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# A further look at type 1 non-uniqueness in the international temperature scale of 1990 above 273.16 K

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# A Further Look at Type 1 Non-Uniqueness in the International Temperature Scale of 1990 above 273.16 K

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**Abstract.** This paper is concerned with the sensitivity of Type 1 non-uniqueness (subrange inconsistency, SRI) to errors in the measurements of Standard Platinum Resistance Thermometers (SPRTs) at the fixed points of the International Temperature Scale of 1990, ITS-90, specifically on pairs of interpolations from the triple point of water (TPW, 273.16 K) up to the freezing points of zinc (FP Zn, 692.677 K) and aluminum (FP Al, 933.473 K). It follows on from a recent survey of SRI, which showed that propagation of uncertainty (error) could be responsible for much of the apparent SRI in using long-stem SPRTs above the triple point of water. The paper considers five possible sources of SRI, related to the definitions and specifications of the scale, the quality of the platinum wires, changes in the SPRT characteristics during calibration and the uncertainties of the measurements themselves. While some systematic offsets in the interpolations are caused by 'scale-intrinsic' SRI, it is clear that in most cases the two experimental sources dominate the SRI, as measured. It is suggested that the scale-intrinsic SRI, which is caused by the ITS-90 specifications rather than as an artefact of the calibration, is best estimated from the mean values of the SRI for groups of SPRTs, but that the standard deviations of historic data do not provide reliable estimates of extrinsic, SPRT-dependent SRI, because they themselves were predominantly due to similar measurement uncertainties, which should not be transmitted to subsequent budgets.

## INTRODUCTION

Non-uniqueness in Standard Platinum Resistance Thermometer (SPRT) calibrations is the term given to differences which arise when a given SPRT is calibrated in different allowed subranges of the International Temperature Scale of 1990, ITS-90 [1], (Type 1 non-uniqueness, or subrange inconsistency, SRI); or to the differences between two or more SPRTs which have been identically calibrated in the same subrange (Type 3 non-uniqueness). Both these types of non-uniqueness are constrained to be zero at the fixed points of the scale which are common to both interpolations, and they typically increase to a peak in the intervals between the fixed points. The ITS-90 was designed so that both types would be small, as far as could be ascertained at the time. (Type 2 non-uniqueness occurs when different allowed interpolation instruments are compared, and does not concern us here.)

Type 3 non-uniqueness is difficult to determine because it requires that a number of SPRTs are compared with high precision at many temperatures within the subrange. For capsule-type SPRTs this can conveniently be done by inserting them into a small copper comparison block in a cryostat whose temperature can be closely controlled as required. Several important sets of data have been produced, which were extensively used in the formulation of the ITS-90 [2] and its later evaluation [3]. This is fortunate, as the interpolations must account for the effects due to impurities and crystal defects in the platinum wires which are variable and become increasingly significant compared with the ideal resistivity of pure platinum, and hence lead to potential non-uniqueness, especially at temperatures below about 50 K.

For long-stem SPRTs (L-SPRTs) which are primarily used above the triple-point of water (TPW, 273.16 K) but often also down to the triple-point of argon (TP Ar, 83.8058 K), the additional resistivities due to impurities and crystal defects in the wires are less variable and Type 3 non-uniqueness in the ITS-90 can be expected to be less significant. However, this is not easily verified, because L-SPRTs are designed to be inserted into furnaces, and the platinum coils are near the closed end of a long silica or steel tube, with the leads emerging through seals at room temperature [4].

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They are therefore quite bulky and it is not easy to assemble a group of L-SPRTs in a temperature-uniform block for precise comparisons. Nevertheless, good comparisons have been made in stirred liquid baths over modest temperature ranges, from ~178 K to 353 K [5], in heat-pipe comparators at much higher temperatures [6], and also at specific temperatures by making measurements at additional 'redundant' fixed points [7], but the coverage and quality of the non-uniqueness data are variable.

Determining the Type 1 non-uniqueness (subrange inconsistency, SRI), by contrast, is in principle relatively simple and requires only that the SPRT is measured at the necessary fixed points, and that the interpolations expressing ($W$ - $W_{\mathrm{ref}}$) as a function of $W$ are derived and compared. In general, if there are incompatibilities between the specified values of $W_{\mathrm{ref}}$, this will lead to a 'scale-intrinsic' SRI, which is systematic and therefore the same for all SPRTs. On the other hand, incompatibilities in the $W$-values measured at the fixed points will produce SPRT-dependent 'extrinsic' SRI, though in this case the situation is complicated by the effects of measurement error.

Considerable banks of calibration data have been acquired and results from several NMIs have been published [8-12] for the most significant case, the SRI between the subranges from TPW to the Zn and Al points, here designated SRI[Zn:Al], which requires only the commonly-made measurements at the freezing points of tin, zinc and aluminum (FP Sn, Zn and Al). The data show that the average peak SRI for L-SPRTs (which occurs near 366 K) is quite small, from ~-0.1 mK to ~0.3 mK, but that there is a substantial dispersion of the values about this mean, the standard deviations being typically 0.3 mK to 0.5 mK.

The situation for SRI[Sn:Zn], which has not been so widely studied, is rather different, because the subrange to FP Sn requires that the FP In is measured, whereas the subrange to FP Zn does not. The consequence of this is discussed later.

In a recent survey of all 16 possible pairs of interpolations between the TP Ar and the FP Al [13] it was found that there was often a significant non-zero mean SRI, such as would occur if some of the ITS-90 reference resistance ratios, $W_{\mathrm{ref}}$, are not fully compatible. The survey also established that the propagation of the uncertainties, or errors, in the measurements at the fixed points, could cause much, if not all, of the extrinsic, SPRT-dependence in the data. This suggests that the scale-extrinsic SRI, the quantity of interest, may be hidden beneath the measurement uncertainties.

This paper first identifies five different possible sources of SRI. It examines the sensitivity of SRI to unit (1 mK) errors in the fixed point measurements, contrasting the results for SRI[Zn:Al] and SRI[Sn:Zn], and then discusses other sources of SRI. Finally, it draws some conclusions about how SRI can be treated in uncertainty budgets for realizations of the ITS-90 (calibrations of L-SPRTs).

## SOURCES OF SRI

The five sources of SRI considered here are:

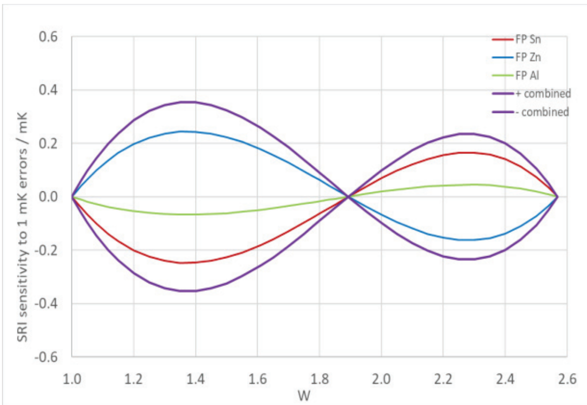
- Incompatibilities between the $W_{\mathrm{ref}}$ values specified in the ITS-90
- Differences arising from the interpolations specified
- Differences due to variations in the samples of platinum wire used
- Changes in SPRT characteristics during the calibration
- Propagation of errors in the measurements at the fixed points.

The first two are 'scale-intrinsic', meaning that they stem from the definitions of the ITS-90. They apply equally to all SPRTs and cause a systematic contribution to the SRI for the pair of subranges. Thus if there is an unexplained offset in the SRI for a group of SPRTs, it may be questioned whether one or more of the $W_{\mathrm{ref}}$ values were correctly chosen, or whether the particular mathematical interpolations were not ideal, due to the choice of equations or the spacing of the fixed points, or both. The third source of SRI can arise from Type 3 non-uniqueness, due to variations in the resistivity characteristics of the SPRTs. Although this principally applies to individual SPRTs, such variations in characteristic may affect the differences between pairs of subranges, and hence the SRI. Finally, the fourth and fifth sources of SRI, are concerned with the experimentation, which inevitably incurs error and uncertainty. This not only applies to the measurement process itself (the fifth source), but also to the behavior of the SPRT during the calibration (the fourth). As it has been found that the effects of uncertainties can account for a significant proportion of the SRI, we should more properly refer to extrinsic SRI as 'apparent SRI'.

All except the third source originate from errors in measured values of $W$ or specified values of $W_{\mathrm{ref}}$, but before examining them further we need to establish the sensitivity of the SRI to such errors.

## SENSITIVITY OF SRI TO ERRORS IN THE FIXED-POINT MEASUREMENTS

The sensitivity curves have been derived from the differences between the propagated 1 mK errors in each subrange for each fixed point involved, and combining them in quadrature (assuming that they are independent). Figures 1 and 2 show the results for the most commonly studied SRI[Zn:Al] and for SRI[Sn:Zn].



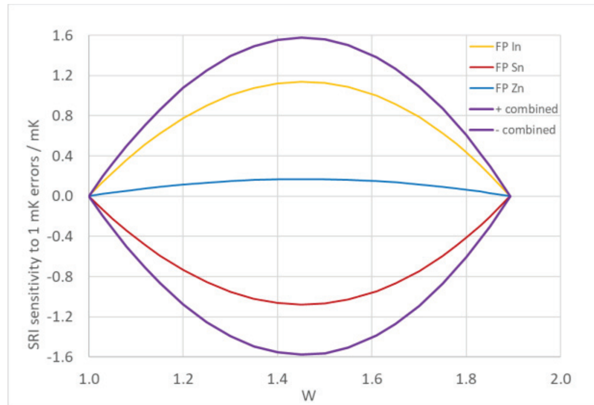



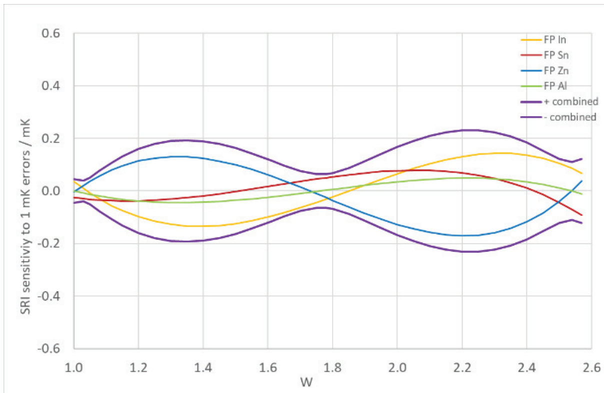

**FIGURE 1** (left) Sensitivity of SRI to 1 mK errors in each fixed point used, for SRI[Zn:Al], and **FIGURE 2** (right) the same for SRI[Sn:Zn].

Figure 1 shows that the effect of the errors in the fixed points in SRI[Zn:Al] is strongly attenuated: only about 25 % of the errors in the tin and zinc points, and 10 % of the error in the aluminum point, appears in the SRI. Overall, the SRI for 1 mK errors is expected to be less than 0.4 mK though, of course, individual cases may exceed this. The published data show mean peak SRI values ranging from ~-0.1 mK to ~0.3 mK [8-12], which implies that the ITS-90 values for $W_{\mathrm{ref}}$(Sn) and $W_{\mathrm{ref}}$(Zn) values are consistent within about half of the 1 mK values assumed in Figure 1. The survey by Peruzzi et al [13], based on data for 15 SPRTs from NRC and PTB, gave a mean peak value of 0.04 mK, which would suggest consistency nearer ±~0.1 mK); the standard deviation of the dispersion in the SRI was 0.3 mK, which implies an incompatibility, principally between the measured $W$(Sn) and $W$(Zn) values , within ~ ±0.75 mK (0.3/0.4 mK).

The situation is rather different in Figure 2, mainly because in this case FP In (at 429.7485 K) is included in one subrange but not the other, so there is no compensation of its error in the SRI. Moreover, $W$(In), at ~1.6, is quite close to $W$(Sn), at ~1.9, so any incompatibility between the two points (in the values of $W$ or $W_{\mathrm{ref}}$) will have a large leverage in the curve, which then rises to a peak in mid-range, before coming back to zero at TPW. The FP Zn has little effect, but overall there is an amplification of the combined 1 mK errors to a maximum of ~1.6 mK. In the Peruzzi survey the mean peak SRI (for 65 SPRTs) was 0.68 mK, and Figure 2 suggests that this could result from an incompatibility between the $W_{\mathrm{ref}}$(In) and $W_{\mathrm{ref}}$(Sn) values of as much as 1.1 mK (0.68 x 1.6 mK). The dispersion of the SRI about the mean was 0.58 mK, suggesting that the measured $W$(In) and $W$(Sn) values could be incompatible by about 0.9 mK (0.58 x 1.6 mK).

In connection with these subranges, it has been suggested, most recently by Žužek [12], that the interpolations would usefully be improved if least-squares fitting is used, with FP In included in all these subranges. Figure 3 shows that including FP In reduces the sensitivity in the lower part of the range to a peak of ~0.2 mK, but has little effect on the peak at $W$ ~ 2.3. In Figure 4 a more significant reduction is seen, from a peak of ~1.6 mK to ~1.0 mK, as the curve is now not forced through the In and Sn points, but can pass between them. (Note that Žužek *et al* also included MP Ga, but this is quite close to TPW and it is not clear that it contributes much, especially as they also forced the curves to pass through 0 at TPW.)

These least-squares interpolations do not, of course, change the previous analysis of the possible inconsistences in the assigned $W_{\mathrm{ref}}$ values, because if Peruzzi *et al* had used these interpolations, they would have found lower SRI, as in these figures. Inconsistences in 'redundant' points, such as FP In with respect to the ITS-90, can be deduced more directly by substitution in the subranges to the Zn or Al points.



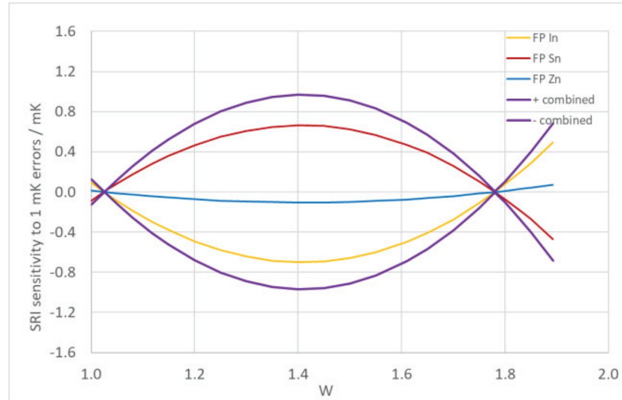



**FIGURE 3** (left) Sensitivity of SRI to 1 mK errors using a least-squares quadratic fit to the freezing points of In, Sn and Zn with respect to a cubic fit to In, Sn, Zn and Al. **FIGURE 4** (right) shows the same for the ITS-90 quadratic to the In and Sn points with respect to a least-squares quadratic to the In, Sn and Zn points. These figures should be compared with Figures 1 and 2.

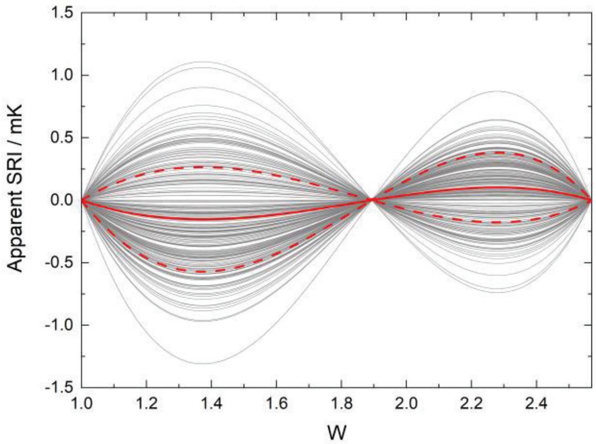
## EXTRINSIC SOURCES OF SRI

The third source of SRI can arise from Type 3 non-uniqueness, due to variations in the resistivity characteristics of the SPRTs, which may affect the differences between pairs of subranges, and hence the SRI. Although the temperature-dependence of the resistivity of platinum is a complex phenomenon which has not been calculated accurately, still less the effect of impurities and crystal defects, it is known that the non-idealities lead to additional components of resistivity which are to a first approximation independent of temperature (Matthiessen's Rule), except for temperatures below ~50 K. Thus, for a constant extra component of resistance δR, the resistance ratio $R_T/R_{TPW}$ becomes $(R_T + \delta R)/(R_{TPW} + \delta R)$. This lowers the temperature coefficient of resistance and it follows that the leading ITS-90 calibration coefficient *a* is also lower for more degraded platinum.

On the other hand, it has been shown [8] that the SRI[Zn:Al)] is given by $(W\text{-}1)(W\text{-}W_{Sn})(W\text{-}W_{Zn})c$, where *c* is the coefficient of the cubic term in the calibration. Thus the SRI is constrained to pass through zero at the fixed points and scales with *c*. Figure 5 shows the apparent SRI for over 150 SPRTs calibrated at NPL between the TPW and the freezing point of aluminum and published some years ago [10]. The mean value (shown by the red line) reaches a peak of ~-0.1 mK near $W = 1.35$, but there is considerable dispersion between the individual SPRTs. The standard deviation of this dispersion (indicated by the dotted red lines) is ±0.41 mK at the first peak. Several other National Measurement Institutes have published similar results, with standard deviations ranging from 0.3 mK to 0.5 mK [8-12].

Figure 6 shows the result of plotting *c* versus *a*, to see if there is a correlation between them, and so indicate whether the SRI is correlated with the quality of the platinum wires and hence the Type 3 non-uniqueness. It is hard to see such a correlation: the data are scattered seemingly at random, apart from a cluster of Tinsley SPRTs which have low *c*- and *a*-values. These cause the 'trendline' to have a small positive slope, which otherwise is almost level. Consequently, we conclude that the quality of the platinum wires does not have a significant effect on this SRI or presumably others, above the TPW.

This brings us to the fourth and fifth sources of SRI, which are concerned with the experimentation, and inevitably incur error and uncertainty. This not only applies to the measurement process itself (the fifth source), but also to the behavior of the SPRT during the calibration (the fourth). It is well known that SPRTs suffer from the effects of the temperature cycling, due to stress in the wires and reversible or irreversible oxidation, and if these are not sufficiently controlled the changes in characteristic will lead to SRI, by an unpredictable amount. However, time pressures do not often permit investigation of such effects during routine SPRT calibrations.



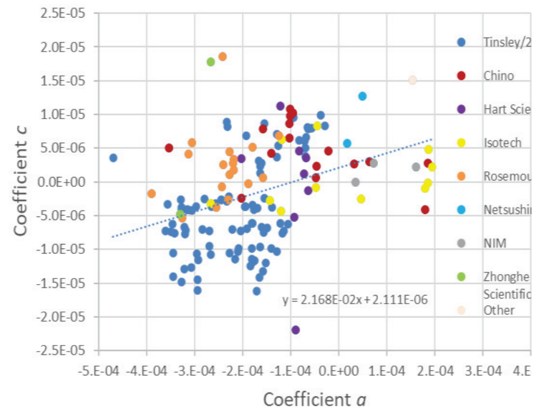




**FIGURE 5** (left) data for the apparent SRI[Zn:Al] for over 150 L-SPRTs accumulated at NPL, and **FIGURE 6** (right) scatter-plot of the coefficients $c$ versus $a$.

## CONCLUSIONS

Five sources of Type 1 Non-uniqueness (Subrange Inconsistency) have been examined, of which two are 'scale intrinsic' and cannot be removed without an amendment of the ITS-90. Chief among these above TPW is the apparent inconsistency between the adopted value for $W_{ref}$(In) compared with $W_{ref}$(Sn), which we infer is responsible for the bias in the SRI[Sn:Zn] in [13]. The third source is SRI due to differences in the quality of the platinum wires used, but positive evidence of this was not found in the set of data investigated.

The two other sources are both experimental and subject to uncertainties: that due to the behavior of the SPRT during calibration, and the propagation of measurement errors. These jointly contribute to the dispersion of SRI data between SPRTs, as in SRI[Zn:Al], Figure 5. The standard deviations of the dispersions can be quite large (~0.3 mK to 0.5 mK have been reported). However, the propagated uncertainties of the calibrations account for much of the effect, estimated in [13] to be about 60 % for this SRI, and up to 100 % or more for other pairs of subranges.

The question arises as to whether, or how, components of uncertainty can be recommended for SRI. It seems necessary to treat the cases of intrinsic and extrinsic SRI differently. For the intrinsic SRI, the mean values reported by Peruzzi et al [13] are systematic offsets of up to -1.23 mK in cases where FP In is used in just one of the subranges, but less than -0.31 mK in other cases). We note that these and other mean offsets could provide a useful basis for investigating the internal consistency of the $W_{ref}$ values adopted in the ITS-90 for the fixed points above TPW.

Given the dominance of experimental uncertainties in the determination of the (apparent) extrinsic SRI, it seems that adopting the dispersion of SRI data in historic studies as the basis for the uncertainty component for the SRI is unwarranted. Similar arguments apply to determinations of Type 3 non-uniqueness, where the uncertainties are such that only upper limits for the effect can be deduced, see [5] for example. In Figure 13 of the Guide to the Realization of the ITS-90, Chapter 5 [4], large Type 1 and Type 3 non-uniqueness components are combined with the uncertainties ascribed to a state-of-the art SPRT calibration, with the result that non-uniqueness is the dominant component in the peak uncertainties between the fixed points, which are almost doubled. We believe that this is excessive because it makes no allowance for the errors and uncertainties inherent in the historic SRI determinations.

With regard to subranges where FP In is used, on its own or coupled with FP Sn, if the results of [13] are substantiated, we suggest that the Guide should note that these subranges are subject to significant uncertainties and are not recommended for use where the highest compatibility within the ITS-90 is required.

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