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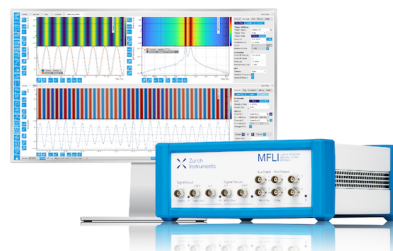
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Realizing the Redefined Kelvin: Extending the life of ITS-90

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Abstract. Following the redefinition of the kelvin, the user is presented with a more nuanced traceability route for temperature through the *mise en pratique* for the definition of the kelvin (*MeP-K-19*). Here we describe research to address several present and potential shortcomings with the current main dissemination route, namely the International Temperature Scale of 1990 (ITS-90). The ITS-90 has served the global temperature measurement community well, providing reliable, low uncertainty traceability for over 30 years. However, there are some potentially life-limiting issues for it. Among these are the impact of the main types (1 and 3) of non-uniqueness which represent an important contribution to the uncertainties achievable with the ITS-90, and the possible need to identify an alternative to the mercury triple point, a key fixed point of the ITS-90 whose use could be banned by an international treaty. Significant progress has been made in addressing these problems through a) new determinations of Type 3 non-uniqueness which have been undertaken in the range -189 °C to 156 °C ; b) a comprehensive evaluation of Type 1 non-uniqueness on a large number of Standard Platinum Resistance Thermometers (SPRTs) across multiple temperature regions; c) comparison of high temperature SPRTs in pressure-controlled heat pipes to characterize Type 3 non-uniqueness between 660.323 °C and 961.78 °C and d) new designs of CO₂ and SF₆ cells for use with long-stem SPRTs. The fixed-point cells have been improved compared to previous versions by using purer gases and more stable and uniform temperature-controlled baths, and by the development of a flexible set-up that can accommodate both capsule and long-stem SPRTs. The effect of replacing mercury on the ITS-90 interpolating equations and uncertainty propagation has also been investigated.

INTRODUCTION

The current temperature scale in use worldwide is the International Temperature Scale of 1990 (ITS-90) [1]. It has been in place since 1990 and has served the global temperature measurement community well, providing reliable, low uncertainty traceability for over 30 years. However, there are several potentially life-limiting issues for it, including the impact of the main types (1 and 3) of non-uniqueness which represent an important contribution to the uncertainties achievable [2,3-6]. There is also a need to identify a possible alternative to the mercury triple point, a key fixed point whose use could be banned by an international treaty, potentially posing an existential threat to the ITS-90.

Following the redefinition of the kelvin [7], the user is presented with a more nuanced traceability route for temperature through the *mise en pratique* for the definition of the kelvin (*MeP-K-19*) [8]. We describe progress in

realizing the redefined kelvin in the context of the European metrology program for innovation and research (EMPIR) Realizing the Redefined Kelvin (Real-K) project [9,10], Work Package 3, the aim of which was to begin to turn the *MeP-K-19* into a reality.

The aim of this activity was to give users continued access to low uncertainty realization of the ITS-90 whilst allowing time for primary thermometry methods to mature. Scale non-uniqueness has been investigated, with the objective of reducing its uncertainty by 30 % [2] through improved determinations of Type 3 non-uniqueness and improved understanding of the impact of measurement error and uncertainty (e.g. double-counting of uncertainties). Possible replacement fixed-points for the mercury triple point have been examined, and the issue of integration within a new temperature scale has been addressed, particularly with regard to uncertainty propagation and non-uniqueness [11-13].

Type 1 non-uniqueness is associated with the difference between the interpolations over different, overlapping ITS-90 subranges for the same SPRT; results have been published [4,13,14-16], mainly for the subrange inconsistency (SRI) between the subranges to the zinc and aluminum points. New results have now been obtained [2]. Type 3 non-uniqueness arises from the difference between individual SPRTs over the same sub-range because of the differences in their resistance characteristics. Here there is a paucity of reliable data, particularly between $-189\text{ }^{\circ}\text{C}$ and $156\text{ }^{\circ}\text{C}$.

The three main candidates for replacing the mercury point (TP Hg, $-38.8344\text{ }^{\circ}\text{C}$) are the triple points of Xe (TP Xe, $\sim -111.744\text{ }^{\circ}\text{C}$) [17], CO_2 (TP CO_2 , $\sim -56.558\text{ }^{\circ}\text{C}$) [18] and SF_6 (TP SF_6 , $\sim -49.595\text{ }^{\circ}\text{C}$) [11]. Investigations so far have mainly been for capsule SPRTs, which is a significant limitation as nearly all commercial calibrations are for long-stem SPRTs. The research described here addresses these problems by performing 1) A comprehensive evaluation of Type 1 non-uniqueness, performed for the first time on a large number of SPRTs; 2) New determinations of Type 3 non-uniqueness which have been undertaken in the range from $-189\text{ }^{\circ}\text{C}$ to $156\text{ }^{\circ}\text{C}$, and between $660.323\text{ }^{\circ}\text{C}$ (FP aluminum) and $961.78\text{ }^{\circ}\text{C}$ (FP silver); 3) New designs of CO_2 and SF_6 cells have been tested with long-stem SPRTs. The effect of replacing mercury in the scale interpolating equations and uncertainty propagation has also been investigated.

In this paper it is noted that the ITS-90 represents a definition and cannot be changed throughout the lifetime of the scale. In very rare cases, amendments might be made. Such amendments must preserve the fundamental things like reference functions and specified temperature values, and it should be avoided if possible.

TYPE 1 NON-UNIQUENESS

A wide-ranging study of Type 1 non-uniqueness (SRI) has been conducted and published by NRC, NPL, IPQ and UL [2] as part of the Real-K project. The study drew on a wide range of data from the EURAMET.T-K9 and CCT-K9 comparisons of SPRTs at the ITS-90 fixed points. In addition, NPL, PTB, NRC and other NMIs provided data from their commercial calibration databases. A comprehensive evaluation of Type 1 non-uniqueness was performed for all pairs of overlapping ITS-90 sub-ranges between $-189.3442\text{ }^{\circ}\text{C}$ (Ar) and $660.323\text{ }^{\circ}\text{C}$ (Al). The SPRTs were representative of manufacturers across the globe. Across all the pairs of overlapping sub-ranges, the mean SRI varied from -1.23 mK to $+0.21\text{ mK}$, and the standard deviation varied from 0.04 mK to 0.62 mK . Both the mean and standard deviation of the SRI exhibited a general increase with increasing temperature; this is particularly pronounced when the lower sub-range requires a fixed point which is not included in the higher sub-range.

To determine the significance of the SRI determinations, the contribution from the uncertainties propagated from the fixed points were also assessed, and it was found that, although the effect of the propagated uncertainty largely cancels out for points common to both sub-ranges, it still accounts for between 59 % and 130 % of the differences between overlapping pairs of sub-ranges. Hence the SRI is probably substantially overestimated since it is convolved with the measurement uncertainty at the fixed points and propagation thereof. The study [2] will help to reduce the uncertainty of Type 1 non-uniqueness as it provides a characterization of this phenomenon over all ITS-90 subranges with an unprecedentedly large and diverse sample of SPRTs drawn from a global dataset, including CCT and regional metrology organization (RMO) key comparison data and commercial calibration data from several leading NMIs.

Table 1 shows a comparison of statistical parameters associated with the SRI (minimum, maximum and mean SRI and the standard deviation) from the current work [2] to those reported in the literature, for the overlapping sub-ranges from the triple point of water (TPW) to FP Zn and TPW to FP Al. All values are in units of mK.

TABLE 1. Comparison of statistical SRI parameters obtained in the current work [2], and in the literature.

Author	Number of SPRTs	Min	Max	Mean	Standard deviation
Peruzzi [2]	15	-0.47	0.70	0.04	0.30
Strouse [13]	13	-0.27	0.40	-	-
Zhiru [14]	58	-0.89	1.00	0.06	0.32
White [4]	60	-0.80	1.70	0.12	0.48
Sun [15]	60	-1.58	0.96	0.20	0.37
Rusby [5]	159	-1.30	1.20	-0.12	0.41

TYPE 3 NON-UNIQUENESS

NPL, CEM and INTiBS have performed comparison measurements on cohorts of up to ten long-stem SPRTs of different manufacture and design. Each cohort comprised at least six locally maintained SPRTs, with two SPRTs which were circulated amongst the participants, to provide linkage between the three local investigations.

The NPL comparisons were carried out in a stirred silicone oil bath at ten temperatures between -95 °C and 30 °C, coupled with measurements at the TP Ar, -189.3331 °C. Similar comparisons were made at CEM at 18 temperatures between 0 °C and 80 °C, coupled with measurements at the freezing point of In (FP In, 156.5985 °C). Finally, comparisons were carried out at INTiBS between -189 °C and 0 °C, coupled with measurements at TP Ar and TP Hg.

The comparisons were made by measuring the ratios R_x / R_{ref} , where R_{ref} is the resistance of an SPRT chosen as the reference, and the R_x ($x = 2$ to 8) are the resistances of the other 7. As the SPRTs have very similar characteristics, these ratios are all close to 1 and are not sensitive to (uniform) changes in the bath temperature. Self-heating corrections were applied. Having measured the ratios R_x / R_{ref} at 0 mA and the resistance R_{ref} at 0 mA, the resistances, and hence the ratios $W(T) = R(T) / R(0.01 \text{ °C})$, and the differences (deviations) $W(T) - W_{ref}(T)$, can all be calculated. These deviations from $W_{ref}(T)$ can now be compared with deviations interpolated using the relevant equations (or the equivalent Lagrange functions) and the deviations at the chosen fixed points.

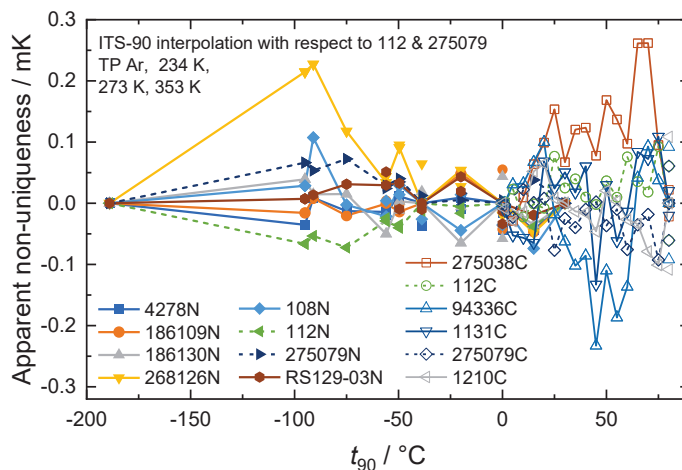


FIGURE 1. Combined results of NPL (from TP Ar to -189 °C) and CEM (from 0 °C to 80 °C).

In Figure 1 the NPL results for the differences between the SPRTs (the apparent non-uniqueness) are merged with those of CEM, both with the baseline of the mean of the two common SPRTs, 112 and 275079. As these two SPRTs agree well with each other, the two sets of results are simply plotted together. ‘N’ against the SPRT serial number refers to NPL, ‘C’ to CEM. The differences measured at INTiBS between -189 °C and 0 °C are unfortunately too large to associate with SPRT non-uniqueness and it seems likely that they are due to systematic but quite repeatable temperature gradients between the SPRTs in the cryostat.

Few, if any, comparisons of long-stem SPRTs have been made so precisely¹, but the measurements reported here still only represent an upper limit, because, in addition to the Type 3 non-uniqueness, they incorporate experimental measurement uncertainty. However, they suggest that an assessment of the Type 3 non-uniqueness uncertainty need be no higher than ± 0.1 mK, at least between -95 °C and 30 °C, rising to ± 0.2 mK at 80 °C.

Additional measurements of Type 3 non-uniqueness are being performed by INRIM between 660 °C and 962 °C by comparing the output of cohorts of high temperature SPRTs (HTSPRTs) in a gas-controlled heat pipe. The HTSPRTs have been calibrated at the fixed points of TPW, Sn, Zn, Al and Ag. Measurements are ongoing.

REPLACING THE MERCURY FIXED POINT

The mercury triple point (TP Hg, -38.8344 °C) is a defining fixed point of the International Temperature Scale of 1990 (ITS-90). It is also a highly toxic heavy metal, and it is conceivable that its use could be banned by an international treaty², potentially posing an existential threat to the ITS-90. Hence there is a need to identify a possible alternative. The three main candidates for replacing the triple point of Hg are the triple points of Xe (TP Xe, ~ 161.406 K or -111.744 °C), CO₂ (TP CO₂, ~ 216.482 K or -56.668 °C) and SF₆ (TP SF₆, ~ 223.555 K or -49.595 °C)³. For Xe and SF₆, investigations have so far been mainly, but not exclusively, for capsule SPRTs, which is a significant limitation as nearly all commercial calibrations are for long-stem SPRTs.

One obstacle to incorporating the Xe, CO₂ and SF₆ fixed points into the temperature scale is the current lack of internationally agreed triple point temperatures with the required uncertainty. The de facto reference temperatures and their standard uncertainties are those reported by Bedford et. al. in 1996 [21] which amount to 161.40596 K ± 0.5 mK, 216.5924 K ± 0.5 mK and 223.554 K ± 5 mK for Xe, CO₂ and SF₆ respectively. For all of these, the determinations of triple point temperature have improved in the last few years. For all three fixed points, the consistency of the most recent measurements (from around 2000 onwards) supports the establishment of an updated consensus value. In particular, the three most recent reported determinations⁴ of the CO₂ triple point temperature fall within a range of 0.4 mK [18,22,23], amounting to 216.5915 K ± 0.0004 K (NPL [23]), 216.5909 K ± 0.00036 K (NMIJ [18]), 216.59136 K ± 0.00037 K (NIM [22]); here the standard uncertainties are given. Determinations of the Xe (161.4060 K ± 0.00032 K, NRC⁵ [24], 161.4058 K ± 0.00027 K, INRiM [25], 161.40579 K ± 0.00029 K, INRIM/NRC⁶ [26]) and SF₆ triple points (223.55523 K ± 0.00049 K, NRC [27], 223.55607 K ± 0.00035 K, NIST [11], 223.55647 K ± 0.00053 K, NMIJ/AIST [28], 223.55603 K ± 0.00054 K, NIM [29] and 223.55545 K ± 0.00055 K (provisional), LNE-Cnam [30]) since 2000 are similarly consistent.

Both the CO₂ and SF₆ triple points have proven to be suitable for use with both capsule SPRTs and long-stem SPRTs, providing adequate immersion⁷. Xe, CO₂ and SF₆ triple points are all suitable for capsule SPRTs where immersion requirements are less demanding. In general, CO₂ and SF₆ fixed-point cells are suitable for use in conventional stirred liquid baths, which most practitioners already have in their laboratories, whereas Xe requires more sophisticated cryogenic apparatus. For this reason, it is anticipated that CO₂ and SF₆ fixed points will be more widely used, as minimal investment is required.

In Real-K, LNE-Cnam have manufactured three new SF₆ triple point cells and constructed a quasi-adiabatic calorimeter to realize them; this system permits simultaneous calibration of both long-stem and capsule SPRTs (Figure 2). In addition, LNE-Cnam, in cooperation with SMU, have characterized the solid–liquid transition of the SF₆ cells with both long-stem and capsule SPRTs, to verify the equivalence between the quasi-adiabatic and fully

¹ Long-stem and capsule SPRTs have similar platinum elements, but the difference is that capsule SPRTs can be compared very precisely, whereas it is very difficult to compare the large and ungainly SPRTs.

² Minamata Convention: <https://mercuryconvention.org/en>

³ However, SF₆ is itself not immune from potential restrictions on its availability in the future. The Intergovernmental Panel on Climate Change (IPCC) considers it to be the most potent greenhouse gas that has been evaluated, with a global warming potential of 23,900 times that of CO₂ when compared over a 100-year period [19], with an estimated atmospheric lifetime of between 800 and 3,200 years [20].

⁴ There are some measurements reported before this that are also consistent with the most recent ones.

⁵ The NRC value from 2020 [17] was obtained with refractive index gas thermometry to measure the thermodynamic temperature T at the T_{90} temperature that was previously determined by the 2005 realization [21].

⁶ Deduced from the difference between the INRIM and NRC cells.

⁷ Tew et. al. [11] demonstrated the conditions under which adequate immersion can be achieved in SF₆ cells suitable for long-stem SPRTs, and that the plateau values from two immersion cells, with different immersion characteristics, were equivalent to those plateaus observed using adiabatic-style cells. Maintaining adequate immersion in a non-metal such as CO₂ or SF₆ is significantly more difficult than for metal or water cells, due to the tendency of the solid mantle to disintegrate during melting. The development of techniques for refining the solid crystals, to remove the lattice distortions, are needed for the larger (i.e. designed for long-stem SPRTs) cells of both SF₆ and CO₂. Mitigating techniques are, however, now well established, at least for adiabatic-style cells (see e.g. Kawamura et. al. [18,28]). The application of those techniques to the larger cells for long-stem SPRTs needs to be further developed.

adiabatic realizations (the thermal environment has been reported as being a major contribution to the measurement uncertainty) and to determine the thermodynamic temperature of the triple point of the SF₆ cells with capsule SPRTs calibrated against an acoustic gas thermometer.

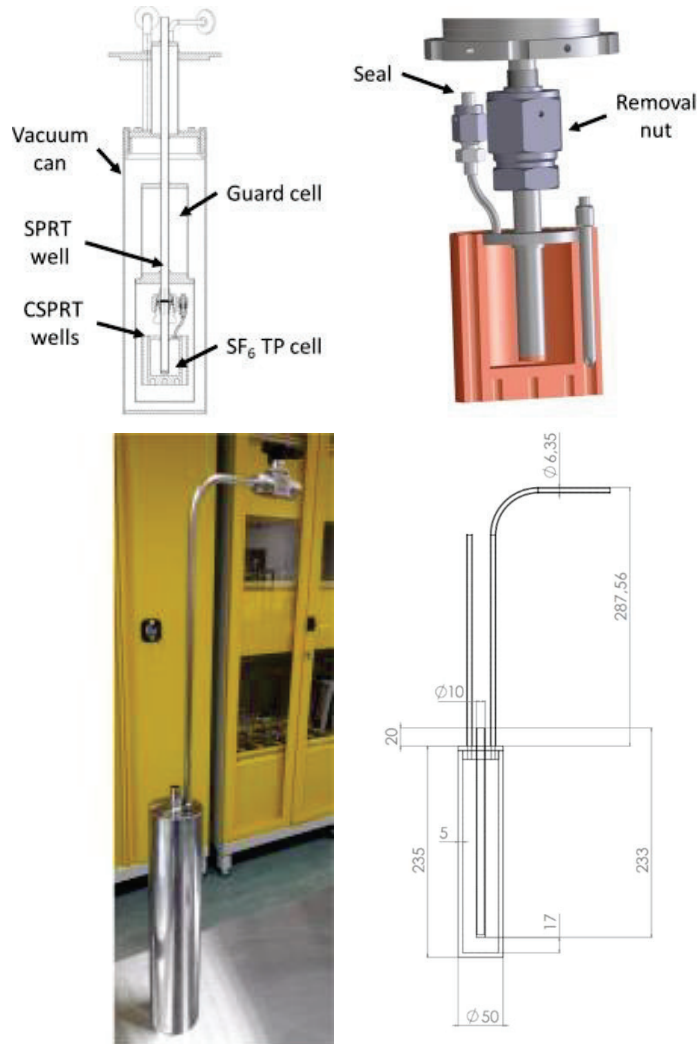


FIGURE 2. Top left: Calorimeter for simultaneous calibration of long-stem and capsule SPRTs developed at LNE-Cnam. Top right: SF₆ triple point cell of LNE-Cnam. Bottom: CO₂ cell of TUBITAK/UME.

It has been found that the same SF₆ cell installed either in a quasi-adiabatic system or in a fully adiabatic one, can provide compatible SF₆ triple point realizations. However, further measurements are necessary to validate this hypothesis. The graphs in Figure 3 suggest that the measurements carried out with CSPRTs in the fully adiabatic system and in the quasi-adiabatic one are compatible within about 1 mK. It is also apparent that CSPRT measurements do not seem to be significantly affected by the presence, or not, of a long-stem SPRT in the central well, meaning that the heat flow brought by the SPRT has a relatively small contribution on the evolution of the phase transition. On the other hand, temperatures measured by the long-stem SPRT appear to be higher than those of CSPRTs, by approximately 2 mK. That might be an effect of heat conduction along the SPRT stem, which is not sufficiently thermally anchored to the cell. The number of triple point realizations is however rather small at this stage, and new measurements are in progress to confirm these hypotheses.

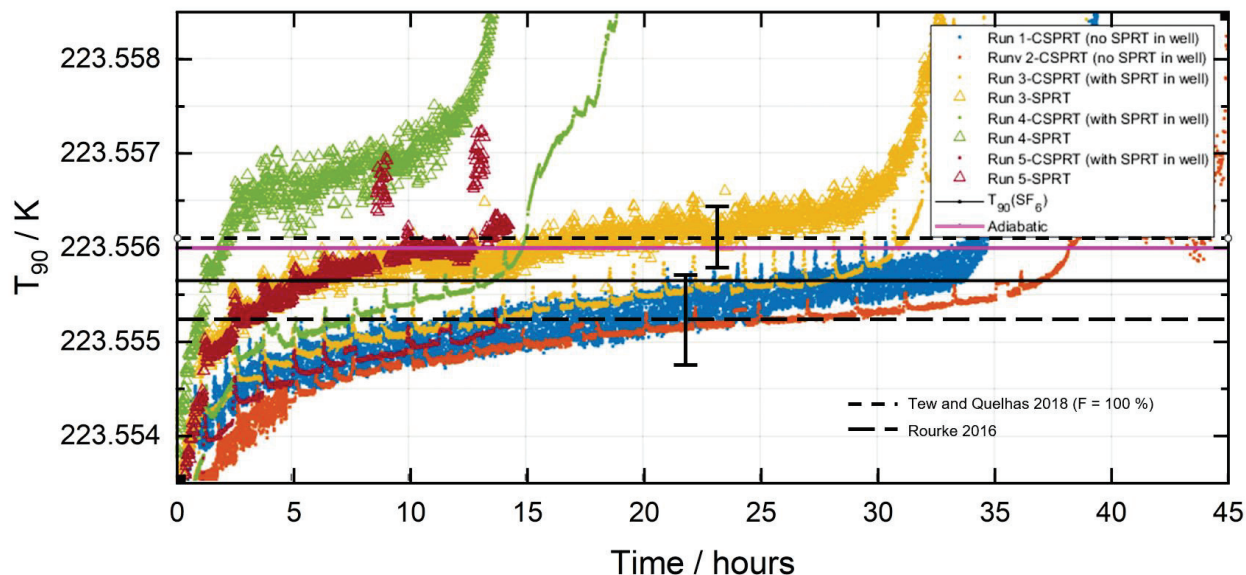


FIGURE 3. SF₆ triple point realizations carried out with the quasi-adiabatic system developed at LNE-Cnam using a CSPRT (dots) and long-stem SPRT (triangles). Solid magenta line is temperature measured with the same cell in a fully adiabatic calorimeter. Solid black line is temperature of the SF₆ triple point calculated as an average of the those measured in [11,27], which are expressed separately as short-dashed line and long-dashed line, respectively.

TUBITAK have manufactured two new CO₂ triple point cells to be realized in a stirred ethanol bath (Figure 2). The stainless steel cell was designed to have two tubes for accessing the main volume in which the CO₂ is located. Each tube can be closed with Swagelok valves. One valve was used for filling, while the second one was used to enhance the rate at which cleaning solvents and subsequent flushing could be performed, in order to optimise the cleaning process. A getter (purifier) was introduced to the CO₂ cell filling system and a chemical analysis was performed on samples of the gases used to fill the respective cells (gas chromatography with discharge ionization detector, GC-DID, was used for the CO₂); this is shown in Table 2. The getter proved effective at trapping O₂, but not other impurities such as H₂, Ar, N₂, CH₄ and CO. The plateau range amounted to about 0.3 mK, with plateau duration more than ten hours. The repeatability amounted to around 0.15 mK; with the more highly purified samples performing slightly better. The overall expanded uncertainty of calibration using the new CO₂ fixed points amounts to about ±0.5 mK (coverage factor $k = 2$, corresponding to 95 % coverage probability); an outline uncertainty budget is shown in Table 3. This uncertainty budget only pertains to the realization of the CO₂ cell using an SPRT and does not include the uncertainty of the triple point temperature or the scale non-uniqueness contributions.

TABLE 2. Impurities detected in the TUBITAK CO₂ cell.

Component	Concentration (mol mol ⁻¹)	Standard uncertainty (mol mol ⁻¹)
Hydrogen	4.43 x 10 ⁻⁸	4.17 x 10 ⁻¹⁰
Argon	1.04 x 10 ⁻⁷	3.48 x 10 ⁻⁹
Oxygen	4.42 x 10 ⁻⁷	7.79 x 10 ⁻⁸
Nitrogen	1.36 x 10 ⁻⁶	1.19 x 10 ⁻⁷
Methane	6.94 x 10 ⁻⁸	2.44 x 10 ⁻⁹
Carbon monoxide	1.37 x 10 ⁻⁷	1.87 x 10 ⁻⁹

TABLE 3. Uncertainty budget for realization of the TUBITAK CO₂ cell using an SPRT.

Uncertainty contribution	Standard uncertainty / mK
Phase transition realization repeatability	0.09
Resistance bridge (repeatability, non-linearity, AC quadrature)	0.02
Reference resistor stability	0.01
Plateau determination	0.10
Chemical impurities	0.15
Hydrostatic head correction	0.03
Propagated uncertainty at the triple point of water	0.08
SPRT self-heating correction	0.03
Heat flux effects	0.10
Combined standard uncertainty	0.25
Expanded uncertainty (coverage factor $k = 2$)	0.50

SMU and NPL have investigated how the fixed-point uncertainties propagate in the ITS-90 sub-range to the TP Ar when TP Hg is replaced with either TP SF₆, TP CO₂ or TP Xe, or with the melting point of gallium, MP Ga, 29.7646 °C. The propagation of uncertainties (or errors) for the TP Hg and for all the candidate replacement fixed points when the interpolation uses the ITS-90 Eq. 13 (as now) is largest when TP Hg is replaced with TP Ga, followed by (in order of decreasing propagated uncertainty) Hg, SF₆, CO₂, Xe. Using a simple quadratic (ITS-90 Eq. 14) instead results in a significant reduction of the propagated uncertainties and reduces the disparity between the different cases, except in the case of Xe which is almost unchanged. This is shown in Figure 4.

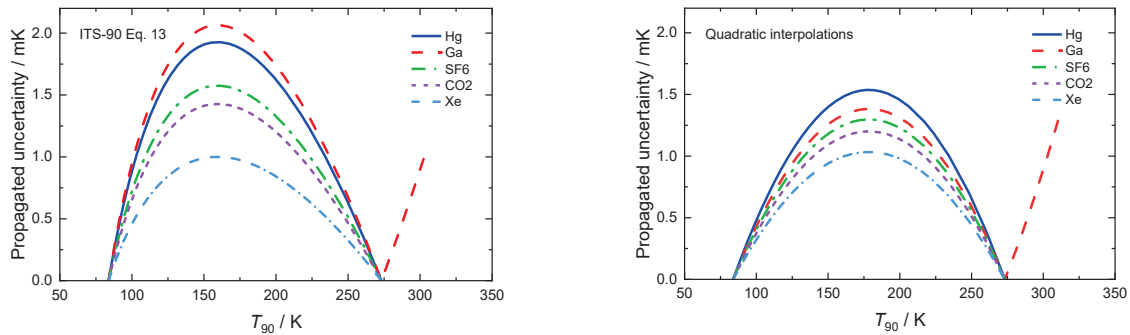


FIGURE 4. Propagation of 1 mK errors at the triple point of mercury and at possible replacement points, the triple points of SF₆, CO₂, Xe, and the melting point of Ga, using the ITS 90 Eq. 13 (left) and Eq. 14 (a simple quadratic, right). In each case the modulus of the error is shown.

As a theoretical exercise to assess possibilities for a future temperature scale, NPL is also investigating alternative interpolations for long-stem SPRTs in which the subranges currently specified in the ITS-90 are extended below the triple point of water without including the mercury point or any replacement for it. Figure 5 shows how cubic interpolations in ($W-1$) which require only $W(\text{Ar})$, $W(\text{Sn})$ and $W(\text{Zn})$ compare with the ITS-90 as defined over this subrange. The data are for 11 SPRTs which participated in the Key Comparison CCT-K9. Above TPW the interpolations are closely bunched together, but there is a bias in the mean values of $\pm \sim 0.25$ mK. At TPW the discontinuity in the first derivative in the ITS-90 caused by the inconsistency between the TP Hg and subranges above TPW is clear to see, and this propagates to an average difference of ~ 1 mK at ~ 113 °C. It is suggested that this and similar equations could, in a future temperature scale, enable simplified interpolations over the full range of use of long-stem SPRTs, without incurring the inconsistencies associated with the mercury point.

A further conclusion arising from this study was that any of the Xe, CO₂ or SF₆ triple points could successfully replace the mercury point, and the choice should be based on their utility, realization uncertainty, and their location in the subrange. The realization uncertainties of the alternative fixed points are likely to be larger than those for the

mercury point, but the propagation of the uncertainties would in all cases be somewhat lower [8,10]. On the other hand, very low uncertainties can be achieved at the melting point of gallium but, being an out-of-range point, the uncertainty propagates poorly.

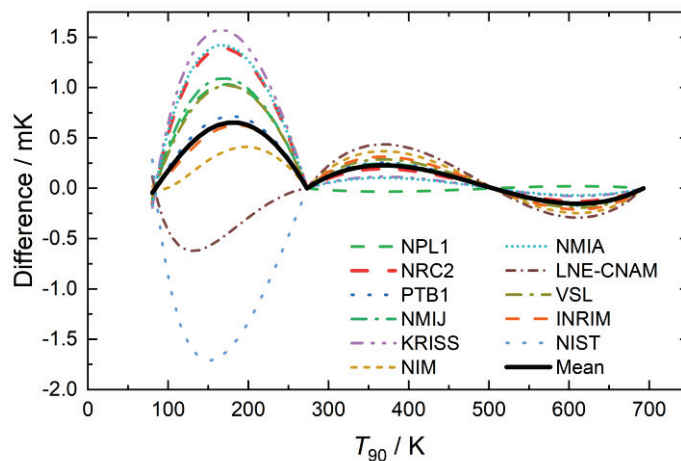


FIGURE 5. Comparison of cubic interpolations in ($W-1$) between TP Ar and FP Zn (using only TP Ar, FP Sn and FP Zn) relative to the ITS-90 as defined using data from CCT-K9.

CONCLUSION

In this paper research has been described that addresses several present and potential shortcomings with the ITS-90. Progress in addressing these problems were described through: a) New determinations of Type 3 non-uniqueness which have been undertaken in the range $-189\text{ }^{\circ}\text{C}$ to $156\text{ }^{\circ}\text{C}$ by direct comparison of SPRTs in stirred liquid baths; b) a comprehensive evaluation of Type 1 non-uniqueness on a large number of Standard Platinum Resistance Thermometers (SPRTs) across multiple regions using data from CCT Key Comparisons and local calibration databases; c) comparison of high temperature SPRTs in pressure-controlled heat pipes to characterize Type 3 non-uniqueness between $660.323\text{ }^{\circ}\text{C}$ and $961.78\text{ }^{\circ}\text{C}$; d) new designs of CO_2 and SF_6 cells for use with long-stem SPRTs.

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