Approximation of ITS-90 with High Temperature Thermometers up to 1085 °C

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Abstract. The upper limit of the ITS-90 in the contact thermometry part of the scale is the silver freezing point 961.78 °C. This limit is justified by the decrease of the stability and reliability of the high-temperature platinum resistance thermometers above the silver point. It was shown in several papers before, that some HTPRTs were able to work up to the gold and copper points with accuracy better than that for thermocouples or pyrometers. So, HTPRTs can be successfully used in some applications in the high-temperature range, such as calibrations of standard thermocouples or pyrometers by comparison with a high-temperature thermometer. To calculate the temperature measured with an HTPRT above the silver point, it is necessary to develop an interpolation function. Some methods for the interpolation have already been suggested in several papers. In the work on developing the new reference functions for noble metal thermocouples (Burns et al. 1992) one interpolation model was applied to a Russian-made HTPRT. In this paper we are investigating 8 interpolation equations, for which 3 to 5 calibration points are used. The functions were applied to 13 Russian HTPRTs calibrated up to 1064.18 °C and 7 HTPRTs calibrated up to 1084.62 °C. The uncertainty of the approximation was found to vary from 3 mK to 25 mK depending on the thermometer and interpolation model.

INTRODUCTION

Although the high-temperature platinum resistance thermometer is exclusively the defining interpolation instrument of the ITS-90 in the temperature range from 660.723 °C to 961.78 °C, there are some applications, in which the use of HTPRTs instead of thermocouples at temperatures up to the gold and copper point would be very desirable. HTPRTs may be employed for the calibration of standard noble metal thermocouples by comparisons with the thermometers, or as reference devices in pyrometry. Several papers were published on investigating the stability and accuracy of Russian HTPRTs at temperatures above the silver point [1], [2], [3]. It was shown that the thermometers were able to retain their performance characteristics in that temperature range.

The dependence of the platinum resistivity on the thermodynamic temperature is chosen as the base function for constructing the ITS-90 scale. From fitting W(T) vs. T_{90} data, obtained with one highly-stable HTPRT, a ninth-order polynomial $W_r(T)$ was generated, that now represents the reference function of the scale over the range 0.01 – 961.78 °C. The reference function was not defined above the silver point. It should be pointed out, that at temperatures above 900 °C two major effects might distort the function: the effect of vacancy defect formation, and the effect of electrical leakage through the insulating parts of an HTPRT. At the gold and copper points the number of possible vacancies in the platinum lattice is significant. The dependence of the resistance on the concentration of vacancies has the exponential form $c \cdot exp(-E_v/kT)$, where c is a coefficient, E_v is the activation energy for the creation of a vacancy, K is Boltzmann's constant, T is the thermodynamic temperature. The insulation resistance of an HTPRT depends on the design of the sensing element, quality of the quartz, presence of moisture inside the thermometer. The uncertainty resulting from the decrease of the insulation resistance depends on the nominal resistance of the thermometer. An exponential form of the insulation dependent term in the $W(T)$ function can also be expected.

There are two ways for developing the interpolation equation for an HTPRT above 961.78 °C. The first is to generate a fit of $W(T)$ vs. T_{90} data from the results of a calibration of the HTPRT through the gold point, trying to get the close matching of the slope of the ITS-90 function at the silver point. This approach was taken in work [3], where a fourth degree polynomial was chosen for the fit.

The second method is to extrapolate the ITS-90 reference function above 961.78 °C and to add a deviation function, calculated from the results at the fixed points. This method is simple and convenient. However, it is necessary to prove sufficient accuracy and smoothness of the interpolating procedure.

In this paper we are investigating several interpolation equations based on the extrapolation of the ITS-90 reference function beyond the silver point. The deviation functions are calculated from the data obtained from the results in different sets of the fixed points.

CHARACTERISTICS OF HTPRTS INVOLVED IN THE STUDY

The results of calibration of thirteen Russian HTPRTs were used for the analysis of the interpolation models. All the thermometers were of Strelkov's design, with quartz insolating parts. The resistance at 0.01 °C was about 0.6 ohm, the diameter of the platinum wire was 0.4 mm. The insulation resistance of HTPRTs of this type was investigated in work [2]. It was found that the resistance of the quartz insulation of the HTPRTs decreased from 75 MΩ at 960 °C to 7 MΩ at 1090 °C. However, the uncertainty in the temperature due to shunting the sensing element by the insulation was only 0.16 mK at 960 °C, and 0.77 mK at 1090 °C.

After the construction, the HTPRTs were stabilized at 1100 °C by short anneals, each lasting not more than 5 h. The total time of annealing was about 100 h. The change in *R(TPW)* observed during the last 20 hours of the stabilization was less than the equivalent of 1 mK. The HTPRTs were calibrated at the fixed points of ITS-90: Sn, Zn, Al, Ag, Au. Seven thermometers were additionally calibrated at Cu fixed point. The calibration measurements were performed with DC bridge Guildline 9975 at two currents 10 and $10\sqrt{2}$ mA. Usual precautions were taken to avoid quenching of the lattice defects. After completing the measurements at Al, Ag, Au points, the HTPRTs were cooled slowly inside the furnace with a speed of about 2 °C/min to 450° C, and then were removed from the furnace. The calibration cycle was repeated three times. The instability of *R(TPW)* was not worse than the equivalent of 1 mK per cycle. The expanded uncertainty of calibration at the high temperature fixed points was within the equivalent of 5 mK. The results of the calibration at Ag, Au, Cu points, calculated as the average of values *W(FP)* obtained in the three calibration cycles are presented in Table 1.

TABLE 1. Results of the Calibration of the HTPRTs at High Temperature Fixed Points.

S/N	Ag	Au	Cu
45	4.285530	4.570567	4.626076
46	4.285072	4.570045	4.625581
47	4.285645	4.570670	4.626219
68	4.285698	4.570737	4.626248
157	4.285088	4.570086	4.625626
181	4.285396	4.570353	4.625891
192	4.285798	4.570823	4.626371
49	4.285569	4.570629	
183	4.285498	4.570445	
184	4.285513	4.570498	
207	4.285381	4.570362	
211	4.285869	4.570896	
212	4.285846	4.570862	

INTERPOLATION EQUATIONS BASED ON ITS-90 DEVIATION FUNCTION

The simplest method for constructing the interpolation function *W(T)* for the range above 961.78 °C is to extrapolate the ITS-90 reference and deviation functions. The deviation function of the ITS-90 has the form:

$$\Delta W(T) = a(W(T)-1) + b(W(T)-1)^2 + c(W(T)-1)^3 + d(W(T)-W(Al))^2 \qquad (1)$$

where $d = 0$ in the range 0.01 – 660.323 °C
d is calculated from the result at Ag point in the range 660.323 – 961.78 °C

We evaluated the difference between the calibration data and the ratios *W(Au)* and *W(Cu)* calculated using equation (1). The results are given in the first column of Table 2. As seen from the table, all the experimental results at Cu point have negative deviations from the extrapolated curve. The largest error is observed for HTPRT S/N 45 at Cu point (-12.9 mK). Excluding this value, the errors for all of the HTPRTs investigated do not exceed -6.1 mK. The extrapolation of the ITS-90 reference and deviation functions was taken as the baseline for our other models.

In this work we do not consider the model in which the additional term, $e(W(T)-W(Ag))^2$ is added to the deviation function (1). The temperature interval between the silver and the gold points is rather small, and the additional independent term will cause the interpolation function to fluctuate considerably.

Besides, there will be no redundant point to check the accuracy of the method.

Two equations were tested for the deviation functions, based on equation (1). For the first function $\Delta W_1(T)$ we calculated coefficient d from the data at Au point, and for the second function $\Delta W_2(T)$ we used the results at Cu point. The difference between the experimental results in the redundant fixed points and the W values calculated from functions $\Delta W_1(T)$ and $\Delta W_2(T)$, are shown in Table 2.

TABLE 2. Difference Between Experimental and Calculated Data at Redundant Points.

	ΔW(T)		ΔW₁(T)	ΔW₂(T)	
S/N	**Au**	**Cu**	**Ag**	**Ag**	**Au**
45	5.6	-12.9	-3.1	6.5	17.3
46	0.9	-3.9	-0.5	1.9	4.5
47	1.3	-2.4	-0.7	1.2	2.2
68	6.1	-1.2	-3.4	5.9	16.8
157	1.9	-3.2	-1.1	1.6	4.8
181	-2.3	-5.5	1.3	2.8	2.6
192	0.3	-3.7	-0.1	1.8	3.6
49	1.2		-0.6		
183	-0.3		0.2		
184	-0.5		0.3		
207	-0.2		-0.4		
211	-0.2		0.1		
212	0.6		0.1		

As seen from Table 2, the extrapolation of the ITS-90 reference function with the deviation function $\Delta W_1(T)$ exhibits a very good accuracy at Ag point for all the thermometers. The use of the deviation function $\Delta W_2(T)$ results in larger errors at Au point than the use of the ITS-90 extrapolation. To assess the smoothness of the models, we calculated the difference between $\Delta W(T)$ and each of $\Delta W_1(T)$ and $\Delta W_2(T)$ functions. The corresponding graphs are shown in Fig.1 and Fig.2.

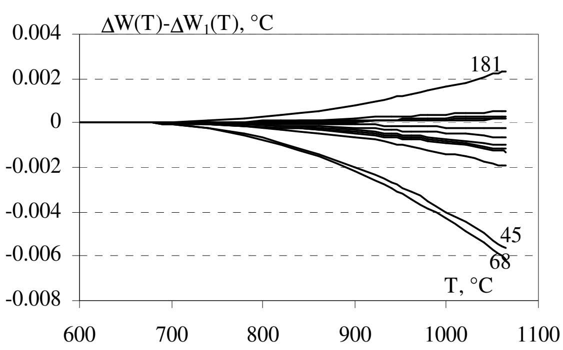

FIGURE 1. Difference between deviation functions $\Delta W(T)$ and $\Delta W_1(T)$.

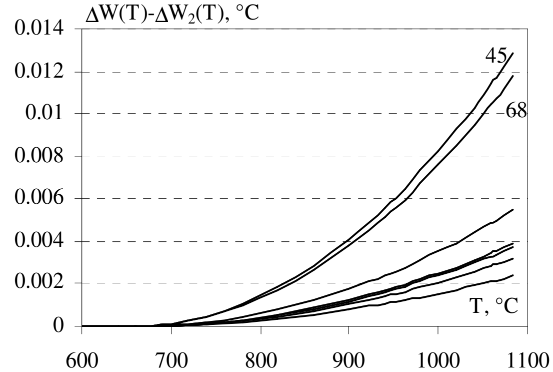

FIGURE 2. Difference between deviation functions $\Delta W(T)$ and $\Delta W_2(T)$.

As seen from the graphs, functions $\Delta W_1(T)$ and $\Delta W_2(T)$ have a smooth junction at Al point with the interpolation function for the range 0.01 - 660.323 °C, the change of the first derivative is small.

Two other functions were tested for the range 660.323 – 1084.62 °C. We tried to increase the order of the polynomials. The last term of equation (1) was changed to $d(W-W_{Al})^3$ in function $\Delta W_3(T)$, and to $d(W(T)-W(Al))^4$ in function $\Delta W_4(T)$. Fig.3 and Fig.4 show the difference between functions $\Delta W_3(T)$, $\Delta W_4(T)$, and the extrapolation of the ITS-90 deviation function up to Cu point, $\Delta W(T)$. The thick curves represent HTPRTs S/N 45 and S/N 68, which showed the greatest departure from the ITS-90 extrapolation in the previous model. As can be noticed from the graphs, the errors at Ag point for these thermometers are not largest of all the others.

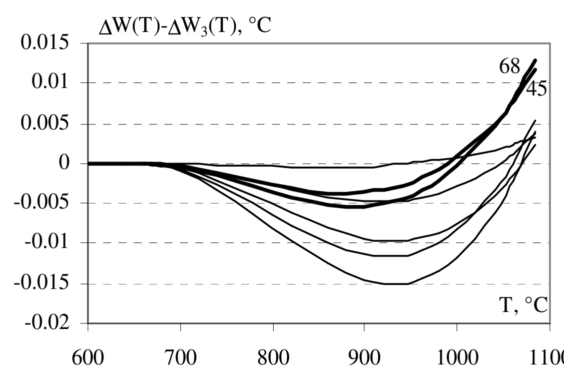

FIGURE 3. Difference between deviation functions $\Delta W(T)$ and $\Delta W_3(T)$.

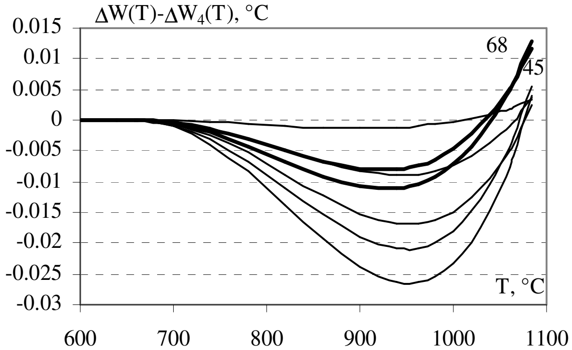

FIGURE 4. Difference between deviation functions $\Delta W(T)$ and $\Delta W_4(T)$.

The increase of the order of the last term of equation (1) has resulted in changing the shape of the curves. The difference between experimental and calculated values at Ag point has become lager for most of the HTPRTs. For some thermometers it approaches –15 mK for the third-order function and -27 mK for the fourth order function. For the second-order function the maximum difference between the calculated and experimental data at Ag point was 7 mK for HTPRT S/N 45.

The deviation function based on using Au point instead of Ag point in equation (1) was tested in work [5] on calibration data of six HTPRTs obtained from publications of NBS and NIM. The errors of the interpolation at Ag point were found to be from 0 to 6.2 mK.

INTERPOLATION EQUATIONS BASED ON A LINEAR DEVIATION FUNCTION IN THE RANGE UP TO ZN POINT

HTPRTs are used usually as standard thermometers for the temperature range above 419.527 °C. In the lower range, 25-Ohm SPRTs serve as defining interpolation instruments. Considering that HTPRTs are made of high-pure platinum and that Matthiessen rule works well for them in the middle-temperature range, we used a linear equation for the deviation from the reference function up to Zn point. In upper temperature ranges a second-order term, similar to that of the ITS-90 function for Al-Ag range, was used. So, the equation for the deviation function in our next model was the following:

$\Delta W_L(T) = a(W(T)-1)$, in the range 0.01- 419.527 °C,

$\Delta W_L(T) = a(W(T)-1) + b(W(T)-W(Zn))^2$,
(2)
in the range above 419.527°C.

We considered two deviation functions of the form (2). In $\Delta W_5(T)$, b is calculated from the result at Au point, and in $\Delta W_6(T)$ b is calculated from the result at Cu point

The advantage of this model is the use of only two fixed points, besides TPW, for the HTPRT calibration. The graphs showing the difference in the temperatures obtained with these deviation functions and with extrapolation of the ITS-90 are presented in Fig.5 and Fig.6.

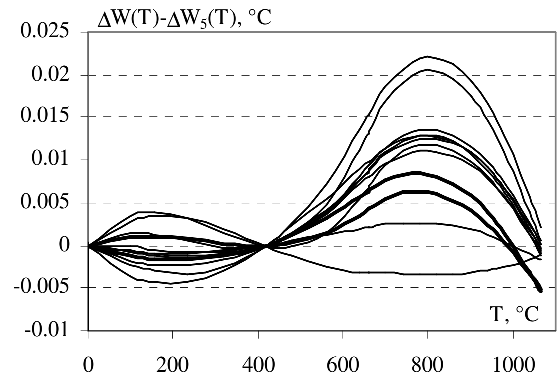

FIGURE 5. Difference between deviation functions $\Delta W(T)$ and $\Delta W_5(T)$.

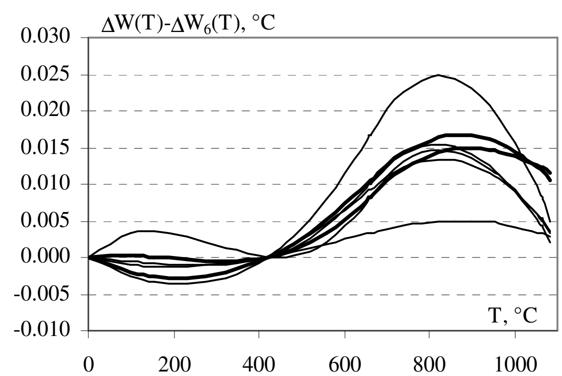

FIGURE 6. Difference between deviation functions $\Delta W(T)$ and $\Delta W_6(T)$.

In the range 0.01 – 419.527 °C the functions investigated deviate from the ITS-90 for not more than ±5 mK. For upper temperature range the error is larger. Comparing the graphs on Fig.3, 4 with the graphs on Fig. 5, 6 one can notice that the deviations from the extrapolated ITS-90 function changed the sign. To assess how the accuracy of the present model changed with respect to the previous one, we give in Table 3 the differences between the experimental results and the results calculated at Al and Ag fixed points.

For all the HTPRTs investigated the error at Ag point does not exceed 20 mK, though, as seen from the graphs, the maximum deviation from the ITS-90 function is observed at about 800 °C and it can approach 25 mK.

TABLE 3. Difference Between Experimental and Calculated Data at Redundant Points.

	$\Delta W_5(T)$		$\Delta W_6(T)$	
S/N	**Al**	**Ag**	**Al**	**Ag**
45	4.2	1.4	8.2	14.4
46	4.7	6.7	8.2	11.2
47	7.5	1.2	10.1	11.4
68	6.4	2.6	10.4	15.6
157	2.2	-0.01	3.3	4.6
181	15.3	14.7	16.6	19.1
192	8.1	6.8	9.2	10.7
49	-3.2	-2.8		
183	20.6	18.4		
184	13.1	12.8		
207	8.6	7.9		
211	9.4	8.5		
212	9.9	7.9		

It is interesting, that HTPRTs S/N 183, 184, that showed negligible errors when using the extrapolation of ITS-90 deviation function, exhibited the largest deviation from the experimental results in Al and Ag points when using this model.

The interpolation method that employs the linear equation below Zn point was previously tested in work [4] using the results of calibration of several Russian and foreign HTPRTs in the range 0.01-961.78 °C. The deviations from the ITS-90 were within 6 mK.

QUADRATIC DEVIATION FUNCTIONS

Two quadratic polynomial functions for the ranges 0.01 - 1064.18 °C and 0.01 - 1084.62 °C were also considered as deviation functions for HTPRTs. The form of equation for them is the following

$$\Delta W_q(T) = a(W(T)-1) + b(W(T)-1)^2 , \quad (3)$$

where coefficients *a* and *b* are calculated from the results at Zn and Au points for $\Delta W_7(T)$, or from the results at Zn and Cu points for $\Delta W_8(T)$.

A disadvantage of the model is that the uncertainty of calibration at the high-temperature fixed points will propagate to the whole temperature range. Advantages of the model are the simple form of the equation and the use of only two fixed points besides TPW for the HTPRT calibration.

The difference between the extrapolation of ITS-90 function and functions $\Delta W_7(T)$, $\Delta W_8(T)$ is shown in Fig. 7 and Fig. 8.

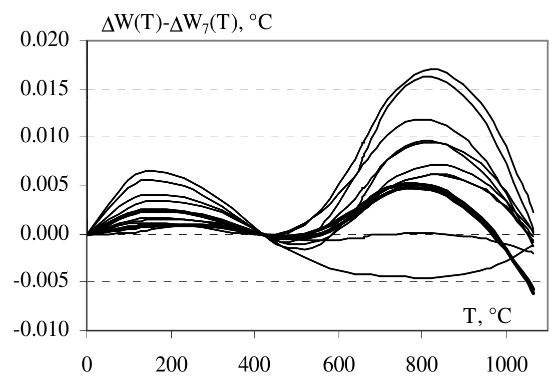

FIGURE 7. Difference between deviation functions $\Delta W(T)$ and $\Delta W_7(T)$.

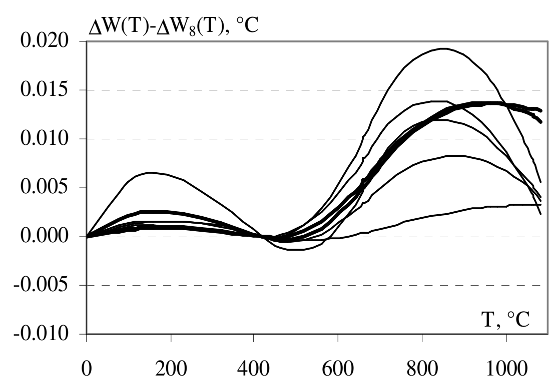

FIGURE 8. Difference between deviation functions $\Delta W(T)$ and $\Delta W_8(T)$.

The error for some of HTPRTs may approach 7 mK at a temperature of about 180 °C. For the most of the HTPRTs the error in the range 0-420 °C does not exceed 3 mK. The deviation from the experimental data at the silver point is within 20 mK and greatly depends on the thermometer. For HTPRTs S/N 45, 68, which are shown in the figures by the thick curves, the use of the quadratic deviation function in the range 0-1064.18 °C leads to smaller errors than those obtained with the ITS-90 extrapolation.

This simple quadratic deviation function for the range up to the gold point was previously suggested and studied in work [6]. The errors for four Russian thermometers at the redundant fixed points were found to vary from 3 to 16 mK.

CONCLUSION

Although the ITS-90 defines the HTPRT as the interpolating instrument only in the range from 0.01 °C to 961.78 °C, some platinum resistance thermometers can be successfully used up to the freezing point of gold and copper. In this work we analyzed several interpolation models, based on the extrapolation of the ITS-90 reference function beyond the silver point. It was found that the application of the same deviation function to different thermometers may result in different errors at the redundant fixed points. The fact that the form of resistance-versus-temperature dependence may vary from one thermometer to another is probably related to varying the properties of the HTPRTs at high temperatures. The thermometers may exhibit different decrease in the insulation resistance, different changes in the electrical purity of the platinum due to contamination, distribution of impurities and defects in the crystal lattice.

In this paper we used the calibration results of thirteen Russian HTPRTs. It was shown that for all of the thermometers under study extrapolation of the reference and deviation functions of the ITS-90 beyond the silver point gives an error within 6.1 mK at 1064.18 °C, and within 13 mK at 1084.62 °C. This result is in contradiction with that obtained in work [3], where the extrapolation of the ITS-90 function for two Russian HTPRTs calibrated at NIST gave an error of about 100 mK at the gold point. The most probable reason for this is a difference between the temperatures of NIST and VNIIM high temperature fixed points.

The best accuracy was obtained for the interpolation function $\Delta W_1(T)$ that was constructed similar to the ITS-90 model but using Au point instead of Ag point. The error at Ag point for this function did not exceed 3.5 mK for all the HTPRTs under investigation. The other models investigated in the paper did not provide an improvement in accuracy. However, taking into account the simplicity of some deviation functions and a small number of the calibration points, it may be worth to use them in the applications where uncertainties of about 20 mK are acceptable.

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