Industrial experience with the primary calibration of high-temperature platinum resistance thermometers

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The International Temperature Scale of 1990 defines the Standard Platinum Resistance Thermometer (SPRT) as the primary interpolation instrument for temperature from −189.34 °C to the freezing point of silver (961.78 °C). In the temperature range from 0 °C to 961.78 °C a newly developed, high temperature SPRT is utilized. Previously, the type S thermocouple was used for temperatures from 630.74 °C to the gold point (1064.18 °C). Though much more difficult to utilize on a regular basis, a greater than tenfold increase in accuracy over the thermocouple has made the high temperature SPRT the preferred instrument for primary calibration to the silver point. This paper explores the difficulties encountered in the use of these devices to support industrial metrology and illustrates specific examples of the reduction of uncertainty in the overall scheme of thermometer calibration.

INTRODUCTION

The industrial metrology environment is quite different from that encountered in a national laboratory. Though identical standards and techniques may be used to realize a temperature scale, the priorities in maintaining the scale for users mandate a decidedly practical approach.

The High Temperature Standard Platinum Resistance Thermometer (HTSPRT), as a primary interpolation instrument on the International Temperature Scale of 1990 (ITS–90), Ref. (1), appears to afford substantial improvement in accuracy over the type S thermocouple. This is certainly true in the specialized area of producing and maintaining primary standards in national laboratories. However, very few industrial processes are temperature critical enough to warrant the use of these devices.

The fragile nature, susceptibility to contamination, and labor intensive calibration procedure make it impractical to use HTSPRTs as working standards. In fact, the overall improvement in accuracy has proven almost academic in the Primary Standards Laboratory at Lockheed. Thus, HTSPRTs offer very little in the way of improving the accuracy of process–oriented calibration required to support the needs of this laboratory.

The demand for timely and accurate calibration makes it cost ineffective to rely on primary standards supplied from outside the laboratory. As such, an ongoing effort to realize the ITS–90 at the primary level has been undertaken at Lockheed. It has therefore become necessary to utilize HTSPRTs and freezing point standards to provide the basis for maintaining the scale in the prescribed fashion.

The development of ITS–90 based calibration of HTSPRTs is described. The difficulties encountered and the advantages gained by virtue of this effort will be evaluated.

MEASUREMENT SYSTEM

The basic measurement system for HTSPRTs utilizes an automatic AC resistance bridge operating at 30 or 90 Hz. AC standard resistors of 1 and 10 ohms are used as bridge references. Due to a decrease in the insulation resistance of thermometer elements at high temperatures, elements of 0.25 and 2.5 ohms (at 0°C) are most often used for the highest accuracy measurements. This ensures that leakage currents through the insulation remain low enough to negligibly affect the resistance determination. Excitation currents of 10 mA were used on the 0.25 ohm thermometers to improve signal to noise ratio (1 mA was used for the 2.5 ohm thermometer). Results are described for two 0.25 ohm and one 2.5 ohm thermometer.

FREEZING POINT REALIZATIONS

In order to realize the ITS–90 from 0 to 961.78°C, HTSPRT resistance values must be obtained at the tin, zinc, aluminum, and silver freezing points as well as the triple point of water. Two temperature controlled furnaces are utilized: A low temperature vertical furnace capable of heating to 500°C for tin and zinc cells; a high temperature vertical, sodium heat pipe furnace capable of heating to 1000°C for aluminum and silver cells. Tin and zinc cells have been used for many years and these freezing points are realized according to already established procedures.

In realizing the aluminum (660.323°C) and silver freezing points (961.78°C) with an HTSPRT special precautions must be taken. If the thermometer is cooled too quickly from 660°C, crystal defects and high temperature dislocations can be frozen into the lattice. This can lead to significant changes in resistance at the water triple point following a freezing point realization. In addition, the quartz thermometer sheath becomes permeable to metallic ions at temperatures above 650°C and severe contamination of the element can occur, Ref. (2)

It is necessary to have available an auxiliary furnace to closely control the cool down rate of the HTSPRT after a silver or aluminum freezing point resistance value has been obtained. This furnace must be designed in such a way as to minimize contamination of thermometers when at temperatures above the aluminum freezing point. This adds complexity in realizing the silver and aluminum freezing points with an HTSPRT.

In this laboratory, furnaces previously used for copper and aluminum freeze point cells were operable. Though the temperature range was not a problem, control was effected by manually varying the level of constant voltage across the heaters rather than by active means, which would have simplified the process. The auxiliary furnace was heated to near the silver point and then allowed to cool with the thermometer inside. Passive cooling (at a rate of ~75°C/hr) was thought to be slow enough to ensure no adverse effects from thermal cycling, Ref. (2). The thermometer was placed in a thick walled alumina tube inside the furnace to reduce contamination by metallic ions.

Currently, only a single HTSPRT is measured on a given silver or aluminum freezing curve, whereas resistance values for five or six SPRTs can typically be obtained on a single zinc freeze. This clearly reduces the efficiency of HTSPRT calibration with respect to that of SPRTs not designed for high temperature use. These problems, though not insurmountable, introduce a great deal of complexity to the calibration effort.

SILVER AND ALUMINUM FREEZING POINT DATA

The adoption of the HTSPRT as an interpolation instrument on the ITS–90 is most significant above 500°C. Tin and zinc freezing points were used in the definition of the International Practical Temperature Scale of 1968 (IPTS–68) and thus are not unique to the ITS–90. Therefore, the realization of these points using HTSPRTs will not be discussed here. Data will be shown only for the aluminum and silver points.

Three HTSPRTs were initially used to realize the aluminum and silver points. Two had nominal resistance values of

0.25 ohms at the water triple point and the third had a resistance of 2.5 ohms. All were measured twice at the silver freezing point. One of the 0.25 ohm HTSPRTs exhibited erratic behavior and was eliminated from evaluation at the aluminum point. The two remaining HTSPRTs were measured twice each at the aluminum freezing point. Thermometer "X10" was the remaining 0.25 ohm HTSPRT and "X03" was the 2.5 ohm HTSPRT.

Triple point (tp) of water measurements were obtained immediately after each freezing point realization (@1 mA for the 2.5 ohm thermometer and @10 mA for the 0.25 ohm thermometer). Results are reported in terms of resistance ratios:

$$W(T) = R(T)/R(273.16\ \mathrm{K}) \tag{1}$$

where R(T) is thermometer resistance at temperature T.

Each HTSPRT was used to obtain a complete freezing curve. The flattest portion of the freezing curve (plateau) was thought to be the best representation of phase equilibrium. The mean value of resistance along this plateau defined the value of R(T).

Table I summarizes the data for the two reliable thermometers. The rows which are marked "range" in Tab. I refer to the differences between maximum and minimum values (expressed in temperature equivalent of ratio) obtained along the freeze plateau for each realization. The rows marked "DELTA(T)", are the differences in the mean ratio values between data sets 1 and 2 shown in terms of temperature. As can be seen, successive realizations reproduced to better than 5 mK for cells and thermometers.

TABLE I. SUMMARY OF FREEZING POINT DATA

HTSPRT#	X10 Ratio	X03 Ratio
Ag Set 1 Range	4.286463 2.0 mK	4.286617 7.3 mK
Ag Set 2 Range	4.286470 3.8 mK	4.286599 6.8 mK
Delta(T)	1.5 mK	4.7 mK
Al Set 1 Range	3.376078 5.6 mK	3.376250 6.8 mK
Al Set 2 Range	3.376094 4.4 mK	3.376259 3.0 mK
Delta(T)	3.5 mK	2.1 mK

Given only two measurement sets for each thermometer, it is difficult to draw conclusions as to what are typical characteristics for freezing point realizations. The large difference in the range of HTSPRT X03 at the silver point as compared to HTSPRT X10 is due to choosing a greater portion of the freezing curve as the plateau region. As this is somewhat arbitrary, more data will be needed to make consistent choices. However, it is clear that the limited data represents a very substantial improvement over what can be expected from thermocouple measurements.

Figures 1 and 2 show a silver freezing point curve and an aluminum freezing point curve, respectively. The chosen plateau regions are also shown. The freezing curves are typical of what was obtained with all thermometers. Optimization of furnace set points could extend the duration of the freeze and reduce the range of temperature variation by minimizing the offset between furnace and cell temperature thus reducing heat leak.

The above data were obtained by AC measurements made at 30 Hz. In an effort to assess the magnitude of reactive effects, measurements were also made at 90 Hz. Differences of no greater than 1 mK were observed. In addition, DC measurements were made during the plateau interval. Differences between AC and DC measurements were of the order of 1 mK.

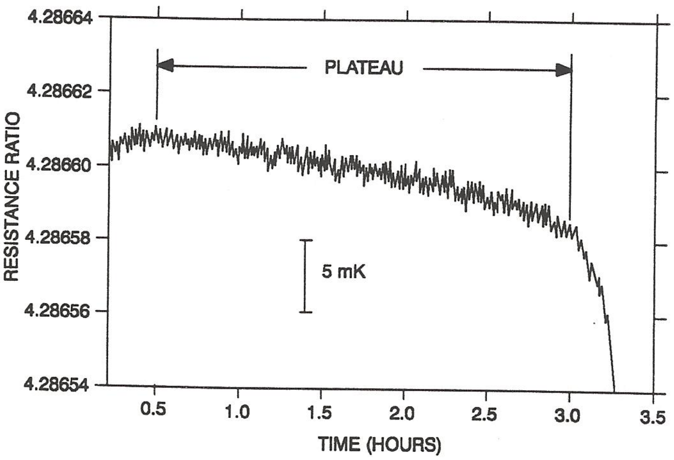

FIG. 1. Freezing curve of silver

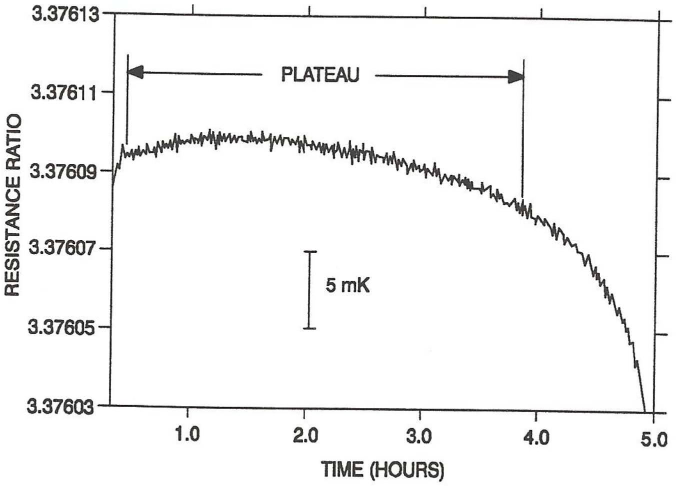

FIG. 2. Freezing curve of aluminum

IMPLICATIONS FOR INDUSTRIAL METROLOGY

It is generally assumed that the best accuracy possible with a type S thermocouple is 0.2 K at 1000°C, Ref. (3). Clearly, HTSPRTs are far superior in this respect. However, for temperatures beyond 500°C, thermocouples are used in industrial applications.

The fragile nature of HTSPRTs makes them impractical for direct application to industrial processes. The increased accuracy offered cannot be conveniently utilized outside the metrology laboratory. Surely, thermocouple accuracy might be enhanced by direct transfer of calibration from an HTSPRT. The design of an apparatus to accomplish this calibration must consider immersion depth effects (such as radiation piping) for which little data is available, Ref. (4).

HTSPRTs can be used to track aluminum and silver freezing point behavior and enhance confidence levels in the reproducibility of these fixed point realizations. Thus, the practical impact of HTSPRTs on industrial processes is very limited.

If a viable working standard existed with inherent stability better than that of the type S thermocouple, the increased accuracies offered by HTSPRTs would be of great practical advantage. The platinum/gold (Pt/Au) thermocouple is garnering much attention as a possible standard. Accuracies to 50 mK or better are indicated and Pt/Au thermocouples are much more rugged than HTSPRTs, Ref. (5). The problems inherent to thermocouple thermometry still exist (contamination, inhomogeneity, and immersion). Physically, Pt/Au thermocouples are daunting to work with being over 6 ft in length. Fabrication is also somewhat troublesome due to substantial differences in thermal expansion coefficients between platinum and gold.

CONCLUSIONS

HTSPRTs offer a substantial improvement in accuracy over the type S thermocouple in the realization of the aluminum and silver freezing points and for temperature measurements within this range. The properties of platinum coupled with the delicate nature of HTSPRTs, makes HTSPRTs unsuitable for direct use in industrial processes. Process–oriented applications at Lockheed, are not temperature critical enough to require the high accuracies offered by HTSPRTs. However, it has been clearly shown that HTSPRTs can be calibrated in an industrial metrology laboratory.

There are no secondary standards readily available for contact thermometry above 660°C other than thermocouples. The increased accuracy offered by HTSPRTs in this range is, therefore, of little use in process oriented calibration. Inherent uncertainty in type S thermocouples is more than an order of magnitude higher than that for HTSPRTs. Pt/Au thermocouples have been viewed as possible working standards. However, commercial availability is not yet assured. It is also not clear that Pt/Au thermocouples are physically suitable for use in an environment other than the metrology laboratory.

Thus, the accuracy afforded by HTSPRTs is a substantial improvement over the previous interpolation instrument, the impact on industrial processes is virtually nil at this time. The implications of choosing a resistance thermometer as a primary interpolation instrument in this temperature range are extremely significant. As HTSPRTs experience more widespread use, which they most certainly have already, practical ways of utilizing their enhanced accuracy will evolve. Secondary standard resistance thermometers robust enough for industrial use will, no doubt, be developed for use above 660°C. As familiarity with techniques for resistance thermometry increases, thermocouples will gradually be replaced as general use thermometers.

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