LONG-TERM RESISTANCE AND RATIO STABILITY OF SPRTS, COMPARING METAL SHEATHS VS. FUSED SILICA SHEATHS

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Abstract – An investigation of re-calibration results of metal-sheathed standard platinum resistance thermometer (SPRT) and fused silica-sheathed SPRTs was reported. The performance of metal-sheathed SPRTs could be as good as that of fused-sheathed SPRTs if the user could take care it very well. However, in fact, the long-term stability of metal-sheathed SPRTs is generally worse than that of fusesilica sheathed SPRTs due to the users' carelessness. The investigation results were discussed based on possible effects due to the sensor contamination, platinum oxidation, and mechnical shock, etc. To reduce calibration uncertainty and improve calibration reliability, two simple methods are introduced.

INTRODUCTION

We have been asked that whether fused silica standard platinum resistance thermometer (SPRT) or metal-sheathed SPRT has better performance, and which type SPRT is better for a specific application. To answer these questions better, we completed an investigation of re-calibration results of fused silica-sheathed SPRTs and metal-sheathed SPRTs recently.

Upon investigation of re-calibration results of SPRTs, it was found that most SPRTs are pretty stable over a few years, just like it should be. However, we did find that the resistances at the triple point of water (Rtpw) of many reference thermometers were significantly different between the two calibrations, although the “bad” reference thermometers had been in use as standards for calibration work. It is difficult for many users to observe and track the drift of the reference thermometer between calibrations. If the reference thermometer drifts beyond the acceptable limit during the calibration interval, the process uncertainties may be compromised requiring recall of calibration work.

In the investigation, it was also found that the performance of metal-sheathed SPRTs could be as good as, may be slight worse than, that of fused silica SPRTs. However, on average, the long-term drifts of the metal-sheathed SPRTs are much greater than those of the fused silica SPRTs. The main reason, it is presumed, is that users treat the fused silica-sheathed SPRTs more carefully because they are believed to be more fragile.

In this paper, we combined our research results that were made in recently years, and discussed the different effects on the stabilities of fused silica-sheathed SPRTs and metal-sheathed SPRT. To reduce calibration uncertainty and improve calibration reliability, two simple methods will be introduced.

INVESTIGATION OF RE-CALIBRATION RESULTS OF SPRTS

Recently, we investigated a collection of fused silica-sheathed SPRTs and metal-sheathed SPRTs calibrated by Hart Scientific over at least four one-year calibration intervals. These SPRTs were made by various manufacturers throughout the world, and their structures vary. As a sample, the drifts of the R(tpw)s of eight fused silica-sheathed SPRTs and eleven metal-sheathed SPRTs are shown in Fig.1 and Fig. 2 respectively. Most SPRTs are stable as a reference thermometer over years. However, the investigation results are still surprising—the R(tpw)s of many SPRTs drifted over 10 mK in at least one calibration interval. The R(tpw) of a few SPRTs drifted as much as 50 mK.

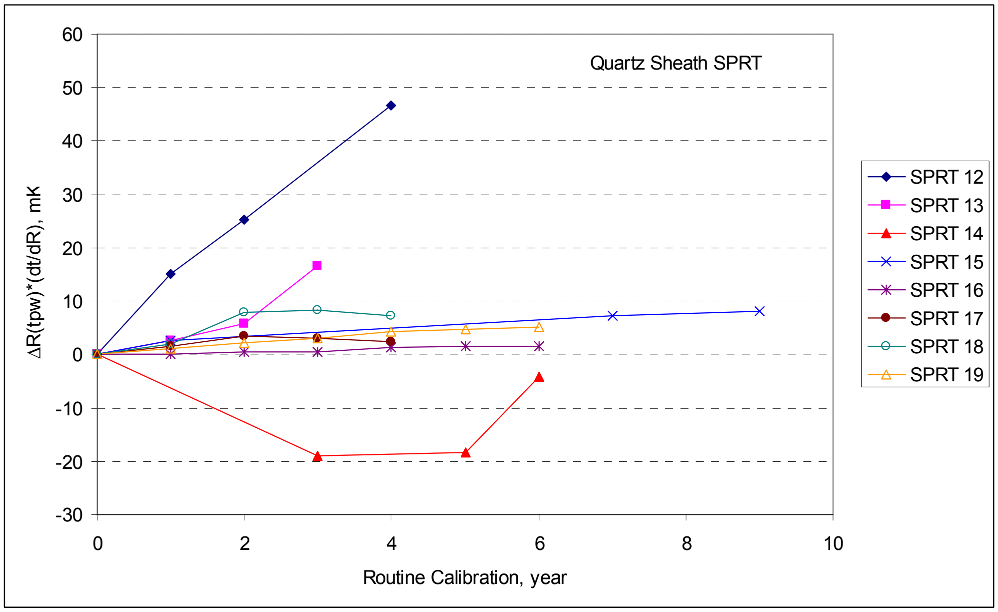

Figure 1: The R(tpw) drifts of fused silica-sheathed SPRTs during routine calibration intervals

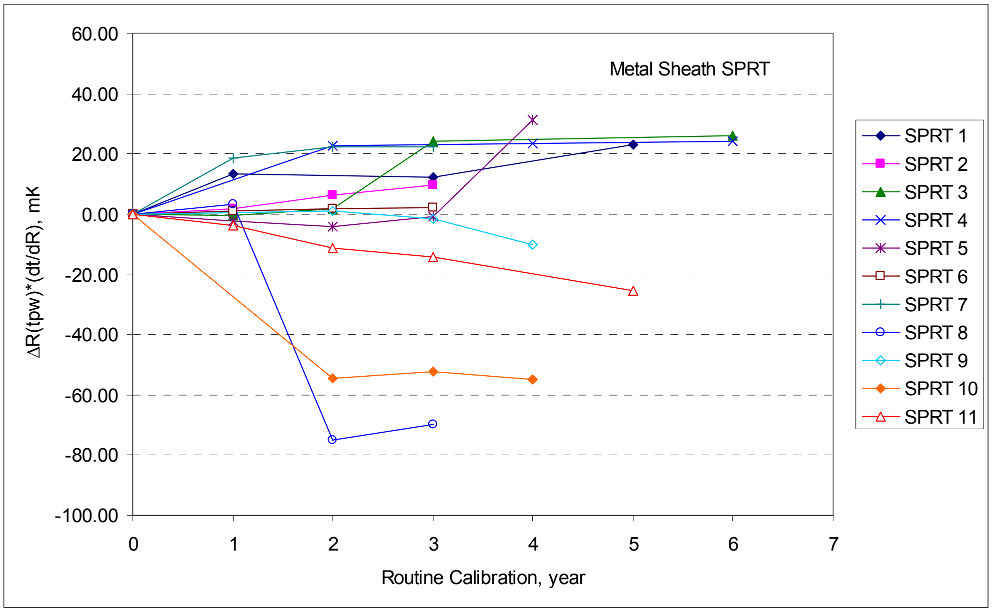

Figure 2: The R(tpw) drifts of metal-sheathed SPRTs during routine calibration intervals

It was found that the R(tpw) might jump significantly in one interval, while the R(tpw) is quite stable or at least acceptable in other intervals. The R(tpw) of metal-sheathed SPRT 8 drifted almost 80 mK between the second year and third year. The R(tpw) of metal-sheathed SPRTs 4 and 10 drifted significantly between the first year and second year, while the same problem happened on metal- sheathed SPRT 5 between the fourth year to fifth year. It is assumed that these SPRTs met unusual treatment during those years.

Comparing Fig. 1 and Fig. 2, the long-term stability of fused silica-sheathed SPRTs is better than that of the metal- sheathed SPRTs. The main reason, it is presumed, is that users treat the SPRTs more carefully because they are expected to be more fragile. Three among eight fused silica-sheathed SPRTs exceeded the SPRT long-term stability limitation. The drift of the R(tpw) of a good fused silcai-sheathed SPRT should be less than 3 mK per year, depending on the usage and handling. An SPRT, whether fused silica-sheathed or metal-sheathed, should be handled very carefully to maintain its excellent stability.

Upon our researches done recently, the performance of metal-sheathed is a little worse than that of fused silica-sheathed SPRT, but they are very close. Under normal use with great care, the annual drift of a fused silica-sheathed SPRT is around 2 mK, while that of a metal-sheath SPRT is around 3 mK. It is well known, the performance of an SPRT, whether fused silica-sheathed SPRT or metal-sheathed SPRT, is effected by sensor platinum oxidation [1] [2] [3] [4], senor contamination [5] [6] [7], mechnical shock [8], etc. The effects on fused silica-sheathed SPRT are different from that on the metal-sheathed SPRT. The differences will be discussed in this paper.

DISCUSSION

Different effects on the stabilities of SPRTs, fused silica-sheathed vs. metal-sheathed

Oxidation

In the 1970s, Berry discovered platinum oxidation effects over the range of -40°C – 500°C [1] [2]. A three-dimensional (3d) form of PtO_2 will grow on a thermally cleaned Pt wire in as little as 5 kPa of O_2 in the temperature range from 300 to 500°C approximately, and a two-dimensional (2d) form of Pt oxide will grow in as little as 0.1kPa of O_2 in the range from -40 to 300°C approximately. The resistance of platinum wire increases because part of its cross-sectional area is replaced by a poorly conducting oxide film. The drifts in the lower temperature range are mainly caused by oxidation of platinum.

Recently years, we did researches on the platinum sensor wire oxidation for fused silica-sheathed SPRT [4] and metal-sheathed SPRT [3]. It was found that there are different effects on the fused silica-sheathed SPRT from that of metal-sheathed SPRT due to the platinum oxidation. The main difference is that the loss of oxygen in the metal-sheathed SPRT's sheath will cause the oxygen partial pressure variable over time due to slow oxidation of the metal, while the oxygen partial pressure in fused silica-sheathed SPRT will stay unchanged.

We have to discuss the contamination problem of the metal-sheathed SPRT when we discuss the oxidation of the metal-sheathed SPRT, since there is a trade-off between the oxidation effect and element contamination in metal-sheathed SPRTs. Excessively high O_2 partial pressure causes the platinum sensor to oxidize, and excessively low O_2 leads to sensor contamination. The oxygen content in a thermometer may become unknown after a period of operation due to slow oxidation of the metal sheath and consequent loss of oxygen in the metal-sheathed SPRT. This can significantly affect the thermometer's performance. The research has shown that a metal-sheathed SPRT may eventually become contaminated due to a deficiency of oxygen surrounding its element, if the SPRT element is not sealed separately [3]. The contamination phenomena of metal-sheathed SPRT is shown figure 3. The cause of the contamination was that the oxygen partial pressure in the metal-sheathed SPRTs dropped too low as a consequence of the oxidation of the inconel sheath at high temperature. As soon as the oxygen partial pressure dropped down to a very low level, the SPRT sensor would be contaminated. It has been clearly shown that the conflict between contamination and platinum oxidation can be solved by sealing the element separately from the sheath [3]. The long-term stability of the metal-sheathed SPRT could be as good as that shown in figure 4, if a good design is adopted.

The R(tpw) of the SPRT will increase and the resistance ratio W at any freezing point will change very little. The W is calculated by W=R(t)/R(tpw). The drift of an SPRT due to the oxidation could be removed through annealing process.

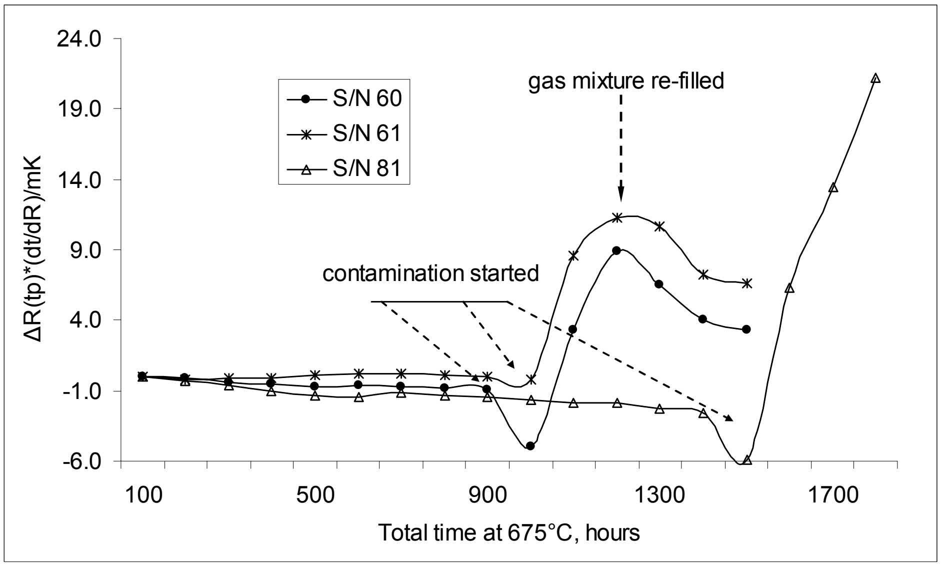

Figure 3: Contamination phenomena of metal-sheathed SPRTs

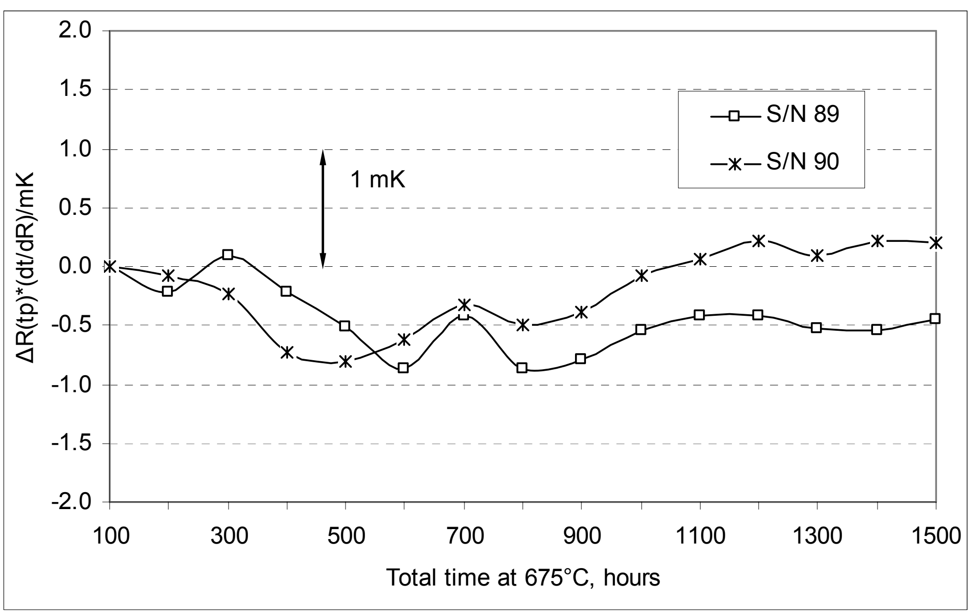

Figure 4: Long-term stability test at the triple point of water for metal-sheath SPRT with sealed elements

Contamination

In most literatures, it is not suggested to expose a fused silica SPRT into base metal surroundings above 500°C. However, our recent research showed that the fused silica-sheathed SPRT would not be contaminated in a base metal temperature block until 660°C [7]. It is well known the fused silica-sheathed SPRT would be contaminated in the base metal surrounding at the temperature above 850°C [5] [6] [7]. It is suggested to anneal the fused silica-sheathed SPRT in a graphite block or alumina block above 660°C [7].

Usually the metal-sheathed SPRT could be used up to 675°C. Since the element design of a metal-sheathed SPRT is usually very well to protect the sensor wire from the contamination of the metal sheath, the metal-sheathed SPRT might be operated in a base metal surrounding. However, since the loss of oxygen in the metal-sheathed SPRT's sheath will cause the oxygen partial pressure variable over time due to slow oxidation of the metal, if the element of the metal-sheathed SPRT is not sealed separated from the sheath, or the element is not sealed very well anymore during the operation, the metal-sheathed SPRT could be contaminated, shown in figure 3.

If an SPRT is contaminated, the R(tpw) of the SPRT will increase, and the resistance ratio W at any freezing point will decrease. Usually the R(tpw) and the W cannot be recovered fully through annealing process. The SPRT might not meet the requirement of ITS-90 after contamination. The difference between the contamination of a fused silica-sheathed SPRT and a metal-sheathed SPRT is that the drifts of the metal-sheathed SPRT might drift significantly in very short time, while the drifts of the fused silica-sheathed SPRT are gradually, shown in figure 3 and figure 5.

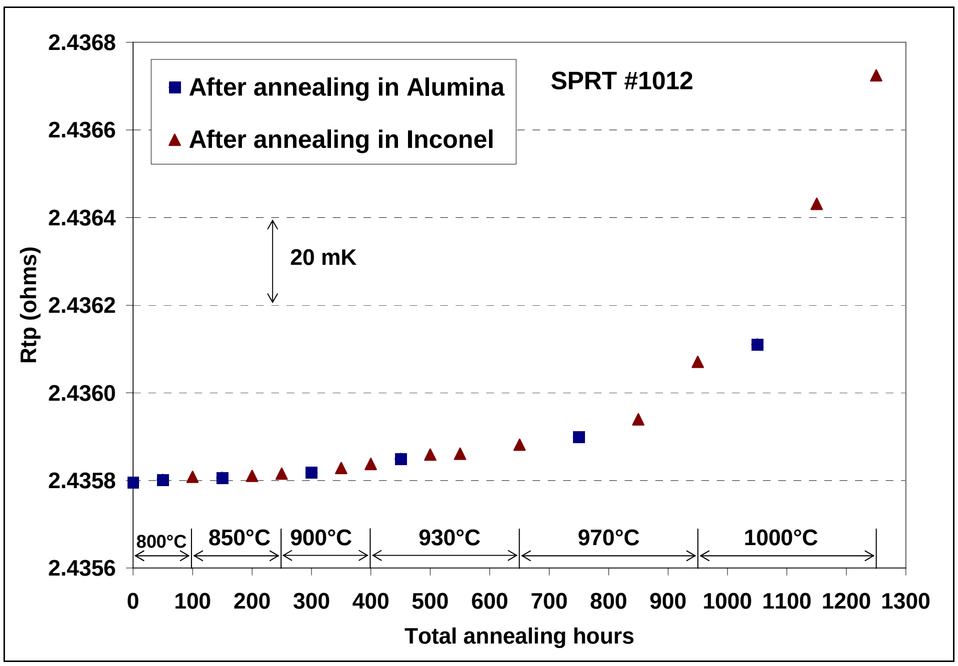

Figure 5 The contamination phenomena of a fused silica-sheathed SPRT

Mechnical shock

An SPRT is a delicate instrument. Shock, vibration, or any other form of acceleration may cause the aire to bend and around its supports, thus producing strains that change its temperature-resistance characteristics. Strains in the platinum resistor normally will increase the resistance and decrease the values of W above 0.01°C (or increase the values of W below 0.01°C) [8].

During the annealing process, the platinum wire becomes very soft. Because the platinum sensor is fragile, it is important to handle the SPRT carefully. Upon to the investigation, comparing Fig. 1 and Fig. 2, the long-term stability of fused silica-sheathed SPRTs is better than that of the metal-sheath SPRTs. The main reason, it is presumed, is that users treat the fused silica-sheathed SPRTs more carefully because they are expected to be more fragile. Just because an SPRT may have a metal sheath, it doesn't make it any less susceptible to mechanical shock. A metal-sheathed SPRT should be handled with the same care as one that has a fused silica sheath. These are delicate instruments and they should not be subject to any vibration, shock or form of acceleration.

The R(tpw) and resistance ratio W drifts due to mechnical shock could be eliminated through annealing process, if the mechnical shock is not significant, i.e., the drifts due to the mechnical shock are not too much. However, if the platinum sensing wire is physically damaged, for example the small cut on the wire or the bamboo structure of the wire, the R(tpw) and W drifts will not recovered through annealing process.

Evaluating an SPRT through the drifts of R(tpw) and W

Based on the analysis on the research results and investigation, we might evaluate the SPRT through the drifts of the R(tpw) and the W to figure out the possible reasons that cause the drifts. The summary is as follows:

1. The R(tpw) went up slightly and W stayed unchanged or very little, the SPRT might be oxidized, or slight mechnical shocked. It should be recovered through annealed process;
2. The R(tpw) went up significantly and W stayed unchanged or very little, the SPRT might be oxidized or sensor wire physically damaged. If the R(tpw) is recovered after annealing, the SPRT was oxidized. If the R(tpw) is getting worse after annealed, the sensor wire of the SPRT is physically damaged;
3. The R(tpw) went up slightly and W went down slightly, the SPRT might be mechnical shocked or contaminated slightly. After annealing, if the R(tpw) is recovered, it is mechnical shock, otherwise, it is contamination.
4. The R(tpw) went up significantly and W went down slightly, the SPRT might be mechnical shocked significantly. The R(tpw) could be recovered partially through annealing;
5. The R(tpw) went up significantly and W went down significantly, the SPRT might be contaminated significantly. The R(tpw) could be worse or not help through annealing;
6. The R(tpw) went down slightly and W stayed unchanged or very little, it should be under normal;
7. The R(tpw) went down significantly and W went up, the sheath of the SPRT might not be sealed anymore (moisture went into the sheath);
8. The R(tpw) went down significantly and unstable, the sensor of the SPRT might be short;
9. The R(tpw) went down continuously during annealing process, it might be caused by the grain growth of sensor platinum;

Methods to improve reliability in a temperature calibration laboratory

During our calibrations and services for customers, it was found that some reference thermometers drifted significantly due to such various reasons as mechanical shock and overheating. Most users had not noticed the drifts until the re-calibration was completed in the upper level temperature laboratories, or because the reference thermometer did not work anymore. If the "bad" SPRT was used as reference thermometer in daily calibration, the process uncertainties may have been compromised and recalls of calibrated work may be necessary. To find the "bad" reference thermometers and improve the calibration reliability, two simple methods are introduced.

Using the resistance ratio W(t)

Usually, the resistance ratio W(t), W(t)=R(t)/R(tpw), of a reference platinum resistance thermometer is more stable over time than the resistance at the triple point of water or those at other temperatures. Therefore, if the R(tpw) could be updated regularly, the calibration uncertainty will improve significantly. As examples, the drifts of the resistance at freezing point of zinc, R(Zn) , the resistance at triple point of water, R(tpw), and the resistance ratio at freezing point of zinc, W(Zn), of a fused silica-sheathed SPRT are shown in Figure 6. The W(Zn) drifted less than 1 mK in the period of six years, while the R(Zn) and

R(tp) drifted 34 mK and 14 mK respectively. These of a metal-sheathed SPRT are shown in Figure 7. The W(Zn) drifted less than 5 mK in the period of four years, while the R(Zn) and R(tp) drifted 82 mK and 30 mK respectively. It is very clear that the resistance ratios are much more stable than resistance values R(Zn) and R(tpw). It is possible to reduce the calibration uncertainty significantly through using the resistance ratio W.

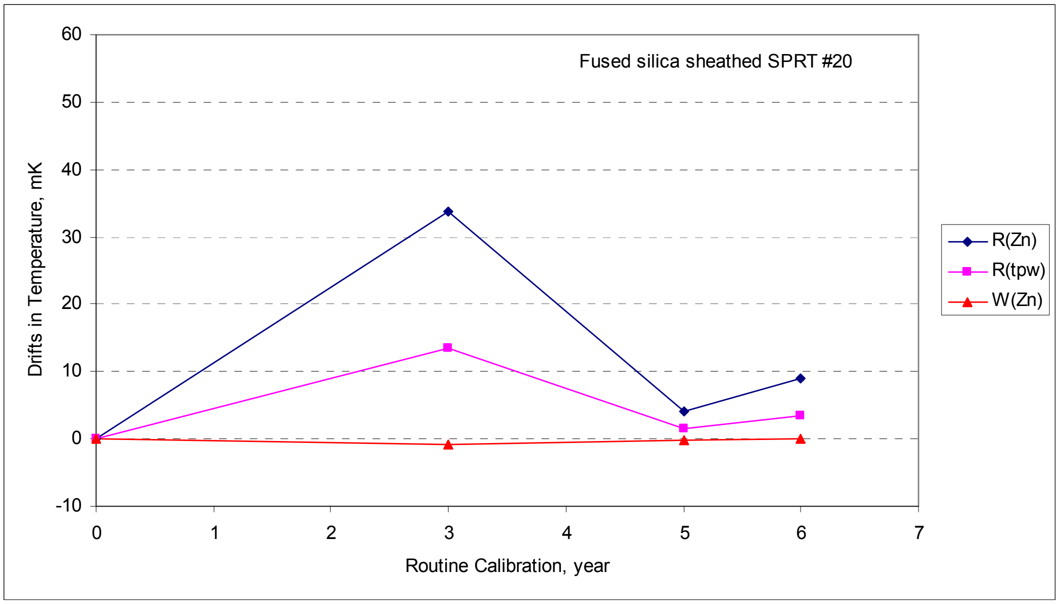

Figure 6: R(Zn), R(tpw), W(Zn) drifts of the fused silica-sheathed SPRT #20

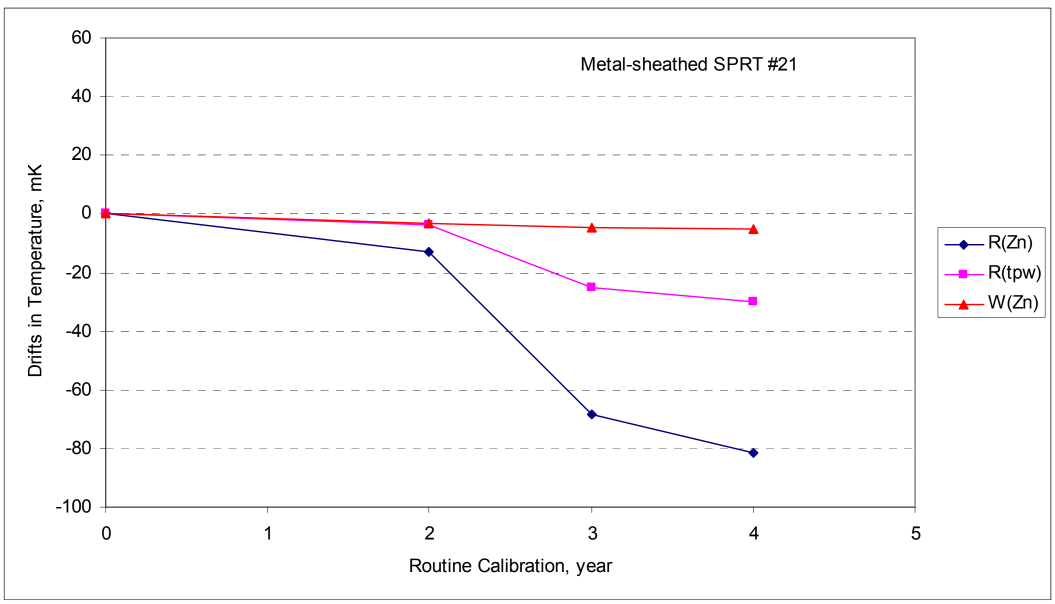

Figure 7: R(Zn), R(tpw), W(Zn) drifts of the metal-sheathed SPRT #21

Using a traditional triple point of water cell, or a mini triple point of water system

To avoid that the reference thermometers outside tolerance limits are still used as the standard in calibration work, and guarantee the reliability in a temperature calibration laboratory, the resistance of the reference thermometers at triple point of water reference thermometer should be checked regularly between the calibration intervals using a traditional triple point of water cell. If this is not practical for a secondary laboratory then the mini TPW system is an excellent and simple apparatus to assist the laboratory in controlling their process [9]. It allows a control chart to be maintained that indicates when a reference thermometer should be sent to an upper level temperature laboratory for re-calibration. Furthermore, it is strongly suggested to use the resistance ratio W(t) and updated R(tpw) to reduce the calibration uncertainty.

SUMMARY

The long-term stability of the metal-sheathed SPRT could be as good as, or a little worse than, that of fused silica-sheathed SPRT, even though there are lots of different factors that effect the performances of these two type SPRTs. However, to reach the best performance of any SPRT, the handling of an SPRT should be extremely careful. It will be very helpful if the user understand the evaluation methods to figure out the possible causes of the drift of an SPRT. To guarantee the reliability in a temperature calibration laboratory, the reference thermometer should be checked regularly, and the resistance ratio W should used in the calibration. It is necessary to maintain a control chart that indicates when a reference thermometer should be sent to an upper level temperature laboratory for re-calibration.

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