NIST CERTIFICATION OF ITS-90 FIXED-POINT CELLS FROM 83.8058 K TO 1234.93 K: METHODS AND UNCERTAINTIES

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ABSTRACT

The certification of ITS-90 fixed-point cells from the Ar triple point (83.8058 K) to the Ag freezing point (1234.93 K) is an integral part of the calibration services offered by the NIST Thermometry Group. This service is used to qualify new fixed-point cells for internal use within the NIST Thermometry Group and by those facilities seeking traceability to NIST for the ITS-90 calibration of SPRTs. The method of certifying an ITS-90 fixed-point cell is a multiple step process that is designed to evaluate the intrinsic repeatability of the fixed-point cell, evaluate the realized temperature difference between the test fixed-point cell and the NIST reference fixed-point cell, assess the interaction of the fixed-point cell with the furnace and SPRT, and estimate the uncertainty of the certification process. This paper gives results of the reproducibility of direct comparison measurements over time, furnace effects on the realized fixed-point temperature, the certification uncertainty budget, and an uncertainty budget showing the required measurements that an end user must perform to assign an uncertainty in the use of the fixed-point cell.

1. INTRODUCTION

An integral part of the NIST Thermometry Group dissemination of the International Temperature Scale of 1990 (ITS-90) is the certification of ITS-90 fixed-point cells from the Ar triple point [TP, (83.8058 K)] to the Ag freezing point [FP, (1234.93 K)] [1]. Customers that calibrate standard platinum resistance thermometers (SPRTs) in terms of the ITS-90 utilize this cell certification service to qualify their fixed-point cells as their reference ITS-90 defining standards, determine uncertainty values, establish traceability, and in some cases satisfy accreditation requirements.

The method of certifying an ITS-90 fixed-point cell is a multiple-step process that is designed to evaluate the intrinsic repeatability of the fixed-point cell, evaluate the realized temperature difference between the test fixed-point cell and the NIST reference fixed-point cell, assess the interaction of the fixed-point cell with the furnace and SPRT, and estimate the uncertainty of the certification process. The NIST Certificate of Analysis contains results of the measurements performed on the test fixed-point cell including a heat flux (immersion) profile to verify that an SPRT tracks the expected hydrostatic head, three freezing curves (where applicable), three melting curves (where applicable), and three sets of direct-comparison measurements against the NIST reference fixed-point cell. From the results, an estimation of the direct-comparison uncertainty and the realized temperature difference between the two fixed-point cells is determined.

A critical aspect in the evaluation of a fixed-point cell is the intrinsic repeatability of the realization temperature of the cell. The repeatability of an SPRT in a fixed-point cell depends on many factors including at least the: measurement system stability, thermal stability and repeatability of the furnace, intrinsic variation in the realization process, the realization method, characteristics of the SPRT, and the operator. Generally, many of these terms depend on the particular laboratory that is realizing the fixed-point cell. To accommodate this dependence and assist in assigning an uncertainty in the use of the fixed-point cell, the NIST Certificate of Analysis includes an uncertainty budget with blank fields for the end user to populate with their own values based on their own measurements. The certification results of NIST In FP cell (In 96-4) are shown with respect to the NIST reference In FP cell (In 96-3) as an example throughout this paper to show measurement results and estimated uncertainty values that are representative for fixed-point cells of comparable quality to those used at NIST. Any fixed-point cell of lesser quality will result in larger uncertainty values.

2. METHOD OF CERTIFICATION

The NIST Certificate of Analysis is designed to give detailed information on the characteristics of a NIST measured test fixed-point cell, NIST-performed measurement uncertainties, and guidance to the customer on what measurements are still required to assign an uncertainty when used by that customer. It is important to note that the NIST Certificate of Analysis does not assign a realization temperature to the fixed-point cell as would be the case with a NIST Report of Calibration.

In most cases, the customer-supplied maintenance system is used when certifying the Ar TP, Hg TP and Ga melting-point (MP) cells. This is the preferred method of certification as the same thermal conditions are present when the fixed-point cell is realized by the customer. For the certification of the metal FP cells (In, Sn, Zn, Al, and Ag) and the H_2O TP cell, the customer cells are usually tested in an appropriate NIST maintenance system. Detailed descriptions of the NIST fixed-point cell maintenance systems are found in Ref. [2-4]. When a fixed-point cell is tested in a NIST maintenance system, there exists an additional burden on the customer to investigate the thermal influence of their maintenance system on their realization of that fixed-point cell.

The instrumentation used for certifying a fixed-point cell includes a commercially-available 9.5 digit ac resistance ratio bridge operating at a frequency of 30 Hz, a thermostatically-controlled (25 °C ±0.01 °C) ac/dc reference resistor and an SPRT [3,5]. For tracing realization plateaus, the SPRT excitation current is 1.0 mA; for the heat-flux (immersion) test and the direct comparisons two excitation currents of 1.0 mA and 1.414 mA are used to calculate 0 mA values. Following each experimental measurement set, the SPRT is measured at the water triple point.

2.1 Heat-Flux (Immersion) Test

The first step in the multiple step process of certifying an ITS-90 fixed-point cell determines if the cell can be properly realized and measured with negligible influence from any extraneous thermal sources (e.g. SPRT stem conduction, furnace). By performing a heat-flux (immersion) test, the interaction of the furnace, SPRT, realization method, and fixed-point cell is evaluated. The results of this test are used estimate a heat-flux (immersion) uncertainty value as part of the direct-comparison measurement uncertainty budget.

In order to validate that the SPRT is in near-thermal equilibrium with the phase transition of the fixed-point cell, the SPRT must track the ITS-90 assigned hydrostatic-head effect for at least 3 cm above the axial midpoint of the SPRT platinum sensor. Since the SPRT measures an average temperature over the length of platinum sensor, the 3 cm criterion is chosen to accommodate the nominal 2.5 cm distance above the platinum-sensor axial midpoint. The heat-flux (immersion) test is performed by measuring the SPRT starting 10 cm from the bottom of the thermometer well, then inserting the SPRT in 2 cm steps until 5 cm from the bottom, at which time the SPRT is then inserted in 1 cm steps until the thermometer well bottom is reached. The immersion depth of the SPRT is calculated from the sensor axial midpoint to the height of the sample column during the fixed-point realization. From these measurements, a heat-flux (immersion) uncertainty (k=1) is calculated as the difference between the 3 cm value calculated from the linear fit of the measurements over the bottommost 5 cm and the ITS-90 assigned hydrostatic-head effect. Examples of heat-flux (immersion) tests are found in Ref. [6].

It is important to note that different designs of the fixed-point cell assembly, maintenance system, or SPRT may change the heat-flux (immersion) characteristics and will require re-determination of the heat-flux uncertainty. Additionally, the realization method and duration of the realization plateau strongly impact the SPRT heat-flux (immersion) test results [7].

2.2 Melting and Freezing Curves

The tracing of the melting and freezing plateaus of a fixed-point cell is part of the certification process that is used to determine if the thermal environment of the maintenance system significantly influences the realization temperature and plateau slope. Additionally, the results given in the NIST Certificate of Analysis can be used by the customer as a baseline to determine if they are properly realizing the fixed-point cell within their own laboratory and to check for possible contamination of the fixed-point cell over time [8].

A simple check for perturbations of the fixed-point realization temperature by the thermal environment can be performed by tracing realization curves of various durations and observing the effect on the slope of the plateau and the reproducibility of the realized temperature. Figure 1 shows how changing the furnace set-point temperature has little effect on the realization temperature reproducibility and the freezing plateau slope. When the furnace set-point temperature (furnace gradient) is changed from 0.3 K to 0.8 K below the freezing-point temperature, there is no difference in the realization temperature. In the case where furnace gradient is set to 75 K below the fixed-point temperature, the realization temperature is depressed by about 0.15 mK and the freezing plateau lasts only 0.8 h. To eliminate this possible furnace effect, the furnace gradients are set such that the freezing plateaus last at least 16 h during direct-comparison measurements.

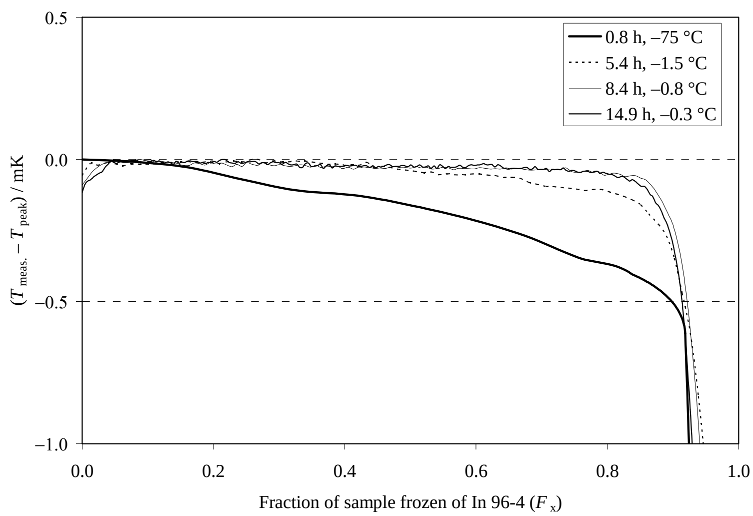

Figure 1: The effect of different furnace set-point temperatures on the realization temperature and the slope of the freezing plateau for the In 96-4 FP cell. The temperature offset in the legend is the difference between the furnace set-point temperature and the ITS-90 fixed-point temperature.

2.3 Direct-comparison measurements

The direct-comparison measurements are used to determine the relative realization temperature differences between the test and NIST laboratory reference fixed-point cells. The direct-comparison measurements are obtained by performing simultaneous realizations for the two cells in two separate furnaces and making three sets of alternate measurements with an SPRT, at equal time intervals, on their realization-curve plateaus. This ensures that the comparison measurements on the two cells are made at approximately the same liquid-solid ratio of the fixed-point samples. Corrections are made for any differences in pressure and hydrostatic head effects in each cell. The test and NIST reference fixed-point cells are measured using an SPRT three times during the direct comparison, and this procedure is repeated two times for a total of nine measurement pairs.

Since the test and NIST reference fixed-point cells are directly compared such that the any thermal non-uniformities negligibly effect the realization temperatures, the realized temperature difference is primarily a function of the purity difference between samples respectively contained within the test and NIST reference fixed-point cells. In Fig. 2, four direct-comparison results obtained over six years demonstrate the SPRT measurement reproducibility and the consistency of realization temperature differences between the test (In 96-4) and NIST reference (In 96-3) fixed-point cells.

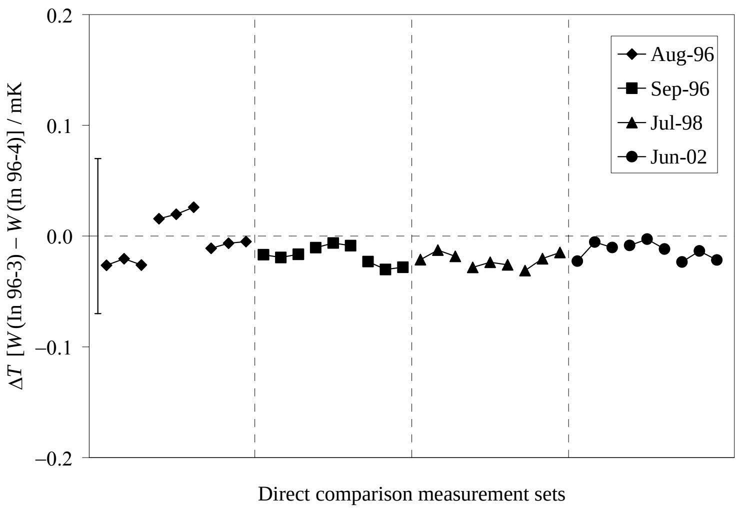

Figure 2: Four direct-comparison results showing the SPRT measurement reproducibility and the realization temperature difference between the test (In 96-4) and NIST reference (In 96-4) fixed-point cells over six years. The uncertainty bar (k=2) is the estimated direct-comparison measurement uncertainty.

The SPRT repeatability uncertainty value used for the direct-comparison measurements is lower than that assigned to the NIST fixed-point realization uncertainty for the calibration SPRTs. The different repeatability uncertainty values are a function of the type of fixed-point cell measurement and the realization plateau duration. In the case of SPRT calibrations, the check SPRT undergoes more thermal cycling and measures the realization plateau over a greater duration, thus the larger repeatability value than for direct comparisons. Table 1 shows the check SPRT repeatability when used for SPRT calibrations as compared to the direct comparison of fixed-point cells.

Table 1: The changes in the In FP check SPRT repeatability value for SPRT calibrations and for the direct-comparison measurements of fixed-point cells. Note that during SPRT calibrations the check SPRT is always measured before and after the customer SPRTs at both the ITS-90 calibration fixed point and the water triple point.

Check SPRT use	s.d. (not of the mean) / mK
SPRT calibrations – before and after readings, n=84	0.04
SPRT calibrations – before readings only, n=42	0.02
Direct comparison (fixed-point certification), n=9	0.01

The long-term direct-comparison measurement reproducibility of two fixed-point cells was studied to determine if the direct-comparison repeatability term is a fair representation for a Type A uncertainty. Table 2 gives the direct-comparison reproducibility of the two indium fixed-point cells directly compared over six years. The temperature difference variation between the two cells is within that of the direct-comparison measurement uncertainty.

As an additional crosscheck on the realization-temperature difference between the test and NIST reference fixed-point cells determined by direct comparisons, the average direct-comparison temperature difference is compared with the temperature difference calculated using the realization curves of the two cells.

Table 2: The direct-comparison reproducibility of the In 96-4 and In 96-3 fixed-point cells over six years.

Date of direct comparison	ΔT / mK	Standard deviation (n=9) / mK
August 1996	–0.01	0.02
September 1996	–0.02	0.01
July 1998	–0.03	0.01
June 2002	–0.02	0.01
All 4 direct comparison sets	–0.02	0.01

3. UNCERTAINTIES

The NIST Certificate of Analysis for a fixed-point cell contains three uncertainty budgets labeled *Appendix A*, *B*, and *C*. *Appendix A* is the direct-comparison uncertainty budget, *Appendix B* is the NIST reference fixed-point cell uncertainty budget, and *Appendix C* is a template for the suggested test fixed-point cell uncertainty budget. *Appendix B* examples are found in Ref. [6].

Table 3 gives an example of the direct-comparison uncertainty budget (*Appendix A*). This uncertainty budget is a subset of the fixed-point cell uncertainty budget (*Appendix B*), but contains only the components that are relevant to determine the uncertainty of the direct comparison. This budget incorporates uncertainty values derived for both the test (In 96-4) and reference (In 96-3) fixed-point cells. Thus, the values used in Table 3 (*Appendix A*) are a function of the quality of the fixed-point cell undergoing certification.

Table 3: Example of a direct-comparison uncertainty budget (*Appendix A* in a NIST Certificate of Analysis) for a direct comparison of a test fixed-point cell (In 96-4) against the NIST reference fixed-point cell (In 96-3) in June 2002.

Uncertainty component	u_i / mK	Remarks
Bridge repeatability, Type A	0.01	Both cells
Direct-comparison repeatability, Type A	0.01	Pooled s.d. of pair differences
Hydrostatic head, Type B	0.02	Both cells, rectangular distribution
SPRT self heating, Type B rectangular	0.02	Both cells, rectangular distribution
Heat flux (immersion), Type B normal	0.01	Both cells, normal distribution
Gas pressure, Type B rectangular	0.00	Both cells, rectangular distribution
Total Standard Uncertainty (k=1)	0.03	
Total Expanded Uncertainty (k=2)	0.07	

Table 4 gives a sample template of an uncertainty budget (*Appendix C* in the NIST Certificate of Analysis) for the customer to use in assigning an uncertainty to the submitted fixed-point cell as realized in their laboratory. Two of the supplied uncertainty values in Table 4 (absolute value of the direct-comparison difference and direct-comparison measurements) are obtained from the direct-comparison measurements and uncertainty budget (*Appendix A*). The third uncertainty value (chemical impurities in the NIST reference cell) is obtained from the NIST fixed-point cell uncertainty budget (*Appendix B*). The suggested application of the supplied values is a conservative approach. Values given in *Appendix B* of the NIST Certificate of Analysis are not to be used to complete *Appendix C*.

The realization uncertainty of a fixed-point depends on many factors including at least the: measurement system stability, thermal stability and repeatability of the furnace, intrinsic variation in the realization process, realization method, characteristics of the SPRT, and operator. Generally, many of these terms depend on the particular laboratory that is realizing the fixed-point cell. Thus, the customer is responsible for assigning an overall realization uncertainty to their certified fixed-point cell as realized in their laboratory by making the necessary measurements using their own equipment, methods and personnel to populate the blank values given in table 4 (*Appendix C*).

Table 4: Example of the suggested template for a customer fixed-point cell uncertainty budget (*Appendix C* in a NIST Certificate of Analysis) as realized in their laboratory using their own equipment, realization method and personnel.

Uncertainty Component	u_i / mK	Remarks
Bridge repeatability		Blank values and Type (e.g. A or B) determined by customer
Bridge non-linearity		
Bridge quadrature effects (AC only)		
Reference resistor stability		
Check SPRT repeatability		
Hydrostatic head		
SPRT self-heating		
Heat flux (immersion)		
Gas pressure		
Slope of plateau		
Propagation of water triple point		
Absolute value of direct-comparison difference	NIST derived	Type B, normal distribution – NIST suggested method of applying these uncertainties
Direct-comparison measurements	NIST derived	
Chemical impurities in NIST reference cell	NIST derived	

REFERENCES

[1] Preston-Thomas, H., "The International Temperature Scale of 1990 (ITS-90)", *Metrologia* **27**, 1990 pp 3-10; *ibid*. p. 107.

[2] Mangum, B. W. and Furukawa, G. T., "Guidelines for Realizing the International Temperature Scale of 1990 (ITS-90)", NIST TN1265, 1990, pp. 190.

[3] Strouse, G. F., "NIST Implementation and Realization of the ITS-90 Over the Range 83 K to 1235 K. Reproducibility, Stability, and Uncertainties," in *Temperature: Its Measurement and Control in Science and Industry*, edited by J.F. Schooley, Vol. **6**, American Institute of Physics, New York, 1992, pp. 169-174,

[4] Strouse, G. F., "Thermal Characteristics of the NIST Fixed-Point Cells, Furnaces, and Maintenance Baths over the Temperature Range from 83.8058 K to 1234.93 K," in *Tempmeko '99: The 7th International Symposium on Temperature and Thermal Measurements in Industry and Science*, edited by J. F. Dubbledam and M. J. Groot, NMi-Van Swinden Laboratorium, Delft, The Netherlands, 1999, pp.153-158.

[5] Kaeser, R. S., Strouse, G. F., "An ITS-90 Calibration Facility", *NCSL Conference Proceedings*, 1994.

[6] Mangum, B. W., *et al.*, "CCT-K3: Key Comparison of Realizations of the ITS-90 over the Range 83.8058 K to 933.473 K", NIST TN1450, 2002, pp. 393.

[7] Strouse G. F., "NIST Realization of the Gallium Triple Point", *Tempmeko '99: The 7th International Symposium on Temperature and Thermal Measurements in Industry and Science*, edited by J. F. Dubbledam and M. J. Groot, NMi-Van Swinden Laboratorium, Delft, The Netherlands, 1999), pp. 147-152.

[8] Strouse, G. F., "NIST Methods of Estimating the Impurity Uncertainty Component for the ITS-90 Fixed-Point Cells from the Ar TP to the Ag FP", 2003, document CCT 03-19, BIPM, Sèvres, France, 2003.

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