An evolutionary approach to updating the International Temperature Scale

Hill, Kenneth D (Ken)

Publisher's version / Version de l'éditeur:
https://doi.org/10.1063/1.4821373
Temperature : Its Measurement and Control in Science and Industry, 8, pp. 71-80, 2012-03-23

An Evolutionary Approach To Updating The International Temperature Scale

Kenneth D. Hill

National Research Council of Canada, Ottawa, Ontario, Canada

Abstract. Since its inception in 1927, the International Temperature Scale has been updated at approximately 20-year intervals to meet the needs of the time: the selection of fixed points and their assigned temperatures have changed, defining instruments have been added and deleted, and the equations have also changed, particularly for the temperature range defined by the platinum resistance thermometer. After presenting the historical development of the PRT-portion of the ITS, a proposal is made to update the ITS-90 in order to achieve closer accord with thermodynamic temperature.

Keywords: International Temperature Scale, ITS-90, platinum resistance thermometer, PRT, thermodynamic temperature.

INTRODUCTION

Since its inception in 1927, the International Temperature Scale (ITS) has changed to meet the needs of the time in a predictable, evolutionary fashion. Occasionally, the changes to its basic formulation might be considered (by some) to be revolutionary. The ITS protocol specifies phase transitions with assigned temperatures (defining fixed points), defining instruments (thermometers), and interpolating (or extrapolating) equations. Over time, the selection of fixed points and their assigned temperatures have changed, defining instruments have been added and deleted, and the equations have also changed. The discussion to follow will focus solely on the portion of the ITS for which the platinum resistance thermometer is the defining instrument.

Over the 22 years since its introduction, the ITS-90 has served its user community well. However, it departs from thermodynamic temperature more than is desirable and also suffers from a slope discontinuity at the triple point of water. These shortcomings can be addressed through an evolutionary change that maintains the mathematical structure of the ITS-90 while updating the reference temperatures of the defining fixed points and the coefficients of the reference functions. This route to ITS-20XX merits consideration due to the relatively modest requirements for its promulgation.

HISTORY OF THE ITS

The capabilities of the platinum resistance thermometer (PRT) were demonstrated by H. L. Callendar in his 1887 publication "On the Practical Measurement of Temperature: Experiments Made at the Cavendish Laboratory, Cambridge" [1] in which he compared a PRT to a gas (air) thermometer. Callendar emphasized the practical nature of the PRT, and stated "There is, in fact, hardly any experimental investigation in which the measurement of temperature is necessary, which may not be more accurately and simply effected by means of a platinum wire thermometer." In 1899, Callendar published his "Proposals for a Standard Scale of Temperature based on the Platinum Resistance Thermometer" [2]. His motivation was expressed as: "The following proposals are submitted in consideration of the importance of adopting a *practical* thermometric standard for the accurate verification and comparison of scientific measurements of temperature. The gas-thermometer, which has long been adopted as the *theoretical* standard, has given results so discordant in the hands of different observers at high temperatures, as greatly to retard the progress of research." The proposed interpolation formula was a quadratic equation in temperature with three calibration points: the melting point of ice (0 °C), the normal boiling point of water (100 °C), and the normal boiling point of sulfur (444.53 °C). He notes that "It may be desirable in special cases to make subsidiary tests at other points, such as the B.P. of oxygen, or the F.P. of silver". Deterioration of the electrical insulation and strain of the wire are among the problems Callendar mentions as becoming increasingly important as temperature increases toward (or exceeds) 1000 °C.

Quinn [3] and Hall [4] give accounts of the events following Callendar's proposal that led to the adoption of the International Temperature Scale (ITS) in 1927 by the Seventh General Conference on Weights and Measures (CGPM). An English version of the text of the ITS-27 was published by Burgess [5] in 1928 in the Bureau of Standards Journal of Research. From 0 °C to 660 °C, ITS-27 is nearly identical to Callendar's proposal: the form of the equation is a quadratic with coefficients determined from calibration at the ice point (0 °C), boiling point of water (100 °C), and boiling point of sulfur (440.60 °C, not the value proposed by Callendar):

$$R_t = R_0\,(1 + At + Bt^2) \qquad (1)$$

Temperatures from -190 °C to 0 °C are determined from an equation proposed by Van Dusen in 1925 [6]:

$$R_t = R_0\,[1 + At + Bt^2 + C\,(t - 100)\,t^3\,] \qquad (2)$$

The coefficient of the cubic term is determined from calibration at the boiling point of oxygen (−182.97 °C). We will not concern ourselves here with the definition of the ITS-27 above 660 °C where it is defined by thermocouple and radiation thermometry.

The Consultative Committee for Thermometry (CCT) was created in 1937 and met for the first time in 1939. At this meeting, a revision of the ITS-27 was agreed but war intervened and the revision could not be approved by the CGPM until 1948. The lower limit of the International Temperature Scale of 1948 (ITS-48) [7-9] increased to −182.97 °C (the oxygen boiling point) because the extrapolation proved to be unreliable. The upper limit of the PRT-defined portion of the scale was reduced from 660 °C to 630.5 °C (freezing point of antimony). The interpolation equations and temperature assignments of the fixed points (oxygen, ice, steam, sulfur) remained the same. The purity of the platinum was further restricted (R_{100} / R_0 > 1.3910; for ITS-27, the requirement was R_{100} / R_0 > 1.390). The "degree Celsius" replaced "degree Centigrade" at this time.

With the International Practical Temperature Scale of 1948, Amended Edition of 1960 (IPTS-48) [10], the triple point of water replaced the ice point and the zinc freezing point (419.505 °C) became a recommended alternative to the sulfur boiling point (which remained a defining fixed point). The purity required for the platinum wire was increased once again, the limiting criterion being $R_{100} / R_0 > 1.3920$.

Though the ITS had remained largely unchanged in form and value for more than 40 years, that familiar circumstance ended with the introduction of the International Practical Temperature Scale of 1968 (IPTS-68) [11,12]. During the 1960s, it was recognized that the ITS needed to be extended to lower temperatures and better accord with thermodynamic temperature was desired [13]. Hall and Barber [14] describe developments from 1948 to 1967 that led to the creation of IPTS-68. Preston-Thomas [15] provides considerable information regarding the context and the process by which the IPTS-68 developed.

Prior to IPTS-68, interpolation from −182.97 °C to 0 °C was based on the Callendar-Van Dusen equation. Although H. Kamerlingh Onnes had liquefied helium in 1908 and discovered superconductivity in 1911, a proposal to extend the ITS to temperatures below the oxygen boiling point did not come about until 1948, when the NBS suggested extending the scale to 20 K by including the boiling point of hydrogen. However, it became apparent that the low-temperature extension of the ITS required greater complexity, and so it was not until 1968 that the low-temperature extension of the ITS came to fruition. To that end, five fixed points were added: the equilibrium hydrogen triple point (13.81 K), the equilibrium hydrogen vapor pressure point at 25/76 standard atmosphere (17.042 K), the equilibrium hydrogen boiling point (20.28 K), the neon boiling point (27.102 K), and the oxygen triple point (54.361 K). The temperature T_{68} is defined by the relation

$$W(T_{68}) = W_{CCT\text{-}68}(T_{68}) + \Delta W(T_{68}) \qquad (3)$$

where $W(T_{68}) = R(T_{68}) / R(273.15\ \mathrm{K})$, $W_{CCT\text{-}68}(T_{68})$ is a standard reference function [16], and $\Delta W(T_{68})$ is a deviation polynomial specific to each sub-range. The sub-ranges are abutting (13.81 K to 20.28 K, 20.28 K to 54.361 K, 54.361 K to 90.188 K, and 90.188 K to 273.15 K), and the coefficients of the deviation functions for each sub-range are determined by measurements at the defining fixed points appropriate to the specific sub-range and by importing the derivative from the higher-temperature abutting sub-range (except for the 90.188 K to 273.15 K sub-range, which requires the resistance ratio at the water boiling point). Compared to the Callendar-Van Dusen equation, this approach to interpolation must have seemed revolutionary. It would have been possible to maintain the IPTS-48 interpolation from the oxygen boiling point to the ice point, but this methodology was not followed "on account of the substantial differences known to exist between the IPTS-48 and corresponding thermodynamic temperatures near 90 K. These differences would have led to severe discontinuities of the various derivatives of temperature at 90 K if the extension was made thermodynamically correct" [15].

Above 0 °C, IPTS-68 retained the customary quadratic equation of Callendar. However, a correction term ("the Moser wobble" [15]) was added to the calculated temperatures in an effort to provide better agreement with thermodynamic temperature. The triple point of water replaced the ice point, the zinc freezing point (419.58 °C) replaced the sulfur boiling point, and the tin freezing point (231.9681 °C) became a permitted alternative to the water boiling point.

THE ROAD TO THE ITS-90

Papers pointing out the defects of the IPTS-68 appeared shortly after its proclamation, and so the seeds for its eventual replacement were sown shortly after its birth. The non-uniqueness of the scale below the ice point was clearly a concern [16-18]. However, such analyses are only as good as the quality of the data on which they are based. The situation was much improved when Ward and Compton published their comparison of 37 capsule-style PRTs [19] in 1979.

The 1976 Provisional 0.5 K to 30 K Temperature Scale (EPT-76) [20,21] was introduced to solve two shortcomings of the IPTS-68: it did not extend to low enough temperatures (the helium vapor-pressure scales [22,23] had not been incorporated) and both the 1958 ^{4}He and 1962 ^{3}He vapor-pressure scales as well as the IPTS-68 deviated significantly (by as much as 7 mK) from thermodynamic temperature (and these deviations were in opposite directions). Further, there was no internationally-agreed temperature scale from 5 K to 13.81 K. The intended purpose of the EPT-76 is best described by its creators: "This introduction of the EPT-76 will satisfy the need for a provisional practical temperature scale which can be used together with the IPTS-68 for temperatures from 0.5 K to above room temperature. As additional thermometric data become available, especially in the lower ranges of the IPTS-68 (below 90 K), firm bases will be laid for the establishment of a new IPTS which is defined down to 0.5 K." [21]

By 1985, a list of the shortcomings of the IPTS-68 had been compiled [24]. The concerns for the PRT portion of the scale were mainly that the IPTS-68 was believed to depart significantly from thermodynamic temperature over much of its range and the non-uniqueness of the low-temperature portion was unnecessarily large due to a poor choice of interpolation function.

With regard to the departure of IPTS-68 from thermodynamic temperature, Working Group 4 (WG4) of the CCT outlined the "Thermodynamic Basis for the ITS-90" in their 1991 publication [25]. The list of references is extensive, with the key thermodynamic data drawn from 31 publications from 1971 to 1989 based on a variety of thermodynamic thermometry principles, including constant-volume gas thermometry, acoustic gas thermometry, dielectric-constant gas thermometry, paramagnetic susceptibility, noise thermometry, total radiation thermometry, and spectral radiation thermometry. The outputs of the WG4 analysis included recommendations for the values of the ITS-90 fixed-point temperatures and a table of $(T - T_{68})$, their estimate of the differences between the IPTS-68 and thermodynamic temperature.

As for the matter of the interpolation, Working Group 3 (WG3) of the CCT published "The Platinum Resistance Thermometer Range of the International Temperature Scale of 1990" [26] in 1991 to explain the rationale and process behind the construction of the interpolation function. ITS-90 partitions the PRT range into a low-temperature portion (13.81 K $\leq T_{90} \leq$ 273.16 K) and a high-temperature range (273.15 K $\leq T_{90} \leq$ 1234.93K). This is much the same as for IPTS-68, except that the upper limit has been increased by more than 300 K to coincide with the freezing point of silver in order to eliminate the Pt/Pt-10%Rh thermocouple as a defining instrument of the ITS. Unlike the IPTS-68, interpolation above 273.15 K requires both a reference function and a deviation function ($W = W_r + \Delta W$, where W_r represents the reference function and ΔW is the deviation function). The rationale is explained as follows: "The definition of the relation between the resistance and the temperature of a PRT by means of a reference function and a set of deviation equations is based on the assumptions that the resistance differences between any pair of PRTs can be described by a relatively simple equation and that it is possible to provide a thermometer with direct or indirect calibration in terms of the best determinations of the thermodynamic temperature used as the reference. Such a thermometer can be either a single real thermometer or an "artificial" thermometer generated by combining the properties of two or more real thermometers. In this way, the reference function accurately expresses the relation of the resistance of a representative PRT to the thermodynamic temperature." [26] Ultimately, the reference functions were based on two *real* PRTs, a 25 ohm Tinsley capsule-style PRT (S/N 217894, α = 0.003927238 °C^{-1}) belonging to the National Physical Laboratory, United Kingdom and included in the Ward and Compton comparison [19] and a 0.25 ohm high-temperature PRT (S/N 18222, α = 0.003927296 °C^{-1}) supplied by the National Institute of Metrology, China and calibrated at the Physikalisch-Technische Bundesanstalt, Germany.

The construction of the high-temperature reference function was described in detail by Jung [27]. Unfortunately, this publication is not widely available so I will elaborate the key details. PRT S/N 18222 was calibrated at the triple point of water and at the freezing points of tin, zinc, aluminum and silver. Based on the tin and zinc measurements, 21 values of W were generated at intervals of 30 °C from 0 °C to 600 °C. For each value of thermodynamic temperature,

t, the corresponding value of $(T{-}T_{68})$ was computed by iteration from the WG4 table. This difference was used to obtain t_{68}. A value for $W(t)$ was then obtained from the usual IPTS-68 equations. From 630 °C to 962 °C, the PRT was calibrated against thermodynamic temperature as provided by the PTB Infrared Pyrometer. The resulting 31 (t, W) pairs (including two "fictitious points" at 690 °C and 750 °C) were fitted with cubic splines. The process relied on manual adjustments to the weights, the W-values of the fictitious points, and "some W biases" in order to "minimize the amplitudes of the residual and to produce a smooth second derivative versus t removing unlikely peaks." [27] The spline functions were used to generate 11 data points over the range 0 °C to 962 °C at the zeros of the Chebyshev equivalent of the equation

$$W(t)=\sum_{i=0}^{N}C_i\left(\frac{t-481}{481}\right)^i \tag{4}$$

As a 10th-order polynomial was found to give no significant reduction in the residuals compared to one of 9th order, the one of lower order was selected as the reference function. However, some adjustments remained. At this point, Jung's reference function was still normalized to $W(0\ °C) = 1$ and its slope at 0.01 °C did not match that of the March 1989 version of the low-temperature reference function, so a linear transformation was applied to $W(t)$ and the coefficients of the reference function:

$$W(t) \rightarrow (k_0\, W(t)\ - 1)\, k_1 + 1 \tag{5}$$

$$C_0 \rightarrow (k_0\, C_0 - 1)\, k_1 + 1 \tag{6}$$

$$C_i \rightarrow k_0\, k_1 C_i \tag{7}$$

with $k_0 = 0.99996012$ and $k_1 = 1.000002837$.

The WG3 publication [26] briefly addresses the development of the high-temperature deviation functions. The full-range form of the equation is

$$W{-}W_r = a(W{-}1) + b(W{-}1)^2 + c(W{-}1)^3 + d(W{-}W_{Al})^2 \tag{8}$$

with $d = 0$ below 660.323 °C. In practice, the number of terms depends on the number of fixed points within the sub-range of interest.

Kemp *et al.* [28,29] had been working for some time to improve the low-temperature interpolation, following-up on the approach introduced by Kirby *et al.* [18]. The development of the ITS-90 reference function has been described by Kemp [30]. The (W, T_{68}) data pairs for PRT 217894 were taken from Ward and Compton [19]. The WG4 tabulation of $(T{-}T_{68})$ was used to form (W,T) pairs as input to the fitting routine. Additional data (resistance ratios at the triple points of neon, argon and mercury) were supplied by NPL, making a total of 51 data pairs. The fitting procedure constrained the value and the first and second derivatives at 273.16 K ($W_r = 1$, $dW_r/dT = 0.003988528\ °C^{-1}$, $d^2W_r/dT^2 = -1.220103\times10^{-6}\ °C^{-2}$) to match the high-temperature reference function. While various mathematical forms were tried, the low-temperature ITS-90 reference function settled upon was

$$\ln[W_r(T_{90})] = A_0 + \sum_{i=1}^{12} A_i\left[\frac{\ln(T_{90}/273.16)+1.5}{1.5}\right]^i \tag{9}$$

In addition to the reference function, interpolation on the ITS-90 requires appropriate deviation functions to account for the individual behavior of PRTs. The general form of the ITS-90 deviation equation is

$$W - W_r = a(W-1) + b(W-1)^2 + \sum_{i=1}^{m} c_i(\ln W)^{i+n} \tag{10}$$

The values of m and n are specific to the sub-range, with m being two less than the number of fixed points for the sub-range in question and n a value chosen to minimize the non-uniqueness. The sub-range from 83.8058 K to 273.16 K does not follow this scheme, and instead has as its deviation function

$$W{-}W_r = a(W{-}1) + b(W{-}1)\ln W \tag{11}$$

The complete definition of the ITS-90 may be found in the article by Preston-Thomas [31]. With regard to the story behind the development of the ITS-90 as related by WG4 and WG3 [25,26], I would like to add that the development of the ITS-90 was very much a human activity to which many contributed and it is fair to say that much of the process remains undocumented in the open literature. H. Preston-Thomas was President of the CCT and presided over its meetings from 1971 (9th meeting) to 1989 (17th meeting), and in that capacity oversaw the development of the ITS-90. In July 1988, I was asked by Preston-Thomas and R. E. Bedford to confirm the calculations of Kemp for the low-temperature PRT-portion of what would become the ITS-90. I was supplied with copies of communications circulating among the participating laboratories. P. Bloembergen, L. Crovini (WG3 chair), R. C. Kemp and R. L. Rusby were frequent contributors to the discussions. There was an air of collaboration (and a hint of competition) as the formulations that would eventually become the

ITS-90 were refined. I suggested an alternative form of the low-temperature deviation equation that was considered for a time but eventually rejected. Bloembergen suggested adding the "n" to Eq. 10, and Kemp and I determined the n that minimized the non-uniqueness of each sub-range. To minimize sub-range inconsistency, I suggested minor adjustments to some of the fixed-point temperatures.

At least five draft versions of the ITS-90 were circulated to the members of the CCT, and my files include versions B (28 March 1988) though E (14 September 1989). As an example of its evolution, version B differed from the ITS-90 in the following ways:

1) the gallium triple point was proposed as the upper limit of the low-temperature sub-ranges
2) the triple point of xenon was included as a calibration point for the low-temperature sub-ranges
3) the mercury triple point was only included in the sub-range from the triple point of mercury to the triple point of gallium
4) the sub-range 0 °C to the indium freezing point required a calibration point at the triple point of gallium
5) the sub-range 0 °C to the zinc freezing point required calibration at the indium freezing point (in addition to tin and zinc)
6) the higher-temperature sub-ranges could be defined using either antimony or aluminum freezing points
7) the reference functions were as yet undefined

During the discussions, concerns were expressed with the xenon point – at the time, it was not considered sufficiently reproducible. Explicit forms of the reference functions were introduced with version C (24 August 1988). With version D (7 March 1989), the low-temperature sub-ranges saw the following changes: mercury replaced the xenon triple point, the upper limit became 273.16 K, and calibration at the gallium point was no longer required. In the high-temperature regime: the deviation function had the ITS-90 form, but calibration at the gallium point was included in the sub-ranges having indium, tin, and zinc as their upper limits.

The final details of the ITS-90 were decided during the 17th meeting of the CCT in September 1989, and the minutes of that meeting [32] capture the process very well. Much of the meeting concerned itself with finalizing the PRT portion of the ITS-90, and it is surprising how many decisions were taken at that time. For example, the sub-range from the neon triple point to 273.16 K had been deleted from the ITS-90 proposal due to its relatively large non-uniqueness, but F. Pavese and G. Bonnier were able to persuade the CCT of the need for its inclusion, despite its deficiencies and the lack of a positive recommendation from WG3.

IS IT TIME TO REVISE THE ITS?

ITS-90 has been the consensus standard for more than 20 years, so it is reasonable to ponder whether or not the time is right to revise the scale. Recently, WG4 estimated the extent to which the ITS-90 differs from thermodynamic temperature [33]. From 14 K to 273 K, the maximum difference of 8 mK occurs near −120 °C. Above 273 K, the difference increases with temperature and reaches 29 mK at 660 °C. These differences exceed by a large margin the uncertainties of platinum resistance thermometry at these temperatures, so a case can be made for such an updating. Figure 1 indicates how (for the most part) successive revisions have improved the agreement with thermodynamic temperature, and the smoothness of the differences is clearly improving as well.

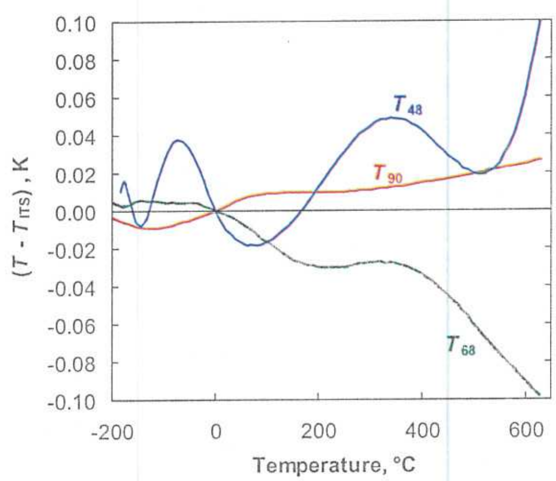

FIGURE 1. Differences of the various ITS scales with respect to thermodynamic temperature, based on WG4's 2010 estimate of $(T–T_{90})$ [33].

The slope difference of $(T–T_{90})$ at 273.16K is another feature seen in Figure 1. While this was commented on shortly after ITS-90 came into effect (see for example [34]), it received increased attention when the feature was confirmed by thermodynamic thermometry [35], and recently by analysis of PRT calibrations [36]. I have long held the opinion that the slope discontinuity at 273.16 K was caused by the forced matching of the first and second derivatives of the two reference functions. In [30], Kemp comments "When the reference function in (2) was forced to have these values the fit immediately below 273.16 K deteriorated and residuals at the triple point of mercury rose to 1.5 mK. These effects are unacceptable and the fit was weighted in this region to reduce the residuals to more acceptable levels." The difficulty in forcing the two functions to match is understandable: S/N 217894 had $\alpha = 0.003927238$ °C while S/N 18222 had $\alpha = 0.003927296$ °C^{-1}. The relative slope difference based on these α-coefficients is 1.5×10^{-5}. Pitre *et al.* reported a slope discontinuity of 4×10^{-5} [35] while Rusby finds values ranging from 0–6 $\times$ 10^{-5}. The approximate expressions recommended by WG4 for $(T-T_{90})$ [33] have a slope difference of 3.1×10^{-5}. The preponderance of evidence suggests that the effect is real.

A revised ITS should have among its goals: to provide the best possible agreement with thermodynamic temperature, to minimize slope discontinuities for abutting sub-ranges, to minimize non-uniqueness among PRTs within each sub-range, and to minimize the sub-range inconsistency among overlapping sub-ranges. The next question is how to proceed.

A PROPOSAL FOR ITS-20XX

While there are undoubtedly many approaches to designing a temperature scale, the one that I will propose here maintains the familiar mathematical forms of the ITS-90 (reference and deviation functions), while updating the fixed-point temperatures and the coefficients of the reference functions. The revised temperatures of the defining fixed points can be obtained from the WG4 estimates [33]. Table 1 provides the updated values alongside the ITS-90 assignments.

TABLE 1. Defining fixed-point temperatures.

Fixed Point	ITS-90, K	ITS-20XX, K
e-H_2 triple point	13.8033	13.8037
e-H_2 v.p.	17.035	17.0355
e-H_2 v.p.	20.27	20.2703
Ne triple point	24.5561	24.5559
O_2 triple point	54.3584	54.3573
Ar triple point	83.8058	83.8014
Hg triple point	234.3156	234.3124
H_2O triple point.	273.16	273.16
Ga melting point	302.9146	302.919
In freezing point	429.7485	429.7586
Sn freezing point	505.078	505.089
Zn freezing point	692.677	692.691
Al freezing point	933.473	933.502
Ag freezing point	1234.93	1234.976

To complete the scale definition, the coefficients of the two reference functions and their respective inverse functions need to be provided. For the range 13.8037 K to 273.16 K:

$$\ln[W_r(T_{XX})] = A_0 + \sum_{i=1}^{12} A_i \left[\frac{\ln(T_{XX}/273.16)+1.5}{1.5}\right]^i \quad (12)$$

$$T_{XX}/273.16 = B_0 + \sum_{i=1}^{15} B_i \left[\frac{W_r(T_{XX})^{1/6}-0.65}{0.35}\right]^i \quad (13)$$

From 273.15 K to 1234.976 K,

$$W_r(T_{XX}) = C_0 + \sum_{i=1}^{9} C_i \left(\frac{T_{XX}-754.15}{481}\right)^i \quad (14)$$

$$T_{XX} - 273.15 = D_0 + \sum_{i=1}^{9} D_i \left(\frac{W_r(T_{XX})-2.64}{1.64}\right)^i \quad (15)$$

TABLE 2. The revised constants of the reference functions and the inverse functions.

A_0	-2.135 287 07	B_0	0.183 321 538
A_1	3.183 374 01	B_1	0.240 963 636
A_2	-1.801 512 31	B_2	0.209 062 179
A_3	0.716 898 83	B_3	0.190 264 326
A_4	0.504 644 36	B_4	0.142 817 262
A_5	-0.618 370 35	B_5	0.079 746 736
A_6	-0.059 226 32	B_6	0.011 405 460
A_7	0.279 655 83	B_7	-0.042 127 080
A_8	0.117 529 88	B_8	-0.072 607 348
A_9	-0.292 491 31	B_9	-0.028 545 314
A_{10}	0.036 398 18	B_{10}	0.074 033 522
A_{11}	0.118 377 63	B_{11}	0.083 379 865
A_{12}	-0.049 991 35	B_{12}	-0.029 391 476
		B_{13}	-0.062 007 293
		B_{14}	0.001 956 247
		B_{15}	0.017 727 617
C_0	2.781 502 69	D_0	439.951 146
C_1	1.646 437 23	D_1	472.440 942
C_2	-0.137 143 85	D_2	37.691 541
C_3	-0.006 531 26	D_3	7.477 486
C_4	-0.002 431 49	D_4	2.953 111
C_5	0.005 431 32	D_5	-0.062 208
C_6	0.001 964 53	D_6	-1.015 101
C_7	-0.002 514 91	D_7	-0.072 361
C_8	-0.000 457 85	D_8	0.209 270
C_9	0.000 651 34	D_9	-0.004 054

In an earlier paper [34], I re-fitted the low-temperature reference function to eliminate the slope discontinuity at 273.16 K using a FORTRAN implementation of the well-known singular-value decomposition routine [35]. This time, I have relied on the MATLAB Curve Fitting Toolbox. The input data for the low-temperature reference function are in Table 3. The W-values are the same as tabulated by Kemp [30] and the T_{XX}-values are Kemp's values adjusted by the WG4 estimates for $(T-T_{90})$ [33]. The fitting residuals appear in Figure 2 as temperature-equivalents. In terms of W, the residuals are low in magnitude and well-behaved. However, when expressed in temperature-equivalent (as in Figure 2), they are slightly higher at the lowest temperatures due to the declining sensitivity of platinum resistivity (Figure 3).

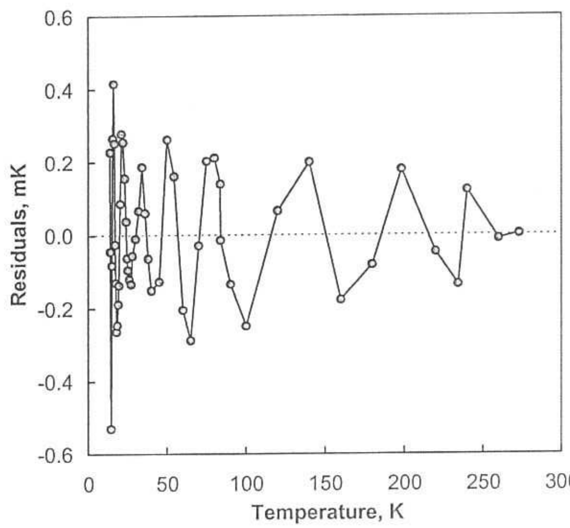

FIGURE 2. The residuals obtained from fitting the low-temperature reference function.

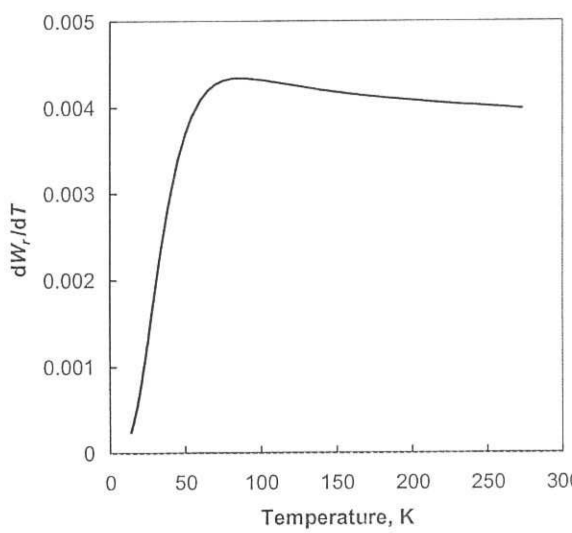

FIGURE 3. The sensitivity of platinum resistivity (the first derivative of the low-temperature reference function) decreases below 90 K and at 14 K is only 6% of its room-temperature value.

TABLE 3. The set of (W, T) data on which the low-temperature reference function $W_r(T_{XX})$ is based. The bold values identify the defining fixed points.

T_{XX}, K	W	T_{XX}, K	W
13.803 78	**0.001 190 12**	35.992 42	0.030 329 11
13.993 31	0.001 236 64	37.993 22	0.035 689 50
14.494 48	0.001 369 47	39.993 91	0.041 447 57
14.994 46	0.001 517 23	44.993 06	0.057 373 65
15.493 85	0.001 680 78	49.993 57	0.075 114 45
15.995 00	0.001 861 91	**54.357 23**	**0.091 718 70**
16.494 35	0.002 060 25	60.001 29	0.114 315 41
17.036 06	**0.002 296 76**	65.004 14	0.135 078 49
17.492 90	0.002 514 43	70.004 95	0.156 280 56
17.992 71	0.002 772 47	75.004 76	0.177 754 92
18.491 59	0.003 051 70	80.005 27	0.199 386 87
18.991 57	0.003 354 07	83.676 37	0.215 316 14
19.490 84	0.003 679 30	**83.801 61**	**0.215 859 29**
20.271 22	**0.004 236 22**	90.191 97	0.243 609 13
20.991 95	0.004 805 15	100.051 98	0.286 323 55
21.992 33	0.005 685 24	120.004 58	0.371 945 69
22.993 02	0.006 675 13	140.003 26	0.456 550 57
23.993 96	0.007 778 86	160.001 23	0.540 105 28
24.556 03	**0.008 449 66**	179.854 43	0.622 219 36
24.994 47	0.008 998 84	198.350 56	0.698 094 38
25.995 11	0.010 338 33	220.001 78	0.786 241 72
27.097 35	0.011953 88	**234.312 26**	**0.844 142 82**
27.994 52	0.013 378 27	240.007 08	0.867 110 14
29.993 03	0.016 904 14	260.040 92	0.947 575 58
31.991 88	0.020 913 48	**273.160 00**	**1.000 000 00**
33.991 57	0.025 394 80		

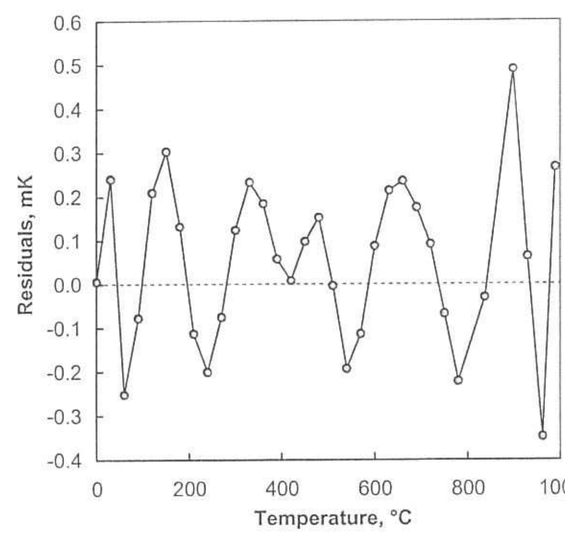

FIGURE 4. The residuals obtained from fitting the high-temperature reference function.

Likewise, the coefficients of the high-temperature reference function can be obtained from the data used by Jung [27]. The W-values in Table 4 are the "smoothed" values of Jung but scaled so that they are in terms of $R(t)/R(0.01\ °C)$ rather than $R(t)/R(0\ °C)$. The temperatures in Table 4 are those of Jung adjusted by the WG4 estimates of $(T-T_{90})$ [33]. The fitting residuals are shown in Figure 4.

The coefficients of both reference functions (Equations (12) and (14)), as obtained by the fitting process described above, are provided in Table 2. For completeness, we also require the coefficients of the inverse functions (Equations (13) and (15)). The coefficients of the inverse functions were obtained by fitting 250 (T,W) data pairs obtained by distributing the values of T uniformly over the respective temperature ranges and with the corresponding W values provided by the appropriate reference function.

TABLE 4. The set of (W, T) data on which the high-temperature reference function $W_r(T_{XX})$ is based.

t_{XX}, °C	W	t_{XX}, °C	W
0.0000	0.999 960 14	480.0187	2.778 143 40
30.0043	1.119 068 97	510.0202	2.880 336 38
60.0077	1.237 089 51	540.0218	2.981 452 81
90.0094	1.354 030 57	570.0234	3.081 483 61
120.0100	1.469 896 98	600.0250	3.180 418 67
150.0100	1.584 693 93	630.5975	3.280 099 07
180.0100	1.698 426 90	660.3245	3.375 916 08
210.0101	1.811 102 14	690.0301	3.470 568 87
240.0103	1.922 725 91	720.1390	3.565 387 78
270.0108	2.033 303 31	750.0336	3.658 418 47
300.0115	2.142 837 84	779.8453	3.750 090 04
330.0123	2.251 331 52	837.0875	3.923 055 08
360.0134	2.358 784 92	898.2316	4.103 444 51
390.0145	2.465 197 04	929.1534	4.192 990 50
420.0158	2.570 564 90	961.8052	4.286 353 20
450.0172	2.674 883 05	988.9654	4.363 104 08

TESTING ITS-20XX

With the reference functions determined, the next task is to test the proposal to ensure that agreement of specific thermometers within the sub-ranges (non-uniqueness) and between overlapping sub-ranges (sub-range inconsistency) are no worse than for the ITS-90. Because the reference functions and deviation functions are nearly the same as those of the ITS-90, the non-uniqueness should be unchanged. Alterations to reference functions and fixed-point temperatures are known to influence sub-range inconsistency, so there is greater need to carry out such tests.

Figure 5 shows the non-uniqueness for the 13.8 K to 273.16 K sub-range using the 35 Ward and Compton [19] thermometers. While other data sets [38] can be used for such testing, the Ward and Compton data have been the most commonly employed for this purpose and are therefore well-suited to evaluating the ITS-20XX formulation. By way of comparison, computation using the ITS-90 reference function and temperature assignments resulted in an identical-looking graph.

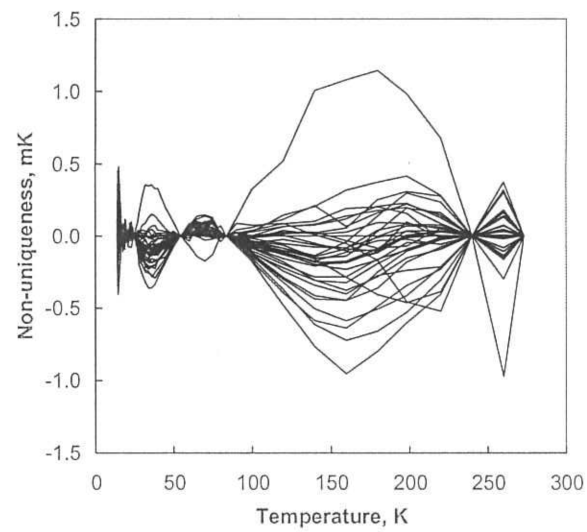

FIGURE 5. Non-uniqueness for the 14 K to 273 K sub-range for the 35 Ward and Compton PRTs [19].

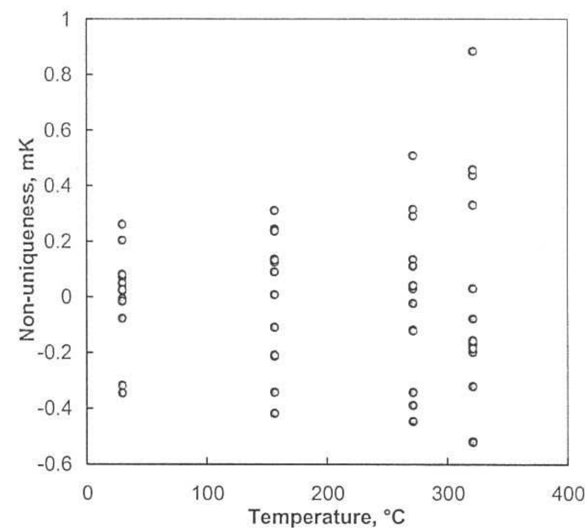

FIGURE 6. Non-uniqueness for the 0 °C to 420 °C sub-range for the 11 Ancsin and Murdock PRTs [40]. The deviations are expressed with respect to the mean.

Above 273.16 K, PRTs tend to be less stable and comparators with the required stability and isothermality and also designed to accommodate long-stem PRTs are rare. Therefore, most of the non-uniqueness estimates are based on measurements of non-defining (secondary) fixed points, such as the freezing point of cadmium. Twenty years ago, as a contributor to this symposium series, I summarized the high-temperature non-uniqueness data available at that time [39]. For the present purposes, the data of Ancsin and Murdock [40] at the gallium, indium, bismuth, and cadmium fixed points will be used to assess the non-uniqueness between 0 °C and 420 °C. The result of the analysis appears as Figure 6. The standard deviations are 0.17 mK, 0.24 mK, 0.29 mK, and 0.42 mK near 30 °C, 157 °C, 271 °C, and 321 °C, respectively. Again, we find no difference in the apparent non-uniqueness between ITS-90 and ITS-20XX.

The test for sub-range inconsistency requires data for all of the fixed points of the overlapping sub-ranges. Such testing was first described in a document submitted to the 17th meeting of the CCT [41]. For the sub-ranges below 273.16 K, we will use the data reported by Hill and Steele [42]. Figure 7 is the sub-range inconsistency assessment that results from using the ITS-20XX temperature assignments from Table 1 and the ITS-20XX reference function coefficients from Table 2. The extent of sub-range inconsistency is similar to that of the corresponding ITS-90 calculation, but the ITS-20XX version is more symmetric about zero, at least for this data set.

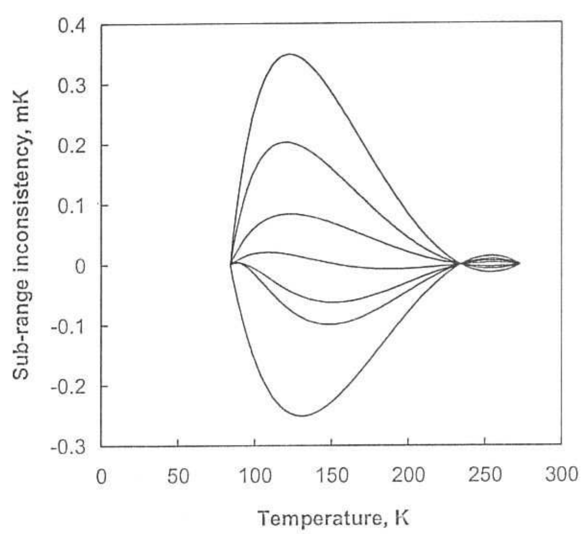

FIGURE 7. Sub-range inconsistency between the 14 K to 273 K sub-range and the 84 K to 273 K sub-range based on the fixed-point data of Hill and Steele [42].

In a similar manner, we can test the sub-range inconsistency above 273.16 K. For this purpose, we will use the NIST data for six Chino PRTs that was circulated privately by B. W. Mangum [43] to those involved in formulating the ITS-90. When the ITS-90 reference function and fixed-point temperature assignments are employed, the non-uniqueness diagram for this set of PRTs is nearly symmetric about the origin. When the proposed ITS-20XX temperature assignments of Table 1 and the reference function coefficients of Table 2 are used, the non-uniqueness exhibits a negative excursion reaching -1.25 mK. When a zinc fixed-point temperature of 419.5445 °C is used, a sub-range inconsistency diagram is obtained (Figure 8) with values very similar to the ITS-90 version. This difference of 3.5 mK in the tin fixed-point temperature is significant, but well within the uncertainty of 6.9 mK estimated by WG4 for this temperature. The need to adjust the tin temperature suggests that some "tuning" of the Table 1 assignments may be necessary in order to minimize sub-range inconsistency.

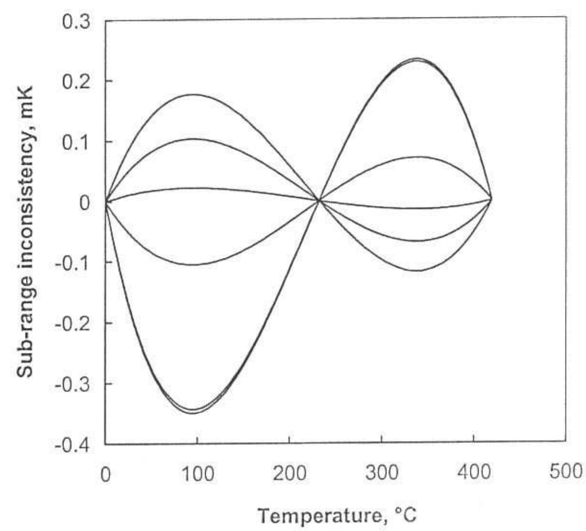

FIGURE 8. Sub-range inconsistency between the 0 °C to 660 °C sub-range and the 0 °C to 420 °C sub-range based on fixed-point data from NIST [43]. (Note: this was generated with $t_{XX}(\mathrm{Zn})$ = 419.5445 °C, not the value in Table 1.)

CONCLUSIONS

The possibility of a revised ITS conforming more closely to thermodynamic temperature than ITS-90 has been demonstrated. Implementation along the lines suggested requires little more than an updating of the coefficients of the reference functions and the temperatures assigned to the defining fixed points. This approach minimizes the need to educate users on the mathematics of the "new" scale, and there is no impact on calibration infrastructure because the ITS-90 fixed points are employed with no additions.

While the ITS-90 design may not be optimal from a mathematical perspective [44], it offers a familiar paradigm that can be updated to improve its accord with thermodynamic temperature. With a clear proposal in place to bring to fruition ITS-20XX, it is clear that we know *how* to revise the ITS. Two questions remain to be answered:
1) *Should* we revise the ITS?
2) If "yes", then *when* should the ITS be revised?
My personal viewpoint is that we should respond "*Yes*" and "*Now*". Those who wish to use ITS-20XX will have the authority and guidance to do so and those who prefer to maintain traceability to the ITS-90 are free to choose that course, just as many measurements

maintained traceability to the IPTS-68 long after the introduction of the ITS-90.

Updating or revising the ITS in the manner described here should not preclude work on a scale that is better-behaved mathematically. Non-uniqueness from 84 K to 273 K could be reduced by replacing the mercury triple point with the xenon triple point due to its superior positioning (~160 K). This has become feasible with the availability of high-purity xenon and the understanding that isotopic effects do not limit the quality of the xenon triple-point realization [42]. Other improvements should be possible by implementing the suggestions of White [44].

REFERENCES

1. Callendar, H. L., *Phil. Trans. R. Soc. Lond. A* **178**, 161-230 (1887).
2. Callendar, H. L., *Phil. Mag. Series 5* **48**, 519-447 (1899).
3. Quinn, T. J., *Temperature*, Second Edition, London: Academic Press, 1990.
4. Hall, J. A., *Metrologia* **3**, 25-28 (1967).
5. Burgess, G. K., *Bureau of Standards J. Res.* **1**, 635-640 (1928).
6. Van Dusen, M. S., *J. Am. Chem. Soc.* **47**, 326-332 (1925).
7. Stimson, H. F., *J. Res. NBS* **42**, 209-217 (1949).
8. Hall, J. A. and Barber, C. R., *Brit. J. Appl. Phys.* **1**, 81-86 (1950).
9. Hall, J. A., "The International Scale of Temperature", in *Temperature, Its Measurement and Control in Science and Industry*, Vol. 2, edited by H. C. Wolfe, Reinhold Publishing Corp, New York, NY, 1955, pp. 115-139.
10. Stimson, H. F., *J. Res. NBS* **65A**, 139-145 (1961).
11. Barber, C. R., *Metrologia* **5**, 35-44 (1969).
12. Barber, C. R., *Nature* **222**, 929-931 (1969).
13. Terrien, J. and Preston-Thomas, H., *Metrologia* **3**, 29-31 (1969).
14. Hall, J. A. and Barber, C. R., *Metrologia* **3**, 78-88 (1967).
15. Preston-Thomas, H., "The Origin and Present Status of the IPTS-68", in *Temperature, Its Measurement and Control in Science and Industry*, Vol. 4, edited by H. H. Plumb, Instrument Science of America, Pittsburgh, 1972, pp. 3-14.
16. Bedford, R.E. and Ma, C. K., *Metrologia* **6**, 89-94 (1969).
17. Tiggelman, J. L. and Durieux, M., "Intercomparison of Standard Platinum Thermometers Calibrated on IPTS-68 Between 13.81 K and 273.15 K", in *Temperature, Its Measurement and Control in Science and Industry*, Vol. 4, edited by H. H. Plumb, Instrument Science of America, Pittsburgh, 1972, pp. 857-864.
18. Kirby C. G., Bedford, R. E. and Kathnelson, J., *Metrologia* **11**, 117-124 (1975).
19. Ward, S. D. and Compton, J. P., *Metrologia* **15**, 31-46 (1979).
20. BIPM, *Metrologia* **15**, 65-68 (1979).
21. Durieux, M., Astrov, D. N., Kemp, W. R. G. and Swenson, C. A., *Metrologia* **15**, 57-63 (1979).
22. Brickwedde, F. G., Van Dijk, H., Durieux, M., Clement, J. R. and Logan, J. K., *J. Res. NBS* **64A**, 1-17 (1960).
23. Sherman, R. H., Sydoriak, S. G. and Roberts, T. R., *J. Res. NBS* **68A**, 579-588 (1964).
24. Preston-Thomas, H., Quinn, T. J. and Hudson, R. P., *Metrologia* **21**, 75-79 (1985).
25. Rusby, R. L., Hudson, R. P., Durieux, M., Schooley, J. F., Steur, P. P. M. and Swenson, C. A., *Metrologia* **28**, 9-18 (1991).
26. Crovini, L., Jung, H. J., Kemp, R. C., Ling, S. K., Mangum, B. W. and Sakurai, H., *Metrologia* **28**, 317-325 (1991).
27. Jung, H. J., "The construction of a reference function for platinum resistance thermometers in the range from 0 °C until 962 °C", Document CCT/89-11, submitted to the 17th Meeting of the CCT (1989).
28. Kemp, R. C., Besley, L. M. and Kemp, W. R. G., *Metrologia* **14**, 137-142 (1978).
29. Kemp, R. C., Besley, L. M. and Kemp, W. R. G., *Metrologia* **21**, 139-146 (1985).
30. Kemp, R. C., *Metrologia* **28**, 327-332 (1991).
31. Preston-Thomas, H., *Metrologia* **27**, 3-10 (1990). Erratum: *Metrologia* **27**, 107 (1990).
32. Comité Consultatif de Thermométrie, *Report of the 17th Meeting*, Sèvres: Bureau International des Poids et Mesures (1989).
33. Fischer, J., de Podesta, M., Hill, K. D., Moldover, M., Pitre, L., Rusby, R., Steur, P., Tamura, O., White, R. and Wolber, L., *Int. J. Thermophys.* **32**, 12–25 (2011).
34. Hill, K. D., *Metrologia* **32**, 87-94 (1995).
35. Pitre, L., Moldover, M. R. and Tew, W. L., *Metrologia*, **43**, 142–162 (2006).
36. Rusby, R. L., *Int. J. Thermophys.* **31**, 1567–1572 (2010).
37. Press, W. H., Flannery, B. P., Teukolsky, S. A. and Vetterling, W. T., *Numerical Recipes, The Art of Scientific Computing*, New York: Cambridge University Press, 1986, p. 818.
38. Hill, K. D. and Steele, A. G., "The Non-Uniqueness of the ITS-90: 13.8033 K to 273.16 K", in *Temperature, Its Measurement and Control in Science and Industry*, Vol. 7, edited by D. C. Ripple, AIP, Melville, NY, 2003, pp. 53-58.
39. Hill, K. D. and Woods, D. J., "A preliminary assessment of the non-uniqueness of the ITS-90 in the range 500 °C to 660 °C as measured with a cesium-filled, pressure-controlled, heat-pipe furnace", in *Temperature, Its Measurement and Control in Science and Industry*, Vol. 6, edited by J. F. Schooley, AIP, Melville, NY, 1992, pp. 215-219.
40. Ancsin, J. and Murdock, E. G., *Metrologia* **27**, 201-209 (1990).
41. Hill, K. D. and Bedford, R. E., "The minimization of sub-range inconsistency by fixed-point adjustment", Document CCT/89-6, submitted to the 17th Meeting of the CCT (1989).
42. Hill, K. D. and Steele, A. G., *Metrologia* **42**, 278-288 (2005).
43. Mangum, B. W., personal communication, August 1989.
44. White, D. R., these proceedings.