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NON-UNIQUENESS OF THE ITS-90 FROM 13.8033 K to 24.5561 K

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ABSTRACT

The International Temperature Scale of 1990 (ITS-90) is defined in the region 3.0 K to 24.5561 K by an interpolating constant volume gas thermometer (ICVGT) that is calibrated at three specified fixed points. From 13.8033 K to 1234.93 K the ITS-90 is defined by means of standard platinum resistance thermometers (SPRTs) calibrated at specified fixed points. Two of the fixed points at which SPRTs are calibrated, at 17.035 K ± 0.010 K and 20.270 K ± 0.010 K, may be realized by using either of two different types of thermometry, yielding two SPRT definitions. Therefore, from 13.8033 K to 24.5561 K the possibility exists for non-uniqueness due to the overlap of three equally valid definitions (one ICVGT and two SPRT) that do not necessarily agree. The NIST apparatus for realizing the ITS-90 below 85 K includes an ICVGT that uses ^{4}He as the working gas and fixed point cells which are used to calibrate the ICVGT and SPRTs below 85 K. We present here a determination of the non-uniqueness of the ITS-90 from 13.8033 K to 24.5561 K by means of direct comparisons of temperatures determined by the three valid definitions. Over this interval, total uncertainties (k=2) in the ICVGT determinations range from 0.16 mK to 0.21 mK, and those from the SPRT determinations range from 0.15 mK to 0.48 mK. The maximum non-uniqueness observed is 1.55 mK ± 0.54 mK, which occurs at 15 K.

1. INTRODUCTION

From 3.0 K to 24.5561 K the International Temperature Scale of 1990 (ITS-90) [1] is defined by an interpolating constant volume gas thermometer (ICVGT) using either ^{3}He or ^{4}He. Furthermore, from 13.8033 K to 1234.93 K the ITS-90 is defined by means of standard platinum resistance thermometers (SPRTs) calibrated at specified fixed points and using specified interpolation procedures. Two of these fixed points (at 17.035 K ± 0.010 K and 20.270 K ± 0.010 K) may be realized by using either of two different equally valid methods; this yields two SPRT definitions. From 13.8033 K to 24.5561 K, the overlap of these three differing definitions results in possible non-uniqueness of the scale, since all definitions are considered equally valid. By the definitions provided for by Working Group 1 of the Comit0 Consultatif de Thermom0trie (CCT), the non-uniqueness between the two SPRT definitions is "Type 1" and the non-uniqueness between the ICVGT and SPRT definitions is "Type 2" [2]. Non-uniqueness can also exist between different SPRT instruments using the same SPRT definition because of their different material compositions, and this is referred to as "Type 3" [2]. The purpose of this paper is to present quantitative determinations of these three types of non-uniqueness of the ITS-90 in this region of the scale.

The ICVGT is calibrated at three ITS-90 fixed points: the triple points of neon (24.5561 K) and equilibrium hydrogen (13.8033 K), and an arbitrary point between 3.0 K and 5.0 K realized by the ITS-90 vapor-pressure/temperature relations of ^{3}He or ^{4}He. The arbitrariness of this lowest point introduces the possibility of Type 1 non-uniqueness to the gas-thermometry definition of the ITS-90. The thermodynamic accuracy and non-uniqueness of the ICVGT are dependent on the thermodynamic accuracy of the temperature assignments to these three defining points. A previous paper investigated the non-uniqueness of the ICVGT definition of ITS-90 when different He vapor pressure points were used as the lowest fixed point [3]. While the non-uniqueness was as large as 0.7 mK below 13.8033 K, it was less than 0.1 mK from 13.8033 K to 24.5561 K.

For the range 13.8033 K to 273.16 K, an SPRT is calibrated at eight fixed points. Six of the fixed points are the triple points of water (273.16 K), mercury (234.3156 K), argon (83.8058 K), oxygen (54.3584 K), neon (24.5561 K), and equilibrium hydrogen (13.8033 K). The other two fixed points are at ≈17.035 K and ≈20.270 K and may be realized by either the vapor pressure of equilibrium hydrogen (e-H_2 VP) or an ICVGT. The opportunity to choose between these two fixed-point realizations adds Type 1 non-uniqueness to the SPRT definition of the ITS-90 in this range. We shall refer to the SPRT definition using the e-H_2 VP fixed points as SPRT(VP) and that using the ICVGT fixed points as SPRT(GT). The SPRT(VP) and ICVGT definitions share two fixed points: the triple points of equilibrium hydrogen and neon. The SPRT(GT) and ICVGT definitions have two additional shared fixed points at 17 K and 20 K. Therefore the SPRT and ICVGT definitions will necessarily agree at these common fixed point temperatures.

If the ITS-90 were perfectly designed and SPRTs behaved ideally, no non-uniqueness would exist because all

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overlapping definitions would agree and all SPRTs would perform equivalently. The non-uniqueness in the ITS-90 which exists over the range 13.8033 K to 24.5561 K occurs as a result of imperfect assignments of thermodynamic temperature values to the fixed-points used by the SPRT and ICVGT definitions, deficiencies in the interpolation equations, and differences between individual SPRTs [2]. Irreproducibility of the scale also occurs due to errors in the realization of any of the relevant fixed points [2].

In this paper, we present comparisons of three different ITS-90 temperature determinations based on its three definitions over the range 13.8033 K to 24.5561 K using our low temperature facility for realization of the ITS-90. One determinations uses an ICVGT with ^4He as the working gas and with the lowest calibration point at 5 K. A second use the SPRT(VP) definition and the third uses the SPRT(GT) definition. The fixed-point calibrations for the ICVGT were made using realizations performed in the NIST low temperature facility for realization of the ITS-90 [3]. The SPRT calibrations were made using fixed-point realizations performed in this same facility [4] except for mercury [5] and water [6], which were performed in the NIST SPRT calibration laboratory. Three different SPRTs were used to represent the SPRT determination. By using three SPRTs, we were able check for Type 3 non-uniqueness between fixed points.

2. APPARATUS

These temperature determinations were performed in NIST's low-temperature ITS-90 realization facility [3,4,7], which was designed to realize the ITS-90 below 84 K using the guidelines published by BIPM [8]. The cells used for realizing the ITS-90 below 84 K are located inside a cylindrical oxygen-free high conductivity copper block. This block contains vapor-pressure cells for ^3He and ^4He, the ICVGT, a vapor-pressure/triple-point cell for e-H_2, and triple-point cells for Ne, O_2 and Ar. The block is 31.8 cm high and has a diameter of 10.2 cm at the location of the gas thermometer. The block has horizontal wells located 1.6 cm from the top and 0.6 cm from the bottom for the insertion of rhodium-iron resistance thermometers (RIRTs). In addition, there are four horizontal wells located in the middle of the block; two of these can contain RIRTS or capsule-type SPRTs and the other two can contain only RIRTs. The gas thermometer cavity has an inner diameter of 7.6 cm and a depth of 22.4 cm. The block also contains a fill-line to the cavity which has a 0.33 cm diameter and a length of 9.4 cm, giving the entire gas thermometer a total volume of 1017 cm^3.

For the vapor pressure and triple point realizations, each gas has its own cell. The ^3He, ^4He, e-H_2 and Ne cells each have a volume of 3 cm^3 and the Ar and O_2 cells have a volume of 20 cm^3. The e-H_2 cell contains about 0.5 cm^3 of FeO(OH) powder, which is used as a catalyst for the conversion of ortho-hydrogen and para-hydrogen to their equilibrium distribution [8,9].

Five of the six thermometer wells can accommodate resistance thermometers used for ICVGT/SPRT comparisons (the last contains an RIRT temperature-control sensor). The resistances of the thermometers are measured with an automatic ac resistance ratio bridge operating at 30 Hz, using a standard resistor calibrated at NIST. The thermostatically controlled ac/dc standard resistors used are 10 Ω for the RIRTs and 1 Ω for the SPRTs. The standard resistors were calibrated shortly before measurements were taken.

The apparatus uses a continuously operating ^3He refrigerator for cooling the copper block. The block is heated with resistive wire. Temperature control is obtained with a PID controller. The sensor for the controller is a RIRT inserted in one of the wells in the middle of the block. The resistance of the thermometer is measured with a second ac resistance bridge, which gives a dc voltage output proportional to the deviation from balance. Temperature stability of better than 0.01 mK over several hours can be achieved with this system.

The pressures inside the vapor-pressure cells and the gas thermometer are measured with a system that includes a gas-lubricated piston gauge, used in the absolute mode, and a differential capacitance diaphragm gauge. Weights are placed on the piston gauge so that when balanced, it generates a pressure within +40 Pa of the sample gas pressure. The difference is measured with the differential gauge. The same piston gauge is used for all cells, but each cell requiring pressure measurement uses its own differential gauge, which can be isolated from the piston gauge by a valve. The gas used between the piston gauge and differential gauge is 99.9999% (by weight) pure nitrogen.

3. REALIZATION TRACEABILITY

The ICVGT realization was performed in November 1995, and was maintained on three rhodium-iron thermometers with serial numbers B168, B174 and B211. Details of the ICVGT realization have been described elsewhere [3]. Uncertainties of the realization (k=2) range from 0.15 mK at 13.8033 K to 0.21 mK at 24.5561 K and increased

approximately linearly with temperature.
The SPRT temperature determinations were performed with three thermometers, which had serial numbers 1004131, 1812282, and 1812284. The SPRTs were calibrated at eight fixed points, six of which were realized in the same copper block where the ICVGT/SPRT comparison was performed. Results from the realizations of the triple points of argon, oxygen, neon and equilibrium hydrogen in the NIST low temperature facility have been published elsewhere

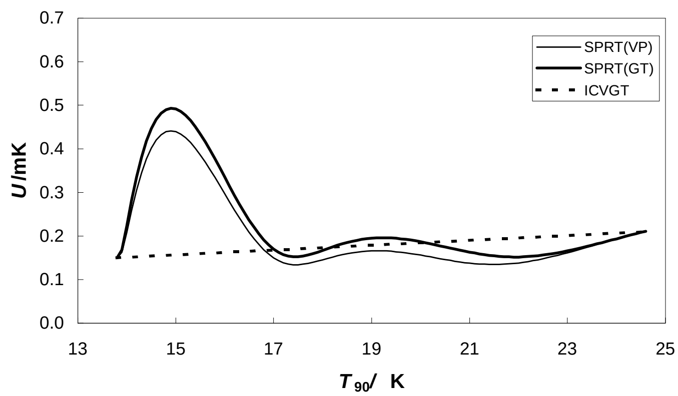
Table 1. SPRT fixed-point uncertainties U (k=2).

Item	**e-H_2 TP**	**17 K**	**20 K**	**Ne TP**	**O_2 TP**	**Ar TP**	**Hg TP**	**H_20 TP**
U/mK	0.15	e-H_2 VP: 0.15 ICVGT: 0.17	e-H_2 VP: 0.15 ICVGT: 0.18	0.21	0.06	0.07	0.20	0.04

[4]. Descriptions of the realizations of the triple points of water and mercury can be found in [5,6]. Expanded uncertainties (k=2) for the triple point realizations are given in Table 1.

The e-H_2 VP realizations were performed at 17.0365 K and 20.2682 K. They were conducted using exactly the same method as the ^{3}He and ^{4}He vapor pressure realizations [7], with one major exception: special care was taken to ensure that the H_2 sample was in ortho-para equilibrium before performing the vapor pressure measurements. First, the condensed H_2 was left exposed to the catalyst at the fixed-point temperature for about 24 h. At that point, the H_2 vapor above the liquid, which was not exposed to the FeO(OH) catalyst, was evacuated for 15 seconds. This vapor was replaced by e-H_2 boiling off from the liquid. A trial vapor pressure measurement was then made. This procedure was repeated several times. Once the trial realization temperature was no longer changed by replacement of the H_2 vapor, it was assumed that the H_2 was in sufficient ortho-para equilibrium for a reliable realization. Total expanded

Figure 1. Uncertainties (k=2) of the temperature determinations for the SPRT and ICVGT definitions of the ITS-90. The SPRT(VP) definition uses the e-H_2 VP fixed points at 17.0365 K and 20.2682 K and the SPRT(GT) definition uses the ICVGT at these temperatures.



uncertainties (k=2) are given in Table 1 above.

SPRT uncertainties are larger between fixed points than they are at fixed-points due to propagation of errors from the fixed points. Figure 1 shows the estimated uncertainties for the SPRT(VP) and SPRT(GT) determinations given the fixed-point uncertainties listed in Table 1. The estimated uncertainties for the ICVGT realization are also shown in Fig. 1.

The low-temperature fixed point realizations used for this study are those performed when SPRT 1004131 was in the copper block. During those realizations, RIRTs B168, B174 and B211 were also in the copper block, and later those RIRTs were used to transfer this realization to SPRTs 1812282 and 1812284. The expanded uncertainty of the transfer of these fixed points is estimated to be 0.04 mK (k=2).

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4. MEASUREMENT PROCEDURE

The first set of ICVGT/SPRT comparisons was made in December 1995. It was performed during the same cooldown as that of the ICVGT realization, which was done one month previously. RIRTs B168, B174, and B211, which were calibrated against the ICVGT realization, were present in the copper block. The SPRT used was 1004131. A second set of comparisons was made in February 1999. For this comparison, RIRTs B168 and B211 represented the ICVGT realization and the SPRTs used were 1812282 and 1812284.

For each comparison temperature, the temperature was controlled at the same temperatures as the ICVGT realization measurements. By making comparisons at these temperatures, we were able to transfer the ICVGT scale exactly rather than relying on the accuracy of a curve fitted to the ICVGT data. The copper block was controlled at the comparison temperature for a minimum of 20 minutes, until temperature drift was unobservable over a 10 minute period. Measurements were made of the thermometer resistance at two currents. For the RIRTs, these were 0.2 mA and 0.2828 mA. For SPRT 11004131, the currents were 2.0 mA and 2.828 mA, and for SPRTs 1812282 and 1812284, they were 2.828 mA and 5.0 mA. For each current, resistance measurements were taken over a five minute period with approximately 15 seconds between measurements. Since ITS-90 realizations were recorded as zero-current resistance extrapolations, similar extrapolations were made for the RIRTs and SPRTs during the comparison measurements. For a given temperature and SPRT, the SPRT(VP) and SPRT(GT) temperature determinations were obtained using the same resistance value; the difference in the temperatures determined was a result of different ITS-90 coefficients used in the interpolation equation.

5. COMPARISON UNCERTAINTIES

The discussion here is based on the ISO guidelines for the evaluation of uncertainties [10]. Type A standard uncertainties are the statistical uncertainty of the resistance measurements, which were s_r=0.04 mK for each current and s_r=0.06 mK for the zero-current extrapolation. Type B standard uncertainties are the temperature drift during the measurements, reference resistance uncertainties, and resistance bridge uncertainties, which we estimate to be u_d= 0.04 mK, u_{rs}= 0.04 mK and u_{rb}< 0.01 mK, respectively. The total expanded uncertainty for the comparison is then calculated to be U_c (k=2) = 0.17 mK.

For the SPRT/ICVGT Type 2 non-uniqueness, the total uncertainty is the quadrature sum of the comparison uncertainty and the two temperature determination uncertainties. For the SPRT(VP)/SPRT(GT) Type 1 non-uniqueness, the total uncertainty is the quadrature sum of the uncertainties of the two temperature determinations, and the uncertainties of the fixed points common to both SPRT definitions are assigned an uncertainty of zero when calculating the SPRT uncertainties over the desired range. Total uncertainties U(k=2) are shown as solid curves in Fig. 2.

6. RESULTS

Results of determinations of the non-uniqueness of the ITS-90 between 13.8033 K and 24.5561 K are shown in Fig. 2. The difference between the SPRT(VP) and ICVGT temperature determinations is shown in Fig. 2a. The largest difference is at 17.0365 K (e-H_2 VP definition) and reflects the 0.65 mK difference between the e-H_2 VP and ICVGT fixed-point values at that temperature. A second maximum in the difference magnitude exists at 20.2682 K (e-H_2 VP definition) and reflects the –0.25 mK difference between the e-H_2 VP and ICVGT fixed-point realizations at that temperature. The SPRT interpolations between the fixed points, as shown by the difference plot, appear very reasonable.

Figure 2b compares the SPRT(GT) and ICVGT temperature determinations. The difference between the two is now zero at 17.0365 K and 20.2682 K, which is natural since the SPRTs were calibrated using the ICVGT at these temperatures. Above 19 K the difference is small, but between 13 K and 17 K its magnitude increases dramatically, with a maximum difference of about –1.3 mK at 15 K. This increase demonstrates the sensitivity of the ITS-90 SPRT temperature determinations over the region between the e-H_2 triple point and the 17 K e-H_2 vapor pressure point to fixed point values. Propagation of fixed-point uncertainties is larger in this region than other regions, as shown by the uncertainty curves. It may be fortuitous that the interpolation over this range is so well-behaved in the SPRT(VP) determination.

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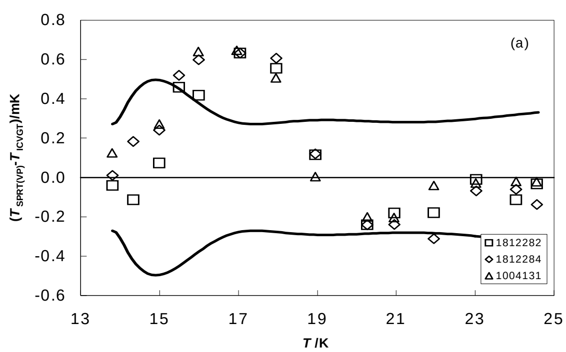
Both plots show no obvious systematic deviations between the three SPRTs. The scatter between the temperature determinations from the different SPRTs is consistent with the uncertainties estimated for temperature drift and statistical variations in the resistance measurements, making Type 3 non-uniqueness unobservable.

In Fig. 2c the difference between the temperatures determined by the two SPRT definitions is shown. No scatter appears in the plot because both determinations result from the same SPRT resistance measurements; the difference is a result of different ITS-90 SPRT coefficients traceable to different fixed-point values at 17.0365 K and 20.2682 K. The difference at 15 K (1.55 mK ±0.51) is the largest non-uniqueness determined over this range from all the comparisons.

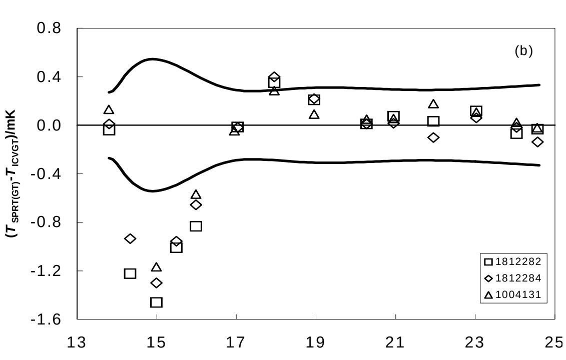
A major source of non-uniqueness in our determination of ITS-90 temperatures over the range shown is the

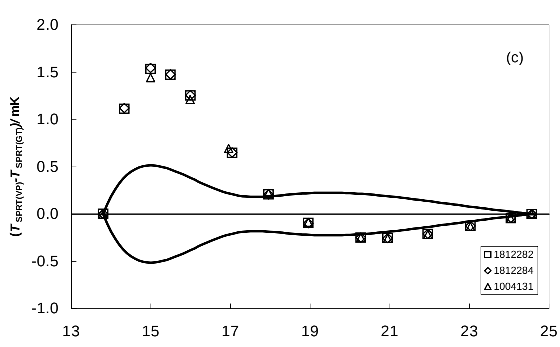
Figure 2. Difference between ITS-90 temperatures determined by equally valid definitions over the range 13.8033 K to 24.5561 K. In the first two plots, the difference is between SPRT and the ICVGT temperatures determined when the 17 K and 20 K SPRT fixed points are from (a) e-H_2 vapor pressure realizations and (b) ICVGT realizations. In (c) the difference is between the two SPRT realizations. In all plots the solid curves show the uncertainty (k=2) of the non-uniqueness of the temperature determinations.

disagreement
between the e-H_2 VP and ICVGT realizations at 17.0365 K and 20.2682 K. This disagreement, which is larger than the combined uncertainties of the realizations at both temperatures, can be studied further by comparing both to the NPL-75 scale [11], which the ITS-90 was partially based upon. All three RIRTs present in the copper block during the e-H_2 VP and ICVGT realizations (B168, B174 and B211) also have calibrations traceable to the NPL-75 scale. Using an average from the RIRTs for temperatures on this T_{75} scale, we determined that at 17.035 K, T_{90}(e-H_2 VP) – T_{75} = 0.16 mK ± 0.28 mK, and T_{90}(ICVGT) – T_{75} = –0.49 mK ± 0.31 mK, where uncertainties are given for k=2. At 20.27 K, we found T_{90}(e-H_2 VP) – T_{75} = –0.08 mK ± 0.28 mK, and T_{90}(ICVGT) – T_{75} = 0.17 mK ± 0.31 mK. While in both cases $|T_{90}(\text{e-H}_2\ \text{VP}) - T_{75}|$ is smaller than $|T_{90}(\text{ICVGT}) - T_{75}|$, both realizations agree with T_{75} to within 0.5



mK at the two temperatures.
Steur and Durieux of Kamerlingh Onnes Laboratorium (KOL) have also used an ICVGT to determine temperatures [12]. In their work, which was performed before the ITS-90 was adopted, they used two calibration points, the first at 4.2 K and the second at 24.5561 K. Their temperature values agree with T_{75} to within 0.6 mK, as do ours [3]. Some of the features of their deviation, $T_{KOL} - T_{75}$, are similar to ours, but not enough to conclude that our results agree better with T_{KOL} than with T_{75}. To our knowledge, no other national laboratory has made recent e-H_2 vapor pressure realizations at 17 K and 20 K with which we can compare our results.





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When calibrating customer SPRTs, NIST has chosen to use the e-H_2 vapor pressure points rather than the ICVGT at 17.0365 K and 20.2682 K. For RIRTs calibrated at NIST, the ICVGT definition of the ITS-90 is used from 5.0 K to 13.8033 K and SPRTs are used as the reference above 13.8033 K. In order to disseminate a unique scale, NIST does not calibrate customer thermometers against the other definitions of the ITS-90 except upon special request.

7. SUMMARY

We have compared three equally valid determinations of ITS-90 temperatures over the range 13.8033 K to 24.5561 K. One determination uses an ICVGT and the other two use SPRTs with different definitions. In one SPRT definition, the 17 K and 20 K calibration points are e-H_2 vapor-pressure points and in the other they are ICVGT points. The maximum non-uniqueness found over the range was 1.55 mK $\pm$ 0.54 mK. This non-uniqueness is an indication of the degree of self-consistency of the ITS-90 in this region. NIST has chosen the e-H_2 vapor pressure fixed points at 17.0365 K and 20.2682 K for its calibration of SPRTs over this range.

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