Uncertainties in the Realization of the SPRT Sub-ranges of the ITS-90

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Abstract   Working Group 3 of the Consultative Committee for Thermometry is responsible for recommending methods to assess uncertainties in contact thermometry. Accordingly, it has now completed a guide summarizing the uncertainties in the

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realization of the standard platinum resistance thermometer subranges of ITS-90 between the triple point of neon (24.5561 K) and the freezing point of silver (961.78 °C). The document provides guidance to assess the uncertainties of both SPRT calibrations and temperature measurements. The document describes all known sources of uncertainty and influence variables, identifies key references in the literature that discuss, model or evaluate each effect, gives an indication of the typical magnitudes of the uncertainties, and provides propagation laws. This article is an overview of the guide emphasizing aspects that may be different from common practice, which includes: associating all uncertainty terms with a physical cause to ensure they can be propagated and to prevent double counting; uncertainty due to the oxidation state of the SPRT; uncertainty due to the isotopic composition of fixed-point substances; uncertainty due to impurities in fixed-point substances; and uncertainty due to non-uniqueness of the SPRT interpolations. The article gives a graphical summary of the total uncertainties in ITS-90 over the SPRT temperature range.

1 Introduction

The last decade or so has seen a large increase in the number and scope of activities in support of the International Committee for Weights and Measures (CIPM), Mutual Recognition Arrangement (MRA) [1]. This is reflected in the number of international comparisons, the number of national laboratories listed in the International Bureau of Weights and Measures (BIPM) calibration and measurement capability (CMC) database, and the number of accredited national laboratories. Earlier, it became apparent that there was a need to harmonize the treatment of uncertainty in order to make meaningful analyses of comparison results and capabilities. In response to this need, several of the working groups of the CIPM's Consultative Committee for Thermometry (CCT) have been preparing uncertainty guides for different aspects of temperature measurement. In 2001, CCT Working Group 3 (CCT-WG3) commenced the preparation of a guide for the assessment of uncertainties in the calibrations of SPRTs at the defining fixed points of the ITS-90. Early versions focused on evaluations of fixed-point measurements to support the MRA related activities, and a summary article was prepared for TEMPMEKO 2004 [2]. Subsequently CCT-WG3 has expanded the text to encompass the uncertainties associated with temperature measurements between the fixed points, and broadened the intended audience to all users of SPRTs. The latest version of the guide can be downloaded from the BIPM website [3].

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The purpose of this article is to give an overview of the guide, and highlight aspects that may be novel or different from common practice. Section 2 gives a brief overview of the guide and outlines its key principles. The following sections then discuss the assessment of fixed-point impurities, isotopic effects in fixed points, SPRT oxidation effects, and SPRT interpolation effects (non-uniqueness). Finally, we present an indicative summary of the total uncertainty in the SPRT sub-ranges of ITS-90 and discuss the future of the guide.

2 Scope and Principles of the Guide

The guide covers all known sources of uncertainty in the SPRT sub-ranges between the triple point of neon (24.5561 K) and the freezing point of silver (961.78 °C). Since the hydrogen point is required for the calibration of SPRTs for the neon-water sub-range, effects associated with the realization of the triple point of equilibrium hydrogen (13.8033 K) are included. The main topics in the guide include:

- Fixed-point effects: hydrostatic pressure, residual gas pressure, impurity and isotopic effects, buoyancy, strain, crystal defects, crystal size, and static and dynamic thermal effects
- SPRT effects: oxidation, vacancies, strain, impurities, insulation, and leakage
- Interpolation effects: Type 1 and Type 3 non-uniqueness
- Resistance measurement effects: reference resistor, connecting cables, resistance bridge effects, and self-heating

Each section provides a short summary of the state of knowledge, identifies all known influence effects, and gives key references to the literature that discuss, model or evaluate each effect, and provides propagation laws for the contributing uncertainties. Throughout the guide, and this article, all uncertainties are expressed as standard uncertainties ($k = 1$).

The final section of the guide provides guidance to evaluate the total uncertainty of a variety of measurements ranging from the fixed-point temperatures, fixed-point resistances, resistance ratios at fixed points, uncertainties in interpolated temperatures, and uncertainties in fixed-point comparisons. The appendices tabulate useful physical constants associated with the fixed points, the range of typical uncertainties in fixed-point measurements, the sensitivity coefficients for fixed-point uncertainties, and a summary of the mathematical foundation for the SPRT subranges of ITS-90 and uncertainty propagation equations.

The main principle of the guide is "guidance" only. Metrology advances principally through the improved understanding and reduction of the causes of uncertainty, and, therefore, most of the contents of the guide are the subjects of ongoing research. Any method for assessing uncertainty described by the guide is therefore a suggestion or recommendation, and is not prescribed. As a matter of principle, the user of the document is free to adopt any approach to uncertainty analysis so long as it is consistent with current physical knowledge and uncertainty practice [4]. Similarly, although the guide occasionally notes the impact of different measurement techniques on uncertainty, it is not a guide to the realization of the scale and should be read in conjunction with the Supplementary Information for the ITS-90 [5].

In the interests of promoting harmonization and ensuring consistency with the ISO Guide to the Expression of Uncertainty in Measurement [4], we have endeavored to associate all uncertainty terms with a physical cause. This ensures that each of the identified sources of uncertainty has a mathematical model allowing estimation and propagation of uncertainty. It also helps ensure that all uncertainty contributions are counted only once. For the same reasons, where Type A assessments are employed, we recommend that all sources of uncertainty contributing to measured standard deviations should be identified, and the measurements should draw samples from the whole of the distribution associated with each uncertainty source. This practice prevents both "double counting" and underestimates of uncertainty. This requirement may preclude the use of nonspecific uncertainty terms such as repeatability or reproducibility [6].

3 Impurity Effects in Fixed Points

Impurity effects in the fixed points have been a long-standing problem in realizing the international temperature scales. There have been problems controlling the sources of the various impurities, it has been difficult to accurately measure the impurity concentrations, and different impurities have different effects on the fixed-point temperatures. However, in recent years, two developments have changed the scene. Firstly, chemical analyses can now measure concentrations of the majority of impurities at concentrations well below the part-per-million level. Secondly, a combination of experiment and thermodynamic modeling has enabled determinations of the low-concentration liquidus slopes in the binary phase diagrams for many of the fixed-point impurities. Working Group 1 of the CCT (definitions) has been watching these developments closely and has now made improved definitions of the fixed-point temperature and recommended methods for correcting for impurities [7]. They recommend two methods for assessing fixed points, known as the sum of individual estimates (SIE) and overall maximum estimate (OME) methods.

3.1 Sum of Individual Estimates (SIE)

Empirically, it is observed that at sufficiently low concentrations, the effects of different impurities are linear with concentration and practically independent. Thus, the fixed-point temperature for the pure substance, T_{pure}, can be found from the experimentally determined liquidus temperature [3,7], T_{liq}, by applying a correction:

$$\Delta T_{imp} = T_{pure} - T_{liq} = -\sum_i \frac{\partial T_{l,i}}{\partial c_{l,i}} c_{l,i} = -\sum_i c_{l,i} m_{l,i} \qquad (1)$$

where $c_{l,i}$ is the equilibrium concentration (mole fraction) of the impurity at the liquidus point for the ith impurity and $m_{l,i} = \partial T_{l,i}/\partial c_{l,i}$ is the initial slope (near $c_{l,i} = 0$) of the liquidus line in the binary phase diagram for the ith impurity.

This method, which sums the individual estimates (SIE) for each impurity, requires the determination of the concentration of each impurity, and knowledge of the liquidus

slope for each impurity. Fellmuth and Hill [8] present an example of the SIE analysis applied to tin. They also discuss and demonstrate the limitations of thermal analysis in the assessment of impurity effects, and compare the SIE method to other methods.

The uncertainty in the impurity correction is due to propagated uncertainties in the various parameters in Eq. 1:

$$u^2_{\text{imp,SIE}} = \sum_i \left[u^2(c_{l,i}) m^2_{l,i} + u^2(m_{l,i}) c^2_{l,i} \right]. \tag{2}$$

It should be noted that at present the uncertainty estimates for chemical analyses provided by analytical laboratories may not be expressed in a manner consistent with the ISO uncertainty guide.

Although the SIE method is the preferred method for correcting and assessing impurity effects, it is not yet fully realizable. The key limitations are that the method requires knowledge of the concentrations of all impurities, and values for the liquidus slopes for all impurities in the fixed-point substance. Unfortunately, not all impurities can be measured with sufficient accuracy, and not all liquidus slopes are known. At present, the most complete table of liquidus slopes is for tin [8]. Some liquidus slopes can be derived from published binary phase diagrams, but usually the diagrams do not have sufficient resolution to calculate the liquidus slopes for binary systems exhibiting phase transformations at low concentrations. In some cases, thermodynamic calculations of the phase diagrams have been used. A number of national laboratories have active research programs for measuring or calculating the liquidus slopes.

3.2 Overall Maximum Estimate (OME)

This method should be applied where either the impurity concentrations or their effect on the liquidus slopes are not well known.

The manufacture of high-purity metals by zone refining relies on the segregation of impurities that occurs while freezing and melting. Thus, for many of the fixed-point substances (not all are zone refined), impurities with a high relative solubility in the solid or liquid phase are preferentially removed. Given this observation, we assume that the effects of most remnant impurities on the fixed-point liquidus temperature lies in the range

$$\left| T_{\text{liq}} - T_{\text{pure}} \right| < \Delta T_{\text{ome,max}} = \frac{c_{l,\text{tot}}}{A}. \tag{3}$$

where $c_{l,\text{tot}} = \sum_i c_{l,i}$ is the sum of all of the impurity concentrations, and A is the cryoscopic constant for the fixed point. If it is assumed that any liquidus temperature in the range of Eq. 3 is equally likely, then the uncertainty in the liquidus temperature is given by

$$u^2_{\text{imp,ome}} = \frac{\left(\Delta T_{\text{ome,max}} \right)^2}{3} = \frac{\left(c_{l,\text{tot}} / A \right)^2}{3}. \tag{4}$$

The method therefore provides an estimate of the uncertainty based on the overall maximum estimate of the concentration of impurities.

Where chemical assays are incomplete, i.e., lacking uncertainties or detection limits, or contain an incomplete list of detected elements, often no further claim can be made beyond the nominal purity (e.g., 99.9999% by mass, metallic elements only).

Where a complete impurity analysis is available, it is possible to use the SIE method for those impurities for which the liquidus slope is known and the OME method for the remainder. The SIE method generally yields smaller uncertainties than the OME method.

4 Isotopic Effects in Fixed Points

It has been known for sometime that the isotopic composition of the fixed-point substances has an effect on the fixed-point temperature. However, since the promulgation of the ITS-90, it has become clear that the natural variations in the isotopic composition of hydrogen, water, and neon are much greater than thought previously, and hence, variations in isotopic composition contribute significantly to the uncertainty in some fixed points. This has necessitated the introduction of a specified isotopic composition for these substances [9, 10], and guidelines for assessing uncertainty due to the departure of the isotopic composition from these values.

4.1 Water Triple Point

Previous definitions of the water triple point (WTP) implied that the water should have the isotopic composition of seawater. Recommendation 2 of the CIPM 2005 [9] has clarified this point and defined the composition to be that of Vienna Standard Mean Ocean Water (V-SMOW), a standard reference material distributed by the International Atomic Energy Agency (IAEA) for the standardization of isotopic analysis, and representative of standard mean ocean water.

Natural fractionation effects ensure that most of the continental surface (fresh) water, from which WTP cells are made, is depleted in the heavy isotope ^{2}H and, to a lesser extent, ^{18}O and ^{17}O, with a strong dependence on the latitude, altitude, and season at the location of the precipitation. During the distillation and degassing processes in the manufacture of the cells, the water may be further depleted or enriched. The combination of effects leads to cells that realize temperatures typically ranging between 10 above and 110 μK below the V-SMOW definition. Owing to the dependence on source water and processing, the isotopic depression in cells is highly dependent on the cell manufacturer. Recently, some manufacturers have begun to spike the source water with enriched water to obtain cells with compositions close to the V-SMOW definition. These cells may have an isotopic composition within $\pm 20 \mu$K of the ideal.

Ideally, the isotopic composition of the cell water should be measured by taking a sample after the cell has been sealed, and a correction applied [10]:

$$\Delta T_{\text{iso}} = -A_{\text{D}}\delta D - A_{18O}\delta^{18}O - A_{17O}\delta^{17}O, \tag{5}$$

where the δD, $\delta^{18}O$, and $\delta^{17}O$ are differences in isotopic composition from V-SMOW according to

$$\delta^{18}O = \left[\frac{(^{18}O/^{16}O)_{\text{sample}} - (^{18}O/^{16}O)_{\text{V-SMOW}}}{(^{18}O/^{16}O)_{\text{V-SMOW}}} \right], \qquad (6)$$

and similarly for δD and $\delta^{17}O$. The delta values are often expressed in permil ($^0\!/_{00}$, per thousand) and are usually negative for most cells. The values for the isotopic depression constants in Eq. 5, currently recommended for use with the ITS-90, are: $A_D = 628\,\mu K$, $A_{18O} = 641\,\mu K$, and $A_{17O} = 57\,\mu K$. The total uncertainty in the isotope correction is given by

$$u_{\text{iso}}^2 = u_{AD}^2\,(\delta D)^2 + u_{A18O}^2\left(\delta^{18}O\right)^2 + u_{A17O}^2\left(\delta^{17}O\right)^2$$
$$+ u_{\delta D}^2 A_D^2 + u_{\delta 18O}^2 A_{18O}^2 + u_{\delta 17O}^2 A_{17O}^2. \qquad (7)$$

The uncertainty is usually dominated by the uncertainties in δD and A_D. For a cell with not more than $100\,\mu K$ from V-SMOW, the uncertainty in the correction is of the order of $4\,\mu K$, which is generally negligible.

If no isotopic analysis is available for the water, the composition is assumed to lie in a rectangular distribution within $+10\,\mu K$ and $-110\,\mu K$ of V-SMOW. Thus, a correction of $+50\,\mu K$ and an uncertainty of $35\,\mu K$ will account for typical variations in isotopic composition of commercially available cells.

4.2 Hydrogen Point

Isotopic effects are the largest source of uncertainty for the equilibrium-hydrogen point. The isotopic composition of commercially available hydrogen varies from about $27\,\mu$mol D/mol H to about $155\,\mu$mol D/mol H. It has been established that the discrepancies previously found at the e-H$_2$ triple point are mainly due to the variable deuterium content in the hydrogen used for its realization. It is therefore specified [10] that the ITS-90 temperature for the triple point of equilibrium hydrogen, 13.8033 K, is taken to refer to hydrogen with an isotopic ratio of

$$D/H = 0.000\,089\,02. \qquad (8)$$

This is the isotopic ratio determined for SLAP (Standard Light Antarctic Precipitation), another standard reference material distributed by the IAEA. The specified isotope ratio is very close to the mean of observed ratios for commercially available hydrogen. Note that, in molecular forms, the isotopic ratio of hydrogen deuteride (HD) is approximately twice the ratio of atomic deuterium.

The isotopic correction for deuterium in the hydrogen triple point is

$$\Delta T_{\text{iso}} = k_D(x_0 - x), \qquad (9)$$

where x denotes the isotopic ratio of the sample in μmol D/mol H, $x_0 = 89.02\,\mu$mol D/mol H, and k_D is the slope of the temperature dependence of the triple-point temperature on the deuterium ratio. The value for k_D currently recommended for the ITS-90 is 5.42(31) μK per μmol D/mol H. The uncertainty in the isotope correction is

$$u_{\text{iso}}^2 = u_{k,\text{D}}^2 (x_0 - x)^2 + k_\text{D}^2 u_x^2. \tag{10}$$

The propagated uncertainty due to the uncertainty of k_D is less than $20\,\mu$K at the two extremes of observed isotopic compositions. Isotopic analysis of D/H may be obtained with standard uncertainties in the range 0.2–$1.5\,\mu$mol D/mol H, which contributes less than $8\,\mu$K uncertainty to the total uncertainty of the fixed-point realization.

If no isotopic analysis is available for hydrogen, then the composition is assumed to lie in a rectangular distribution within $\pm 65\,\mu$mol D/mol H of the standard composition, x_0, based on the observed distribution of the composition of commercially available hydrogen. The resulting uncertainty due to the unknown isotopic composition is therefore $200\,\mu$K.

4.3 Neon Point

Neon occurs naturally as three isotopes, ^{20}Ne, ^{21}Ne, and ^{22}Ne. The isotopic composition of atmospheric neon, which is normally taken to be the "natural composition", has the isotopes in the proportions 90.48%, 0.27%, and 9.25%, respectively. Note, particularly the large fraction of ^{22}Ne, which has a triple point temperature about 134 mK higher than neon of the natural composition and about 147 mK higher than that of ^{20}Ne.

Recent research on the composition of commercially available neon [11] suggests that most commercial sources are enriched in ^{22}Ne by the temperature equivalent of between 100 and $400\,\mu$K, with the composition strongly supplier-dependent. The natural variations in the ^{21}Ne contribute to variations in the triple-point temperature of less than $5\,\mu$K so are insignificant in comparison to the effect of ^{22}Ne.

In principle, the composition should be measured and corrected to the natural composition. However, at present this is impractical. There are very few laboratories that can provide accurate assays of the composition, in part because there is no convenient reference material for the calibration of mass spectrometers. There are also unresolved discrepancies between historical measurements (including atmospheric neon) and the more recent (and probably more accurate) measurements. The situation is complicated further because the composition of the neon used in the measurements that formed the basis of the ITS-90 is unknown. Until this situation is resolved, we have adopted a literal interpretation of the definition of uncertainty: that it characterizes the range of values that can reasonably be attributed to the neon point. We assume that the five independent samples measured by [11] are drawn from the full distribution of compositions of commercially available neon. We also assume that the neon used to define ITS-90 had a composition in the same range (so that no correction should be applied). The standard uncertainty in a realization of the neon point due to the isotopic composition is therefore

$$u_{\text{iso}} = 175\,\mu\text{K}. \tag{11}$$

Where expanded uncertainties are being calculated, a small number of effective degrees of freedom ($\nu = 4$) should be used. This recognizes the small number of independent samples of neon used to estimate the range of triple-point temperatures.

5 Oxidation Effects in SPRTS

5.1 Behavior of the Oxides

The chemical interactions between platinum and oxygen are extremely complex, with as many as a dozen possible oxides and allotropes. Two of these oxidation states, usually described as the two-dimensional and three-dimensional oxides, are of direct interest to platinum thermometry, and without appropriate care, the effects can cause hysteresis errors of many tens of millikelvin.

The potential energies of the oxidation states are such that, at room temperature, the 3D oxide is more stable than the 2D oxide, which is in turn more stable than metallic platinum. Above 0 °C, the rate of formation of the 2D oxide on the surface of the wire increases with temperature until about 380 °C, when it begins to dissociate. Annealing the SPRT at 450 °C will completely dissociate the 2D oxide.

The 3D oxide shows similar behavior but is restricted to a temperature range from 350 to 600 °C. The formation of the 3D oxide is autocatalytic, i.e., once started, it tends to proceed indefinitely. Modern SPRTs are generally constructed with a low partial pressure of oxygen to suppress the formation of the 3D oxide. An SPRT affected by the 3D oxide will exhibit a steadily increasing triple-point resistance. Annealing at 600 °C will cause the 3D oxide to rapidly dissociate and should largely restore the SPRT.

Berry [12] found that the effect of the 2D oxide is equivalent to a low-conductivity semiconductor layer about half of one atomic layer in thickness. The resulting changes in the resistance of the SPRT are related according to

$$\frac{\Delta R(t)}{R_{\text{H}_2\text{O}}} = ZW \frac{\Delta R_{\text{H}_2\text{O}}}{R_{\text{H}_2\text{O}}} \tag{12}$$

where $\Delta R_{\text{H}_2\text{O}}$ is the increase in the triple-point resistance due to oxidation, $\Delta R(t)$ is the increase in SPRT resistance at temperature, t, due to oxidation, and Z is a dimensionless parameter a little less than 1.0 and dependent on temperature and the relative electrical conductivities of the platinum oxide and platinum metal. The error in the resistance ratio calculated using a triple-point resistance measurement taken immediately after the measurement of $R(t)$, so that the SPRT is in the same oxidation state, is

$$\Delta W_{\text{ox}} = (Z - 1)\,W(t)\frac{\Delta R_{\text{H}_2\text{O}}}{R_{\text{H}_2\text{O}}}. \tag{13}$$

Note that W decreases with oxidation since $Z < 1$. Berry found that the factor $(Z - 1)W(t)$ was almost purely quadratic with values of 0.023, 0.081, and 0.22 at 100, 230, and 420 °C, respectively. Equations 12 and 13 show that the effect of oxidation is substantially reduced if the resistance ratio is calculated using the triple-point resistance of the SPRT in its oxidized state.

In order to avoid errors of several millikelvin due to 2D-oxidation effects, it is necessary to manage the effects. There are two main options.

5.2 High-Accuracy Measurements

For the highest-accuracy measurements, at fixed points for example, the resistance ratio should be calculated using the triple-point resistance measured immediately after the liquidus measurement at the fixed point (if SPRTs are allowed to stay hot in the fixed point or cool slowly below 450 °C, the oxidation may increase). All measurements for the Ga, In, Sn, and Zn fixed points should be measured this way. The uncertainty in the measured resistance ratio due to oxidation is then

$$u_{W,\mathrm{ox}}^2 = (1 - Z)^2 W(t)^2 \frac{u_{R,\mathrm{ox}}^2}{R_{\mathrm{H_2O}}^2} \qquad (14)$$

where $u_{R,\mathrm{ox}}$ is the uncertainty in the triple-point resistance due to oxidation estimated from the range of water-triple-point resistances observed during calibration. The relative uncertainty in the $(Z - 1)W$ term is small, less than 10^{-2}, so its contribution to the total uncertainty is usually negligible. An uncertainty of 2 ppm in triple-point resistance due to oxidation yields an uncertainty of about 100 μK at 400 °C. The effect scales approximately linearly with temperature, so the uncertainty would be about 25 μK at 100 °C.

5.3 General Purpose Measurements

The procedure above requires a water-triple-point-resistance measurement after each temperature measurement, which is impractical in automated calibration systems. For example, if the resistance ratios are calculated using a triple-point resistance taken at any another time when Eq. 12 does not apply, then the uncertainty in the calculated resistance ratio is very much larger.

The mean and range of triple-point-resistances observed when the SPRT is in typical use should be recorded. If the mean is used to calculate the resistance ratio W for the unknown temperature, then the uncertainty in the measured resistance ratio can be estimated as

$$u_{W,\mathrm{ox}}^2 = Z^2 W(t)^2 \frac{u_{R,\mathrm{ox}}^2}{R_{\mathrm{H_2O}}^2} \approx W(t)^2 \frac{u_{R,\mathrm{ox}}^2}{R_{\mathrm{H_2O}}^2}, \qquad (15)$$

where the uncertainty $u_{R,\text{ox}}$ is estimated from the range of observed triple point resistances. A 2 ppm uncertainty in the triple-point resistance yields an uncertainty of 2.0 mK at 400 °C.

6 Non-uniqueness

Ideally, the SPRT interpolating equations of ITS-90 should accommodate the real variations in the $W(t)$ relationship for different SPRTs. In practice, the functional form of the equations is insufficient to characterize the many complex physical effects that cause the variations, and hence the SPRT calibration equations are subject to interpolation error, conventionally described as non-uniqueness.

Historically, it has been unusual to include non-uniqueness in estimates of total uncertainty, in part because it is implicit in the ITS-90 definition, and in part because of the paucity of data. It is clear now that it is one of the most significant sources of uncertainty, contributing up to 0.5 mK or more uncertainty to temperatures interpolated between fixed points.

Non-uniqueness is manifest as variations in the scale because more than one equation is used with a single thermometer (Type 1 non-uniqueness, also called subrange inconsistency), more than one type of interpolating instrument is used (Type 2 non-uniqueness), or there are different instances of the designated interpolation instrument (Type 3 non-uniqueness) [13]. The guide considers only Type 1 and Type 3 non-uniqueness; Type 2 non-uniqueness contributes only between the e-H_2 point (13 K) and the Ne point (24 K) where the SPRT and gas thermometer subranges overlap. Any correlation between the two types of non-uniqueness is not known, presently, we assume they are not correlated.

The definition of the uncertainty for non-uniqueness is problematic because of the multiple subranges and definitions, some of which are infrequently used, each of which gives rise to very different, typically non-normal distributions of temperatures. There is also a paucity of data in some subranges. To yield a consistent uncertainty characterizing "the range of values that ITS-90 attributes to the temperature," the standard uncertainty assigned to non-uniqueness is calculated as the standard deviation of the differences from the mean of all possible formulations of the scale (i.e., averaged over different SPRTs, different subranges). Figures 1 and 2 below give examples of the two types of non-uniqueness. Note that both types of non-uniqueness have zeros at each of the fixed points used to calibrate the SPRTs.

7 Conclusions

7.1 Total Uncertainty in the SPRT Subranges of ITS-90

Figures 3 and 4 show the total uncertainty in the calibrations of SPRTs over two of the SPRT sub-ranges of ITS-90. It is important to note that the values shown are indicative or, in some sense, typical; they are not values taken from a real example. Also, the graphs exclude uncertainties that arise in the use of the SPRTs, which would be very application dependent. However, these graphs do give an indicative summary of the
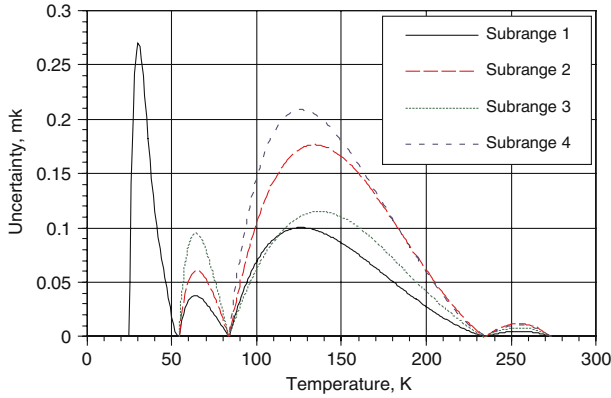
Fig. 1 Uncertainty ($k = 1$) due to Type 1 non-uniqueness over the range from 24 to 273 K [14]
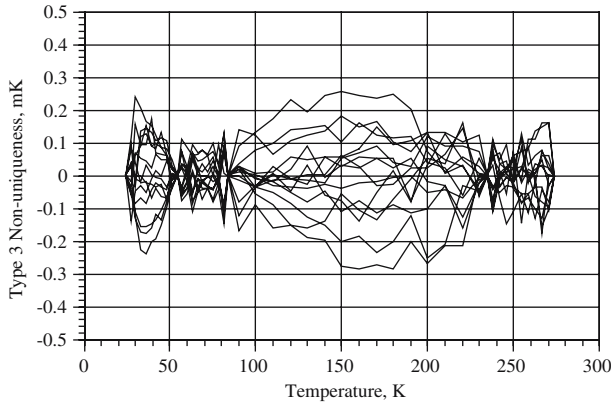

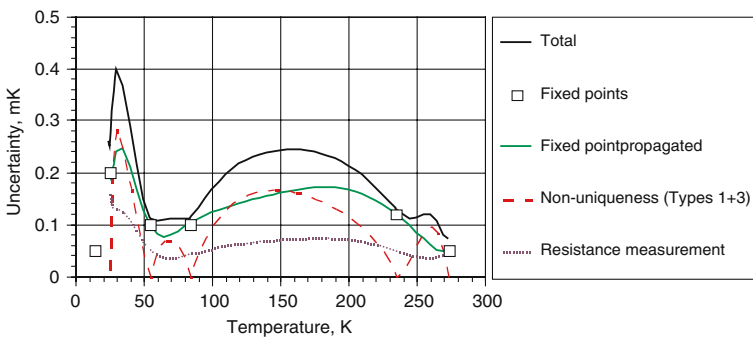**Fig. 2** Type 3 non-uniqueness of ITS-90 between 24 and 273.16 K [15]

Fig. 3 Contributions to the total calibration uncertainty ($k = 1$) for a capsule SPRT calibrated over the neon-water subrange
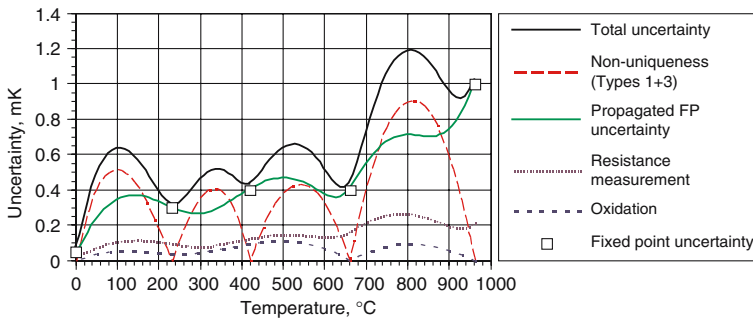
Fig. 4 Contributions to total uncertainty ($k = 1$) for a long-stem SPRT calibrated over the water-silver sub-range

calibration uncertainty achievable with SPRTs, and indicate the relative significance of major uncertainty terms.

In the low-temperature subranges (below $0\,°C$), the fixed-point uncertainties and the non-uniqueness are the most significant contributors to total uncertainty, in approximately equal measure. In the high-temperature sub-ranges (above $0\,°C$), the same components dominate again, but the non-uniqueness is demonstrably more significant between the fixed points.

7.2 Further Research

During the preparation of the guide, it became apparent that there were a number of aspects of SPRT thermometry where the uncertainty analysis is handicapped by a lack of understanding of an effect, or the lack of data, or both. We therefore encourage research into the following areas: impurities in the triple point of water, evaluation of the liquidus slopes for fixed-point impurities, validation of the SIE and OME approaches for assessment of uncertainty due to impurities, isotopic effects in fixed points (including fractionation in use), strain and crystal defects in fixed points, SPRT non-uniqueness (especially in the temperature ranges above $0\,°C$), SPRT insulation and leakage effects, SPRT oxidation, and static thermal effects in non-adiabatic fixed points.

7.3 Future of the Guide

The completion of the approximately 80-page guide represents the endpoint of significant work for many people over a long period, not including the efforts of the many researchers responsible for the more than 150 key references. But, it is nevertheless merely an overview and snapshot of the current state of knowledge. Uncertainty analysis has already advanced beyond the guide with the several dozen articles presented at this TEMPMEKO 2007 conference that make significant contributions to the understanding of the ITS-90 and its sources of uncertainty. Users of the guide are therefore

expected to follow up through the references in order to complete their uncertainty assessments and to supplement the guide with more recent publications.

The future of the guide is planned in the context of a major change in the definition of the kelvin expected in 2011 [16]. The CCT, through Working Group 1, will integrate the guide into revised supplementary information for the ITS-90, which will be incorporated in the new *mise en practice* [10] for the realization of the definition of temperature.

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