Platinum Resistance Thermometers Stable To ±0.001°C Per Year

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Abstract. Those who purchase SPRTs and those who manufacture SPRTs usually specify the performance in terms of the drift of R_{TPW} during a year.

Unfortunately this is a parameter that varies with handling and use, in fact SPRT calibration certificates print W tables which allows for drifts in R_{TPW} whilst maintaining the usefulness of the certificate.

The paper analyses the stabilities both of R_{TPW}, W_{ga} and W_{Hg} of SPRT's calibrated over a number of years and concludes that W_{ga} and W_{Hg} are much safer guides to the quality and performance of SPRTs.

Keywords: Platinum Resistance Thermometer, Stability, R_{TPW}, W_{ga}, W_{Hg}
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INTRODUCTION

Globally, those purchasing SPRT's specify that the water triple point resistance be stable to ±0.0001Ω (0.001°C) per year.

Transportation and use mean that in practice this requirement is never met and in any case is not within the control of the manufacturer. Manufacturers themselves are guilty of specifying SPRT's in terms of R_{TPW} drift.

Is there a better way for manufacturers and purchasers to specify the performance of an SPRT?

THERMOMETER CONSTRUCTION

What factors affect a platinum thermometer's resistance? Firstly how is a thermometer made. A platinum resistor contains a length of platinum wire of a known diameter and purity.

For typical 25.5ohm SPRT this may be 500mm of 0.1mm diameter wire whose purity is 99.9999%. The wire is formed into a coil of some 500 turns and the coil wound onto a quartz cross or mandrel. Each end of the coil is welded to 2 platinum or gold lead wires.

This assemblage is inserted into a quartz or metal sheath from which the lead wires exit via a resealable hermetic seal.

A partial pressure of nitrogen and oxygen is introduced into the thermometer which is then sealed permanently.

Following manufacture the thermometer is stabilised by thermally cycling it a number of times to its maximum and minimum temperatures.

Frequent Water Triple Point values are measured until the thermometer's triple point temperature repeats to within 0.2mK between thermal cycles. This is equivalent to a length change of 0.4μmm or a diameter change of 3.2nmm.

Lastly W_{ga} is measured to ensure it is greater than 1.11807 as specified in ITS-90.

Now in its fully annealed state the platinum has the hardness of butter from a fridge!

One of two things happens; either the SPRT is transported to a customer, or it is moved locally for calibration.

The local calibration laboratory begins by measuring R_{TPW} and comparing it to the annealing sheet.

A sequence of fixed point resistances are then measured according to the requirements of the customer. R_{TPW} is measured many times during the calibration and finally a table of W values is printed, together with the first and last R_{TPW} values.

R_{TPW} may change by 1mK during the complete calibration process which can take up to 2 weeks.

Whether calibrated or not, eventually the SPRT must be transported to the customer.

1. <u>Hand Carrying</u>; they may chose to collect their thermometer. One client collected four SPRT's, took a taxi to the airport, and kept them in his overhead locker followed by a taxi to his laboratory.

All thermometers had R_{TPW} increased by 2 to 4mK during his transportation. He was able to restore the R_{TPW} by annealing to within 0.5mK of the factory values.

2. Delivery by Courier; the SPRT in its padded case is suspended by bungee cords inside a much larger case to minimise shock and vibration during transportation. Even so increases in R_{TPW} have been measured up to 40mK and most of this change is permanent.

The manufacturer has no control over what happens after the thermometer leaves his factory and yet the specification says ±1mK per year!

What Do SPRT Manufacturers Say About The Stability Of Their Products?

I says under long term drift of its 670 SPRT "*from 0.001°C per annum depending on use*".
R states 0.002°C drift per 100 hours at maximum temperature 0.01°C per annum (162CE).
H says less than 0.008°C per annum regular usage less than 0.002°C/100H at 661°C (model 5681).
Y stability not specified.
C stability not specified.

In other words, those who do try and specify drift use R_{WTP} and hedge the numbers with extreme temperature drift or dependent on usage statements. None refer to stability of W_{ga} or W_{Hg}.

Why have manufacturers and those who specify SPRT's become obsessed with R_{TPW} when the true performance of an SPRT is dependent on the stability of the W Table?

A Different Approach

Through shock, vibration and thermal cycling R_{TPW} will inevitably change with usage.

However the purity of the platinum wire will not, and provided the thermometer is annealed, the resistance change with temperature (W value) will remain the same.

It is not coincidence that a calibration certificate presents a table of W values as well as R_{TPW}.

Provided the user regularly updates the R_{TPW} value the certificate remains valid for a long time.

And so specifications should state that the W values must remain within ±0.001°C per annum and not R_{TPW} which as we have already stated above is outside the control of the producer once it leaves his factory.

Uncertainties

Choosing Δ W_{ga} or W_{Hg} as a stability criterion enables tracking of these values to a high degree of accuracy because most uncertainties drop out of W value calculation, and provided the same cells are used, their absolute values are not important assuming they are stable.

Measurement procedure is very important and must be adopted consistently if accurate tracking is to be achieved.

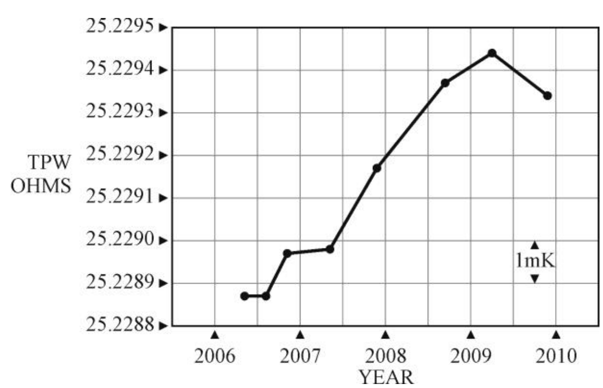
Actual SPRT's

A number of actual thermometers have had their performance monitored over a number of years.

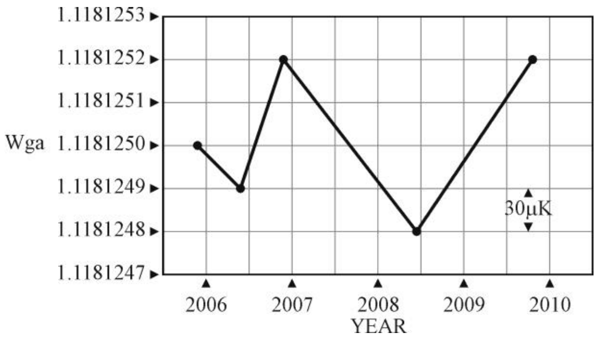
Example 1: Thermometer 670SQ/25.5/002

This thermometer is from a batch of five made in 2006 to evaluate a new design. It has been used on a day to day basis for research projects mainly at the aluminium point. No special precautions in thermal cycling have been taken; infrequently R_{TPW} and W_{ga} have been measured.

Graph 1 shows the change since November 2006 in R_{TPW}. It can be seen that the resistance has increased by around 0.0006Ω (6mK) over the three years covered by the data. Contrast this with graph 2 which charts W_{ga} over the same time span and shows an equivalent variation of ±60μK which is within the measurement uncertainty.



GRAPH 1. Change in R_{TPW} 2006-2010 of 670SQ/25.5/002.



GRAPH 2. Change in Wga 2006-2010 of 670SQ/25.5/002.

Example 2: The Resistance Drift of Platinum Resistance Thermometers

Shu-Fei Tsai in her excellent article "*The Resistance Drift of Platinum Resistance Thermometers*" Tempmeko 2004 [1] analysed the resistance variations of 32 PRTs belonging to 21 customers and originating from seven commercial manufacturers calibrated over 10 years from -190 to 420°C.

She concluded that the equivalent temperature at WTP increased between 0.14mK to 9.9mK per year, and that this is the reason why ITS-90 adopts resistance ratio, and not resistance itself to determine T_{90}. She analysed W_{Hg} and stated that the drift rate was 0.01mK to 0.51mK per annum; with limited data on W_{ga} she noted maximum change of 0.92mK per annum.

Her article is essential reading for all who are interested in thermometer stability.

Example 3: An Investigation of Long-Term Stability of a Precision Platinum Resistance Thermometer up to 660°C

An article presented at NCSL in 2003 [2] analysed the performance of a thermometer kept at 665°C for 20,000 hours.

Over the first 5,000 hours R_{TPW} dropped by the equivalent of 50mK thereafter a further 20mK over the next 15,000 hours W_{AI} increased by around 15mK over the same period.

Example 4: 670/SQ/A/014

From the control chart of this thermometer used to monitor an aluminium cell it was noted that R_{TPW} dropped 4mK over its first 4,000 hours followed by a fairly random ±2mK over the following 15,000 hours.

W_{AI} increased around 10mK over the first 4,000 hours followed by 7 to 8mK over the subsequent 15,000 hours.

Example 5: W_{Zn}

Shu-Fei does not have enough data for W_{AI}, but for W_{Zn} she quotes between 6 and 18mK drift over 9 years.

Example 6: Thermometer Drift

The same article as 3 above reports the drift in 7 thermometers that were regularly calibrated for clients over 3 years. Drifts are shown to vary between -7mK and +20mK.

Discussion

We have two sets of parameters to consider

Initial stabilisation; it seems that around 6 months or 4,000 hours at max temperature (665°C) will remove most of the initial strain in a 25.5ohm thermometer, however further changes in R_{TPW} will always occur with temperature cycling.

Handling; the two articles summarised that deal with regular recalibration of customers SPRT's suggest change in R_{TPW} vary from +20mK to -7mK over 3 years [2] or 0.14 to 9.9mK per annum [1].

From the above, specifying a drift of 1mK per annum in R_{TPW} seems unrealistic unless this is the stability in terms of shelf life.

However if W_{ga} or W_{Hg} is considered then ±1mK per annum encompasses all 32 SPRT's in Shu-Fei's article and ±0.5mK would cover the best SPRT's after 4000 hours stabilisation at maximum temperature.

Conclusion

PRT's stable to ±0.001°C per year.

The common expectation that an SPRT can retain a WTP resistance stable to the equivalent of 0.001°C per year is unrealistic unless it is left in its case on a shelf.

More realistic is the expectation that W_{ga} or W_{Hg} will remain stable to the equivalent of 0.001°C per year. Those purchasing SPRT's and those manufacturing SPRT's should change their specifications accordingly.

Authors Note

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