

The Role of High-purity Noble Metals in Precision Thermometry

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Abstract

A variety of alternate calibration schemes which approximate the ITS-90 are possible when using high-purity noble metals. The high purity of the sensor materials allows the use of correlations that exist between the measured properties at fixed point temperatures. The data from NIST Standard Reference Materials 1749 and 1750 serve to illustrate the degree to which such schemes may succeed using comparable material. The result is a variable cost versus accuracy trade-off in calibration procedures that can be customized to the measurement needs of various industry sectors.

1. Introduction

The costs associated with maintaining accuracy in any thermometer are predominately tied to the supporting calibration infrastructure. This infrastructure is the hierarchical system of traceable measurements necessary to ensure the validity of results at each tier of accuracy.[1] As the accuracy and/or the range demands on a thermometer increase, the number of calibration points, and hence the costs, also increase. This is a common feature of all artifact thermometers where the device characterization is to a certain extent unique to each device.

The traditional approach employed in the industrial environment to keep these calibration costs under control has been to exploit device interchangeability. This is the property of devices to reproduce equivalent characteristics from one device to the next. It is the lot-to-lot chemical uniformity of the sensor material within each device which allows this interchangeability to be realized.

In contact thermometry, interchangeable devices have long existed in several forms, including base metal thermocouples,[2] metal resistance thermometers,[3] some types of metal-oxide thermistors,[4] and semiconductor diode thermometers.[5] In each case, however, conformance to recognized standard curves is subject to the accidental variations in the chemical composition and physical state of the sensor material.

The degree of interchangeability possible in thermometers when using pure noble metals as the sensor material is superior to all other materials. This can be demonstrated in two examples presented here: the gold versus platinum (Au/Pt) thermocouple and the Pt resistance thermometer. For

these noble metals, the sample to sample uniformity and the intra-sample homogeneity that is achievable today permit the derivation of universal reference functions. A well known application of these reference functions is to support the use of standard type and secondary type interpolating thermometers. An additional potential benefit, perhaps less well appreciated, is the use of these noble metal devices to reduce the calibration overhead costs in various industrial applications.

2. Preliminaries

Thermocouples constructed from pure elements, the Au/Pt or Pt/Pd thermocouple for example, [6,7] do not suffer from preferential oxidation problems. This fact has several important consequences: pure element thermocouples are inherently more thermoelectrically homogeneous, and their thermoelectric stability is not limited by shifts in alloy composition caused by preferential oxidation. Additionally, because pure element thermocouples do not require adjustments of alloy composition to match a reference function, the interchangeability of thermocouples manufactured from sufficiently pure elements is excellent and the deviations of actual thermocouples from the appropriate reference function are small. In the case of Au/Pt thermocouples, homogeneity and initial calibration tolerances are superior to those of a type S or type R thermocouple by over an order of magnitude, and no long-term drift has been detected over 1000 hours of use. [6]

Platinum Resistance Thermometers (PRTs) have well established standard specifications for industrial use.[8,9] These industrial PRTs (IPRTs) are normally differentiated according to two or more tolerance classes, but all IPRTs are designed to conform to the nominal curve of platinum having a temperature coefficient of resistance of $\alpha=0.00385\text{ K}^{-1}$ between $0\text{ }^{\circ}\text{C}$ and $100\text{ }^{\circ}\text{C}$. The curves of the industrial specifications span the ranges between $-200\text{ }^{\circ}\text{C}$ and $600\text{ }^{\circ}\text{C}$ or in some cases $850\text{ }^{\circ}\text{C}$. These specifications are designed for only a moderate purity grade of platinum, but it is not difficult to produce platinum elements of significantly higher purity.

Platinum of sufficiently high purity exhibits temperature coefficients of resistance of 0.003926 K^{-1} or higher. Suitably constructed PRTs made from this grade of wire can be used with the Pt reference function $W_1(T)$ as specified in the International Temperature Scale of 1990 (ITS-90).[10] This

Table 1. Standard Reference Materials for thermometers utilizing high purity noble metals in their construction.

SRM	Temperature Range	Type	Output range	Sensitivity	Stability
1749	273.16 K to 1234.93 K	Au-Pt thermocouple	0 μ V to 16,100 μ V	(5 to 25) μ V/K	15 mK/1000 h
1750	13.8033 K to 430 K	SPRT capsule	0.03 Ω to 41.0 Ω	(0.006 to 0.1) Ω /K	

reference function facilitates the interpolation of temperature to both higher and lower limits than what is specified in the industrial standards. Interpolation of temperature can be also much more accurate with this grade of platinum. While Standard PRTs (SPRTs) are more delicate than IPRTs, the advantages conveyed by the use of the higher purity material do not always require use of a traditional SPRT design. Most of the properties we will discuss here would in fact convey to some of the more robust element designs encountered in IPRTs, providing the Pt is of sufficient purity.

3. Results

We present results from two sets of thermometers prepared for the Standard Reference Material[®] (SRM[®]) Program at NIST: the SRM 1749 gold versus platinum thermocouple, and the SRM 1750 capsule standard platinum resistance thermometer (SPRT). Table 1 shows a summary of their respective properties.

3.1. SRM 1749

Although the SRM 1749 thermocouple operates on the same physical principles as all other thermocouples, advances in the fabrication and annealing techniques result in a thermocouple thermometer that has vastly superior accuracy and homogeneity relative to other thermocouples over the range 0 °C to 1000 °C.

Eighteen SRM 1749 thermocouples were constructed from 0.5 mm diameter Au and Pt wire of the highest purity available, typically 99.999 wt%. The fabrication techniques followed previous practice.[6,7] The annealing of the Au and Pt wire is a critical process in producing thermoelements that are thermoelectrically stable and uniform along the length of the thermoelements. High temperature annealing serves to relieve any mechanical strains in the wire and may reduce the quantity of impurities in the wire by either driving off volatile impurities or by oxidizing reactive impurities. Two common methods of annealing are either to anneal the wire electrically by suspending a loop of wire from two clips and heating the wire by passing AC current through the wire, or to anneal the wire by placing the wire in a uniform zone of a furnace. Au has insufficient mechanical strength to be reliably anneal electrically, so the Au wires were annealed only in a furnace. The Pt wire was electrically annealed, and then both Pt and Au wires were furnace annealed by pulling segments of the wire into the bores of a high-purity alumina insulator tube, and placing the alumina tube into a three zone furnace. Furnace annealing schedules are 10 h at 1000 °C and

overnight at 450 °C for Au, and 1 h at 1100 °C and overnight at 450 °C for Pt.

Following annealing, pull wires were used to thread the thermoelements into the 1.6 mm bores of a twin bore, high-purity alumina tube. A relatively large bore diameter allows the thermoelements to move easily through the bores as they expand with heating. Three annealed segments of Au or Pt needed to be butt welded to form thermoelements of sufficient overall length. To minimize any effects of inhomogeneity caused by the welding, the butt welds occur at locations along the thermocouple length that are exposed only to room temperature during calibration or use. To prevent mechanical strain of the thermoelements, and the thermoelectric changes that would accompany strain, it is important to allow for the differential thermal expansion of the Au and Pt. As shown in Fig. 1, a four or five turn coil of 1 mm diameter constructed from 0.12 mm diameter Pt wire was used to connect the thermoelements at the measuring junction, thereby allowing unconstrained thermal expansion of both the Au and Pt wires.

At the end of the thermocouple opposite the measuring junction, the thermocouple wires were insulated with flexible fiber-glass tubing, and in the region where the thermoelements emerged from the alumina insulator a cylindrical sleeve of soft copper was crimped over the fiber-glass tubing. This crimp tube compresses the fiber-glass tubing against the thermoelements to anchor the wires near the end of the alumina insulator. A pair of insulated copper lead wires was soldered to the ends of the thermoelements opposite the measuring junction, and the Cu/Au or Cu/Pt junctions are the reference junctions of the thermocouple. Both copper wires were cut from one spool to minimize any thermal emf caused by slight mismatches in the copper composition.

After construction, each thermocouple was furnace annealed in air for 1 h at 1000 °C, slowly cooled to 450 °C, and held at 450 °C overnight. Then, the effects of inhomogeneity of the thermocouple were determined by measuring the thermocouple emf during a freeze of the Ag, over a period of 90 min. Measurements were performed while inserting the thermocouple in steps into the cell, and while withdrawing the thermocouple. At immersions greater than 8 cm, the thermocouple measuring junction was in thermal equilibrium with the freezing metal. Any deviation from a constant value of emf was taken as an indication of inhomogeneity or drift of the thermocouple. An immersion curve of a typical Au/Pt thermocouple is shown in Fig. 2. The insensitivity of the thermocouple emf to depth of immersion is an indication of high homogeneity of the Au and Pt.

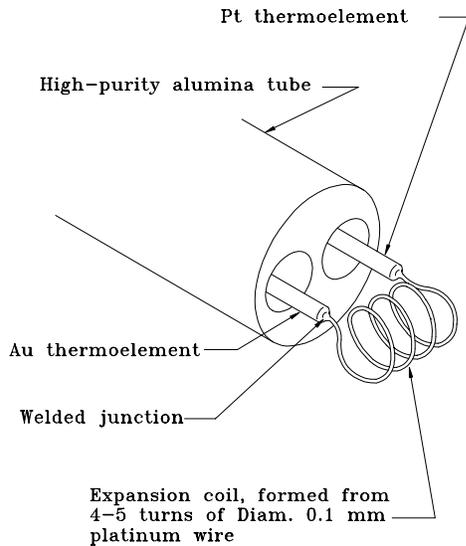


Figure 1. Schematic drawing of the thermal expansion coil at the measuring junction of a Au/Pt thermocouple.

A reference function for Au/Pt thermocouples on the ITS-90 has been measured at NIST over the range 0 °C to 1000 °C [6]. Au/Pt thermocouples can readily be calibrated by measuring the thermocouple emf at fixed points defined on the ITS-90. The fixed points used are ice (0 °C), indium (156.5985 °C), tin (231.928 °C), zinc (419.527 °C), aluminum (660.323 °C), and silver (961.78 °C). The reference junctions of the thermocouples were maintained at 0 °C in an ice bath when measurements were made. The ice point is not commonly used as a calibration point for thermocouples, because the theory of homogeneous thermocouples predicts an emf value of zero when the measuring junction and reference junctions are at identical temperatures. However, there are small deviations from this ideal behavior due to

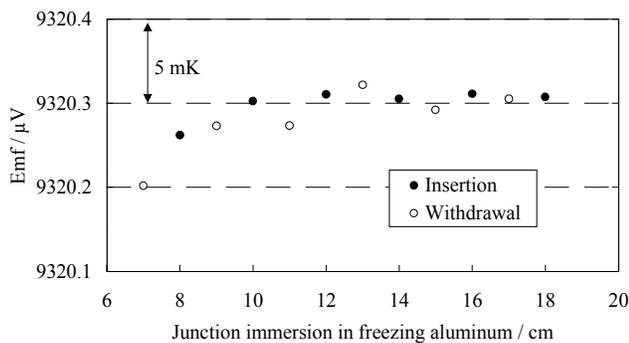


Figure 2. Values of emf measured for an SRM 1749 thermocouple on insertion into and withdrawal from the Al freezing-point cell during a freeze.

small inhomogeneities in either the thermoelements or the copper lead wires. To attain the highest accuracies, a calibration at the ice point is necessary to correct for these inhomogeneities.

When the emf values computed from the reference function are subtracted from the measured values, the resulting emf deviation can be modeled by a quadratic function of temperature. Coefficients of the quadratic function are determined by the method of least squares, and addition of these coefficients to those of the reference function will give the calibration function for the particular thermocouple under test.

The standard uncertainty of the calibration is approximately 4 mK over most of the range of the thermocouple, and rising to 7 mK at 1000 °C. Figure 3 shows the dominant components of the calibration uncertainty of the SRM 1749 thermocouples. As seen in Figure 3, no single uncertainty component dominates the combined uncertainty over the full temperature range. At low temperatures, the uncertainty of the reference function is dominant. Above 962 °C, the reference function is based on an extrapolation of the ITS-90, which is not well known, and this becomes the dominant uncertainty. For intermediate temperatures, the thermocouple reproducibility, the uncertainty of the emf measurements, and the thermocouple inhomogeneity are all significant.

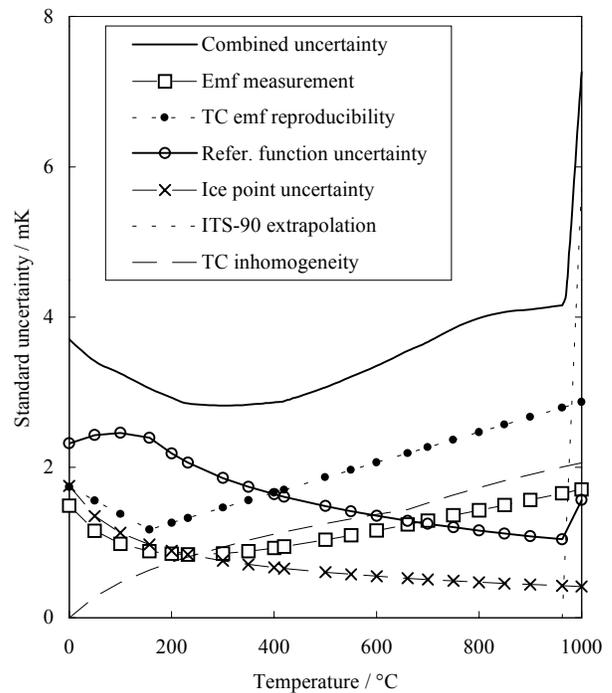


Figure 3. Calibration uncertainties and subcomponent uncertainties for the SRM 1749 thermocouples. Only subcomponents that are significant over some range of temperature are shown.

The results of the fixed-point measurements for all 18 SRM 1749 thermocouples that were constructed are shown in Fig. 4. The emf versus temperature responses of the SRM 1749 thermocouples deviate from the reference function by no more than 16 mK. The very close agreement of the SRM 1749 to the reference function indicates that Au and Pt of

reproducibly-high purity can be obtained, allowing a high degree of interchangeability with Au/Pt thermocouples. The maximum spread of the thermocouple emfs for all of the SRM 1749 thermocouples is approximately 8 mK for all fixed points in the range 0 °C to 962 °C. This very small spread demonstrates that with care in fabrication and annealing, the thermoelectric response of Au/Pt thermocouples is highly repeatable for a single lot of Au and Pt wire.

For industrial sensors where an additional uncertainty of the order of 10 mK is allowable, the thermoelectric calibration of Au/Pt thermocouples does not require calibration of each sensor at all of the ITS-90 fixed-points shown in Figure 4. Instead, it is possible to a) calibrate only representative samples from the lot and/or b) calibrate the thermocouples at only a subset of fixed points: the melting point of ice and the freezing points of zinc and silver, for example.

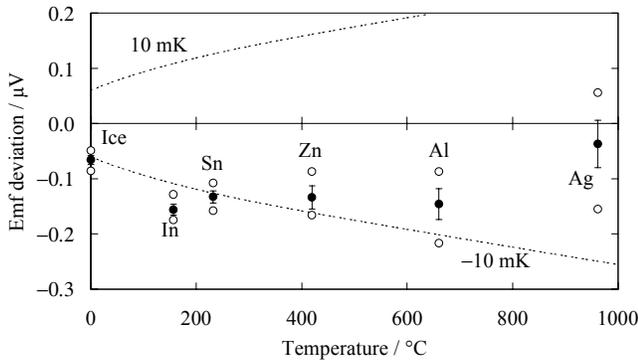


Figure 4. Difference between the measured emf values for the SRM 1749 thermocouples and the reference function for Au/Pt thermocouples. Solid circles indicate the average value for all thermocouples, the open circles indicate maximum and minimum values, and the error bars indicate one standard deviation variations in the emf values.

3.2. SRM 1750

The SRM 1750 is a set of 20 capsule type SPRTs which have been calibrated at NIST between 13.8 K and 430 K according to ITS-90 definitions.[11] Each capsule is a hermetically-sealed sample of 76 μm diameter Pt wire, which has been fully annealed prior to encapsulation.

The SRM 1750 is evaluated with respect to the established ITS-90 reference function for Pt. In general, most Pt wire found in SPRTs will exhibit resistance ratios $W(T)=R(T)/R(273.16\text{ K})$ which are slightly less than those given by the reference function $W_r(T)$ for $T>273.16\text{ K}$ or slightly greater than those given by the reference function for $T<273.16\text{ K}$. The reference function is shown in Figure 5 along with the ITS-90 defined fixed points. This function spans more than 3 1/2 decades in resistance ratio over almost two decades in temperature.

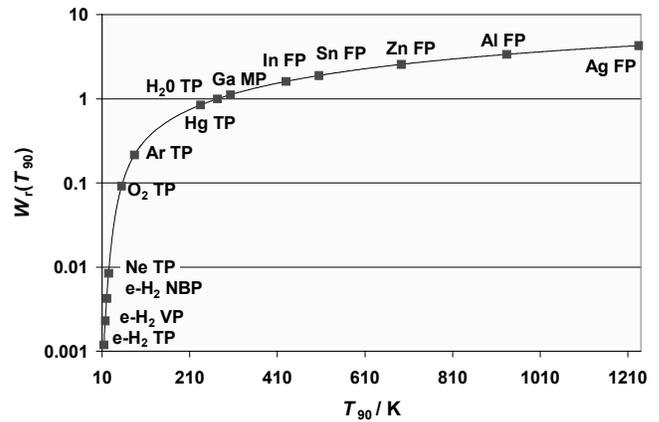


Figure 5. The ITS-90 Pt reference function and the defined values for the 14 fixed points used in SPRT calibrations. MP=Melting Point; FP=Freezing Point; TP=Triple Point; NBP=Normal Boiling Point; VP=Vapor pressure Point.

The degree to which a given sample of Pt approximates $W_r(T)$ is quantified as the deviation $\Delta W(T)=W(T)-W_r(T)$. In the case of SRM 1750 Pt, the $\Delta W(T)$ values are all less than 2.4×10^{-5} in magnitude in the range between 234.3 K and 302.9 K. This is illustrated in Figure 6 in relation to the ITS-90 minimum purity criteria for $\Delta W(\text{Ga MP})$ and $\Delta W(\text{Hg TP})$. This figure also illustrates the high degree of correlation which exists between $\Delta W(T)$ values (or $W(T)$ values) in the SRM 1750 Pt at these two fixed point temperatures. In fact, similar correlations are a common feature to all high purity Pt, not just the SRM 1750 Pt, over the entire range of ITS-90 calibration temperatures.

A set of correlation lines for the SRM 1750 are shown in Figure 7 for the lowest seven SPRT calibration points on the ITS-90 with the Ga MP. The correlations are parameterized in terms of ΔW values expressed as equivalent temperature deviations in units of mK.

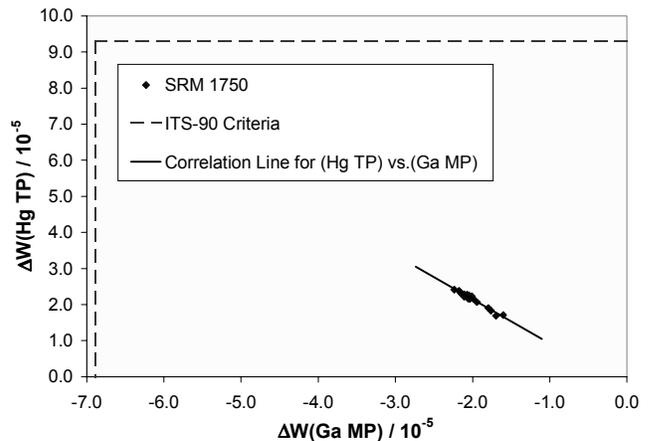


Figure 6. The measured deviations of SRM 1750 Pt samples at the Hg TP and Ga MP in relation to the ITS-90 criteria bounds for SPRTs.

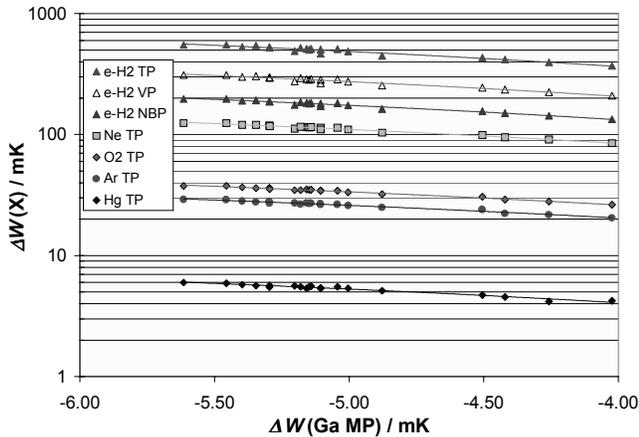


Figure 7. SRM 1750 correlation lines for the seven lowest SPRT calibration points of ITS-90 with the Ga MP.

It is also possible to use calibration fixed points which are not defined in the ITS-90 reference function or, in some cases, even below the lower temperature limit of 13.8 K. A convenient choice for such an additional fixed point is the normal boiling point of liquid ^4He , ($T=4.22$ K), which approximately represents the residual effects of impurities in the Pt. For SRM 1750 Pt, the deviations at the lowest four ITS-90 fixed points temperatures are in fact better correlated with their $W(4.22$ K) values than with $\Delta W(\text{Ga MP})$ values. This suggests substitution of the values correlated with $W(4.22$ K) for some or all of these lower temperature calibration fixed points. The more common parameterization for this point is the Residual Resistance Ratio, or “RRR”, which is approximately given by $RRR=0.99996/W(4.22$ K). Correlations for the lowest six SPRT calibration points on the ITS-90 with the RRR values of the SRM 1750 are shown in Figure 8.

The existence of correlations between ΔW values at fixed point temperatures in high purity platinum is to be expected given the normal assumptions made in modeling pure metal resistivity. A basic underpinning in most such models is the separability of different resistivity contributions due to the different electron scattering mechanisms which predominate in different temperature ranges. This separable feature is best known in the form of “Matthiessen’s Rule” and is known to be approximately true for many high purity metals in addition to Pt.[12] One consequence of this model is that the correlations shown in Figures 7 are, to a certain extent, independent of those in Figure 8.

The observed correlations for SRM 1750 are not perfect, particularly for the RRR data, which is an indication of deviations from Matthiessen’s rule, or sample dependence. The resulting dispersion of the data forming this or any other reference material batch must be taken into account when evaluating the accuracy of any calibration approximation scheme.

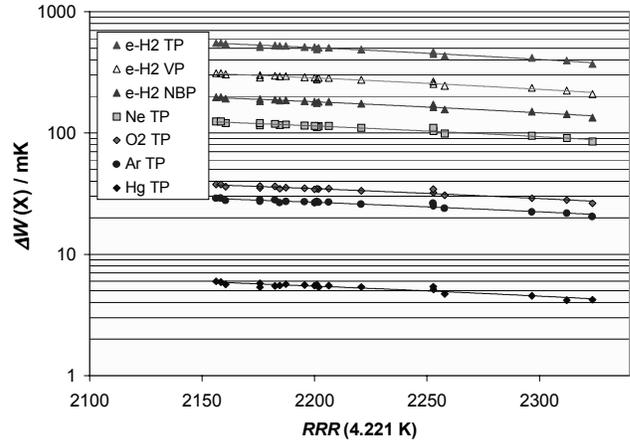


Figure 8. SRM 1750 correlation lines for the seven lowest SPRT calibration points of ITS-90 with the RRR.

Once a set of correlation lines have been established for a particular grade of Pt over a selected range of temperatures, this information can be utilized to streamline a calibration procedure for PRTs made from material in that lot. Depending on the particular range of use, one or two convenient fixed points can be chosen to calibrate a known lot of PRTs and the previously established correlations to those fixed point deviations then serve to complete the process. The purity of the starting material allows this to be accomplished with a moderate, but often acceptable, degree of inaccuracy.

The calibration accuracy versus cost trade-off for PRTs is most apparent in the ITS-90 sub-range between 13.8 K and 273.16 K. Eight calibration fixed points, forming seven independent W values, are normally required for this sub-range definition. The difficulty here is related to accounting for the increasing sample dependence in any PRTs resistance as the temperature is lowered below 70 K. The correlations between the various fixed-point W values, however, can be used to establish approximate W values without going to the expense of making all the required measurements. As an example, the two sets of ΔW correlations in SRM 1750 Pt as shown in Figures 7 and 8 are applied to this calibration sub-range. This procedure allows interpolation errors of less than 50 mK over the entire range and less than 10 mK for temperatures above 37 K with just three fixed points, the ^4He NBP, H_2O TP, and Ga MP. Figure 9 is a plot of the total propagated calibration uncertainty under these conditions. The uncertainties at the fixed-point temperatures are estimated from the known dispersion of the correlation data at those temperatures.

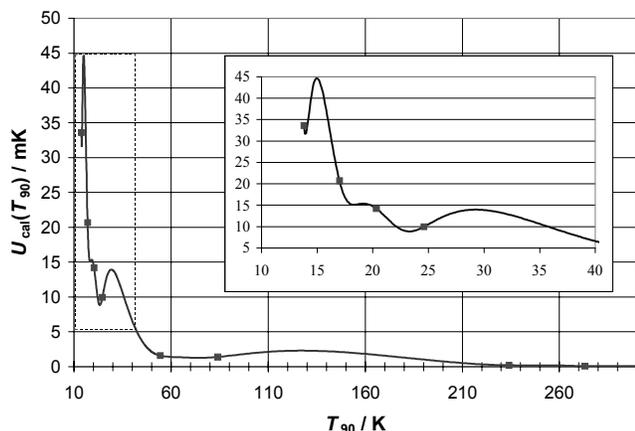


Figure 9. The total expanded ($k=2$) calibration uncertainty for a three-point correlation calibration using the ITS-90 sub-range definition for 13.8 K to 273.16 K. The RRR and Ga MP correlations are combined to approximate the ΔW values at the required fixed points.

Similar procedures such as this are currently being utilized in the aerospace industry to facilitate improvements in PRT calibration process efficiency.[13] In that case, the Pt is of a moderate purity, with temperature coefficients of resistance as low as 0.00391 K^{-1} . The temperature range of 20 K to 273 K is particularly well suited to this approach as long as one of the calibration fixed points chosen is $\leq 20 \text{ K}$. The use of a three point calibration scheme (4.22 K, 77.35 K, and 273.15 K) allows interpolation in this temperature range to within an approximate uncertainty of 100 mK.

4. Summary

Temperature sensors constructed from high-purity noble metals exhibit the highest degree of interchangeability and stability in comparison to all other artifact thermometers. This feature not only permits their use in temperature standards work, but also allows for a wide flexibility in the calibration approach depending on the accuracy requirements. Results derived from the SRM 1749 and SRM 1750 demonstrate the viability of alternative calibration strategies that could reduce the unit-to-unit and point-number measurement requirements when applied to well characterized lots of similar material. In certain industrial applications, the use of sensors derived from material of similar quality could translate into reductions in calibration costs.

Acknowledgements

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