

Analysis of the requirements to SPRTs in the ITS-90 definition

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The temperature range from 83.8 K to 1234.93 K is the most widely used range for scientific and industrial measurements. The ITS-90 is defined in this range through the physical law of changing the resistivity of pure platinum with temperature. Since this law can not be derived theoretically with sufficient accuracy, the approximating equation was obtained from the experimental calibration data of a real “reference” PRT against the fixed points of the ITS-90. Thus, the temperature scale and the temperature unit are essentially determined by the unique function $W_{\text{ref}}(T)$, which is, in the range above 0 °C, the ninth-order polynomial with defined coefficients. The ITS-90 definition gives the method of obtaining the function $W_{\text{ref}}(T)$ in any laboratory using available standard platinum resistance thermometers and fixed points. The SPRTs should be calibrated at the fixed points, and the equation $W(T) - \Delta W(T) = W_{\text{ref}}(T)$ should be calculated, using polynomials $\Delta W(T)$ specified for different temperature sub-ranges [1].

The non-uniqueness of the scale is caused by the anomalies in the shapes of SPRT individual interpolation functions with respect to the reference function $W_{\text{ref}}(T)$. For the thermometers calibrated at the same set of the fixed points, the shapes of the $W(T)$ functions may be affected by the physical-chemical properties of platinum, the detailed designs of the thermometers, and the properties of the insulating material.

The question “what PRT is acceptable for the approximation of the $W_{\text{ref}}(T)$, so that this will not result in a large non-uniqueness of the ITS?” is solved in the ITS-90 by setting the requirements on the purity of the platinum ($W(\text{Ga}) \geq 1.11807$, $W(\text{Hg}) \leq 0.844235$) and stating that the platinum wire must be strain free. One more requirement, which is intended to restrict the electrical leakage across the insulators, is given only for high-temperature thermometers at 961.78 °C, $W(\text{Ag}) \geq 4.2844$.

It was interesting to try to investigate, how the shape of the interpolation function $W(T)$ is affected by two parameters: the purity of the platinum and the decrease in the insulation resistance of a PRT. What non-uniqueness is actually allowed by the definition of the ITS-90?

The non-uniqueness of the scale is usually evaluated as the difference between the calculated $W(T)$ values in the redundant fixed points and the measured values. However, if the redundant fixed points are not available, or the measurements in the redundant points have not been made, an alternative method can be suggested for the estimation of the change in the shape of the $W(T)$ curve with respect to $W_{\text{ref}}(T)$. One can approximate both functions by a polynomial $W_{\text{ap}}(T)$ of a lower order, and to calculate the deviation of $[W(T) - W_{\text{ap}}(T)]$ from $[W_{\text{ref}}(T) - W_{\text{refap}}(T)]$. In the middle temperature range a good choice for the approximating function would be a second order polynomial, such as the CVD function. In Fig.1 the deviation of the ITS-90 reference function from its quadratic approximation is shown as a function of temperature for two temperature ranges. In paper [2] the deviation of the ITS-90 individual interpolation function from the CVD function was estimated for PRTs of a large $W(100)$ range. We are presenting here the table from

that paper, which shows the difference between the $[W_{\text{ref}}(T) - W_{\text{refCVD}}(T)]$ curve and the same curve for the individual calibrations.

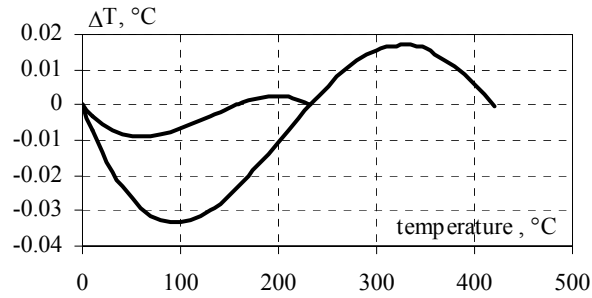


Fig.1

Difference between $W_{\text{ref}}(T) - W_{\text{refCVD}}(T)$ and $W(T) - W_{\text{CVD}}(T)$ in maximums, mK

PRT S/N	W(100)	temperature ranges			
		0 – 420 °C		0 – 232 °C	
		100 °C	330 °C	60 °C	200 °C
SPRT 4185	1.3927	0.01	0.01	0.03	0.01
SPRT 74	1.3926	0.03	0.02	0.03	0.01
SPRT 012	1.3927	0.05	0.04	0.04	0.01
IPRT V-1	1.3921	0.31	0.31	0.05	0.03
IPRT V-5	1.3920	0.35	0.35	0.10	0.05
IPRT V-9	1.3915	0.33	0.30	0.12	0.04
IPRT L-3	1.3854	1.23	0.80	0.36	0.10
IPRT L-7	1.3854	0.94	0.59	0.38	0.08
PRT 1	1.3861	2.04	0.30	0.35	0.09
PRT 2	1.3865	2.58	0.98	0.36	0.09
PRT 3	1.3798	0.15	0.26	0.38	0.08
PRT 4	1.3891	0.18	0.17	0.12	0.03
PRT 5	1.3909	0.20	0.16	0.10	0.02
PRT 6	1.3916	0.11	0.09	0.13	0.04
PRT 7	1.3905	0.25	0.21	0.14	0.03
PRT 8	1.3883	0.26	0.24	0.16	0.04
PRT 9	1.3862	0.62	0.53	0.30	0.07

The range of the $W(100)$ values for the SPRTs was from 1.3798 to 1.3927, which corresponds to the range of the $W(\text{Ga})$ values approximately from 1.11425 to 1.11812. The differences are smaller for SPRTs. However, analyzing the rest of the data, we can not observe any clear relationship between the $W(100)$ values and the values of the differences. The small values obtained for the SPRTs seem to be a result of their better stability. It can be concluded, that the impurity concentration in platinum does not have an noticeable effect on the shape of the interpolation function over the large range of $W(\text{Ga})$. On the other hand, the impurities can cause instability of the resistance, which is a serious problem especially at high temperatures. The analysis of the instability of some HTPRTs at temperatures above 900 °C reported in paper [3] suggested that the requirement on $W(\text{Ga})$ for HTPRTs in the definition of the scale should be increased to about 1.11810.

The main factor which can cause an anomaly in the $W(T)$ function at high temperatures is the change in the insulation resistance. The ITS-90 reference function was developed from the results obtained with a long-stem, quartz-sheathed HTPRT of a certain design. Apparently, the detailed designs of the thermometers used for ITS-90 realizations may be different, and the properties of the insulating material may be different also. The definition of ITS-90 refers to the

“Supplementary Information for the ITS-90” for current good practice, in particular concerning permissible leakage resistance of SPRTs. However, in that document, one can find only the requirement on the insulation resistance for a 25 ohm thermometer: not less than 70 MΩ at 500 °C, and the recommendation to use low-resistance sensing elements for HTPRTs.

In the ITS-90 definition itself, there is a requirement on $W(\text{Ag})$, which is supposed to limit the behavior of the $W(T)$ function at high temperatures. To investigate the non-uniqueness of the ITS-90 allowed by the present restriction on the value of $W(\text{Ag})$ we analyzed two large sets of HTPRT calibration results. The first set is the results taken from the paper [4], which was presented to the CCT meeting in 1987, and which included the results published by NIM, NBS, NPL, PTB. The second set is the results obtained with Russian HTPRTs calibrated at VNIIM. Some of those results were published in [5], [6]. When choosing the results for the analysis we were trying to cover a large range of the $W(\text{Ag})$ values. In Fig. 2 the calibration results at the silver point are shown versus the results at the zinc point.

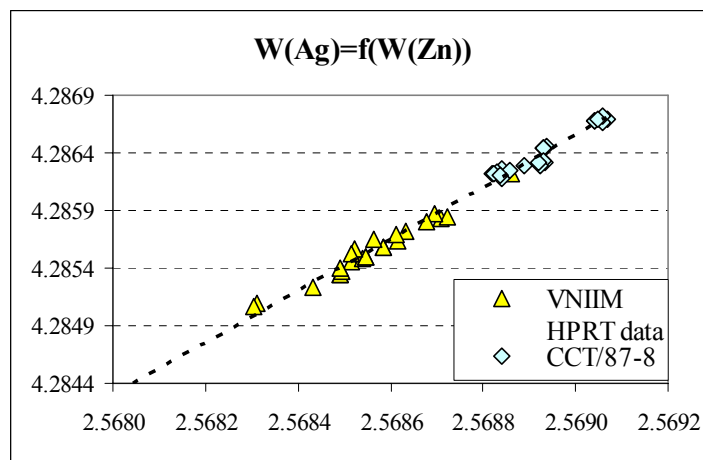


Fig. 2

Fitting the data with a linear function results in the equation

$$W(\text{Ag}) = 2.253186 W(\text{Zn}) - 1.501881 \quad (1)$$

Thus, at the point $W(\text{Ag}) = 4.2844$ we have $W(\text{Zn}) = 2.568044$, that approximately corresponds to $W(\text{Ga}) = 1.118073$. As can be seen, the requirement on $W(\text{Ag})$ in the ITS-90 is consistent with the lowest value of $W(\text{Ga})$. But, what about the other permissible $W(\text{Ga})$ values? It turns out, that the definition of the ITS-90 does not restrict the behavior of the $W(T)$ function for high-purity thermometers, or, more correctly, the $W(T)$ has more freedom for high- $W(\text{Ga})$ thermometers than for low- $W(\text{Ga})$ thermometers. It is interesting to see how the shape of the $W(T)$ function will change, if we use a high-purity HTPRT having a $W(\text{Ag})$ value equal to the minimum permissible value of the scale. What non-uniqueness is actually allowed by the definition of the ITS-90? For the analysis of the non-uniqueness we have to choose an approximating equation, which allows some redundant fixed points and exhibits a small error with respect to the ITS-90 interpolation. Our previous experience in investigating the interpolation equations for HTPRTs showed that one of the best alternative models for the deviation function could be the following:

$$\begin{aligned} 0\text{-ZN} & \quad \Delta W_a(T) = a (W_a(T) - 1) \\ \text{ZN-AG} & \quad \Delta W_a(T) = a (W_a(T) - 1) + b (W_a(T) - W_a(\text{Zn}))^2, \text{ where } a \text{ is taken from the } 0\text{-ZN range} \end{aligned}$$

The interpolation method that employs the linear equation below the Zn point was previously tested in work [6] using the results of calibration of several Russian and foreign HTPRTs in the range 0.01 to 961.78 °C. The deviations from the ITS-90 were within 6 mK. This method gives the opportunity to use the redundant Al point for the estimation of the non-uniqueness.

For all the calibrations presented in Fig.2 we calculated the difference between the ITS-90 interpolation model and the alternative model. This difference at the Al point is shown in Fig.3 (upper row of diamonds).

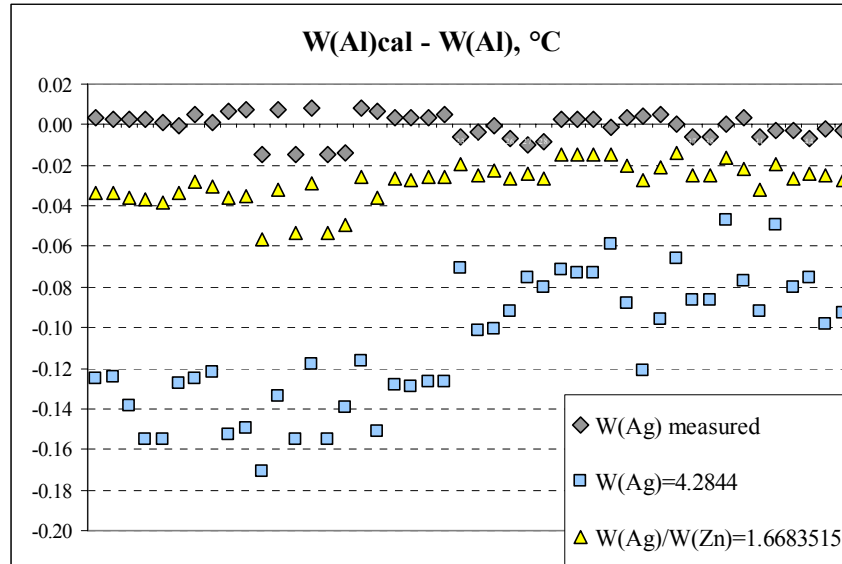


Fig.3

The results are randomly distributed above and below zero, and their spread comprises possible differences in the fixed points, the methods of calibrations and the instability of the HTPRTs. In order to estimate how much the change in the Ag point will distort the shape of the $W(T)$ function, we set the value of $W(Ag)$ to 4.2844 and recalculate the graph. The result is shown in Fig.3 by grey squares. The deviation of the points from the axis became much greater, the average for the high- $W(Ga)$ thermometers was about -0.14 °C, that can be considered as the possible non-uniqueness of the scale. This estimation suggests, that the change in the shape of the $W(T)$ function occurred only at high temperatures, the $W(Al)$ being at the normal level. This imaginary behavior of the $W(T)$ can be ascribed to the decrease in the insulation resistance, which is known to depend exponentially on temperature. However, we should admit that this situation is not natural for standard quartz-sheathed HTPRTs.

There are two possible ways to improve the definition of the ITS-90 in order to reduce the allowance for the insulation resistance. First, is to set the requirement on the permissible deviation from the fitting line in Fig.2. However, it would be too complicated to use the equation in the definition of the scale. The second way is to set the requirement on the ratio $W(Ag)/W(Zn)$. It is clear from equation (1), that the ratio $W(Ag)/W(Zn)$ depends on the $W(Zn)$:

$$W(Ag)/W(Zn) = 2.253186 - 1.501881 / W(Zn) \quad (2)$$

However, the range of possible ratios is not large. The smallest value corresponding to $W(Ag) = 4.2844$, would be $W(Ag)/W(Zn)=1.6683515$. For each of the HTPRTs we calculated $W(Ag)$ from $W(Zn)$ using this value of the ratio, and evaluated $W(Al)$ using the alternative interpolation method described above. The difference between the calculated $W(Al)$ values and the calibration results at the Al point is shown in Fig.3 by triangles. The non-uniqueness became substantially smaller than that derived from setting the requirement on $W(Ag)$ only.

The experience in using commercially available Standard HTPRTs does not show any serious concern about the $W(\text{Ag})$ being inconsistent with $W(\text{Ga})$. The HTPRTs have quartz insulation parts and a low nominal resistance at 0.01 °C. However, it is not forbidden to develop thermometers using different insulation materials. Besides, if the value $W(\text{Al})$ has been restricted by the ITS-90 for low- $W(\text{Ga})$ thermometers, why we should not do so for the whole range of the permissible $W(\text{Ga})$ values? **The requirement $W(\text{Ag})/W(\text{Zn}) \geq 1.66835$ would be more justified than $W(\text{Ag}) \geq 4.2844$.**

It is well known, that commercial middle-range IPRTs may show a large deviation from the quadratic function at temperatures above 600 °C. As a rule, it is a result of a substantial electrical leakage, occurring between the leads of the sensing element coming through the capsule seal. In the Standard documents on the methods of calibration for IPRTs it is recommended to measure the resistance of the thermometers that are used above 450 °C at the end of the working range to check the correspondence with the standard table. The problem for industry is very inconvenient designs for SPRTs suggested in the “Supplementary Information for the ITS-90”. The thermometer, which has a long quartz sheath and does not withstand any vibrations, can not be used in many applications. This situation initiates the development of SPRTs of different designs, which are sometimes similar to those used in industrial PRTs, but employ pure platinum wire. One can consider from the definition of the ITS-90, that if he takes pure platinum and makes a PRT, which, he believes, is “strain free”, he will obtain a standard thermometer. Probably, it is necessary to pay more attention to the requirements on the insulation resistance for SPRTs and HTPRTs in the definition of the scale and in the “Supplementary Information for the ITS-90”.

References

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