Internal Measurement Assurance for the NIST Realization of the ITS-90 from 83.8 K to 1234.93 K

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Abstract. The National Institute of Standards and Technology (NIST) is responsible for realizing, maintaining, and disseminating the International Temperature Scale of 1990 (ITS-90) to the United States of America. The ITS-90 fixed-point cells necessary to calibrate standard platinum resistance thermometers (SPRTs) require an extensive internal measurement assurance program to insure that the assigned fixed-point cell uncertainties are achieved. There are six interactive elements for the realization of an ITS-90 fixed-point cell that contribute to the uncertainty of an SPRT calibration. These six elements are the fixed-point cells, furnace/maintenance systems, SPRT, measurement system, realization techniques, and measurement assurance. Within these six elements, there are twenty-eight parameters that are used to quantify and maintain the NIST-assigned fixed-point cell and SPRT calibration uncertainties.

INTRODUCTION

The Platinum Resistance Thermometry (PRT) Laboratory of the National Institute of Standards and Technology (NIST) uses thermometric fixed-point cells to calibrate standard platinum resistance thermometers (SPRTs) as a means of disseminating the realized International Temperature Scale of 1990 (ITS-90) over the temperature range from 83.8 K to 1234.93 K [1,2]. As part of the Quality System for the ITS-90 realization of fixed-point cells and the calibration of SPRTs, an extensive internal measurement assurance program (IMAP) was instituted in 1990 in order to quantify, minimize, and verify the associated uncertainties [3].

This IMAP encompasses six interactive elements for the realization of the ITS-90 fixed-point cells and the subsequent calibration of SPRTs. As shown in Table 1, the six elements are the Fixed-Point Cells, Furnace/Maintenance System, SPRT, Measurement System, Realization Technique, and Measurement Assurance. Within those six elements, there exist twenty-eight parameters that contribute to the uncertainty of a NIST ITS-90 realized fixed-point cell phase transition and a SPRT calibration. The parameters within each element are described in the order of importance (most to least).

TABLE 1. The NIST ITS-90 Internal Measurement Assurance Program.

Interactive Elements	Measured Parameters	
1. Fixed-Point Cell	sample purity	corrections
	phase transition repeatability	design/assembly
	constant pressure	
2. Furnace/ Maintenance System	vertical gradient	fixed-point cell interaction
	set-point control	
3. SPRT	heat flux	contamination
	immersion depth	wetness
	self heating	light piping
	stability	
4. Measurement System	repeatability	ac quadrature
	non-linearity	current
	ratio error	number of readings
	ohm	
5. Realization Technique	duration of realization curve	SPRT immersion profile
6. Measurement Assurance	check SPRT	SPRT calibration
	fixed-point cell certification	external comparisons

ELEMENT 1: FIXED-POINT CELL

The Sample Purity parameter is the effect of impurities on the realized temperature (Type B, normal distribution) and is one component used to assign an overall uncertainty to the fixed-point cell. The sample purity of all of the NIST fixed-point cells is at least 99.9999 wt. % pure [3]. All of the fixed-point cells [except the H_2O triple point (TP)] are manufactured at NIST. A supplied material assay of the sample gives the type and amount of impurities.

There are three methods that use variations of Raoult's Law of Dilute Solutions to estimate the effect of impurities on the realization of the fixed-point cell temperature: 1) total wt. % impurities, 2) total mole fraction impurities, and 3) derivation from analysis of experimental freezing curves [4]. Description of the three methods of the analysis and examples are found in references 5-9. The first method uses the total wt. % impurities, which gives an estimate that is usually low by at least a factor of two. This method does not take into account the effect associated with the different molecular weights of the impurities. The second method gives a better estimate by using a binary analysis of each impurity in the matrix metal that incorporates the different molecular weights of each impurity. This method is used at NIST to estimate the effect of impurities contained within the sample on the realization temperature of the fixed-point cell. The third method uses an analysis of experimental freezing curves to estimate the amount of impurities contained within the fixed-point cell. This method is implemented on a six-month interval basis as a part of the IMAP to check for degradation of the cells with use [5-9]. Figure 1 compares the results of the three methods for a Sn sample containing impurities of 0.1 µg/g of Ca, 0.1 µg/g of Si, and 0.1 µg/g of Ag.

The Phase Transition Repeatability parameter is the repeatability of an SPRT used to measure multiple realizations of a fixed-point cell. This parameter is used as one of the components of uncertainty (Type A, standard deviation of the measurements) for assigning an overall uncertainty to the fixed-point cell. As further described in section Element 6: Measurement Assurance, the check SPRT is measured at the beginning and end of every phase transition realization. This phase transition repeatability value gives statistical process control information on the fixed-point cell realization [2,3].

The Constant Pressure parameter is the gas pressure maintained inside each fixed-point cell, which affects the realized temperature. The uncertainty of

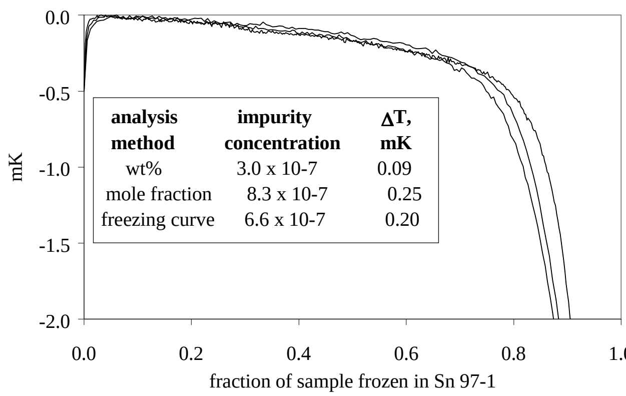

FIGURE 1. Comparison of the three methods to estimate the impurity effect on the realization of a Sn freezing point cell containing impurities of 0.1 µg/g of Ca, 0.1 µg/g of Si, and 0.1 µg/g of Ag.

this value is one component (Type B, rectangular distribution) used to assign an overall uncertainty to the fixed-point cell. The NIST freezing and melting point cells are open to a gas handling system for setting the pressure during realization (101.3 kPa ± 0.027 kPa) [10]. The gas pressure is recorded daily. The sealed triple-point cells are checked for integrity using a dedicated check SPRT.

The Corrections parameter is the two pressure corrections of gas pressure and hydrostatic head applied to the realized temperature of the fixed-point cell [1]. The uncertainty of these corrections on the realized temperature is one component (Type B, rectangular distribution) used to assign an overall uncertainty to the fixed-point cell.

The Design/Assembly parameter is the interaction of the fixed-point cells during realization with the furnace/maintenance systems. This parameter is closely coupled with the Fixed-Point Cell Interaction parameter found in section Element 2: Furnace/Maintenance System. Detail of the designs of the fixed-point cells, furnaces and maintenance systems are found in references 1 and 5-16.

ELEMENT 2: FURNACE/MAINTENANCE SYSTEM

The Vertical Gradient parameter is measured over the length of the fixed-point cell sample crucible. The maximum temperature non-uniformity for any of the furnace/maintenance system for a fixed-point cell is 10 mK. Examples are given in reference [16]. The Vertical Gradient parameter is checked once per year.

The Set-Point Control parameter influences the duration time of a phase-transition realization of the fixed-point cell. During a phase transition realization, the set point temperature control stability of the furnace/maintenance system is ±10 mK. Examples are given in references 10 and 16. This parameter is checked every six months.

The Fixed-Point Cell Interaction parameter is the interaction of the realized fixed-point cell with the furnace/maintenance system. This interaction is dependent on the designs of both the fixed-point cell and the furnace/maintenance system. The furnace/maintenance systems are designed to optimize the NIST-designed fixed-point cell realization. While not directly measurable, this parameter is closely coupled with the Design/Assembly parameter found in Element 1: Fixed-Point Cell. Details of the designs and the interactions of between the furnace/maintenance systems and fixed-point cells are in references 1,5-16.

ELEMENT 3: SPRT

The Heat Flux parameter is one of the few ways to adequately verify that the method used to realize the fixed-point cell is performed properly and that the SPRT is near thermal equilibrium with the phase transition interface. The effect of heat flux on the temperature measured by the SPRT is one of the components (Type B, normal distribution) used to assign an overall uncertainty to the fixed-point cell.

The Heat Flux parameter is quantified by using the SPRT to measure the immersion profile of the phase transition realization of a fixed-point cell. For the SPRT to be near thermal equilibrium, the SPRT must be able to track the ITS-90 hydrostatic head effect over the bottommost 3 cm [2,3,16]. This immersion profile is used to estimate the heat flux uncertainty component. Figure 2 gives an example of an immersion profile of an SPRT in an Al fixed-point cell during a freezing-point realization. This parameter is checked yearly for each fixed-point cell type with the corresponding check SPRT. The immersion profiles of untested SPRT designs are tested prior to calibration.

The Immersion Depth parameter is the effect of the depth of immersion of the SPRT sensor on the assigned fixed-point cell temperature. This parameter is one of the components (Type B, rectangular distribution) used to assign an overall uncertainty to the fixed-point cell. Two variables are used to estimate this uncertainty component of the immersion depth parameter: 1) the estimated depth of immersion of the SPRT sensor below the free sample surface, and 2) the estimated liquid to solid ratio of the sample [17].

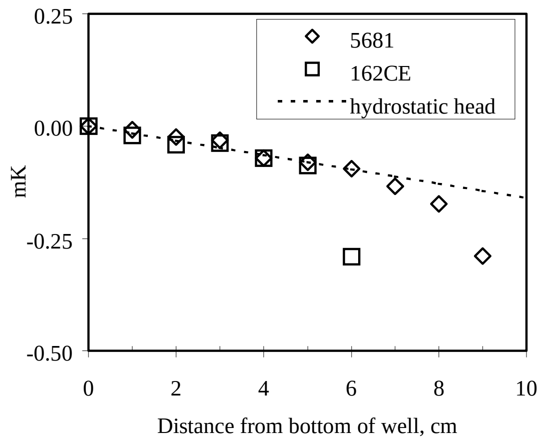

FIGURE 2. An example of an immersion profile for two SPRTs in an Al fixed-point cell during a freezing-point realization used to estimate heat flux uncertainty. The dashed line is the ITS-90 assigned hydrostatic head effect.

The Self-Heating parameter is the SPRT sensor self-heating effect on the realized fixed-point cell temperature. The uncertainty of this parameter is one of the components (Type B, rectangular distribution) used to assign an overall uncertainty to the fixed-point cell. The uncertainty component is calculated from making SPRT measurements with five excitation currents at each fixed-point cell and calculating the range in the zero current extrapolation from the possible current combinations. The Self-Heating parameter is checked yearly using representative SPRTs of different models [2,3].

The Stability parameter checks whether the SPRT is considered stable enough to achieve compliance with the SPRT Calibration parameter within Element 6: Measurement Assurance. Two measurements of stability are used for this determination: 1) prior to a calibration, the SPRT resistance, R, must repeat at the H_2O TP to within the equivalence of 0.2 mK between annealing [1-3]; and 2) the SPRT resistance must repeat at the H_2O TP to within the equivalence of 0.75 mK during the calibration process [1-3].

The Wetness parameter tests for moisture within the sheath of an SPRT. The first test is to measure the R(H_2O TP) of the SPRT at currents of 1 mA, 1.41 mA, and 1 mA. The two 1 mA values of SPRT resistance should repeat to within 2 μΩ. A lower second 1 mA value (≥10 μΩ) may indicate that water within the sheath of the SPRT is condensing on the sensor. The second test involves measuring the amount of time the SPRT requires to come to equilibrium at the H_2O TP from ambient conditions. A “dry” SPRT will be within 0.1 mK of equilibrium within 5 minutes. The third test involves placing the sheath of the SPRT through the bottom of a polystyrene cup such that the rim of the cup is near the head of the SPRT. After allowing for the SPRT to equilibrate at the H_2O TP, the cup is filled with crushed dry ice. If the SPRT is "wet", the condensed water will move from the sensor to the dry ice location along the SPRT sheath and a different $R(H_2O\ TP)$ will be measured. Based on the results of the three tests, a "wet" SPRT is rejected.

The Contamination parameter influences the stability of an SPRT during calibration. The SPRT $R(H_2O\ TP)$, W(Ga MP) sensitivity, and the magnitude of the d coefficient are used to check for contamination of the Pt sensor [1]. Details on using Pt protection tubes to prevent metal ion contamination above 700 °C are found in references 1, 2, and 18.

The Light-Piping parameter is the influence of the room lights on the SPRT measurement of the realized temperature of the fixed-point cell. This parameter directly influences the heat flux parameter within Element 2: SPRT. The light-piping effect along an SPRT sheath is the difference obtained when measuring an SPRT in a realized fixed-point cell with the room lights on and the room lights off.

ELEMENT 4: MEASUREMENT SYSTEM

The Repeatability parameter of the Measurement System Element is determined from making two similar measurements. The first method is to measure a thermostatically controlled (±10 mK) reference resistor over at least a 10 h period to determine the repeatability of only the resistance ratio bridge. The second method is to measure an SPRT in either a H_2O TP cell or a Ga TP cell over at least a 10 h period to determine the repeatability of the measurement system under nominal SPRT calibration conditions. For either method, the repeatability is expected to be within 4 μΩ peak-to- peak. The second method is used to assign a value to the bridge repeatability uncertainty component (Type A) [3,19]. A graphical example is found in reference 19. The Repeatability parameter is checked once every six months.

The Non-Linearity parameter is measured using a commercially available Hamon Box network designed for ac measurement systems [19,20]. The Non-Linearity parameter is checked once per year.

The Ratio Error parameter is used to assign a value to the ratio error uncertainty component (Type A). The results are obtained using both a commercially available Hamon Box and a commercially available ratio turns unit, and verified by the results from a two-way ratio complements check. [19,20]

The Ohm parameter is comprised of two parts. The first part is the maintenance of the ohm. The reference resistors (1 Ω, 10 Ω, and 100 Ω) are calibrated biannually at NIST. The second part is the thermostatic control of those reference resistors. An oil bath is used to maintain the reference resistors at a temperature of 298.15 K ± 0.01 K [2,10]. The reference resistor uncertainty component is calculated from the determination of the effect of the two parts of the Ohm parameter. The second part of the Ohm parameter is checked twice per day.

The AC Quadrature parameter is ac quadrature /frequency dependence of an ac resistance ratio bridge. The ac quadrature uncertainty (Type B, rectangular) is the difference between the low frequency (30 Hz) and the high frequency (90 Hz) measurements of an SPRT in a realized fixed-point cell [19]. No separate parameter is assigned for the difference between ac and dc measurements. This parameter is checked once per year.

The Current parameter is the measurement of the two excitation currents (e.g. 1 mA and 1.41 mA) supplied by the ac resistance ratio bridge used to measure the SPRTs. The excitation current is calculated from the determination of the R(SPRT) and the measured the voltage across the voltage leads of the SPRT [3,10]. The determined excitation currents are used to calculate the zero power R(SPRT) values. This parameter is checked daily during SPRT measurements

The Number of Readings Parameter is a fixed number of readings measured at each excitation current. Four sets of nine readings at each current are used to calculate a mean and standard deviation.

ELEMENT 5: REALIZATION TECHNIQUE

The Duration of a Realization Curve parameter determines the amount of time available in which to make SPRT measurements of a fixed-point cell phase transition. The furnace set-point temperature is adjusted so that a fixed-point cell realization curve lasts a minimum of 16 h. This is so that SPRT measurements are made over the first half of the realization curve where the smallest amounts of impurities are segregated into the solid sample [1-3]. This parameter is checked as part of the Check SPRT parameter of the Measurement Assurance Element.

The SPRT Immersion Profile parameter is the result of the Heat Flux parameter measurements discussed in Element 3: SPRT. This parameter verifies that the SPRT is in near thermal equilibrium with the fixed-point cell phase transition [2,3,16].

ELEMENT 6: MEASUREMENT ASSURANCE

The Measurement Assurance Element is divided into three internal and one external measurement assurance parameters. The three internal parameters verify that the SPRT is calibrated to within the stated calibration uncertainties. The external parameter verifies that the NIST realization temperatures of the fixed-point cells and assigned uncertainties are consistent with other National Metrology Institutions.

The Check SPRT parameter is the most critical measurement parameter for the daily calibration of SPRTs. A check SPRT is assigned to each fixed-point cell type and measured only at that fixed point and the H_2O TP cell. A check SPRT is measured at the beginning and end of the measurements of the fixed-point cell realization curve during the calibration of SPRTs. For the fixed-point cell realization to be acceptable for the calibration of SPRTs, a maximum allowable change is assigned for the difference between the first and second measured values of the check SPRT. The check SPRT is used as a total system check and statistical process control on the whole calibration process of an SPRT [1-3]. Figure 3 is an example of a check SPRT statistical process control chart for the Ga melting point (MP). This parameter is checked for every phase-transition realization of a fixed-point cell.

The Fixed-Point Cell Certification parameter is used to certify new and re-certify current reference fixed-point cells. New fixed-point cells undergo certification prior to becoming NIST ITS-90 defining standards. This process includes analyzing three melting and three freezing curves (freezing curves not applicable for a Ga MP or H_2O TP cells), an SPRT immersion profile, and three direct comparisons with the current reference cell. The realization temperature of a new fixed-point cell must agree with the realization temperature of the laboratory reference fixed-point to within the expected impurity effect difference and measurement uncertainties (k=2). Every six months a new phase transition realization curve of the current reference standard is performed to compare with the previous realizations [3, 6-9].

Within the SPRT Calibration parameter, there are several ITS-90 and NIST criteria that the calibrated SPRT must meet to be designated as an ITS-90 defining standard with the NIST-assigned calibration uncertainties. Failure of the SPRT to meet any of the

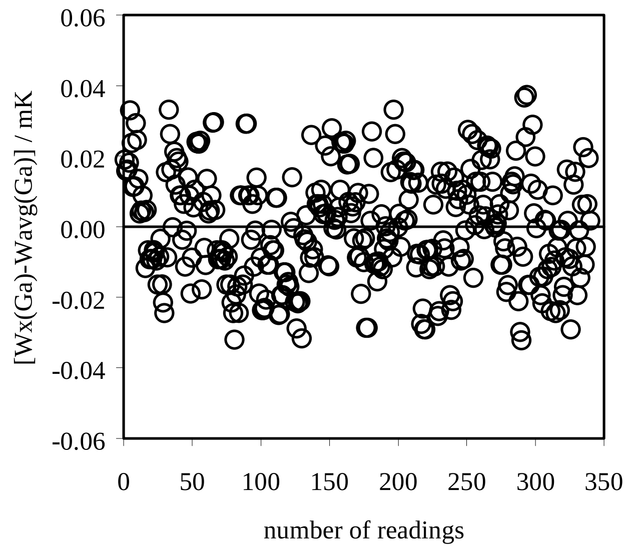

FIGURE 3. An example of a check SPRT statistical process control chart for the Ga melting point cell.

criteria described below results in the rejection of the SPRT for use as a defining standard, and the SPRT is returned without calibration values.

The ITS-90 defined criterion is the minimum purity requirement of the platinum sensor as determined from the W(Ga MP) or W(Hg TP) and the W[Ag freezing point (FP)] for use above 660.323 °C [1].

The six NIST criteria verify that the SPRT is calibrated to within the NIST assigned uncertainties. There are three criteria for the SPRT stability at the R(TPW). The SPRT must repeat at the R(TPW) after an annealing cycle to within the equivalent of 0.2 mK within five annealing cycles. The SPRT must not change by more than the equivalent of 0.3 mK for the R(TPW) measured before and after each other fixed-point cell. The total SPRT R(TPW) change during a calibration must not exceed the equivalent of 0.75 mK.

The measurement excitation currents of 1 mA, 1.41 mA, and 1 mA are used to measure the SPRT. For the SPRT to be in equilibrium, the two 1 mA values of R should repeat to within 2 μΩ.

The SPRT is measured at all of the ITS-90 fixed points over a given temperature subrange or subranges. The redundant fixed points (not required in the calculation of ITS-90 coefficients) give a measure of the error/non-uniqueness associated with the calibration of the SPRT. Based on measurements of a set of SPRTs (n > 30), the error/non-uniqueness at the Ga MP and the In FP should not exceed ±0.2 mK and ±0.3 mK, respectively [21]. Since no redundant ITS-90 fixed points exist between the Ar TP and the H_2O TP, the >0 °C temperature subrange is extrapolated to the Hg TP temperature to check the measured *W*(Hg TP). Based on measurements of a set of SPRTs (*n*>1000), this extrapolation should be within ±1.5 mK.

The External Comparison parameter consists of three types of comparisons: key, bilateral, and supplemental comparisons. Results of these types of external comparisons are used at NIST to improve both the fixed-point cell realizations and SPRT calibrations; and assess the uncertainties assigned to the both the NIST ITS-90 fixed-point cells and SPRT calibrations. Detailed information regarding these types of comparisons is given in references 22-24.

CONCLUSION

The IMAP six interactive elements described above are part of the Quality System implemented in the NIST PRT Laboratory for the ITS-90 calibration of SPRTs. The twenty-eight parameters contained within the six elements provide adequate measurement assurance for uncertainties assigned to the NIST realization of the ITS-90 fixed-points and calibration of SPRTs for use as ITS-90 defining standards.

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