Development of a stand–alone calibration capability for long stem SPRTs

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The task of supporting contemporary aerospace manufacturing and research efforts requires ongoing maintenance of reference standards of the highest precision. The continued cycling of such standards to national calibration laboratories to ensure the highest traceable accuracy becomes impractical and is not cost effective. In order to ensure support of program requirements, a stand–alone system has been developed for the primary calibration of Standard Platinum Resistance Thermometers (SPRTs). Utilizing thermodynamic fixed point cells and precision instrumentation, calibration accuracies to a few millikelvins are regularly achieved. Data and uncertainty analysis are shown for the calibration of SPRTs on the International Temperature Scale of 1990 (ITS–90) from −189° to 660 °C.

INTRODUCTION

The priorities governing thermometer calibration in an industrial primary standards laboratory are very different from those in a national laboratory. Support for research, manufacturing, and process control must be expedient and accuracy levels must be continuously maintained and improved. Given the fragile nature of SPRTs, and the sometimes inordinate amount of time necessary to obtain calibration from outside laboratories, the above priorities become expensive and difficult to satisfy.

In the temperature range −189° to 660°C, the primary interpolation instrument for establishing and maintaining the ITS–90 scale is the Standard Platinum Resistance Thermometer (SPRT). Curves which define the behavior of the thermometer element with temperature are established by virtue of standard reference functions and measurements made at defining fixed points. Thermometer resistance at the triple point of water (R_{tp}) is used to define the resistance ratio $W(T_{90})$ for the thermometer at all other points ($W = R_T/R_{tp}$).

Between −189° and 0°C, the triple points of argon and mercury are used. The melting point of gallium and the freezing points of indium, tin, zinc, and aluminum are used from 0° to 660°C.

All necessary fixed point cells and associated fixtures for utilizing them are readily available commercially as are precision instrumentation and associated reference standards. Any laboratory with the appropriate financial and personnel resources can initiate a complete program for primary calibration of SPRTs on the ITS–90. The following describes the development of such a program at Lockheed Missiles and Space Co. (LMSC).

DESCRIPTION OF APPARATUS

The essential apparatus is comprised of metal freezing point cells of the ITS–90 specified materials as well as triple point cells of water, mercury and argon. The gallium melting point is also a recognized fixed point. A temperature controlled vertical furnace, capable of heating to 500°C, is used for indium, tin, and zinc freezing point realizations and a sodium heat pipe furnace, capable of heating to 1000°C, is used for realizing the aluminum point. The gallium melting point is realized in a small, dedicated module, Ref. (1).

The mercury triple point is realized in a dedicated apparatus utilizing conventional refrigeration techniques. The argon triple point cell is contained in a dewar of liquid nitrogen. By controlling the pressure above the liquid, the nitrogen boiling point can be raised above the argon triple point temperature thus driving the argon through the triple point state. A sealed, re–entrant thermometer well allows for direct measurement of argon cell temperature.

Automated data acquisition greatly enhances control and understanding of the processes and often allows for unattended operation. The work described here uses an instrument controller and real–time graphics to monitor SPRT behavior during fixed point determinations. The baths and furnaces are currently under manual control.

A refrigerated water bath is used to maintain water triple point cells. This bath keeps ice mantles in water cells intact for approximately two months. The bath has capacity for four cells and through proper scheduling at least two cells are always available for use as references.

Resistance ratios are measured using an AC resistance bridge which can resolve ratios to 0.2 ppm at unity. AC standard resistors, in temperature controlled enclosures, are used as bridge references.

DEVELOPMENT EFFORT

Descriptions provided for fixed point behavior by the National Institute of Standards and Technology (NIST) Monograph 126 were used to evaluate the merit of fixed point realizations. Freezing point realizations were performed in accordance with manufacturer's instructions and all measurements were made using NIST calibrated SPRTs.

Fixed point characteristics are determined through analysis of the constant temperature plateau which occurs during phase change equilibrium. The length of the plateau, the range of temperature variation along it, and its overall reproducibility determine the viability of a given cell.

Provided cells are of proper construction, the thermal environment has the greatest effect on cell behavior. Ideally, the cell itself should be a passive element and not contribute to thermal transport within the furnace. During the course of evaluating cells and their associated thermal drivers, it was discovered on several occasions, that heat transport through the cells was too strong a function of the thermal profile within the furnace.

This led, in some cases, to substantial modifications of apparatus in order to isolate cells and reduce process gradients and fluctuations. All modifications were made in–house and yielded significant improvements in behavior and control.

VERIFICATION OF FIXED POINTS

Before fixed point devices can be used in regular calibration, their behavior and thermometric reproducibility must be verified. Sealed freezing point cells will typically show a slight offset from the scale assigned temperature due primarily to pressure effects. In addition, corrections for hydrostatic head must be considered. A temperature value must therefore be assigned to all sealed, two phase fixed points in use. Triple point equilibria occur at fixed temperature and pressure and so no pressure corrections are necessary.

It is convenient to assign cell temperature at the location of the thermometer element within the cell. The temperature at the thermometer element in a water triple point cell is below the defined value of 0.01°C (due to the hydrostatic head of water above the element). The measured resistance value is corrected to represent 0.01°C as this is the reference temperature for determining resistance ratios on the ITS–90.

The development program was initiated before ITS–90 was promulgated, therefore thermometers calibrated on the International Temperature Scale of 1968 (IPTS–68) were used to verify fixed point temperatures. The temperatures of the defining mechanics fixed points above, were established using NIST calibrated SPRTs. Figure 1 shows a typical melting curve obtained for the argon triple point.

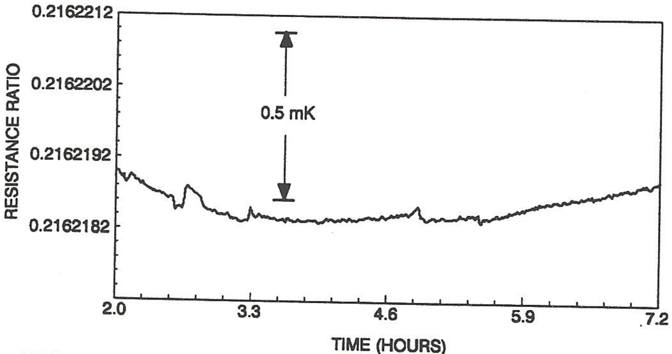

FIG. 1. Melt Plateau of Argon

The data shown in Tab. I are the result of multiple measurements of each fixed point used. IPTS–68 temperatures were determined based on one or more calibrated SPRTs. The values appearing in column 2 of Tab. I are the temperatures as measured at the thermometer element (except for the water triple point). The absolute thermodynamic temperatures of the fixed points have not changed, however, the ITS–90 assigned values are different from those on IPTS–68. The values listed in column 2 were determined from repeated measurements of the fixed points. The temperatures in parenthesis in column 2 are the officially assigned fixed point values on the IPTS–68.

TABLE I. SUMMARY OF FREEZING POINT DATA

Cell Type	IPTS–68 (T)	ITS–90 (T)	1 STD DEV
Zinc (Assigned)	419.5823°C (419.580°C)	419.5293°C (419.527°C)	0.68mK
Tin (Assigned)	231.9702°C (231.9681°C)	231.9301°C (231.9280°C)	0.64 mK
Indium (Assigned)	156.6370°C (156.634°C)	156.6015°C (156.5985°C)	0.45 mk
Gallium (Assigned)	29.7716°C (29.772°C)	29.7642°C (29.7646°C)	0.12 mK
Water	0.0100°C	0.0100°C	0.10 mK
Mercury (Assigned)	–38.8407°C (–38.842°C)	–38.8331°C (–38.8344°C)	0.12 mK
Argon (Assigned)	–189.3520°C (–189.3520°C)	–189.3442°C (–189.3442°C)	0.47 mK

It can be seen that the measured values exhibit an offset from those assigned. This same offset is assumed for the ITS–90 fixed point temperatures. Thus, the ITS–90 temperatures of the cells used are as listed in column 3. As in column 2, the values in parenthesis are the officially assigned ITS–90 temperatures.

The standard deviation from the mean of the fixed point values measured is shown for each cell in column 4. These are assumed to be the random uncertainties (at the 1 sigma level) associated with realization of the fixed point. A complete analysis will follow which includes additional components.

Since the calibrated thermometers in use were not designed to be exposed to temperatures much above 500°C, aluminum does not appear in Tab. I. Separate measurements were made with two suitable thermometers to assess the behavior of the cell without assigning a temperature directly.

Each thermometer was used to measure the aluminum freezing point twice. The mean value of the ratio along the plateau for thermometer 1 repeated to about 1 mK. The difference between the maximum and minimum value along the plateau, defined as the "range", was around 5 mK in both cases. The second thermometer repeated to within 2 mK with a range of ~7 mK on one plateau and ~3 mK for the other.

The aluminum cell in use is of the sealed variety, the pressure therefore is unknown. Pressure dependence of the freezing temperature is ~7.0 mK/atmosphere, Ref. (2). Given the overall range and reproducibility of the plateau, a 10 mK uncertainty in the freezing point temperature is quite reasonable as an over–pressure of more than 0.5 atmospheres is unlikely. Therefore, the aluminum point will be assigned the ITS–90 value of 660.323°C ± 10 mK.

MAINTENANCE AND CONTROL OF FIXED POINTS

Having established values for the fixed points and practical methods for their use, reliability must be assessed for the system to be complete. This requires an ongoing effort utilizing SPRTs dedicated to specific cells. These SPRTs are uncalibrated and essentially gauge the variation in fixed point realization. Overall reproducibility can be determined in the long term. In addition, any abrupt change in the fixed point value will become obvious (SPRT integrity is always assessed through triple point of water measurements made immediately after the fixed point).

Presently, control SPRTs are in use on all fixed point cells. Figure 2 shows control charts generated for zinc, tin, and argon cells. Fixed point values obtained for each of the three cells shown, repeat to within ±1.0 mK. This reflects the overall variation in the mean value of freezing plateaus as determined by SPRT measurements. As the development effort continues, specific SPRTs will be dedicated to all cells in regular use.

ANALYSIS OF UNCERTAINTIES

Uncertainties are broadly divided into two types:

Type A – errors arising from purely statistical analysis

Type B – errors arising from all other sources

The type A error shown in Tab. II is the standard deviation of plateau values obtained by repeated measurements using a single SPRT in a given cell ("Repro" in Tab. II). Two Type B errors are considered in Tab. II. The first, B(1), is the difference between the maximum and minimum values of resistance ratio along the freeze plateau ("Range" in Tab. II).

Resistance ratios are determined from the individual resistances measured at the fixed point and the water triple point. The bridge has an inherent uncertainty of 0.2 ppm at unity ratio. Standard resistor uncertainty is estimated to be 1 ppm of value. The uncertainty in the thermometer resistance measurement is the sum of the product of measured ratio and standard resistor uncertainty plus the product of the standard resistor value and ratio uncertainty.

The parameter used for temperature interpolation is the resistance ratio. As such the errors from individual resistance measurements are added in quadrature to determine the error in resistance ratio. This value, B(2), is reported as Ratio(T) in Tab. II. The B components are combined as root sum square (RSS) and rectangular probability distributions are assumed. The RSS value is multiplied by the $1/\sqrt{3}$, as a result of normalizing the rectangular probability distribution, to yield the net Type B uncertainty.

Finally A and B net are added in quadrature to approximate 1 sigma totals.

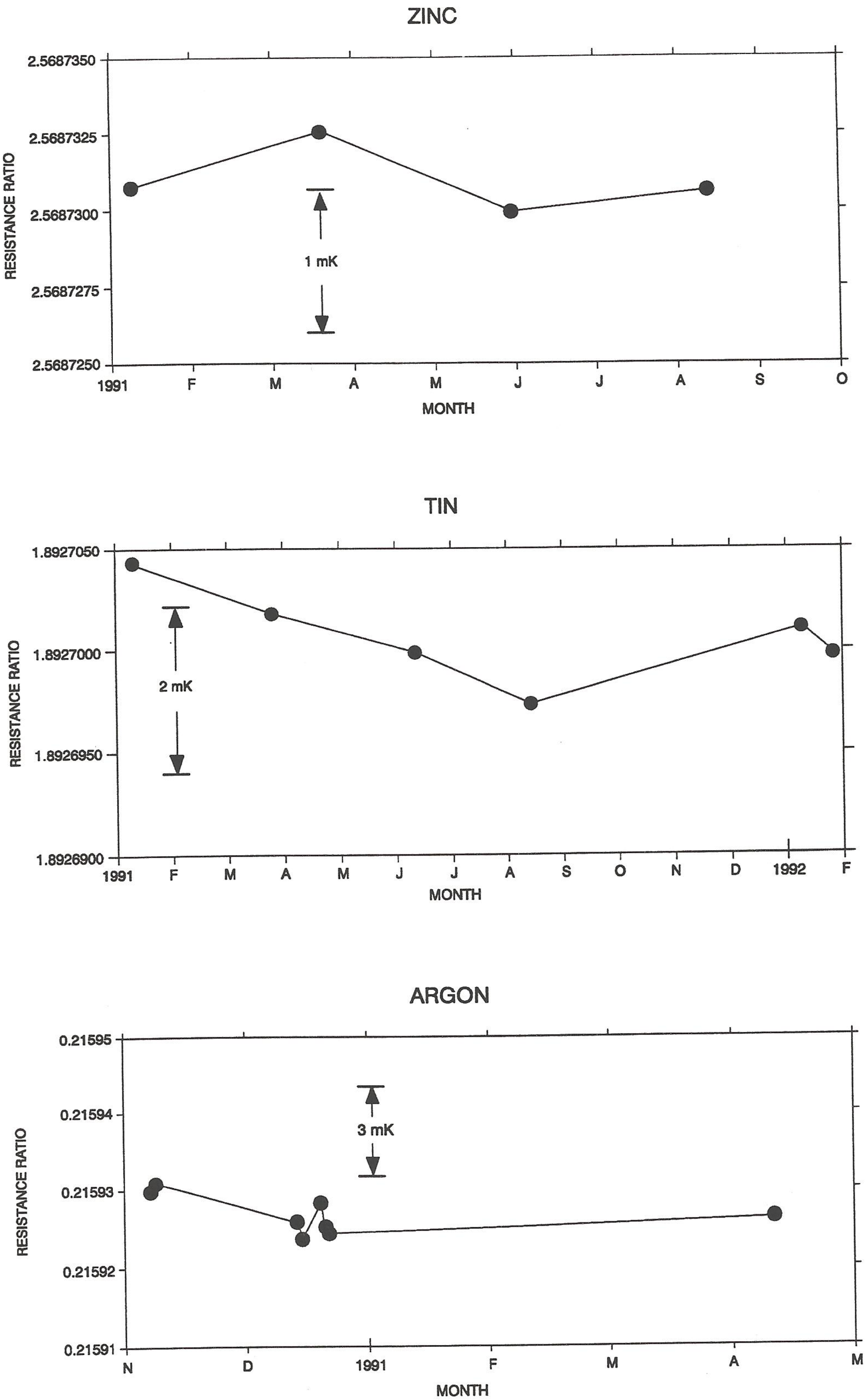

FIG. 2. Fixed Point Cell Control Charts

TABLE II. UNCERTAINTY IN FIXED POINT REALIZATIONS

Error Source		Argon mK	Mercury mK	Gallium mK	Indium mK	Tin mK	Zinc mK
TYPE A ERRORS							
Repro	A(1)	0.30	0.25	0.30	0.25	0.30	0.50
A	$\sqrt{A(1)^2}$	0.30	0.25	0.30	0.25	0.30	0.50
TYPE B ERRORS							
Range	B(1)	0.30	0.25	0.30	0.25	0.30	0.50
Ratio(T)	B(2)	0.28	0.40	0.44	0.48	0.38	0.39
$1/\sqrt{3}\ \sqrt{\sum B(i)^2}$	B_{Net}	0.24	0.27	0.31	0.31	0.28	0.36
U	$\sqrt{A^2 + B^2}$	0.38	0.37	0.30	0.40	0.41	0.62

CONCLUSIONS AND FUTURE PLANS

It has been demonstrated that a system for the primary calibration of long stem SPRTs can be developed from commercially available equipment. Though externally calibrated thermometers were used to establish fixed point temperatures, uncertainty levels appear to be low enough to ensure a stand alone capability for temperature calibration at LMSC from –189° to 660°C.

Open cells of zinc and tin, obtained from NIST, will soon be evaluated and used to transfer values to the sealed cells used above. This will unequivocally establish the freezing point temperature of these cells with respect to the national standards. As argon and mercury are triple points, the ITS–90 can then be realized independently from –189° to 420°C through intrinsically defined fixed points.

The aluminum point will require further evaluation via intercomparisons and transfer thermometers to reduce the uncertainty in the temperature value assigned via measurements made at LMSC.

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