

Uncertainties in the SPRT Subranges of ITS-90: Topics for Further Research

D. R. White · M. Ballico · D. del Campo · S. Duris · E. Filipe · A. Ivanova · A. Kartal Dogan · E. Mendez-Lango · C. Meyer · F. Pavese · A. Peruzzi · E. Renaot · S. Rudtsch · T. Wang · K. Yamazawa

Received: 8 March 2010 / Accepted: 18 September 2010 / Published online: 6 October 2010
© Springer Science+Business Media, LLC 2010

Abstract The CCT has completed the guide summarizing the uncertainties in the realization of the SPRT subranges of ITS-90 between the triple point of neon (24.5561 K) and the freezing point of silver (961.78 °C). This article identifies aspects of standard platinum resistance thermometry where either data or models are lacking and further research is required. In the calibration of SPRTs, the two main concerns are the need for data on liquidus slopes for the different impurities in the fixed points and improved understanding of the impact of the thermal environment of the fixed point on the realized temperature. In the use of SPRTs, the two largest sources of

D. R. White (✉)
Measurement Standards Laboratory of New Zealand (MSL), Lower Hutt, New Zealand
e-mail: r.white@irl.cri.nz

M. Ballico
National Measurement Institute of Australia (NMIA), Sydney, Australia

D. del Campo
Centro Español de Metrología (CEM), Madrid, Spain

S. Duris
Slovak Institute of Metrology (SMU), Bratislava, Slovakia

E. Filipe
Instituto Português da Qualidade (IPQ), Monte de Caparica, Portugal

A. Ivanova
D.I. Mendeleev Scientific and Research Institute for Metrology (VNIIM), St Petersburg, Russia

A. Kartal Dogan
TUBITAK Ulusal Metroloji Enstitüsü (UME), Gebze-Kocaeli, Turkey

E. Mendez-Lango
Centro Nacional de Metrología (CENAM), Queretaro, Mexico

uncertainty are Types 1 and 3 non-uniqueness and oxidation. The causes of Type 3 non-uniqueness are not yet understood, especially at low temperatures, and there is a paucity of data for the high-temperature subranges. In respect of oxidation, there is a need for validation of the models developed in the 1980s, especially in light of the reduced partial pressure of oxygen used in modern SPRTs. A range of other effects including vacancy effects in SPRTs, isotopic effects in fixed points, and improved statistical methods are discussed.

Keywords Fixed points · Impurity · Standard platinum resistance thermometer · Uncertainty

1 Introduction

In October 2009, Working Group Three (on uncertainties) of the CIPM's Consultative Committee for Thermometry (CCT) released the guide *Uncertainties in the Realisation of the SPRT Subranges of the ITS-90* [1]. The main purpose of the document is to provide users of the International Temperature Scale of 1990 (ITS-90) [2–4] with guidance for assessing the uncertainty in calibrations and temperature measurements employing standard platinum resistance thermometers (SPRTs). Additionally, it promotes harmonization of the assessment of calibration and measurement capabilities in support of the CIPM's arrangement for the mutual recognition of national measurement institutes [5].

The guide provides a brief description of all known sources of uncertainty and influence variables, identifies key references in the literature that discuss, model or

C. Meyer

National Institute of Standards and Technology (NIST), Gaithersburg, MD, USA

F. Pavese

Istituto Nazionale di Ricerca Metrologica (INRIM), Torino, Italy

A. Peruzzi

VSL Dutch Metrology Institute (VSL), Delft, The Netherlands

E. Renaot

Laboratoire Commun de Métrologie LNE-CNAM (LNE-INM), Paris, France

S. Rudtsch

Physikalisch-Technische Bundesanstalt (PTB), Berlin, Germany

T. Wang

National Institute of Metrology (NIM), Beijing, China

K. Yamazawa

National Metrology Institute of Japan (NMIJ), AIST, Tsukuba, Japan

evaluate each effect, gives an indication of the magnitudes of the uncertainties, and gives propagation laws so that the total uncertainty may be determined. The guide is necessarily a snapshot of the state of knowledge *circa* 2008, and ongoing research continues to provide greater understanding of the practical limitations of ITS-90 and standard platinum resistance thermometry. The purpose of this article is to identify areas where further research is required, in particular, where more data are required or where there are opportunities for improved models. Occasionally, the article notes recent publications that add to material presented in the guide.

The sources of uncertainty identified here fall into two main groups: those associated with the realizations of the fixed points and those associated with the SPRTs. Section 2 deals with the first group and includes impurity effects, a variety of thermal and pressure effects, and isotopic effects. The second group deals with oxidation, vacancy effects, insulation breakdown, and non-uniqueness. Finally, we draw some conclusions and discuss the current limitations in ITS-90 and the possibility of improved uncertainty analyses allowing a reduction in the uncertainty in temperatures measured according to ITS-90.

2 Fixed Points

2.1 Impurity Effects

During the preparation of the SPRT uncertainty guide, it became clear that more confidence could be placed in Van't Hoff's relation than previously thought. The relation describes the elevation or depression of freezing points caused by impurities:

$$T_{f,\text{imp}} = T_f + \frac{RT_f^2}{\Delta H_f} \sum_i (k_{0,i} - 1)X_i, \quad (1)$$

where T_f is the freezing temperature of the pure substance, X_i 's are the amount of substance fractions of the i impurities in the liquid phase of the substance, $k_{0,i}$'s are the equilibrium distribution coefficients for each impurity, R is the gas constant, and ΔH_f is the molar enthalpy of fusion for the fixed-point substance. The factors $RT_f^2(k_{0,i} - 1)/\Delta H_f$ in Eq. 1 are the liquidus slopes, $dT_{f,\text{imp}}/dX_i$, for each impurity.

Van't Hoff's relation is believed, for both empirical and theoretical reasons, to be correct at the limit of zero impurity concentration [6]. Therefore, because of the very high purity of the substances used for fixed points, typically better than 99.9999 %, it possibly describes the effects of every impurity in all of the ITS-90 fixed points. In combination with analysis of the chemical composition of the fixed-point substance, Van't Hoff's relation provides the means for correcting observed liquidus temperatures for impurity effects, and is the basis of the sum of individual estimates (SIE) method for the impurity corrections and uncertainty analysis recommended by the Guide [1, Sect. 2.3].

2.1.1 Validity of the Model

The range of validity of Van't Hoff's relation is difficult to predict. At the low concentrations typical of fixed-point substances, the equation is expected to be valid. However, there remains the possibility, because of nearby phase transitions (e.g., due to the formation of other compounds at very low concentration) that it is not applicable for some combinations of impurities and fixed-point substances. Two avenues of research need to be explored. First, an expanded impurity model, which identifies additional influence variables and includes the next order of effects on liquidus temperatures, would increase confidence in the application of Van't Hoff's relation and help identify any impurity/fixed-point combinations for which the relation does not apply. Secondly, the phase diagrams for the fixed-point substances should be explored, in the regions of very low concentrations, for phase transformations that would signal the inappropriate use of Van't Hoff's relation.

2.1.2 Water Triple Point

At the time of the CCT-K7 comparison of water triple-point cells during 2002 to 2005, impurities were the major sources of uncertainty in the realization of the triple point of water, contributing up to 200 μK peak-to-peak variation in cell temperatures [7]. Observations by Hill [8] linking dissolution of glass to drift in cell temperatures, followed by chemical modeling of glass dissolution by water [9], has subsequently led to the use of fused silica for the triple-point-of-water cells. Recent measurements, e.g., [10, 11], have demonstrated that impurity effects can now be reduced to levels below 10 μK . It remains to be seen whether new CCT comparisons, which will almost certainly use cells of a wider variety of ages and manufacturers, yield such good results.

2.1.3 Cryogenic Fixed Points

For the most part, the cryogenic fixed points operate at such low temperatures that there can be few impurities dissolved in the fixed-point substance during the realization. Pavese [12] has cataloged the k_0 values for all the most common impurities, and chemical analysis is available to determine the chemical composition of the cells. Van't Hoff's relation, therefore, provides the means for applying corrections for each of the impurities in the cryogenic points. There are, however, two unresolved issues. Equation 1 can be expressed in terms of the impurity concentration in the liquid or the solid, giving different, but mathematically equivalent, expressions for the solidus and liquidus temperatures. At present, the liquidus- and solidus-slope data for fluorine in argon and for xenon in oxygen are not mutually consistent. This may be because the k_0 values are relatively close to 1.0, so that the two curves are difficult to distinguish experimentally, or it may be because the model breaks down in these cases. Further work is required to resolve these issues.

2.1.4 Metal Fixed Points

Impurity corrections based on Eq. 1 require knowledge of the liquidus slopes of all possible impurities, and complete data are not yet available for any of the metal fixed points. The problem has been complicated by the recent observation [13] that in metal fixed points containing some oxygen, a notable number of impurities precipitate as insoluble oxide and do not significantly affect the realized temperature. This means that Eq. 1 should be summed over only those impurities soluble in the fixed-point substance. The discovery also raises the possibility that other compounds may form and possibly precipitate.

Working Group One of the CCT has been collating the k_0 values for the impurities and, at present, the most extensive tables are for tin and aluminum. Another difficulty is that some combinations of impurities are difficult to distinguish chemically with the required low uncertainty. At present, therefore, Eq. 1 cannot be used to apply corrections for all impurities in the metal fixed points. The best approach is a hybrid method that makes corrections where the k_0 values and impurity concentrations are known, and determines an overall maximum estimate (OME) of the impurity effect [1] for the impurities for which the k_0 values are unknown. Further work is required to determine the k_0 values for the remaining impurities, and to investigate the precipitation process and residual solubilities.

2.1.5 Alternatives to SIE and OME Methods

The two uncertainty assessment methods for impurities that are described by the guide, and currently endorsed by the CCT, can be treated as occupying the extreme ends of the “knowledge spectrum.” At one end, the SIE method requires complete knowledge of the concentrations and k_0 values for every impurity, and determines a correction and uncertainty consistent with Van’t Hoff’s relation. At the other end of the spectrum, the OME method assumes only a total impurity concentration and the least knowledge on the behavior of impurities. This leads to a zero correction, based on the assumption that the mean temperature depression or elevation is expected to be zero, and yields a larger calculated uncertainty than appropriate for some fixed points. In principle, the application of any additional information on the behavior of the impurities should enable a reduction in the uncertainty below that for the OME method. For example, for some fixed points, all or almost all impurities depress the freezing point so that a correction can be applied and the OME uncertainty can be more than halved [14]. More work is required to establish such methods and identify the fixed points to which they can be applied.

2.1.6 Origin of Impurities

For most of the fixed points, impurities are the largest source of uncertainty. In addition to the impurities present in the highly purified substance, impurities are introduced via the cell or crucible materials, the processes used to fill the points, and (for the melting and freezing points) the ideally inert gas above the fixed-point substance. While many of these sources of impurity are understood for the cryogenic fixed points, the high

mobility of potential contaminants at temperatures above 600 °C makes the high-temperature fixed points particularly prone to contamination, and at present our knowledge of the origins of the impurities, the effects of particular impurities in the fixed point, and means of preventing the migration of impurities, is weak. Significant progress has been made with investigations of impurity effects in aluminum (e.g., [15–18]), but more work is required.

2.2 Isotopic Effects

Isotopic effects in the fixed points are very closely related to impurity effects, and occur at significant levels in the water triple point, the equilibrium-hydrogen point, and the neon point. In recent years, the CCT has addressed isotopic problems with the water triple point and the equilibrium-hydrogen points by defining the isotopic composition for the water or hydrogen to be used, and providing, in the *mise en pratique for the kelvin*, correction constants to be used when the substance departs from this value [19,20]. However, there remains a serious problem in the neon point due to the large natural variation in isotopic composition giving rise to a standard uncertainty of about 175 μK in the realized temperature. In principle, it is a simple matter to define a nominal composition and correction constant, as has been done for water and equilibrium hydrogen. In practice, a major technical obstacle is the lack of readily available and accurate means for measuring the isotopic composition of neon, in part due to the scarcity of suitable mass spectrometers and in part due to the lack of certified reference materials for calibrating the spectrometers for neon isotopes. The solution is possibly beyond our community's resources, and we may have to wait for analytical techniques to advance.

There is a possibility of significant isotopic effects in other fixed points; aluminum is the only fixed-point substance that exists as a single isotope and is, therefore, known to be free of isotopic effects. However, the magnitude of isotopic effects falls rapidly with atomic mass (approximately $(M_1 - M_2)/(M_1 M_2)$, where M_1 and M_2 are the atomic masses of the isotopes), so a significant effect becomes less likely as the atomic mass and freezing-point temperature increase. The isotope problem is almost certainly not a problem for gallium because there is very little variation in natural abundance, and measurements have established that there is no effect at the level of 10 μK to 20 μK [21]. However, tin and mercury have several isotopes with large differences in atomic mass and in high abundance, and large natural variations in abundance. If the variations in natural abundance are correlated with the fractionation factors (as they usually are), then there could be as much as 100 μK variation between cells due to isotopic effects. Preliminary results for mercury suggest any effect is probably below 100 μK [22], but further work is required for both tin and mercury.

2.3 Thermal Effects in Fixed Points

The aim with any fixed-point realization is to establish in the fixed-point substance a solid–liquid interface that completely surrounds the SPRT and maintains it at the defined temperature. This is most nearly achieved in the cryogenic triple points by

the calorimetric method, in which the fixed point is maintained in an adiabatic environment. This is necessary to enable tight control of the few joules of total energy required to melt the sample over a period of many hours. Additionally, simple experiments enable the quantification of background heat fluxes and empirical modeling of the first-order thermal response of the fixed point, which in turn enables remaining thermal errors to be corrected and minimized.

In contrast with cryogenic fixed points, which operate adiabatically in vacuum and at low temperatures, the metal fixed points are operated in air at higher temperature so that the thermal resistance between the furnaces and the fixed-point cell are very much lower and it is difficult to reduce the heat fluxes below a few watts. The usual solution is to rely on the establishment of two solid–liquid interfaces in the fixed-point cell. With this practice, the outer interface provides the temperature regulation for the inner interface, which is then in near-isothermal conditions. However, there remain several complications including the initiation of the freeze, SPRT immersion effects, and impurity segregation. A few experiments have investigated operating procedures that approximate adiabatic conditions, e.g., [23], but much more work is required to understand melting and freezing process in fixed-point cells.

2.3.1 Initiation of Freezing Points

The high surface energy of very small crystals makes them thermodynamically unstable at temperatures near the nominal freezing point of the fixed-point substance. For this reason, pure substances must be supercooled sufficiently below the freezing point to trigger the formation of crystals of sufficient size to nucleate the remainder of the freeze. Once initiated, the freeze accelerates, the crystals grow over the walls of the cell, enthalpy of fusion is released, and the cell temperature rapidly recovers to the freezing point. With appropriate cooling of the furnace and insertion of cool rods into the thermometer well, complete interfaces can be grown on the inner and outer walls of the cell. At present, the procedures for initiating the freeze in any fixed-point cell are highly empirical; every fixed point supercools differently, the degree of supercool depends on purity, every fixed-point furnace requires unique adjustments, and every cell requires a different number of rods to be inserted. In this respect, our understanding of the initiation process has advanced little since the work of McLaren [24]. Possible complications include the formation of incomplete interfaces either due to the incomplete formation of solid on the cell walls, or because of dendrite growth between the two solid layers.

In recent years, a number of publications demonstrate apparently good realizations with a single solid–liquid interface, e.g., [25]; although, there has been little evaluation of the differences between the two methods. It may be that the advent of heat-pipe furnace liners and improved temperature control have improved the uniformity of the furnace temperature so that a second solid–liquid interface is no longer required to mitigate possible thermal breaches in the first. While a poor fixed-point initiation is evident in a slow recovery from recalescence and from sensitivity to the furnace temperature, there are no guidelines or criteria for the development of initiation procedures. The furnace oscillation test [26] provides a good test of the completeness of

the phase boundary, but the test has not yet been applied to the evaluation of different initiation procedures.

2.3.2 *Interactions Between Thermal and Impurity Effects*

There are also interactions between the thermal treatment of a cell and impurity effects. For most fixed points, there is a significant difference between the melt and the freeze plateaus. In the absence of thermal coupling to the furnace or cryostat, the effects must be due to the segregation of impurities during freezing and dispersion of impurities during melting. In principle, because of segregation effects, the liquidus point is the only point on a melt or freeze plateau that enables modeling and correction of impurity effects. The differences between melts and freezes raise two key questions relating to the current working definition of the fixed-point temperature as the liquidus point. First, how long must a fixed point be maintained in the molten state prior to freezing to allow diffusion of the impurities? This is not often a major issue for the cryogenic fixed points because they are implemented as melting points and relatively rapid freezing does not allow significant segregation to occur, and because the impurities are uniformly distributed in the gas phase (prior to freezing). Secondly, how quickly must recalescence be completed to prevent segregation effects from affecting the highest recorded temperature on the plateau, which is taken to be the liquidus temperature [27]? To answer these questions, more information is required on the diffusion coefficients of the impurities and the vertical distribution of impurities within a cell. Both may be required to interpret the changes in temperature that occur as a freeze or melt progresses.

2.3.3 *SPRT Immersion Characteristics*

With a few exceptions, the high purity required of the fixed points makes fixed-point cells expensive items, and most laboratories are limited to the use of relatively short fixed-point cells with marginally adequate immersion for the SPRT. Adequate immersion is necessary to eliminate coupling between the SPRT and the furnace and the laboratory environment. There are two tests for satisfactory immersion, the furnace oscillation test and the immersion profile measurement. The furnace oscillation test measures the degree of coupling between the furnace and the SPRT, but cannot demonstrate the absence of coupling with the laboratory environment. The immersion profile measurement, which should track the hydrostatic correction line as the SPRT is withdrawn from the cell, demonstrates by the absence of any exponential decay in error versus immersion depth, that both forms of SPRT coupling are absent. The immersion profile test is commonly used in many laboratories, but there is little published on the typical results of such tests to clarify the difference between satisfactory and unsatisfactory results.

A few publications indicate that bushings or silicon oil improve the immersion characteristics for cells at temperatures below 200 °C, where the combination of the low thermal conductivity of air and poor radiation exchange yields a high value for the heat transfer coefficient between the SPRT and the cell. Bushings have also been

found useful in water, though some care is required with the choice of material [28]. More quantitative analysis is required to understand and quantify the possible benefits.

2.4 Pressure Effects in Fixed Points

For the most part, pressure effects in fixed-point cells are easily managed and corrected. However, for sealed fixed-point cells, the internal pressure is not measurable and the user is entirely reliant either on the manufacturer having sealed the cells at the correct pressure, or on an independent calibration with an open cell. A simple model derived in the guide [1, p. 5] shows that it is simple, in principle, if not in practice, to seal cells within 1 % or so of the correct pressure. This suggests that sealed cells should be repeatable to better than 100 μ K. Recent comparisons of cryogenic cells [29], many of which are sealed, have established that there is no major problem with sealed triple-point cells. Although there have been preliminary investigations into the reliability of sealed metal fixed-point cells [30], a comparison of sealed cells from different manufacturers and of different ages would be a valuable confidence-building exercise.

There is also a small possibility of a pressure-related effect in realizations of the triple point of water. At present the hydrostatic correction is based on the pressure exerted by the water at the depth of the SPRT sensing element. However, because of the 8 % difference in the density in the water and the ice, the pressure within the ice at a depth may be different from that in the water, and the ice may not be at isobaric conditions. Indications are that the water penetrates the grain boundaries within the mantle raising the local pressure so that the level of the liquid is the appropriate measure for calculating the correction, but this has not been established conclusively.

A second unexplained problem with the triple point of water relates to the measured hydrostatic pressure gradient being higher than the theoretical value [31,32], although typically within the uncertainty. The deviation is weakly correlated with the diameter of the thermometer well [7], and is suppressed by the use of bushings, e.g., [28], so the cause may be related to convection effects.

3 SPRT-Related Effects

3.1 Oxidation Effects

Currently, the largest source of uncertainty in the important temperature range from -40 °C to 450 °C is due to oxidation effects in long-stem SPRTs. Depending on the diameter of the platinum wire used in the SPRTs and the thermal treatment of the SPRT, errors of 5 mK or more are possible. While the oxidation effects are very well known in a qualitative sense, because most laboratories see the effects every day, we are entirely reliant on the work of Berry [33,34] for quantitative information on oxidation effects. Further, since Berry's work, SPRT manufacturers have reduced the partial pressure of oxygen in SPRT sheaths to reduce oxidation effects. It is, therefore, important to confirm Berry's quantitative observations and model of oxidation effects, and to characterize the magnitude of the effects for modern SPRTs of all designs.

3.2 Non-uniqueness

Over most of the SPRT subranges of ITS-90, the dominant contribution to uncertainty is the non-uniqueness of the SPRTs. This is the main factor limiting the accuracy of ITS-90.

3.2.1 Type 1 Non-uniqueness

Type 1 non-uniqueness, also known as subrange inconsistency, arises as the differences in the temperature indicated by a single SPRT when different calibration equations are used. The effect occurs because the interpolating equations defined by ITS-90 approximate the behavior of any SPRT. When an SPRT is calibrated over a different subrange, using different fixed points and/or different equations, the calibration equations differ. There are three contributions to this effect. First, the reference resistance ratios defined by ITS-90, between which the equations interpolate, are not consistent with the behavior of all SPRTs. Secondly, each SPRT has its own peculiar variations in its resistance–temperature relation, which are manifest as inconsistencies in deviations from the defined reference resistance ratios. Thirdly, differences caused by errors in the practical realization of the fixed points also give rise to inconsistencies between subranges. The uncertainties due to errors in the fixed-point realization are evaluated separately.

At present, the guide suggests a single Type B uncertainty to characterize the subrange inconsistency and that this should be applied to all SPRTs. However, it seems likely that some SPRTs have better interpolating qualities than others [35], at least over some subranges. It remains to be determined whether we can select SPRTs with a low subrange inconsistency or assign a fraction of the subrange inconsistency to a specific SPRT. For all the subranges, except perhaps the water–zinc subrange, there is a shortage of data on subrange inconsistency.

Subrange inconsistency is also manifest where subranges meet, as a discontinuity in the slope dT_{90}/dT . Most especially, this occurs at the triple point of water where all but one of the subranges terminate. Although most users of ITS-90 will not notice, there is the potential for measurements of some thermophysical properties to reflect the discontinuity. The same effects are responsible for the unexpectedly large subrange inconsistency between the mercury–gallium subrange and the other overlapping subranges [36]. More published values of the resistance ratios for the gallium and mercury points for SPRTs would aid in fully characterizing the discontinuity.

3.2.2 Type 3 Non-uniqueness

Type 3 non-uniqueness is manifest as different temperatures measured using different SPRTs in the same subrange, and arises again because the ITS-90 interpolations do not characterize fully the behavior of SPRTs. In the subranges above 0.01 °C, there is still a shortage of good quality data to assess the magnitude of the effect because the measurements are affected by the variable oxidation of the SPRTs and SPRT drift. In the high-temperature range, Matthiessen's rule, $R(T) = R(T)_{\text{ideal}} + \Delta R$, captures perhaps 90 % of the differences between different SPRTs, so that linear and quadratic

interpolation equations work remarkably well [35]. At temperatures below ~ 150 K, Matthiessen's rule does not work so well, which indicates at least one major physical effect for which we do not have a physical model. There are few data sets on which our assessments of this source of uncertainty is based. More data from different laboratories covering a wider range of thermometers would be useful.

3.3 Vacancy Effects

At temperatures above 600 °C or so, the resistance of SPRTs is increased by the thermally induced vacancies in the crystal lattice of the platinum wire. The resistance increases according to

$$\Delta R \propto R(0.01 \text{ }^\circ\text{C}) \exp\left(\frac{-E_v}{kT}\right), \quad (2)$$

where E_v is the energy required to create the vacancy. In principle, knowledge of the value of E_v is not required because the equilibrium resistance is established very quickly at high temperatures. However, it is when cooling or annealing the thermometer that an understanding of the vacancy generation process is required. It has a direct impact on maximum rates of cooling and the minimum annealing times following exposure at higher temperatures. At present, there are no widely accepted guidelines for annealing or any indication of the compromise between annealing temperatures and times versus residual vacancy effects. The thermal process is probably complicated by the presence of higher-order (and higher-energy) defects at the highest temperatures where SPRTs are used. This problem was addressed by Berry [37,38], but more work is required to demonstrate and prove annealing procedures.

3.4 Long-Term Drift

There are at least three mechanisms contributing to the long-term drift of SPRTs: mechanical and three-dimensional oxidation damage, which changes the dimensions of the wire; the accumulation of high-energy defects that cannot be removed by annealing; and the contamination of the platinum wire. To a limited extent, the different types of damage can be distinguished from the history of usage and behavior of the SPRT during annealing. But better understanding of the mechanisms at different temperatures, typical rates of change for each mechanism, and distinguishing features of the mechanisms, would enable better assessments of uncertainty due to drift. This problem was also addressed by Berry [39].

One of the problems with contamination of high-temperature SPRTs is that not much is understood about the origin of the contamination. A few substances like copper are known to diffuse through fused silica, but little is known of other potential contaminants or the temperatures at which such diffusion begins to take place. Additionally, what are the possible protection strategies? Platinum foil barriers work to some degree and a voltage bias on the SPRT appears to prevent the migration of some impurities, e.g., [40], but otherwise we have no quantitative models or explanations.

3.5 Insulation Breakdown Effects

One of the significant sources of uncertainty for temperatures near the silver point (~ 960 °C) is the variable insulation resistance of SPRTs. The complex insulation breakdown effect, which can contribute several millikelvin uncertainty even for 0.25Ω thermometers, is thought to be caused by the formation of metal-semiconductor diodes (Schottky or point-contact diodes) at the points of contact between the silica insulators and the platinum wire of the sensor and lead wires [41,42]. The recognition of the diodes may yet result in improvements to SPRT design, e.g., use of sapphire rather than fused silica insulation disks in the SPRTs. However, the problem remains of how to assess the uncertainty due to insulation breakdown in existing SPRTs. One possibility may be to exploit the sensitivity of the diode resistance to a dc bias voltage. For example, several papers report that a change in a bias voltage applied to the resistance measurement circuit affects the reading [43–45]. However, interpretation of such a change in resistance is complicated because the bias voltage is typically applied via the furnace heater. The complexity arises from the different possible heater supplies, their polarity and electrical connections, the type and dimensions of the materials used to insulate the furnace and the cell assembly, and the temperature distribution along the length of the thermometer. Further research is required on both the breakdown effect and the assessment of its magnitude.

4 Conclusions

A wide range of possible research areas has been identified with the potential to improve the quality of measurements made with SPRTs. No doubt, many of the topics will be the subject of papers at this TEMPMEKO 2010 conference. The effects where there is the greatest opportunity to reduce uncertainty or improve confidence in current models and analysis are associated with the SPRT itself: non-uniqueness and oxidation effects. For temperature measurements made near fixed points, the greatest contribution to the uncertainty continues to be impurity effects, and research on thermal effects, diffusion constants, and distribution coefficients are all required to make significant progress.

References

1. D.R. White, M. Ballico, V. Chimenti, S. Duris, E. Filipe, A. Ivanova, A.K. Dogan, E. Mendez-Lango, C. Meyer, F. Pavese, A. Peruzzi, E. Renaot, S. Rudtsch, K. Yamazawa, CCT Working Document CCT/08-19/rev. (2009)
2. H. Preston-Thomas, *Metrologia* **27**, 3 (1990)
3. H. Preston-Thomas, *Metrologia* **27**, 107 (1990)
4. H. Preston-Thomas, P. Bloembergen, T.J. Quinn, *Supplementary Information for the ITS-90* (BIPM, Sevres, 1990)
5. International Committee for Weights and Measures (CIPM), in *Mutual Recognition of National Measurement Standards and of Calibration and Measurement Certificates Issued by National Metrology Institutes* (BIPM, Sèvres, 1999)
6. A. Prince, *Alloy Phase Equilibria* (Elsevier, Amsterdam, 1966)

7. M. Stock, S. Solve, in *CCT-K7: Key Comparison of Water Triple Point Cells Report B* (BIPM, Sevres, 2006)
8. K.D. Hill, *Metrologia* **38**, 79 (2001)
9. D.R. White, C.J. Downes, T.D. Dransfield, R.S. Mason, in *Proceedings of TEMPMEKO 2004, 9th International Symposium on Temperature and Thermal Measurements in Industry and Science*, ed. by D. Zvizdić, L.G. Bermanec, T. Veliki, T. Stašić (FSB/LPM, Zagreb, 2004), pp. 251–256
10. G.F. Strouse, M. Zhao, *Int. J. Thermophys.* **28**, 1913 (2007)
11. M-K. Nguyen, M. Ballico, *Int. J. Thermophys.* **29**, 1761 (2008)
12. F. Pavese, *Metrologia* **46**, 47 (2009)
13. M. Fahr, S. Rudtsch, *Metrologia* **46**, 423 (2009)
14. D.R. White, *CCT Working Document CCT/05-09* (BIPM, Sèvres, 2005)
15. J.V. Widiatmo, H. Katsuhiko, M. Arai, in *Proceedings of TEMPMEKO 2004, 9th International Symposium on Temperature and Thermal Measurements in Industry and Science*, ed. by D. Zvizdić, L.G. Bermanec, T. Veliki, T. Stašić (FSB/LPM, Zagreb, 2004), pp. 239–244
16. E. Renaot, *CCT Working Document CCT/08-10* (BIPM, Sèvres, 2008)
17. S. Gerasimov, A. Pokhodun, E. Renaot, *Int. J. Thermophys.* **28**, 1957 (2007)
18. E. Renaot, M.H. Valin, M. Elgourdou, *Int. J. Thermophys.* **29**, 852 (2008)
19. International Committee for Weights and Measures (CIPM), in *Procès-Verbaux des Séances du Comité International des Poids et Mesures*, vol. 73 (2005), p. 235
20. International Committee for Weights and Measures (CIPM), in *The Mise en Pratique for the Definition of the Kelvin* (CIPM, Sevres, 2006)
21. B.W. Mangum, D.D. Thornton, *Metrologia* **15**, 201 (1979)
22. D. del Campo, V. Chimenti, J. Reyes, J.A. Rodriguez Castrillon, M. Moldovan, J.I. Garcia Alonso, *Int. J. Thermophys.* **29**, 93 (2008)
23. R. Morice, G. Bonnier, J.C. Barbaras, N. Fleurence, V. Le Sant, P. Ridoux, J.R. Filtz, *Int. J. Thermophys.* **29**, 1785 (2008)
24. E.H. McLaren, E.G. Murdock, *Can. J. Phys.* **46**, 369 (1968)
25. K. Yamazawa, J.V. Widiatmo, M. Arai, *Int. J. Thermophys.* **28**, 1941 (2007)
26. M. Fahr, S. Rudtsch, *Int. J. Thermophys.* **29**, 126 (2008)
27. B.W. Mangum, P. Bloembergen, M.V. Chattle, B. Fellmuth, P. Marcarino, A. Pokhodun, *CCT Working Document CCT/2000-13* (BIPM, Sèvres, 2000)
28. P.P.M. Steur, R. Dematteis, *Metrologia* **45**, 529 (2008)
29. F. Pavese, J. Ancsin, D.N. Astrov, J. Bonhoure, G. Bonnier, G.T. Furukawa, R.C. Kemp, H. Maas, R.L. Rusby, H. Sakurai, S-K. Ling, *Metrologia* **20**, 127 (1984)
30. E. Renaot, Pres. CAFMET, Cairo (2010)
31. M. Hiti, J. Bojkovski, V. Batagelj, J. Drnovšek, *Meas. Sci. Technol.* **16**, 2375 (2005)
32. H. Sakurai, *Trans. Soc. Inst. Cont. Eng. (Japan)* **38**, 590 (2002)
33. R.J. Berry, *Surf. Sci.* **76**, 415 (1978)
34. R.J. Berry, in *Temperature: Its Measurement and Control in Science and Industry*, vol. 5, ed. by J.F. Schooley (AIP, New York, 1982), pp. 743–752
35. D.R. White, G.F. Strouse, *Metrologia* **45**, 101 (2009)
36. Y.P. Singh, H. Maas, F. Edler, Z.H. Zaidi, *Metrologia* **31**, 49 (1994)
37. R.J. Berry, J.L.G. Lamarche, *Phys. Lett. A* **31**, 319 (1970)
38. R.J. Berry, in *Temperature: Its Measurement and Control in Science and Industry*, vol 4, ed. by R.P. Hudson (ISA, Pittsburgh, 1972), pp. 937–949
39. R.J. Berry, *Metrologia* **2**, 80 (1966)
40. N.P. Moiseeva, A.I. Pokodun, B.W. Mangum, G.F. Strouse, in *Proceedings of TEMPMEKO '99, 7th International Symposium on Temperature and Thermal Measurements in Industry and Science*, ed. by J.F. Dubbeldam, M.J. de Groot (Edauw Johannissen bv, Delft, 1999), pp. 371–376
41. D.R. White, M. Arai, A. Bittar, K. Yamazawa, *Int. J. Thermophys.* **28**, 1855 (2007)
42. K. Yamazawa, M. Arai, D.R. White, *Int. J. Thermophys.* **28**, 1843 (2007)
43. J.P. Evans, *J. Res. Natl Bur. Stand. (U.S.)* **89**, 384 (1984)
44. R.J. Berry, *Metrologia* **32**, 11 (1995)
45. K. Yamazawa, M. Arai, in *Proceedings of TEMPMEKO 2004, 9th International Symposium on Temperature and Thermal Measurements in Industry and Science*, ed. by D. Zvizdić, L.G. Bermanec, T. Veliki, T. Stašić (FSB/LPM, Zagreb, 2004), pp. 409–414