 7 manufacturers were included. Calibrations were performed by fixed point and then by comparison. Solutions were calculated for the ITS-90 with the fixed point data and for the ITS-90 and four additional equations with the comparison data. The comparison data solutions were calculated with several different temperature schemes for each of the 4 equations. Due to the equipment available in this laboratory, and on the advice of some of the manufacturers represented, the temperature range investigated was limited to ≈77.65 K to 693.15 K (-195.5 °C to 420.0 °C). The experimental measurements were carried out in a process very close to the actual calibration processes employed in the laboratory. The PRT's were numbered in two batches of seven. Therefore, numbers 0 and 7 are the same manufacturer/model, 1 and 8 are the same manufacturer/model, etc. Whenever possible, the tables and graphs will be structured to indicate this relationship.

THE FIXED POINT MEASUREMENTS

EXPERIMENTAL DETAILS

The fixed point measurements were performed in the Primary Thermometry Laboratory. This laboratory is equipped for primary calibration of SPRT's and noble metal thermocouples. The equipment used is as follows: An ASL F18 AC Resistance Bridge with a Tinsley 100 Ω AC/DC Standard Resistor and a Vishay 300 Ω metal film resistor are used for the resistance measurements. The resistors are maintained in oil at 25.000 °C in a Guildline Oil Bath. The cells are Isotech sealed fixed point cells of 99.9999% or better purity. A Pond Engineering furnace is used to realize the zinc freeze, a YSI furnace is used to realize the tin freeze, and a modified Tenney oil bath is used to realize the mercury triple point. The realization process is conventional in all respects and is described elsewhere[4]. Each fixed point has a dedicated SPRT and the measurements are maintained in a state of statistical control. This laboratory does not have an argon triple point apparatus. As a result, the triple point of argon fixed point is substituted by comparison calibration to a NIST calibrated capsule SPRT in a modified commercially available comparison apparatus. The comparison can be made in liquid nitrogen or liquid argon and also has a dedicated SPRT for statistical control. Due to the assorted sizes of the subject PRT's, this apparatus could not be employed and the liquid nitrogen comparison had to be done in the conventional manner utilizing a nickel plated copper block suspended in an open dewar of LN_2.

Fixed point calibrations are carried out starting with a baseline resistance measurement at the triple point of water (R_{TPW}). This measurement has several purposes. First, it shows the initial condition of the thermometer as received in the laboratory. Second, if the thermometer belongs to another laboratory, it indicates any damage that may have occurred during shipping (provided the R_{TPW} was observed by the user before it left for calibration). Finally, it is the baseline measurement used to determine what was accomplished during the annealing process. The purpose of the annealing procedure is to stabilize the thermometer element both physically with respect to strain and chemically with respect to oxidation. Thermometers to be calibrated over the previously stated temperature range are normally annealed for approximately 4 hours at 723.15 K (450.00 °C). After the initial annealing, the R_{TPW} is measured a second time.

Generally, the R_{TPW} has decreased the equivalent of from 1 to 3 mK (in the experience of this laboratory, however, decreases of over 5 mK have been observed). Very rarely does the R_{TPW} increase on annealing. The process is repeated and the R_{TPW} generally decreases less than the equivalent of 0.5 mK after the second annealing. If necessary, the process is repeated a third time. If the thermometer is not stable after the third annealing, alternative annealing procedures[5] are undertaken until the thermometer is stable or it is determined that it cannot be calibrated. The annealing procedure is considered successful when two successive R_{TPW} values differ by less than a few tenths of a mK. Again, in the experience of this laboratory, most thermometers prove stable after the second annealing.

The values discussed above apply to SPRT's. At the beginning of this experiment, it was not known exactly what to expect from the subject PRT's. Therefore, the limit for the stability of the R_{TPW} was set to 5 mK. The annealing procedure outlined above was carried out for each of the PRT's with the following exception. One manufacturer recommended that their thermometers not be subjected to temperatures above 673.15 K (400.00 °C) for any significant period of time. The zinc freezing point is approximately 693 K (420 °C) and would require exceeding this recommended upper limit. It was decided that these thermometers could withstand the minor excursion required without damage if the magnitude of the excursion was kept as low as possible and the duration was limited to as short a time as possible. As a result, an annealing temperature of approximately 698 K (425 °C) was chosen and the procedure outlined above was followed.

Following successful annealing of the PRT's, the actual fixed point measurements are undertaken in the following order: (1) zinc point, (2) TPW, (3) tin point, (4) TPW, (5) mercury point, (6) TPW, (7) LN_2 comparison, and (8) TPW. The TPW measurements are used in the ITS-90 calculations as well as indications of the stability of the PRT during calibration. For quartz sheath SPRT's, if the R_{TPW} changes by more than the equivalent of 0.7 mK during the calibration, it is reannealed and calibration is attempted a second time. For metal sheath SPRT's, the limiting value is 1.0 mK. As mentioned earlier, it was not known exactly what to expect from these PRT's, therefore, it was decided that the maximum change in R_{TPW} would be reported and no calibrations would be repeated. The measurement process provides a graphical representation of the bridge reading in real time for all of the data being collected. Therefore, any unusual trends can be observed while the measurement is in progress.

Following the fixed point measurements, the data are fitted to the ITS-90 functions. There are two general equations for all PRT's on the ITS-90. Also, there are two reference functions and two corresponding deviation functions for the temperature range in question. (The form shown below may be slightly different from that in the official version in the ITS-90.) The equations are expressed in terms of the ratio of resistance at some temperature T to that at the TPW. The resistance ratio is designated W, such that:

$$W\left(T_{90}\right) = \frac{R\left(T_{90}\right)}{R_{TPW}} \tag{1}$$

The reference function is related to the deviation function with the following expression:

$$\Delta W\left(T_{90}\right) = W\left(T_{90}\right) - W_r\left(T_{90}\right) \tag{2}$$

The reference functions and the deviation functions for the ranges of interest are shown below.

Reference function for the range 13.8033 K to 273.16 K (-259.3467 °C to 0.01 °C):

$$\ln\left(W_r\left(T_{90}\right)\right) = \sum_{i=0}^{12} A_i \cdot \left(\frac{\ln\left(\frac{T_{90}}{273.16}\right) + 1.5}{1.5}\right)^i \tag{3}$$

Deviation function for the subrange 83.8058 K to 273.16 K (-189.3442 °C to 0.01 °C):

$$\Delta W_4\left(T_{90}\right) = a_4 \cdot \left(W\left(T_{90}\right) - 1\right) + b_4 \cdot \left(W\left(T_{90}\right) - 1\right) \cdot \ln\left(W\left(T_{90}\right)\right) \tag{4}$$

Reference function for the range 273.15 K to 1234.93 K (0.00 °C to 961.78 °C):

$$W_r\left(T_{90}\right) = \sum_{i=0}^{9} C_i \cdot \left[\frac{\left(T_{90} - 754.15\right)}{481}\right]^i \tag{5}$$

Deviation function for the subrange 273.15 K to 692.677 K (0.00 °C to 419.527 °C):

$$\Delta W_8\left(T_{90}\right) = a_8 \cdot \left(W\left(T_{90}\right) - 1\right) + b_8 \cdot \left(W\left(T_{90}\right) - 1\right)^2 \tag{6}$$

The designations 4 and 8 in the deviation functions , eqs. (4) and (6) were inserted by NIST for identification of specific subranges. The values for the coefficients A_i and C_i in the reference functions, eqs. (3) and (5) are given in Table 1.

Coefficient	Value	Coefficient	Value
A_0	-2.135 347 29	C_0	2.781 572 54
A_1	3.183 247 20	C_1	1.646 509 16
A_2	-1.801 435 97	C_2	-0.137 143 90
A_3	0.717 272 04	C_3	-0.006 497 67
A_4	0.503 440 27	C_4	-0.002 344 44
A_5	-0.618 993 95	C_5	0.005 118 68
A_6	-0.053 323 22	C_6	0.001 879 82
A_7	0.280 213 62	C_7	-0.002 044 72
A_8	0.107 152 24	C_8	-0.000 461 22
A_9	-0.293 028 65	C_9	0.000 457 24
A_{10}	0.044 598 72		
A_{11}	0.118 686 32		
A_{12}	-0.052 481 34		

Table 1. ITS-90 Reference Function Coefficients

The a and b coefficients of the deviation functions, eqs. (4) and (6) are obtained by simultaneous solutions with the observed W and the calculated W_r at the calibration points.

RESULTS

The results of the annealing process for all of the thermometers are shown in Table 2.

PRT	RUN 1		RUN 2		PRT	RUN 1		RUN 2	
#	ΔR Ω	ΔT mK	ΔR Ω	ΔT mK	#	ΔR Ω	ΔT mK	ΔR Ω	ΔT mK
0	0.0119	29.6	0.0033	8.2	7	0.0070	17.6	0.0013	3.3
1	0.0006	1.6	0.0000	0.0	8	-0.0008	-2.0	0.0002	0.6
2	0.0381	95.2	-0.0906	-226.5	9	0.0571	142.7	-0.3171	-792.7
3	-0.0054	-13.5	0.0002	0.6	10	0.0016	3.9	-0.0001	-0.3
4	-0.0002	-0.4	0.0013	3.3	11	0.0003	0.8	0.0012	2.9
5	0.0122	30.5	0.0017	4.2	12	0.0117	29.2	0.0030	7.6
6	0.0002	0.4	0.0008	1.9	13	0.0022	5.5	0.0010	2.5

Table 2. Results of PRT Annealing Process

There are three interesting patterns shown in Table 2. First, the range of changes in R_{TPW} is quite large. From a minimum of 0.0 mK for PRT number 1, to a maximum of -792.7 mK for PRT number 9. Second, in 6 out of the 14 PRT's (numbers 2, 4, 6, 9, 11, and 13), the second annealing caused a larger shift in the R_{TPW} than the first annealing. Finally, in 22 out of 28 instances, the annealings caused an increase in R_{TPW} rather than the expected decrease. These trends suggest that strain related changes are occurring to the platinum element on heating which mask the minor changes normally brought about by annealing. Based on the results of the annealings and the criteria established for the stability of R_{TPW}, PRT's 0, 2, 9, and 12 were omitted from the freeze point experiments.

PRT #	ΔR Ω	ΔT mK	Minimum R_{TPW}	Maximum R_{TPW}
3	0.00066	1.65	TPHg (-0.97)	FPZn (+0.58)
4	0.00114	2.85	FPSn (-1.74)	LN_2 (+1.12)
6	0.00362	9.04	LN_2 (-5.71)	FPZn (+3.15)
7	0.00889	22.20	initial (0.00)	LN_2 (+22.20)
8	0.00117	2.92	initial (0.00)	LN_2 (+2.92)
10	0.00055	1.37	FPSn (-1.37)	initial (0.00)

Table 3. Stability of R_{TPW}

During the zinc freeze point measurements, it was noted that several PRT's would not stabilize. The resistance would climb at rates of from several mK/hour to tens of mK/hour. This was deemed excessive and the PRT's in question were omitted from the remaining fixed point measurements. These PRT's were numbers 1, 5, 11, and 13. The maximum ΔR_{TPW} of the remaining PRT's is shown in Table 3. Also shown are the minimum and maximum values and where in the measurement process they occurred. Two of the PRT's exhibited large changes in their R_{TPW} values as shown in the table above. The R_{TPW} of PRT number 6 increased ≈3 mK after measurement at zinc and decreased ≈5 mK after the LN_2 comparison. On the other hand, the R_{TPW} of PRT number 7 increased steadily with each measurement. The R_{TPW} values for the remaining PRT's shifted much less dramatically. As with the annealing exercise, the data suggest that thermal stress is the major contributor to instability in the PRT's.

The values calculated for the ITS-90 coefficients are shown in Table 4. These values are somewhat larger than those usually found in SPRT's. (In the experience of this laboratory, a and b coefficients are generally smaller in magnitude than 2.5 E-4 and 5 E-5 respectively.) This is to be expected because these PRT's do not strictly comply to the ITS-90 criteria. In fact, PRT's 3,4, and 10 did not meet the ITS-90 and PRT's 6,7, and 8 did. The coefficients reflect this finding in that those of PRT's 6,7, and 8 are smaller in magnitude and thus closer to the reference functions.

PRT #	a_4 coefficient	b_4 coefficient	a_8 coefficient	b_8 coefficient
3	-1.1438379 E-3	-2.1691373 E-5	-1.1230225 E-3	-5.7161044 E-5
4	-1.9563214 E-2	-2.7173720 E-4	-1.9605024 E-2	-1.2188608 E-4
6	-5.9625133 E-4	-1.1169149 E-4	-5.9525574 E-4	-1.1216576 E-4
7	-4.4322528 E-4	-1.4973503 E-4	-3.7985061 E-4	-1.6605156 E-4
8	-2.6213169 E-4	-4.4578613 E-5	-2.0397072 E-4	-4.1597463 E-5
10	-1.4615288 E-3	-6.0940130 E-5	-1.4805889 E-3	-4.9890149 E-5

Table 4. Calibration Coefficients for Subject PRT's

Figures 1 and 2 illustrate the difference between the resistance ratio (W) and the ITS-90 reference functions (W_r) for the subject PRT's and an SPRT. For clarity, the difference is shown as equivalent temperature difference. All of the PRT's are shown in Figure 1, whereas PRT number 4 is omitted from Figure 2. The relationship between the coefficients listed in Table 4 and the slope of the curves can be clearly seen. (When referring to Figures 1 and 2, recall that PRT's 3,4, and 10 did not meet the ITS-90 with reference to the W requirements.)

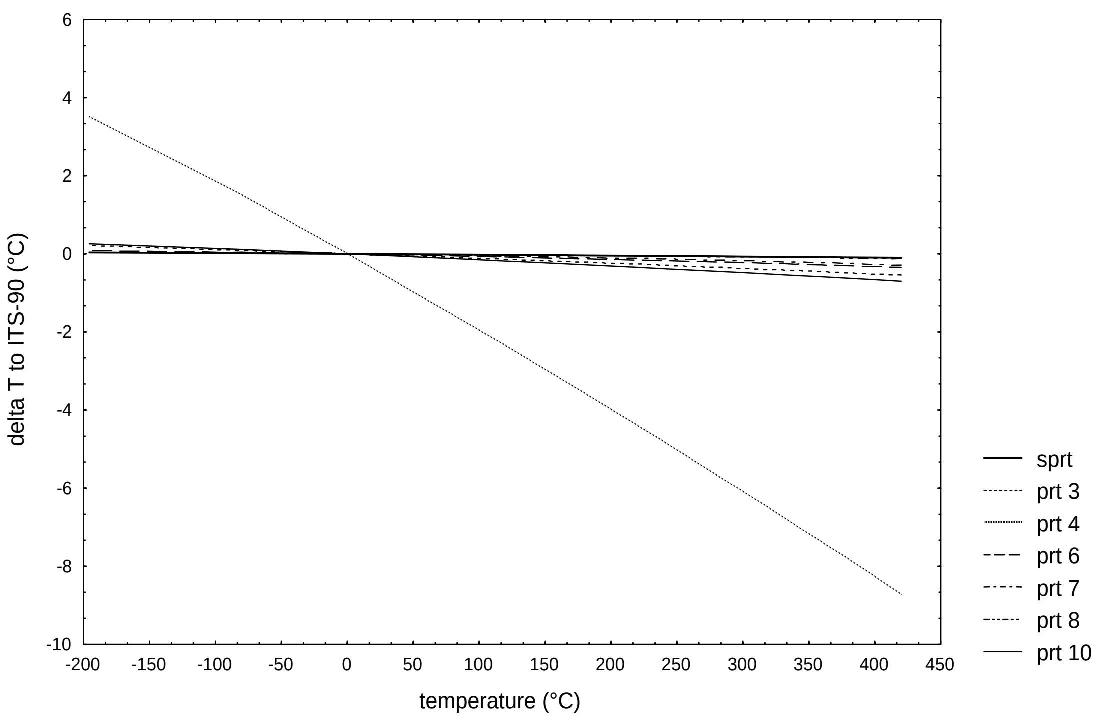


Figure 1. ΔT vs. temperature

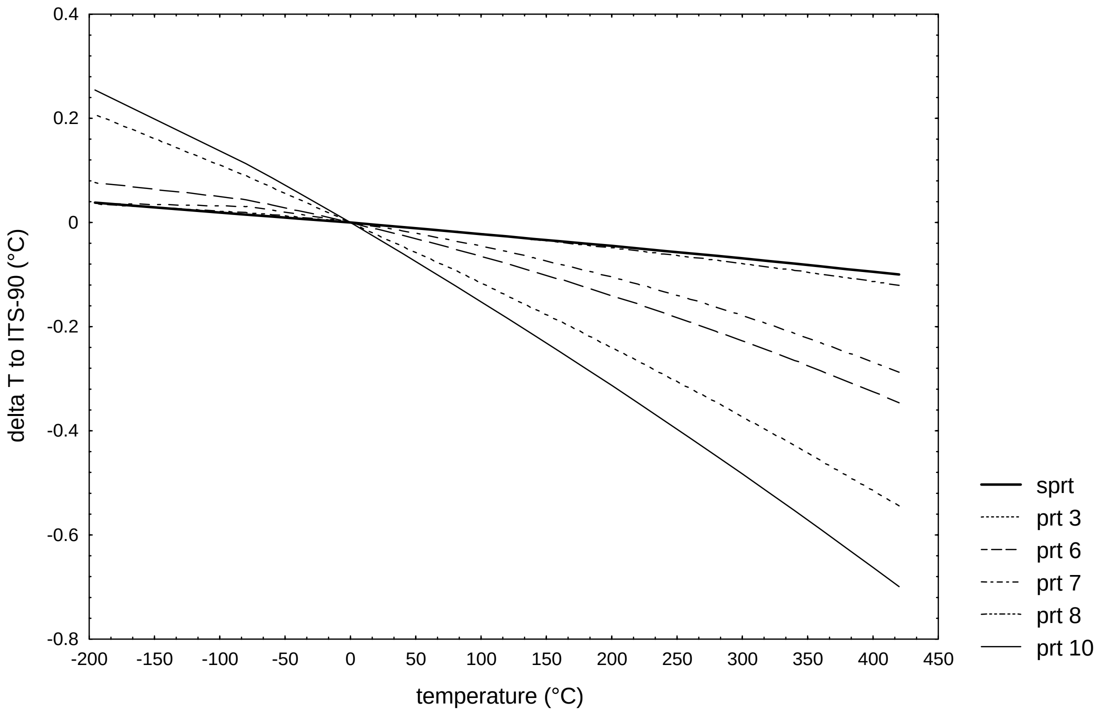


Figure 2. ΔT vs. temperature

Following the fixed point measurements, the PRT's were compared against an SPRT in various calibration baths. (The technique utilized for the comparison measurements will be discussed in the next section.) The measured resistance was then compared to the resistance calculated from the fixed point calibration. The differences were converted to equivalent temperature differences and are shown graphically in Figure 3. Except for PRT 4, the differences are relatively small up through 473.15 K (200 °C). Beyond that, there is considerable error between the measured resistance and the predicted resistance. There is no obvious pattern or trend to the errors except that they tend to increase with increasing temperature and they tend to increase at the points where the calibration baths were changed. It is noteworthy that the errors do not approach zero at the temperatures close to the fixed points. If the errors were primarily the result of a curve which does not fit the PRT's, then the errors would approach zero at the temperatures common to the fit and the comparison. The errors shown appear unrelated to the fixed point temperatures. These observations indicate that, for the most part, the observed errors are due to the PRT's actually changing from thermal cycling (or physical shock) during the time between the first fixed point measurement and the final comparison measurement. As a result, the accuracy of fit is masked by the rather large errors due to the changing characteristics of the PRT's. Additionally, the stability of the R_{TPW} corresponds loosely to the performance at the various temperatures.

Based on the observed instability at the TPW and the relatively poor results from the fixed point calibration, it appears that either better results can be obtained from comparison measurements utilizing more points, and/or a different procedure must be developed for these PRT's to minimize the effects of thermal shocking. At the very least, it appears that these PRT's do not warrant the added expense or time required for fixed point calibration.

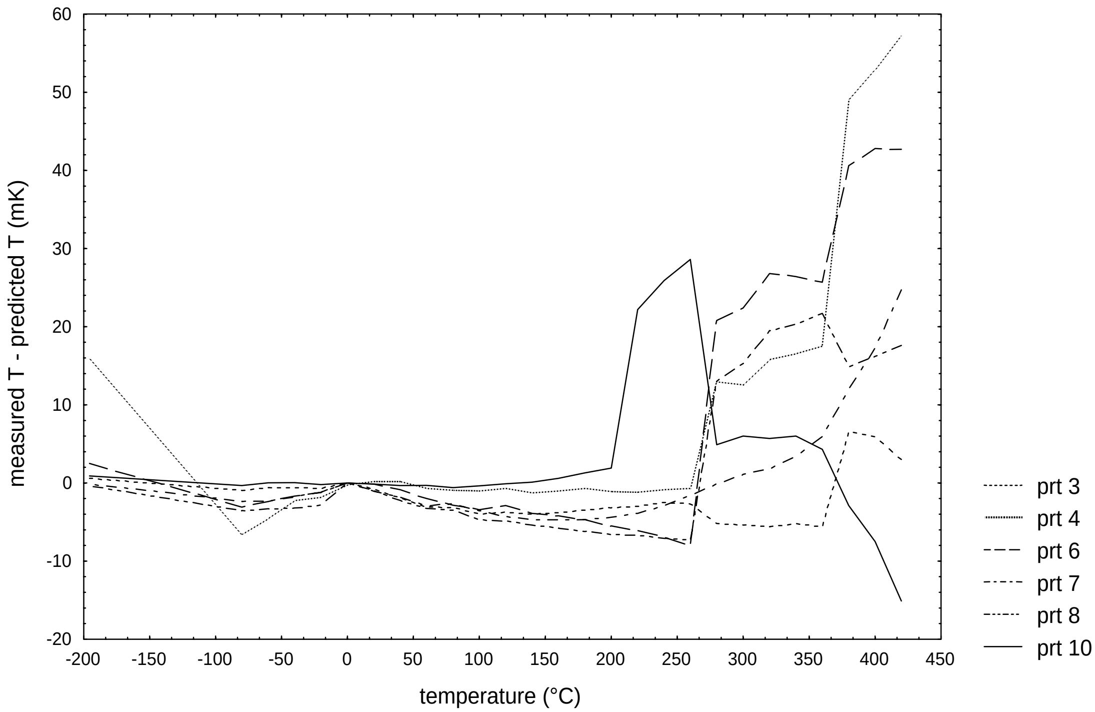


Figure 3. Error vs. temperature

THE COMPARISON MEASUREMENTS

EXPERIMENTAL DETAILS

The comparison measurements were performed in the Temperature/Humidity Laboratory. This laboratory is equipped for comparison calibration of SPRT's, PRT's, as well as a variety of other temperature and humidity instrumentation. The equipment used is listed in Table 5.

Temperature Range	Manufacturer/Model	Nomenclature	Notes
77.65 K to 693.15 K (-195.5 °C to 420 °C)	ASL F17	AC Bridge	
77.65 K to 693.15 K (-195.5 °C to 420 °C)	Rosemount 162 CE	SPRT	
77.65 K to 693.15 K (-195.5 °C to 420 °C)	Data Proof 320A	Scanner	
193.15 K to 393.15 K (-80.0 °C to 120.0 °C)	Rosemount 913AB1	Bath	methanol bath fluid / Dow Corning 200 fluid
413.15 K to 533.15 K (140.0 °C to 260 °C)	Rosemount 913AC1	Bath	Dow Corning 704 diffusion pump fluid
553.15 K to 693.15 K (280.0 °C to 420 °C)	Hart Scientific 6050	Bath	liquid salt
≈ 77.65 K (-195.5°C)	Pope	6" x 24" Dewar	boiling LN_2

Table 5. Equipment Used for Comparison Measurements

The comparison measurements were carried out in 20 K intervals from 693.15 K to 193.15 K (420 °C to -80 °C) and at ≈77.65K (-195.5 °C). The SPRT and PRT's were inserted into a specially made equilibrating block of nickel plated oxygen free copper. The block was suspended in the test media with common hanger wire. The thermometer wells in the block were drilled specifically for the SPRT and subject PRT's. A very close fit between the thermometers and the block was achieved. The Bridge and Scanner were under computer control and a measurement was taken every 30 seconds for a total of 10 readings per PRT per temperature. The Scanner channel was switched and then 30 seconds was allowed to elapse before the reading was taken. In this way, the PRT's were allowed to preheat and the Bridge was allowed to settle. The data was logged for later analysis. The block and thermometers were removed and cleaned with each change in calibration baths and reinserted for the next range. The SPRT was connected to the R_S leg of the Bridge and the PRT's were connected through the Scanner to the R_X leg. The R_{TPW} of the SPRT was taken either before or after the group of measurements depending on range and recorded for use in the analysis.

Following the comparison measurements, the SPRT calibration coefficients and the corresponding R_{TPW} value were used to calculate the resistance at the test temperatures. These values were then used with the logged data to determine the subject PRT's resistance at temperature. The PRT data were then fitted to the ITS-90 and four additional equations, each with a few variations of temperature points included in the fit. The ITS-90 equations (ranges) were discussed in the previous section and need not be covered here. The four additional relations are shown below.

The first will be referred to as ITS-90 ancillary[6] and is a "substitute" for the ITS-90. It was developed for SPRT's and has 10th, 12th, and 15th order variations. This equation is similar to the ITS-90 in that it is expressed in terms of resistance ratio (W). Also, it consists of reference functions, deviation functions (one in this case) and inverse reference functions (again, one only). Unlike the ITS-90, the deviation function and the inverse reference function is continuous from 83.15 K to 933.473 K (-190 °C to 660.323 °C), but will be used here from 77.65 K to 693.15 K (-195.5 °C to 420 °C). After some experimentation, the 12th order variation was selected as the version to fit to the subject PRT's. Both equations are in terms of °C rather than K.

The deviation function is used with the actual ITS-90 reference function for the appropriate temperature range. Over the temperature range of interest here, both ITS-90 reference functions, eqs. (3) and (5) are required. The relationship between ΔW and $W(T90)$ remains the same as that shown in eq. (2). The ancillary deviation function is as follows:

$$\Delta W\left(T_{90}\right) = a\cdot\left(W\left(T_{90}\right) - 1\right) + b\cdot\left(W\left(T_{90}\right) - 1\right)^2 + c\cdot\left(W\left(T_{90}\right) - 1\right)^3 \qquad (7)$$

The reference function shown is a substitute for the ITS-90 inverse reference functions for the ranges covering 83.15 K to 933.473 K (-190 °C to 660.323 °C).

$$t_{90} = \sum_{i=0}^{n} A_i \cdot \left(2 \cdot \ln\left(W_r + 0.8\right) - 1\right)^i \qquad (8)$$

The values for the coefficients A_i in eq. (7) are given in Table 6.

Coefficient	n = 10	n = 12	n = 15
A_0	-37.699 480	-37.699 593 1	-37.699 585 7
A_1	204.268 949	204.274 720 7	204.278 630 8
A_2	57.791 890	57.783 997 5	57.775 537 2
A_3	11.090 159	11.014 870 9	10.943 439 3
A_4	3.137 047	3.238 260 1	3.371 801 8
A_5	0.199 905	0.427 525 4	0.752 644 2
A_6	-0.166 787	-0.524 651 0	-1.196 713 3
A_7	0.271 323	0.095 681 0	-0.345 385 0
A_8	-0.151 819	0.310 903 6	1.721 135 2
A_9	0.067 704	-0.025 710 2	-0.199 241 9
A_{10}	-0.009 397	-0.189 960 8	-1.403 186 7
A_{11}		0.113 336 0	0.845 853 2
A_{12}		-0.019 722 6	0.201 586 4
A_{13}			-0.361 821 9
A_{14}			0.130 840 4
A_{15}			-0.016 131 8

Table 6. Ancillary ITS-90 Function Coefficients

The second equation is a commonly used variation of the Callendar Van Dusen equation as shown below:

$$R_t = R_0 \cdot \left[1 + a \cdot t + b \cdot t^2 + c \cdot (t - 100) \cdot t^3 \right] \qquad (9)$$

The third and forth equations are both a 4th order polynomial. The difference is that the third is calculated continuously from 77.65 K to 693.15 K (-195.5 °C to 420 °C) whereas the forth is divided into two ranges with the break point at 273.15 K (0.0 °C). The equation is shown below:

$$t_{90} = \left(a + b \cdot R + c \cdot R^2 + d \cdot R^3 + e \cdot R^4\right) \qquad (10)$$

The comparison measurements were made at 20 K intervals from 693.15 K to 193.15 K (420 °C to -80 °C) and at ≈77.65K (-195.5 °C) providing 27 temperature vs. resistance points with which to fit the solutions. Various combinations of temperature points were chosen to fit these solutions. Fit 1 is the extreme overdetermined solution (more knowns than unknowns) with all of the data used in the fit. Fit 6 is the extreme square solution (equal number of knowns and unknowns) with extrapolation required beyond the end points provided by the data used in the fit. Matrix methods were used to solve the sets of equations. The overdetermined matrix method is shown in eq. (11) and the square matrix method is shown in eq. (12):

$$\text{coefficients} = \left(A^T \cdot A\right)^{-1} \cdot \left(A^T \cdot B\right) \tag{11}$$

$$\text{coefficients} = A^{-1} \cdot B \tag{12}$$

Table 7 shows which temperature points were used in each of the fitting schemes. Not all of the equations could be fitted with each of the schemes. For example, fit 5 could not be used with the version of eq. (10) split at 273.15 K (0.0 °C) because there are insufficient points for the fit.

Temperature	Fit 1	Fit 2	Fit 3	Fit 4	Fit 5	Fit 6
693.15 K (420 °C)	X	X	X	X	X	
673.15 K (400 °C)	X					
653.15 K (380 °C)	X	X				
633.15 K (360 °C)	X		X			
613.15 K (340 °C)	X	X		X		X
593.15 K (320 °C)	X					
573.15 K (300 °C)	X	X	X			
553.15 K (280 °C)	X					
533.15 K (260 °C)	X	X				
513.15 K (240 °C)	X		X	X	X	
493.15 K (220 °C)	X	X				
473.15 K (200 °C)	X					
453.15 K (180 °C)	X	X	X			X
433.15 K (160 °C)	X					
413.15 K (140 °C)	X	X				
393.15 K (120 °C)	X		X	X		
373.15 K (100 °C)	X	X				
353.15 K (80 °C)	X					
333.15 K (60 °C)	X	X	X			
313.15 K (40 °C)	X					
293.15 K (20 °C)	X	X				
273.15 K (0 °C)	X	X	X	X	X	X
253.15 K (-20 °C)	X					
233.15 K (-40 °C)	X	X	X	X	X	X
213.15 K (-60 °C)	X	X				
193.15 K (-80 °C)	X	X	X	X		X
77.65 K (-195.5 °C)	X	X	X		X	

Table 7. Fitting Schemes

RESULTS

Based on the data obtained during the fixed point annealing process, it was decided to omit PRT's 2 and 9 from the comparison experiment as well as the fixed point experiment (refer to Table 2). Figures 4, 5, and 6 illustrate the difference between the resistance ratio (W) and the ITS-90 reference functions (W_r) for the remaining 12 PRT's and an SPRT. As with the previous figures, the difference is shown as equivalent temperature difference. All of the subject PRT's are shown in Figure 4, PRT's 4 and 11 are omitted from Figure 5. The similarities between PRT's from a common manufacturer are becoming evident. In Figure 6, the PRT's are displayed in pairs by manufacturer with the SPRT shown for reference.

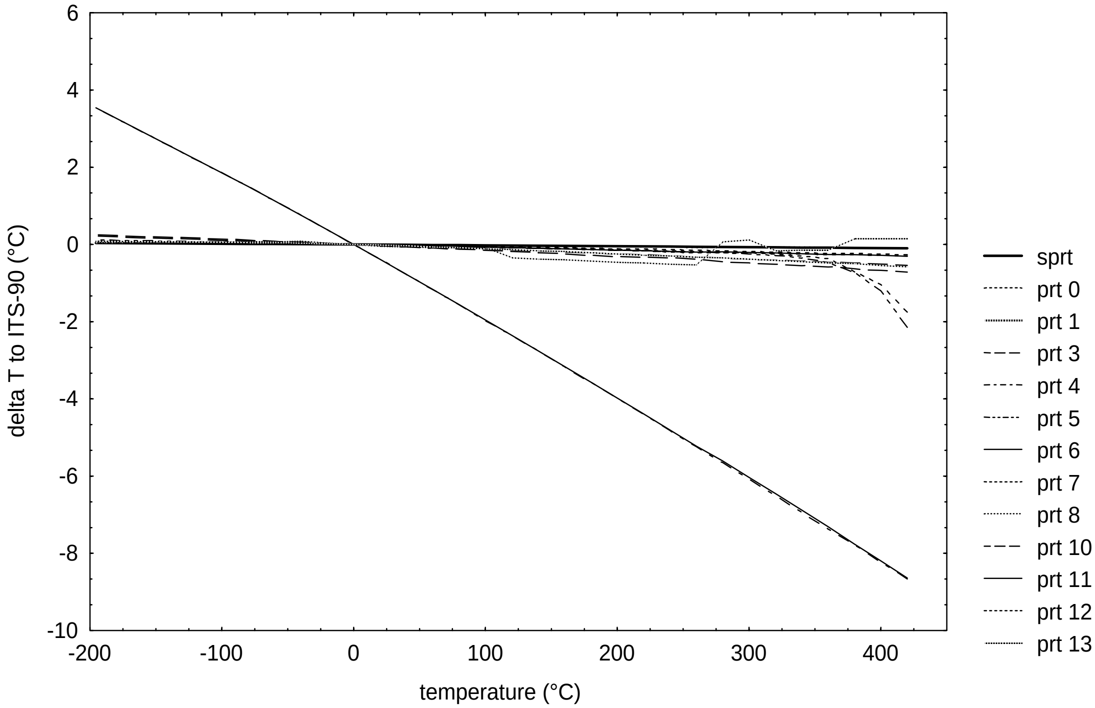


Figure 4. ΔT vs. temperature

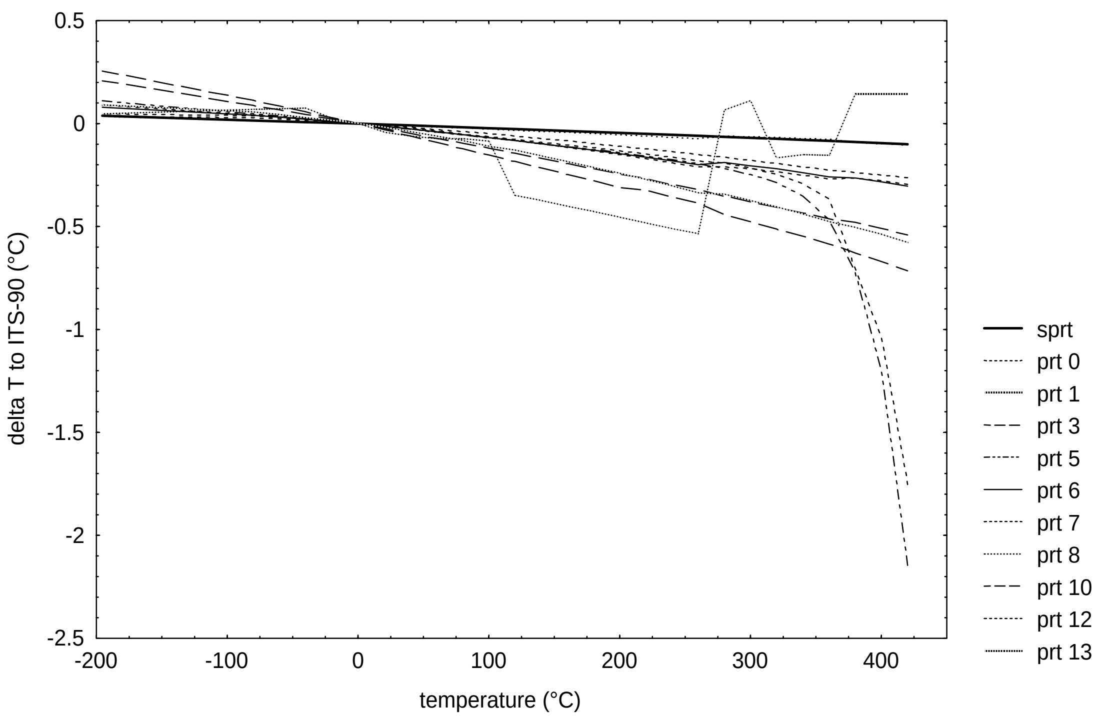
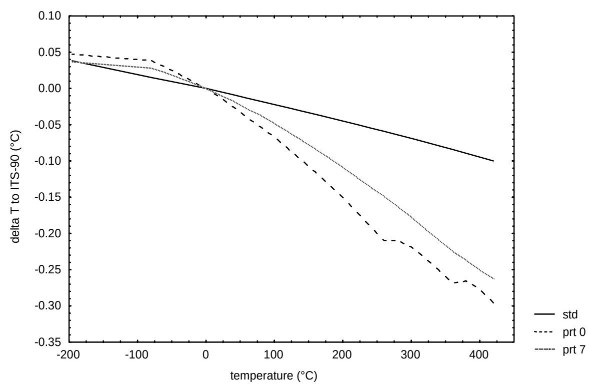
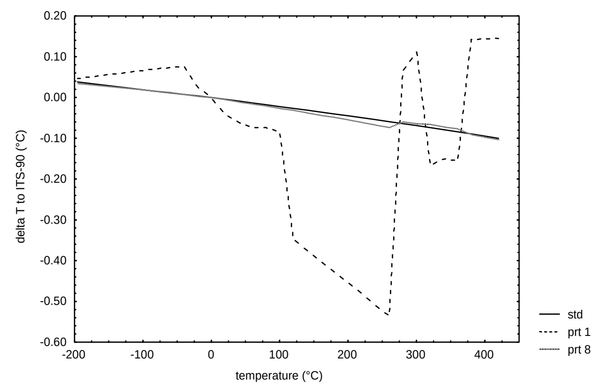


Figure 5. ΔT vs. temperature

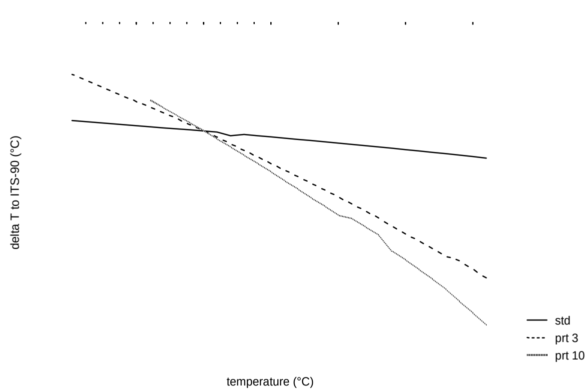
Although the following graphs seem to indicate that the PRT's from each manufacturer are unique to that manufacturer, the differences between the curve shapes from one manufacturer to the next is more a matter of slope than shape. The three exceptions to this are PRT 1 shown in Figure 6(b) and PRT's 5 and 12 shown in Figure and 6(e). PRT 1 seems to have had a failure during the experiment and was simply unstable. It's sibling PRT corresponded very closely to the SPRT and was very stable. On the other hand, PRT's 5 and 12 had a curve shape very different from the other PRT's and the reference function.



(a)

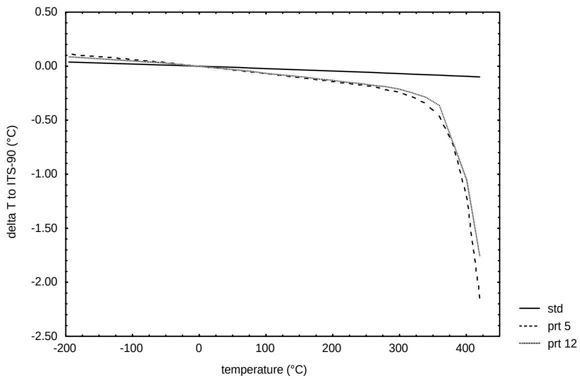


(b)

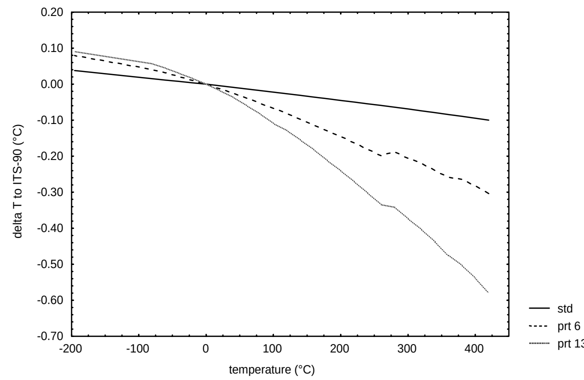


(c)

(d)



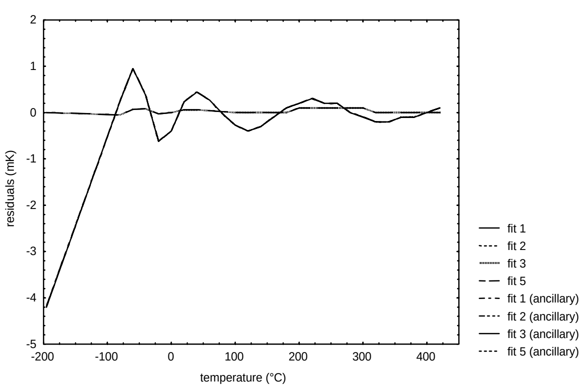
(e)



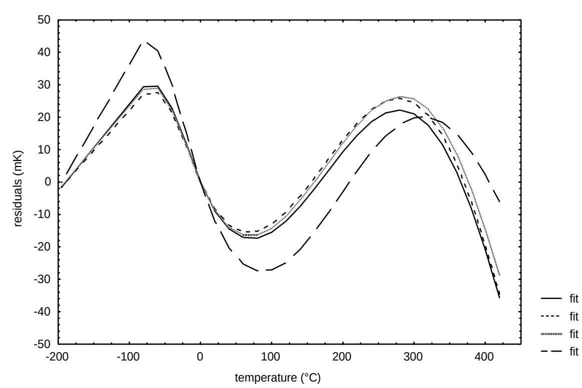
(f)

Figure 6. ΔT vs. temperature by manufacturer

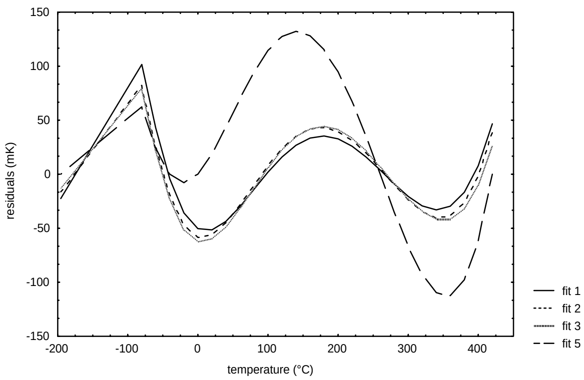
The analysis for accuracy of fit was divided into two temperature ranges: the first range consists of the entire tested range. The second range is the center portion from 213.15 K to 533.15 K (-60 °C to 260 °C). These ranges were chosen because they appear to be of wide interest to users of PRT's. Additionally, some PRT users have expressed interest in extrapolation of their PRT's beyond the end points of calibration. It seems that large errors can be expected in the extrapolated region(s). The magnitude of the errors is of interest. Therefore, this issue is investigated as well. The following figures illustrate the residuals from the various equation/fitting scheme combinations for an SPRT and then the best and worst PRT's in the experiment. The residuals are plotted over both temperature ranges discussed above.



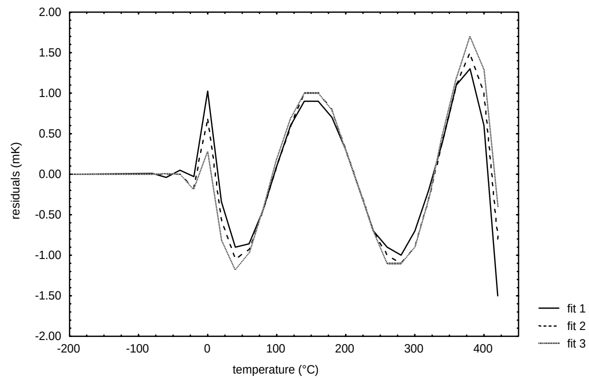
(a) ITS-90 and ancillary ITS-90



(b) Callendar Van Dusen



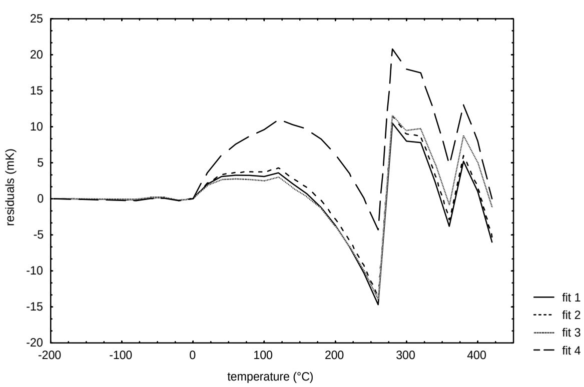
(c) 4th order equation, continuous



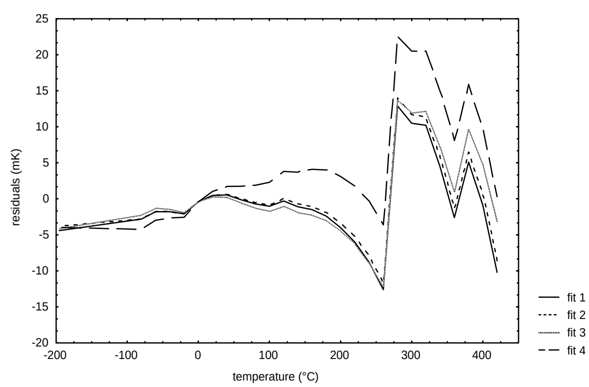
(d) 4th order equation, split at 273.15 (0.0°C)

Figure 7. Residuals for an SPRT over the range 77.65 K to 693.15 K (-195.5 °C to 420 °C)

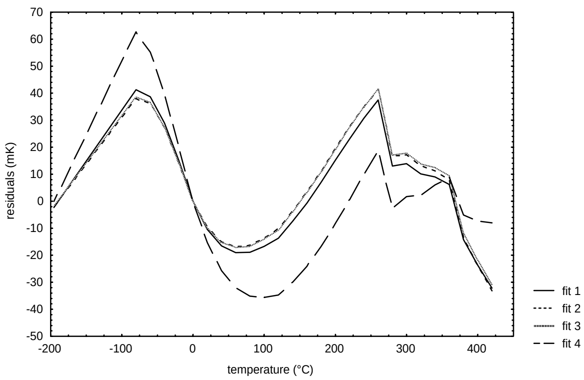
The plots above were generated from fitting the calculated resistance of an SPRT to the four equations. As a result, Figure 7 is more an indication of the differences between the equations themselves and the ITS-90 than an indication of any one SPRT's performance. As such, Figure 7 likely represents the best that can be expected from the following analysis. Figure 7(a) suggests that the ancillary ITS-90 equation is a very close match to the ITS-90 and should result in a good fit. Figures 7(b) and (c) show that the CVD and the continuous version of the 4th order polynomial do not comply well to the ITS-90 and probably should not be used for precision measurements. On the other hand, the split version of the 4th order polynomial left very small residuals over the entire range and should work for most situations.



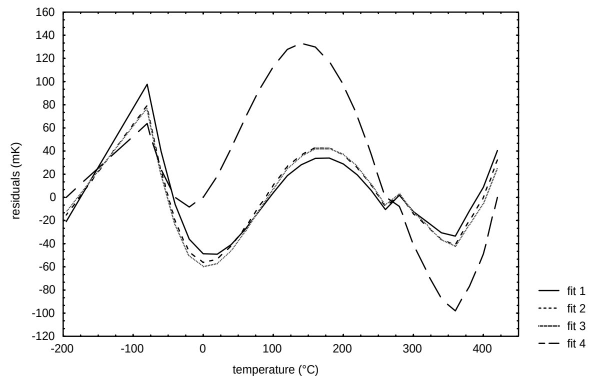
(a) ITS-90



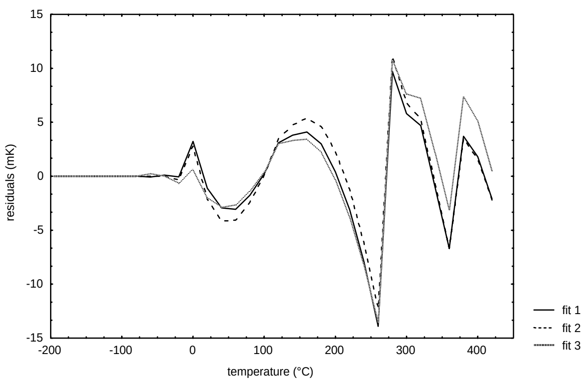
(b) Ancillary ITS-90



(c) Callendar Van Dusen



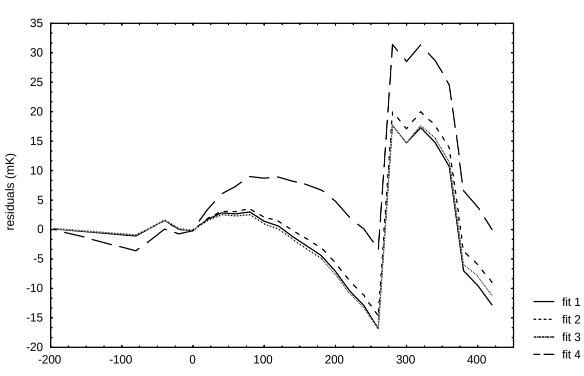
(d) 4th order equation, continuous

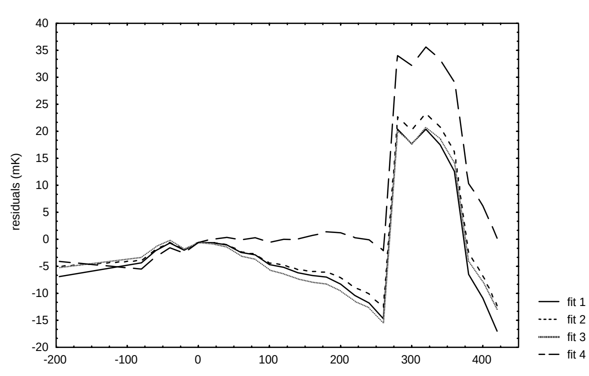


(e) 4th order equation, split at 273.15 (0.0°C)

Figure 8. Residuals for PRT 7 over the range 77.65 K to 693.15 K (-195.5 °C to 420 °C)

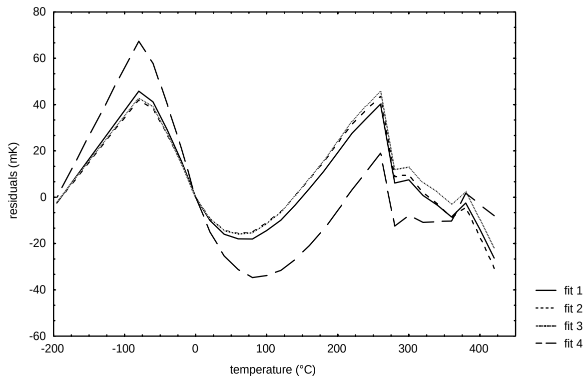
PRT 7 seems to follow the same basic trends as the SPRT depicted in Figure 7. Although the residuals are much larger, the fit for the ITS-90, the ancillary ITS-90, and the 4th order split version are much better than the 4th order continuous and the CVD. Also, the accuracy of fit obtained with fitting schemes 1, 2, 3 is superior to that obtained with fitting scheme 4. The difference between fitting schemes is more pronounced in the two equations which did not fit well and left large residuals.

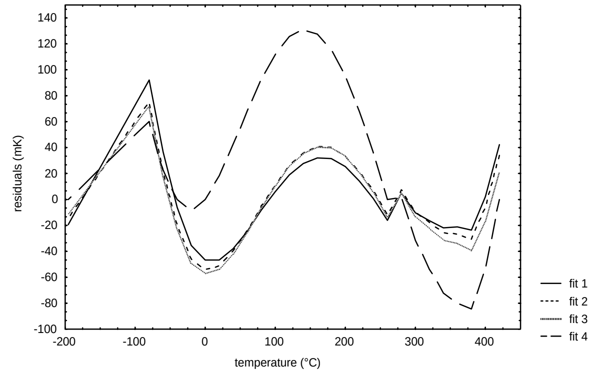




(a) ITS-90

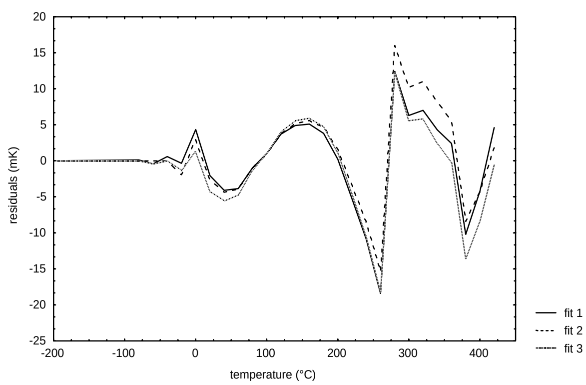
(b) Ancillary ITS-90





(c) Callendar Van Dusen

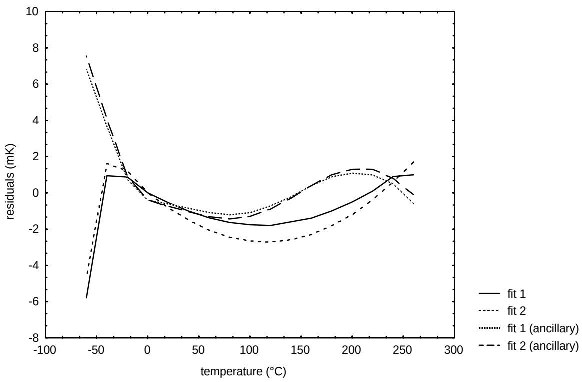
(d) 4th order equation, continuous



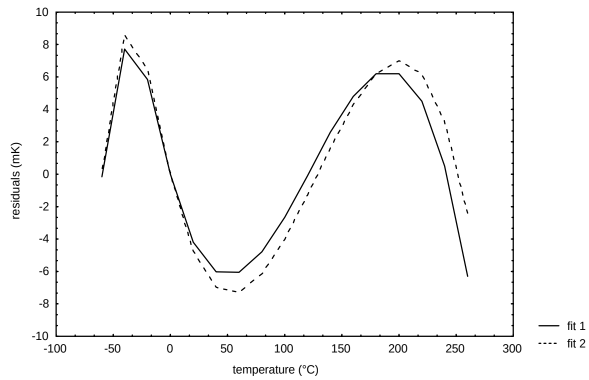
(e) 4th order equation, split at 273.15 (0.0°C)

Figure 9. Residuals for PRT 11 over the range 77.65 K to 693.15 K (-195.5 °C to 420 °C)

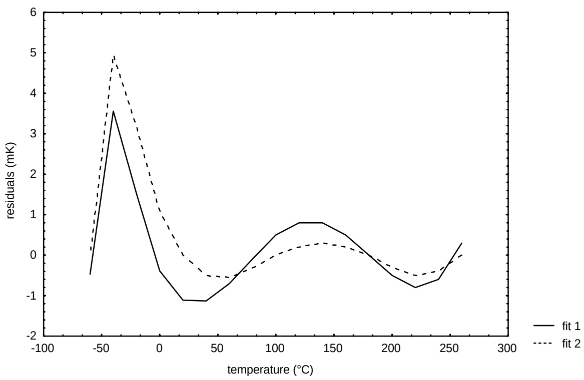
The set of residual plots for PRT 11 is very similar to PRT 7. The difference being one of the magnitude of the residuals rather than the location. Both PRT's seem to fit well up to and including 533.15 K (260 °C). The errors at the tested temperatures above that may be the result of physical or thermal shock. (Recall that the bath was changed at 553.15 K.) As expected, the 4th order continuous version and the CVD had the largest residuals. Note, however, that plots (c) and (d) from PRT 7 are nearly identical to plots (c) and (d) from PRT 11.
The residual plots for the SPRT over the range 213.15 K to 533.15 K (-60 °C to 260 °C) is shown below. The values were generated in the same manner as those in Figure 7. The ITS-90 reference function and range used has a lower limit of 243.15 K (0.0 °C). Note that the magnitude of the maximum ITS-90, ITS-90 ancillary, and CVD residuals is about the same. In this case, the fit obtained with the 4th order polynomial is considerably better.



(a) ITS-90 and ancillary ITS-90



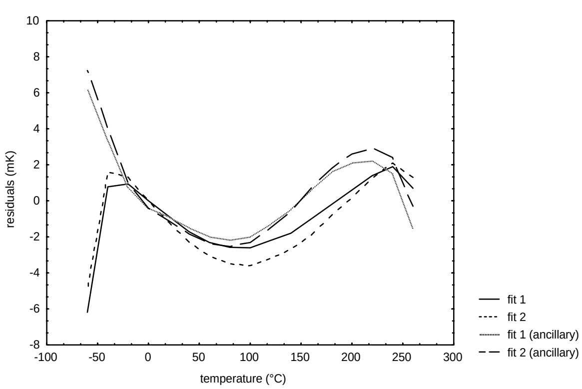
(b) Callendar Van Dusen



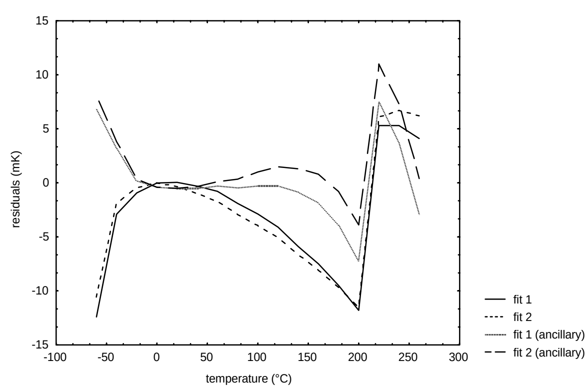
(c) 4th order equation, continuous

Figure 10. Residuals for an SPRT over the range 213.15 K to 533.15 K (-60 °C to 260 °C)

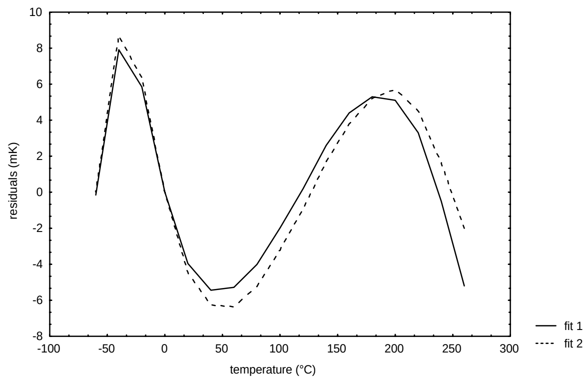
The best and worst PRT's over this temperature range are shown together in Figure 11. The trends indicated follow the SPRT very closely. The fit obtained with the 4th order polynomial is somewhat superior to that obtained with either the ITS-90, ITS-90 ancillary, or the CVD. Again, however, the CVD fits quite well over this narrow temperature range.



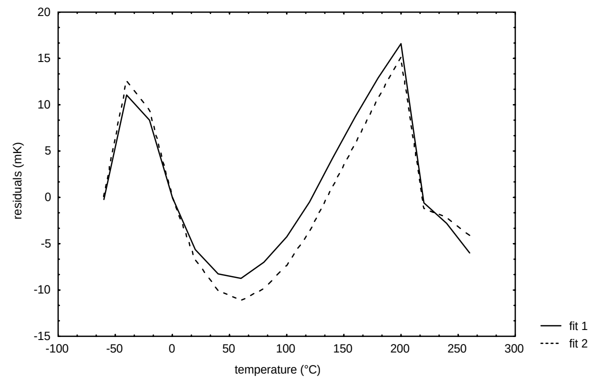
(a) PRT 5, ITS-90 and ancillary ITS-90



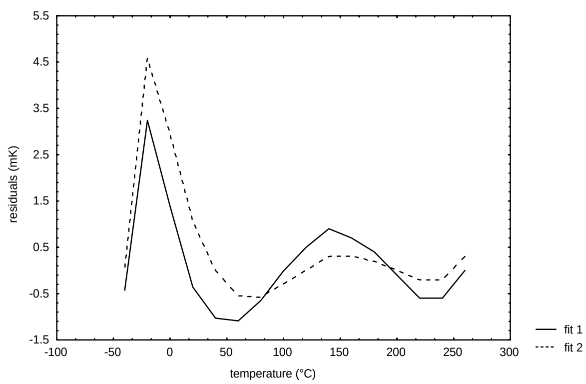
(b) PRT 10, ITS-90 and ancillary ITS-90



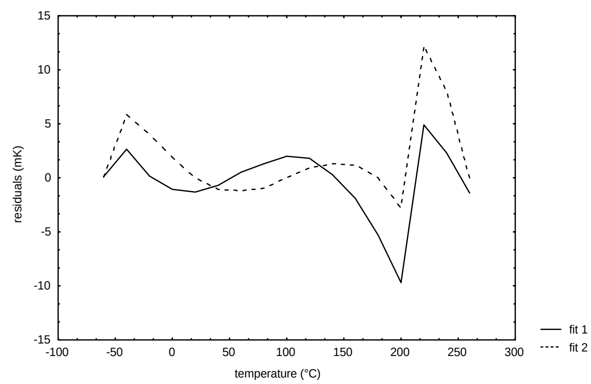
(c) PRT 5, Callendar Van Dusen



(d) PRT 10, Callendar Van Dusen



(e) PRT 5, 4th order equation, continuous



(f) PRT 10, 4th order equation, continuous

Figure 11. Residuals for PRT's 5 and 10 over the range 213.15 K to 533.15 K (-60 °C to 260 °C)

The following figures illustrate the standard deviation of fit for the SPRT and all of the subject PRT's over both temperature ranges discussed above. Figures 12 and 13 suggest that, for the most part, the accuracy of fit is more dependent upon the equation chosen than the number of points fit after a sufficient number of points is reached. That is, fit 5 resulted in a significant reduction in precision for two of the equations and a moderate reduction in precision for the other two. However, the reduction in precision is smaller than the differences between ITS-90 and the CVD. (Except for the case of fit 5 with the continuous 4th order polynomial, which is clearly insufficient.)

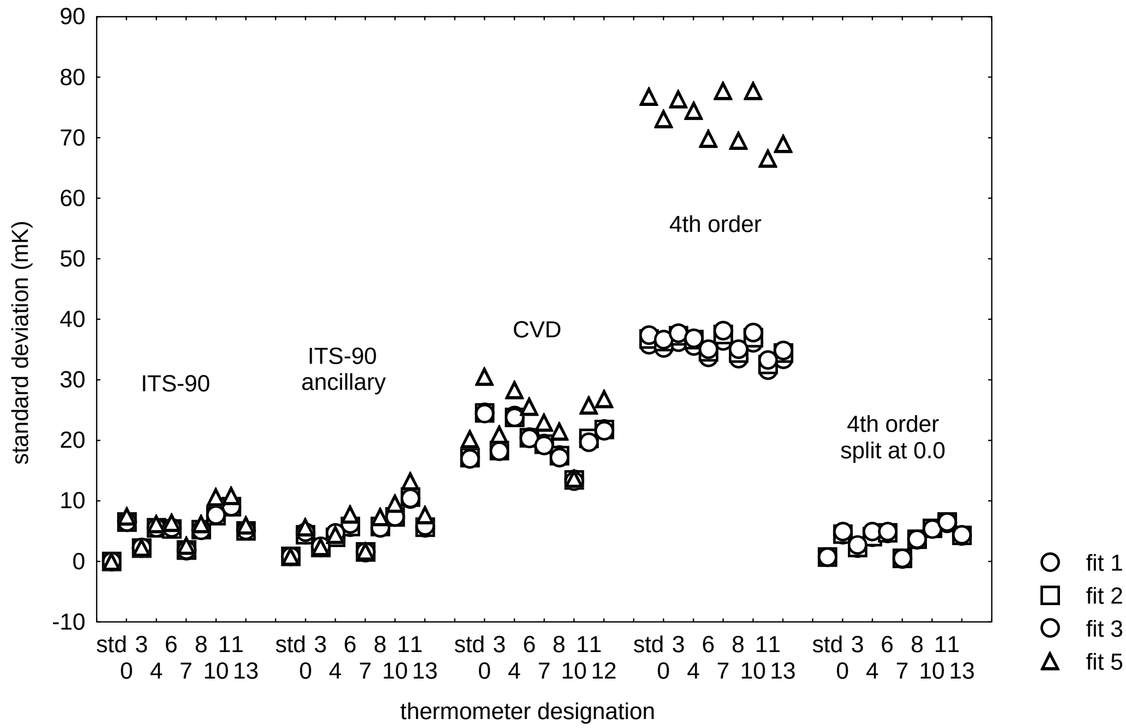


Figure 12. Accuracy of fit for range of 77.65 K to 693.15 K (-195.5 °C to 420 °C)

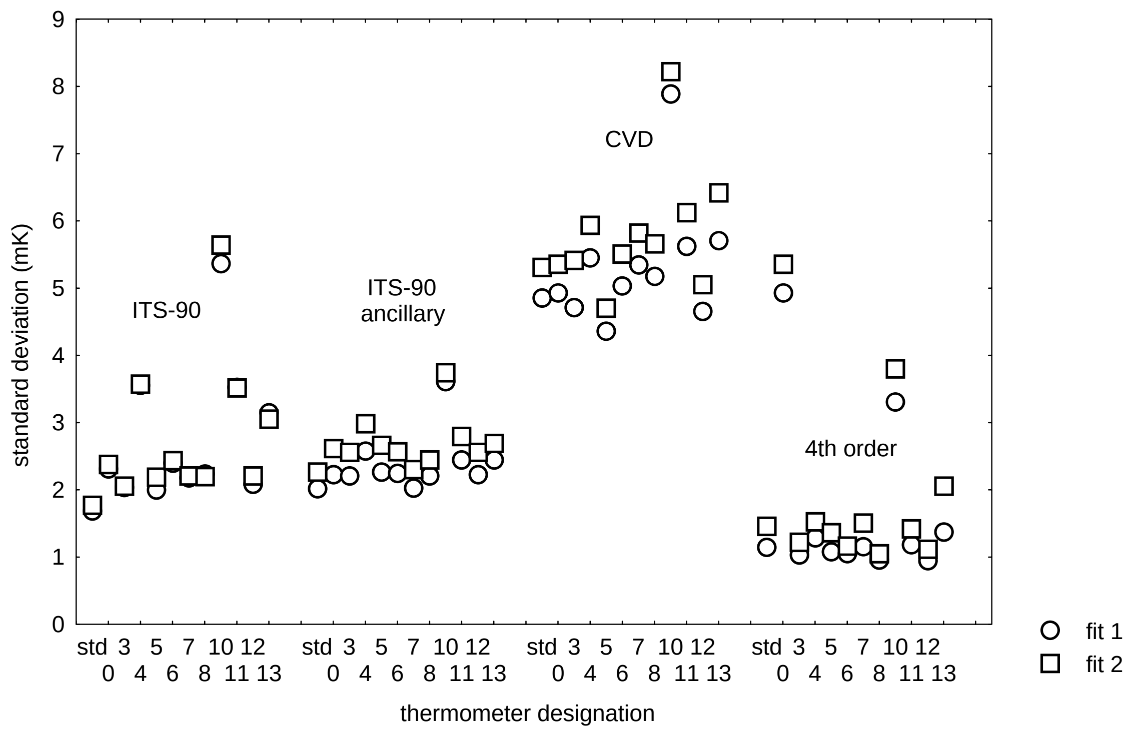


Figure 13. Accuracy of fit for range of 213.15 K to 533.15 K (-60 °C to 260 °C)

Figure 14 illustrates the standard deviation of fit for the SPRT and all of the subject PRT's over the extrapolated range. Except in the case of the ITS-90 and ancillary ITS-90, extrapolation created very large errors. This is to be expected because polynomial extrapolation seldom provides good results. The limited success achievable in extrapolation of the ITS-90 and ancillary ITS-90 is due in large part to the reference function - deviation function structure.

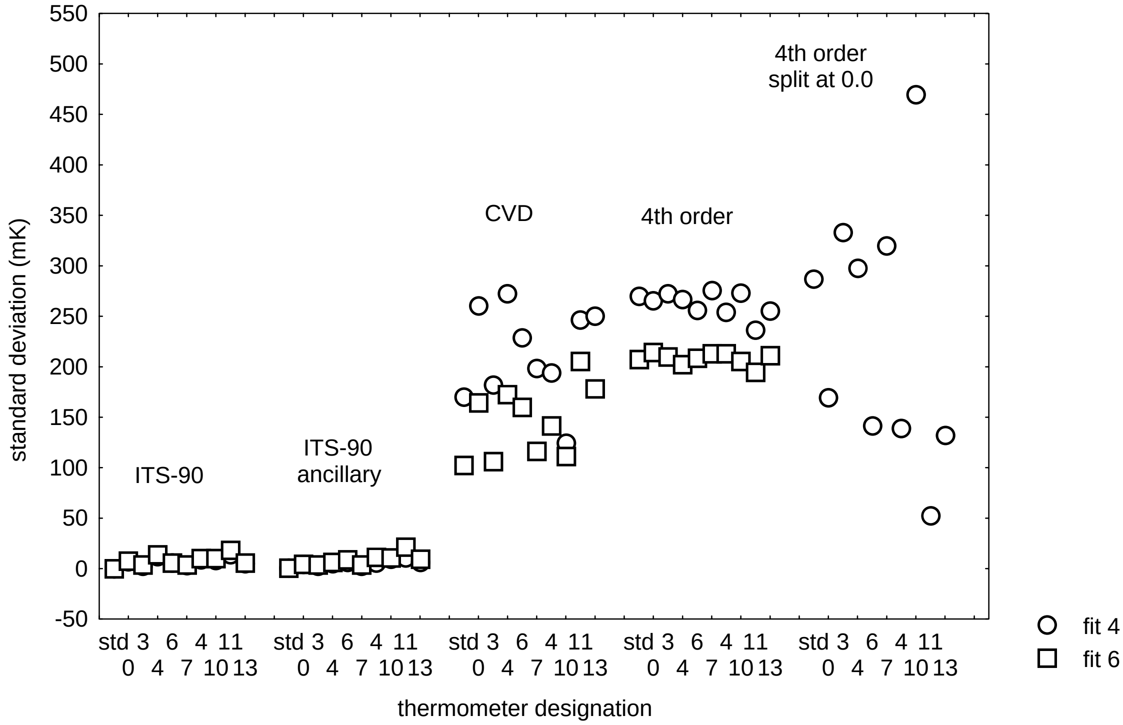


Figure 14. Accuracy of fit for range of 77.65 K to 693.15 K (-195.5 °C to 420 °C) with extrapolation

CONCLUSION

The ITS-90 compliance and thus the accuracy obtainable for secondary standard PRT's is dependent in large part on the equation used to describe the resistance (or resistance ratio) vs. temperature relationship. Some of the commonly used equations are inadequate to describe the PRT over wide temperature ranges with the required degree of accuracy. However, over narrow temperature ranges, all of the equations fitted seemed to be adequate. Additionally, it appears beneficial to use more than the mathematically required number or data points to achieve the highest accuracy of fit, regardless of which equation is used. Also, the data suggest that even under the most cautious circumstances, secondary PRT's can exhibit some error due to thermal or physical trauma. Manufacturers should note the results obtained with the ancillary ITS-90 equation. It is continuous as well as far less complex than the ITS-90, but provides an accuracy of fit similar to that of the ITS-90 equations.

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1. Burns Engineering Inc., 10201 Bren Road East, Minnetonka, MN 55343,
2. Eaton Corp., Pressure Sensors Division, 15 Durant Ave., Bethel CT 06801 (612) 935-4400
3. Logan Enterprises, 8844 US 68 North, West Liberty, Ohio 43357 (513) 465-8170
4. Minco Products, Inc., 7300 Commerce Lane, Minneapolis, MN 55432, (612) 571-3121
5. RDF Corporation, (603) 673-7332
6. Rosemount Aerospace, 1256 Trapp Road, Eagan, MN 55121, (612) 681-8900
7. SDI, 1809 Olde Homestead Lane, Suite 106, Lancaster, PA 17601, (717) 295-2311

Disclaimer: Certain commercial equipment, instruments, or apparatus are identified in this paper in order to properly describe the experimental procedure used. Such identification does not imply recommendation or endorsement by this laboratory, nor does it imply that the equipment or instrumentation identified are necessarily the best available for the purpose.

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