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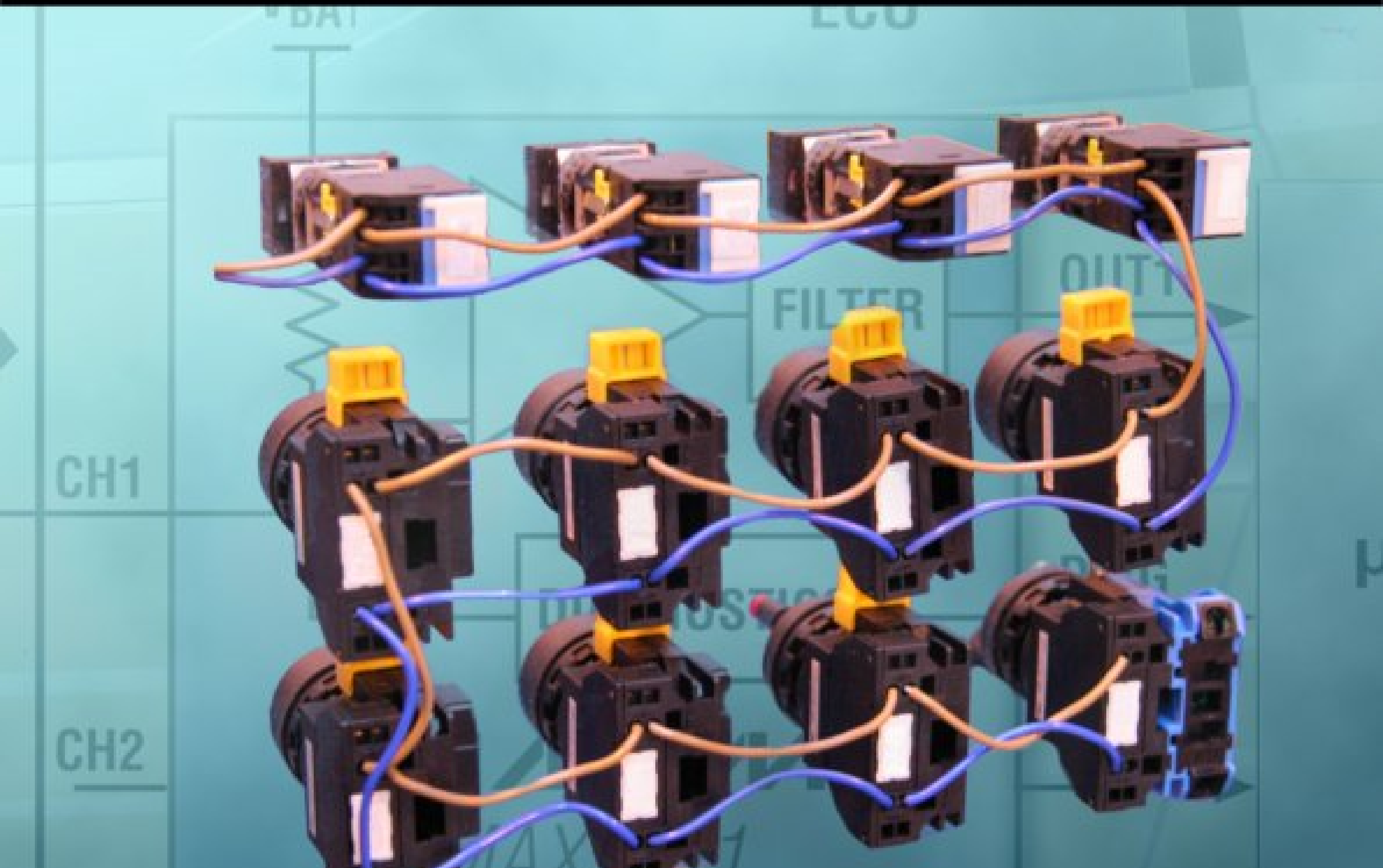

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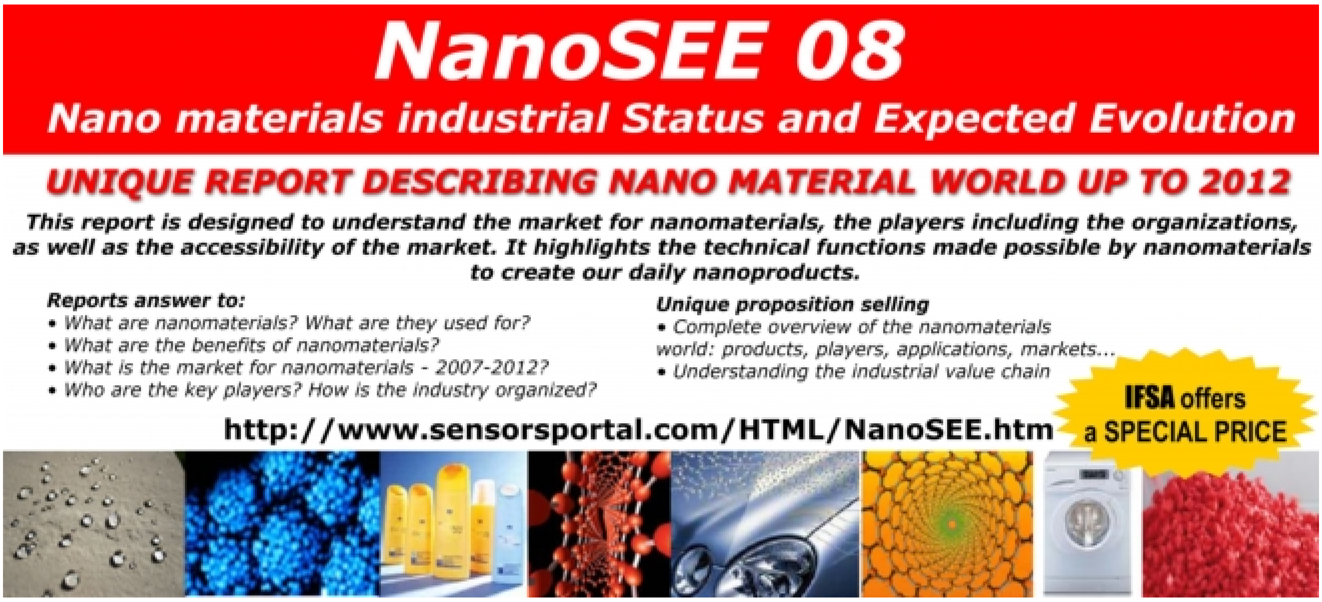

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Stability of High Temperature Standard Platinum Resistance Thermometers at High Temperatures

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Abstract: An investigation of the stability of high temperature standard platinum resistance thermometers HTSPRTs has been carried out for two different designs thermometers (with nominal resistance 0.25 Ω and 2.5 Ω) from two different suppliers. The thermometers were heated for more than 160 hours at temperatures above 960 ^{0}C using a vertical furnace with a ceramic block. A study was made of the influence of the heat treatment on the stability of the resistance at the triple point of water, and on the relative resistance $W_{(Ga)}$ at the melting point of gallium.

The thermometers showed a correlation between the drift note and the values of $W_{(Ga)}$. It was found also that the HTSPRT which has a sensor with strip shaped support and low nominal resistance is more stable than the HTSPRT which has a sensor in the form of a coil wound on silica cross. The 0.25 Ω thermometer has better stability ≅ $7x10^{-6}$ $^{\mathbf{0}}$C (at TPW) after 40 hour. Factors affecting the stability and accuracy of HTSPRT also will be discussed. *Copyright © 2010 IFSA.*

Keyword: HTSPRT, Melting point of gallium, Triple point of water

1. 1. Introduction

The International Temperature Scale of 1990 (ITS-90), extended the temperature range of the standard platinum resistance thermometers from 660.723 ^{0}C to 961.78 ^{0}C. However, the experience of using large numbers of HTPRTS in calibrations and in comparison showed that some difficulties appeared in obtaining the desired long term stability of the HTSPRTs at high temperature. The reasons for losing the stability are possibly due to the properties of platinum and quartz, materials used for constructing PRTs, also the growth of large crystals in platinum wire during long treatment times of an HTSPRT at temperatures above 960 ^{0}C [1]. This will cause the HTSPRT to be very sensitive to vibrations and may result in increase of its resistance. This process is considered to be non-reversible. A second reason for the increase of the HTSPRT resistance is caused by quenching vacancies in the crystal lattice of platinum by fast cooling from high temperature, this process is reversible and can cause an upward shift in resistance that at the triple point of water can be more than 35 mK. The effect of quenched-in vacancies can be reversed by an annealing process as we shall describe in this paper. The third reason for the increase of the platinum resistance at the triple point of water was discussed by Berry [2]**.** He gave an explanation for SPRT shifts in calibration due to platinum oxidation. The net effect of the oxide layer formation is to reduce the effective diameter of the platinum wire, with an increase in $R_{(TPW)}$ and in $R_{(Ga)}$, and essentially no change in $W_{(Ga)}$. The fourth reason is much more difficult to bring under control. Above 500 ^{0}C the quartz sheath of the HTSPRT becomes porous and the platinum sensor can be contaminated by metal ions surrounding the quartz sheath, which may be ceramic, graphite, Inconel or a fixed point cell which contained graphite crucible. Above 500 ^{0}C metal ions can pass freely through the quartz sheath. This effect can cause an increase in $R_{(TPW)}$ and a decrease in $W_{(Ga)}$. It was suggested to use a platinum tubes pocket around the thermometer to protect it from the contamination [3].

For a platinum resistance thermometer to be acceptable as an ITS-90 interpolating instrument, it must be made from pure platinum and exhibit a resistance ratio at the gallium melting point $W_{(Ga)}$ larger than 1.11807 [4].

The purpose of the present work was to study the stability of HTSPRTs by heating at temperatures above 960 ^{0}C, and to investigate the influence of the previous factors on the stability of the resistance at the triple point of water $R_{(TPW)}$ and the $W_{(Ga)}$ of the thermometers. Two different designs of HTSPRTs were used in this study, with nominal resistance 2.5 Ω and 0.25 Ω.

2. Factors Affecting the Stability and Accuracy of HTSPRT

2.1. Instability due to Contamination of HTSPRT by Silver

Many investigators such as Ansen and Hill [5] found that both quartz and graphite allow diffusion of Ag at these temperatures into the space within the thermometer well where they gradually reach concentrations sufficient to measurably contaminate the PRT's. It was found that a thin platinum tube (0.1 mm wall thickness) provides a sufficient barrier to protect PRT's from contamination. For that purpose in our experiments we have used a thermometer platinum pocket.

2.2. Effect of Electrical Insulation Leakage in HTSPRT at High Temperatures

At temperature above 600 ^{0}C it is increasingly difficult to achieve high accuracy due to electrical insulation leakage between the silica support and the platinum sensor. This insulation leakage forms a shunt across the sensor resistor producing systematic temperature measurement errors. It has been well established by Berry [6, 7] and many others that insulation leakage in commercial SPRT's can cause significant temperature measurement errors in the range 600 ^{0}C to 1000 ^{0}C. These errors are large when a sensor of resistance Ro at 0 ^{0}C is 25 Ω, which is commonly used in medium ranges for this purpose commercial HTSPRT do in fact use lower Ro values such as 2.5 Ω or 0.25 Ω, in order to reduce this error to more acceptable levels. The drawback to reducing R_o is that the sensitivity (dR/dt) of the thermometer is also reduced, and consequently the measurement of its resistance requires higher precision for the same precision in temperature.

2.3. The Instability of the HTSPRT due to Strain Effects

Several experimental investigations in the past decades have shown that thermometers exhibits predictable resistance change (drift rates) when heated for long times at high temperatures and then cooled to room temperature and then measured at the triple point of water. It has been found that Ro the resistance of the thermometer at 0 ^{0}C changes rapidly due to the strain. Berry [7] had observed this change in Commercial thermometers and explained that, as due to the quenching effects which occur in SPRT's when they are transferred from a high temperature environment >500 ^{0}C into a room temperature environment.

Regardless of the magnitude of quenching effects in platinum resistance thermometer it has been shown that it is always possible to completely remove the quenched in defects by suitable annealing. From these study and other studies [7, 8], it is apparent that the necessary annealing programmer would involve placing the thermometer in a separate annealing furnace at a temperature about 50 ^{0}C below that measured, and not higher than 800 ^{0}C, then reducing the temperature in 50 ^{0}C steps every 10 to 20 minutes until 450 ^{0}C is reached and it is safe to take out the thermometer at that temperature. This programmer gives complete as well as highly efficient annealing.

2.4. Reactions between the Platinum and the Refractory Materials, used as the Insulators and as a Sheath

The construction of a thermometer requires the use of non-metallic refractory materials for electrical insulation and for sheathing the thermometer. Many refractories can be highly reactive with platinum in atmosphere of argon. This can be avoided if the thermometer contains a partial pressure of O_2. More important are the reactions that platinum may have with impurities in relatively unreactive refractory materials. Walker, Ewing and Miller [9] found that the largest effects were caused by iron in commercial refractory oxide insulation. Contamination of the platinum was observed even without direct contact of the platinum with the ceramic, which implies that iron or iron oxide can be vaporized out of the ceramic into the ambient gas at high temperature.

Better understanding of the high temperature chemistry of platinum may help to improve the stability situation of the platinum thermometers.

3. Equipment

3.1. Thermometers

The thermometer design is most important for a good HTSPRT. In the present study we have used two HTSPRTs of different design and from different sources. One thermometer was constructed by ISOTECH England. The other thermometer was constructed by Hart Scientific, USA. The design details of the thermometer sensors are shown in Fig (1).

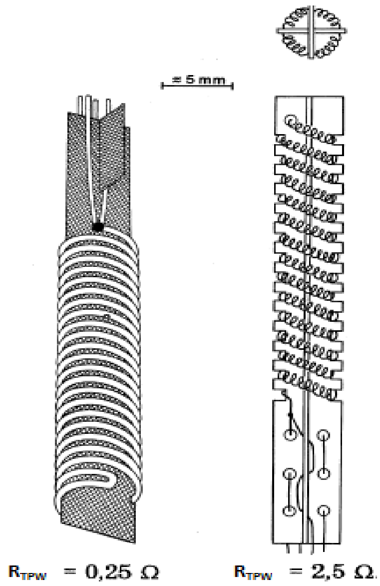

Fig. 1. Typical designs of the two HTSPRTs; $R_{TPW} \cong 0.25\ \Omega$ and $R_{TPW} \cong 2.5\ \Omega$.

The sensor design of the 0.25 Ω thermometer has a strip-shaped support with notches made of silica and the platinum wire of 0.3 mm diameter was wound bifilarly around the support. In order to improve the thermal characteristics, the platinum wire is placed as near as possible to the inner surface of the silica sheath.

The sensor of the 2.5 Ω thermometers is bifilar helix design, but the support is the customary silica crass. Table (1) gives the general features of both thermometers.

The four platinum leads of the thermometers are separated and insulated by disks with four holes and small silica tubes. The discs were roughened and the outside of the silica sheath was sand blasted for reducing the radiation losses along and inside the sheath.

Table 1. General features of both thermometers.

Nominal resistance at 0.01 °C	0.25 Ω thermometer	2.5 Ω thermometer
HTSPRTs overall length	75 cm	77 cm
Header length	12 cm	9 cm
External sheath length	63 cm	68 cm
Nominal sheath diameter	7.4 mm	7.0 mm
Header diameter	2.5 cm	2.1 cm
Sensing element shape	Strip shape	coil wended on the silica cross
Resistor former	Notched silica blade	Notched silica cross
Resistor coil length	45 mm	52 mm
Resistor wire diameter	0.4 mm	0.2 mm
Lead insulator type	Silica tube and disk	Long silica tubes
Lead wire diameter	0.3 mm	0.3 mm
Length of roughened sheath	350 mm	350 mm

3.2. Thermometer Bridge

The resistance measurements were conducted automatically under programmed computer control. An Automatic Systems Laboratories, Inc. (ASL) Model F18 AC bridge, which is capable of 9.5 digit resistance-ratio measurement resolution, was used with thermostated ac/dc Tinsley reference resistors of 10 Ω for 2.5 Ω HTSPRTs and 1 Ω for 0.25 Ω HTSPRTs, giving effectively 0.05 Ω and 0.005 Ω resolution, respectively. The bridge was operated at 30 Hz (with detector gain at 5.90 x10^4, bandwidth of 0.1 Hz and quadrature detector gain at x10).The resistors are maintained at a constant temperature of (23±0.5) ^{0}C in a thermo-stated bath. The bridge and switch box are controlled with an IBM compatible personal computer for automatic operation and digital data recording during a plateau. The bridge has an uncertainty of ± 0.1 ppm of the maximum ratio and a resolution of 0.1 ppm of the reference resistor. The current supplied to the thermometers was uniformly 10 mA, giving rise to self-heat of less than 1 mK in a WTP cell. The values of resistance given by this HTSPRT are used in calculations without adjustment of zero current.

3.3. Furnace

The furnace was used in the present work is home made one [(8)]. It is water cooled with a non-uniform main heater winding to provide balancing of end losses, the heater tube length is 600 mm long, and controlled by a feedback loop employing a Type-N thermocouple for the sensor.

Fine compensation of end losses is obtained with separately controlled end heater. The electrical noise, a series-regulated DC power supply is used, and the winding of the heater is designed to be non-inductive. Powers are adjusted to give a gradient of less than 0.05 ^{0}C over 20 cm around the ceramic block.

4. Stability and Calibration of HTSPRTs Following Heat Treatment

Initially, each thermometer was heated in a quartz-lined tube furnace for 160 hours at approximately 1000 ^{0}C, and checked for, stability. Subsequently, thermometers were heated and/or temperature cycled for various lengths of time to evaluate shifts in R_o with time and temperature.

Annealing of HTSPRT is very important to avoid grain growth of the sensing platinum wire. Normally the grain size is small. When using the HTSPRT at high temperatures for long periods of time, the grain size will increase. A large grain size causes the HTSPRT to lose structural strength and become less stable.

The temperature stability with time in the resistance of the HTSPRTs at TPW comparing to the resistance value after each heating cycle (20-hour interval period) are summarized in Table 2 and shown graphically in Figs. 2 and 3.

Each HTPRT is usually given the following annealing treatment at 1000 ^{0}C. The thermometer is inserted into the annealing furnace when the temperature in the furnace is about 500 ^{0}C. Then the thermometer is heated slowly to 1000 ^{0}C, exposed at that temperature for 5 hour, cooled to 500 ^{0}C over 3.5 hour and removed from the furnace.

Table 2. The variations with time in the resistance of the HTSPRTs at TPW comparing to the initial resistance value.

Annealing time in hour	ΔR in Ω of 0.25 Ω thermometer	ΔR in Ω of 2.5 Ω thermometer
20	0.0000111	0.000376
40	0.0000131	0.000294
60	0.0000091	0.000299
80	0.0000091	0.000313
100	0.0000081	0.000347
120	0.0000081	0.000330
140	0.0000091	0.000349
160	0.0000091	0.000346

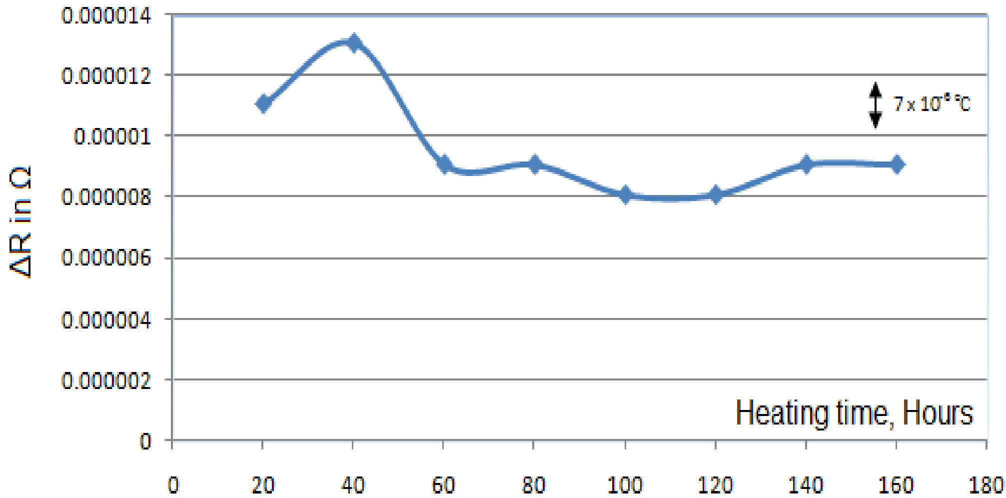

Fig. 2. The variations with time in the resistance of the 0.25 Ω at TPW comparing to the initial resistance value after each heating cycle (20-hour interval period).

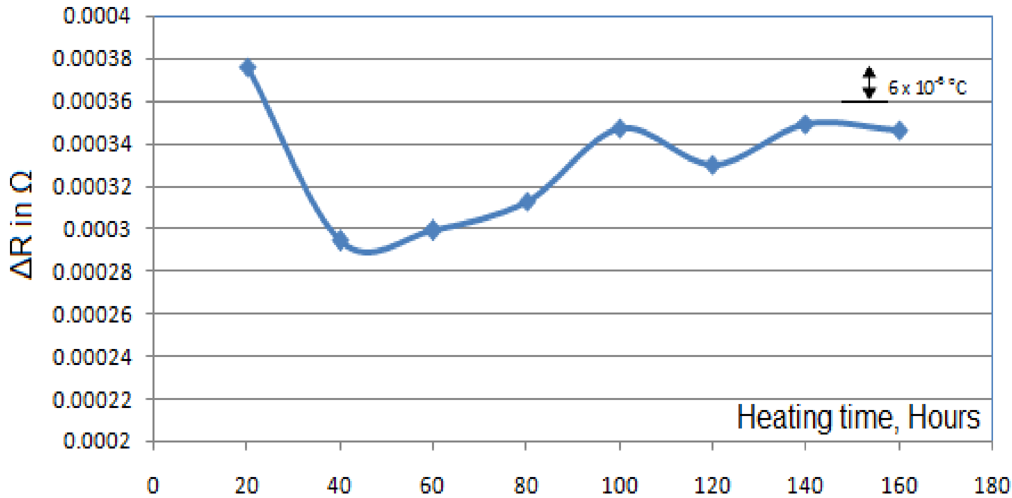

Fig. 3. The variations with time in the resistance of the 2.5 Ω at TPW comparing to the initial resistance value after each heating cycle (20-hour interval period).

Each annealing cycle is followed by the measurements of the resistance at the triple point of water $R_{(TPW)}$ and at the melting point of gallium. The stabilization curves show that both an increase and a decrease of $R_{(TPW)}$ may be observed during the course of the initial stabilization. The resistance ratio $W_{(Ga)}$ was calculated, based on the formula $W_{(Ga)}=R_{(Ga)}/R_{(TPW)}$.

The drift of $R_{(TPW)}$ was equivalent to less than 0.00003 ^{0}C for each thermometer, during the 160 hours of heating up to 1000 ^{0}C as shown in Fig. (3).

Table 3 shows the variations with time in $W_{(Ga)}$ (gallium melting point) during this study. The test results indicate that the $R_{(TPW)}$ and $W_{(Ga)}$ tend to be stable for each thermometers. The trend of $W_{(Ga)}$ is more pronounced than that of $R_{(TPW)}$. This is because the resistance of the thermometers at the triple point of water includes long-term drift in addition to the elimination of strain, while the drift of the resistance ratio (usually) does not include $R_{(TPW)}$ drift. Long-term stability tests are not yet complete and will last for years.

Table 3. Variations with time in $W_{(Ga)}$ (at gallium melting point) during this study.

Annealing Time/hour	$W_{(Ga)}$ of 0.25 Ω thermometer	$W_{(Ga)}$ of 2.5 Ω thermometer
0	1.1181585	1.118115
80	1.1181659	1.118123
160	1.1181750	1.118075

The cooling of the thermometer rapidly from high temperatures to room temperature can quench excess lattice-site vacancies in the platinum crystal structure causing the $R_{(TPW)}$ of the thermometer to increase [10].

The $W_{(Ga)}$ went up fast for the first heating cycles and then $W_{(Ga)}$ tended to be stable with a gradual rate of increase. The stability of $W_{(Ga)}$ was better than 1mK for each thermometer after over 160 hours in three cycles at 1000 ^{0}C.

5. Uncertainty of the Results

The budget of uncertainties in our results at melting point of gallium are estimated according to ISO recommendation [11] as shown in Table 4, the type A uncertainties are taken as the calculated standard deviation of the mean of the series of the experiment given in table (4) (U_A). The type B uncertainties include the maximum estimated allowances (U_B) for the thermometer drift, self heat of the thermometers, effect of impurities, heat flux effect and others.

5. Discussion

The low R_o of the HTSPRTs permits the use of heavier platinum wire and relieves the problem of insulation leakage, but may require a reassessment of a laboratory's ability to measure electrical resistances of low level and, at the higher temperatures, often in the presence of noise.

From the experiments performed in this study, some important observations can be made about the effects of the heat treatment conditions at high temperature on the stability of HTSPRTs:

Table 4. The budget of uncertainties in our results at melting point of gallium for the HTSPRTs.

Uncertainty factors	**0.25 Ω thermometer**	**2.5 Ω thermometer**
Type A combined (mK) Realization of Repeatability and Stability	2.00	6.50
Type B uncertainty component (mK) 1. Chemical impurities, isotopes 2. Hydrostatic head correction 3. Standard resistor 4. Bridge measurement 5. Uncertainty Propagation from TPW 6. Self heat error 7. Heat flux immersion error Type B combined (mK)	 0.06 0.01 0.01 0.02 0.08 0.05 0.01	 0.06 0.01 0.01 0.02 0.08 0.05 0.01
Standard combined uncertainty (mK)	2.00	6.50
Expanded combined uncertainty, k=2 (mK)	**4.00**	**13.00**

- From table (2) and Figure (2 and 3), the 0.25 Ω thermometer has stability ≅ 7 x 10^{-6} ^{0}C (at TPW) after 40 hour annealing but the 2.5 Ω thermometer has stability ≅ 12 x 10^{-6} ^{0}C after the same heating period;
- The relative resistance W(Ga) at the melting point of gallium was used as criteria to check the HTSPRT efficiency according to ITS-90 [4] requirements. From the above results it's clear that 0.25 Ω thermometer has higher stability than 2.5 Ω thermometers after heat treatment;
- The drift rates of R(TPW) depend on the diameter of the platinum wire, which forms the sensor. Where, the 0.25 Ω thermometer with 0.4 mm platinum wire sensors has a less drift rates than the 2.5 Ω HTSPRTs with 0.2 mm platinum wire sensors;
- The shifts which may be observed when a thermometer is cooled to rapidly are due to quenched-in crystal lattice vacancies. These can usually be removed, and the thermometer restored, by heating the thermometer, with the rise time precautions given above, to 960 ^{0}C, and holding it there for 30 to 60 minutes; then gradually cooling to below 500 ^{0}C before withdrawing the thermometer. A check at the triple point of water point will indicate whether the treatment has been adequate, or whether it needs to be reported [12];
- Even with careful use, changes of 2 or 4 mK at the triple point water (TPW) are typical. These changes can be attributed to thermal cycling, slight mechanical shock or oxidation.

6. Conclusion

The experimental technique used in the present work will offer the Egyptian calibration network accredited laboratories to check the quality and choice among a group of HTSPRTs supplied by different manufactures.

The 0.25 Ω thermometer has better stability ≅ 7x10^{-6} ^{0}C (at TPW) after 40 hour annealing but the 2.5 Ω thermometer has stability 12x10^{-6} ^{0}C (at TPW) after the same heating period. The investigation verified that the 0.25 Ω thermometer is an excellent temperature standard for high temperature up above 660 ^{0}C.

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Guide for Contributors

Aims and Scope

Sensors & Transducers Journal (ISSN 1726-5479) provides an advanced forum for the science and technology of physical, chemical sensors and biosensors. It publishes state-of-the-art reviews, regular research and application specific papers, short notes, letters to Editor and sensors related books reviews as well as academic, practical and commercial information of interest to its readership. Because it is an open access, peer review international journal, papers rapidly published in *Sensors & Transducers Journal* will receive a very high publicity. The journal is published monthly as twelve issues per annual by International Frequency Association (IFSA). In additional, some special sponsored and conference issues published annually. *Sensors & Transducers Journal* is indexed and abstracted very quickly by Chemical Abstracts, IndexCopernicus Journals Master List, Open J-Gate, Google Scholar, etc.

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Contributions are invited on all aspects of research, development and application of the science and technology of sensors, transducers and sensor instrumentations. Topics include, but are not restricted to:

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- Theory, principles, effects, design, standardization and modeling;
- Smart sensors and systems;
- Sensor instrumentation;
- Virtual instruments;
- Sensors interfaces, buses and networks;
- Signal processing;
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- Nanosensors;
- Microsystems;
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