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THERMOELECTRIC PROPERTIES OF A SELECTED LOT OF GOLD VERSUS PLATINUM THERMOCOUPLES

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ABSTRACT

Gold versus platinum thermocouples have uncertainties superior to all other thermocouples over the range 0 °C to 1000 °C. In this paper, we describe the properties of 21 specially-constructed gold versus platinum (Au/Pt) thermocouple thermometers, each calibrated on the International Temperature Scale of 1990. The best 18 thermometers were selected as a Standard Reference Material, with an expanded uncertainty (k=2) less than 9 mK from 0 °C to 962 °C. Each thermocouple was calibrated at fixed points over the range 0 °C to 962 °C. At both the aluminum (660.323 °C) and silver (961.78 °C) freezing points, the thermocouple inhomogeneity was characterized by measuring the immersion profiles in the fixed-point cells during a freeze. The resulting body of data for the best 18 thermocouples revealed that:

a. thermocouple inhomogeneity over a 10 cm range of immersion contributed only 2 mK to the standard uncertainty;
b. the emf values for all 18 thermocouples differed by less than the equivalent of 8.5 mK at every fixed point;
c. the average emf at each fixed point deviated from the NIST reference function by less than 14 mK; and
d. for individual thermocouples, emf values measured at fixed points adjacent in temperature (e.g., aluminum and silver, or indium and tin) were correlated, indicating that the variance in emf values was partly due to metallurgical differences of the thermoelements.

These data demonstrate the level of performance that can be achieved with careful wire selection and preparation.

1. INTRODUCTION

The Standard Reference Material® (SRM®) 1749 thermocouple is a specially-constructed and annealed gold versus platinum (Au/Pt) thermocouple, with integral lead wires and a protective silica-glass sheath. The expanded uncertainty (k=2) of its calibration is less than 8.3 mK from 0 °C to 962 °C. Previous publications have documented the performance attainable with individual gold versus platinum thermocouples. In this paper, we present results illustrating the uniformity that can be attained in the fabrication of a set of thermocouples from the same wire lots. Although the Au/Pt thermocouple operates on the same physical principles as all other thermocouples, the inherent metallurgical stability of gold and platinum, coupled with advances in fabrication, annealing, and calibration techniques, results in a thermocouple thermometer that has superior accuracy and homogeneity relative to other thermocouple types over the range 0 °C to 1000 °C. A more comprehensive discussion of the SRM 1749 thermocouples is given in Ref. [1].

2. FABRICATION AND CALIBRATION OF THE THERMOCOUPLES

The SRM 1749 thermocouples were constructed from 0.5 mm diameter gold and platinum wire of the highest purity available, typically 99.999 % mass fraction. The fabrication techniques generally followed previous practice [2,3], and are described in detail in Ref. [1]. Special care was taken to anneal the gold and platinum thermoelements at a uniform temperature, and to avoid straining the thermoelements during the fabrication process. Of 21 thermocouples fabricated, the 18 thermocouples with the best thermoelectric homogeneity and closest agreement to the average emf-temperature response were chosen for SRM 1749.

The thermocouples were calibrated at the melting point of ice (0 °C) and the freezing points of indium (156.5985 °C), tin (231.928 °C), zinc (419.527 °C), aluminum (660.323 °C), and silver (961.78 °C). Between each fixed-point measurement, the thermocouples were annealed at 450 °C overnight. Each fixed-point cell had a glass tube, closed at one end, extending into the well of the cell; consequently the thermoelements were exposed to air for all measurements. All of the emf measurements were made with an 8 ½ digit multimeter and scanner that were tested for linearity and accuracy at low voltages [1]. Special care was taken to correct for stray thermal emf of the wiring and scanner by measuring the emf of each scanner channel, shorted with a bare copper wire, before and after each fixed-point. Stray emf caused by heating of the relays on the scanner cards was minimized by keeping the duty cycle of every channel below 20 %. The reference junctions of the thermocouples were maintained at 0 °C in an ice bath during the measurements.

Because of the low Seebeck coefficient of Au/Pt thermocouples near 0 °C (6.04 μV/K), it is critical to calibrate the thermocouples at the ice point to attain an expanded uncertainty less than 10 mK for temperatures below the indium point. When both reference and measuring junctions are at 0 °C, an emf still may result because of small inhomogeneities in the copper lead wires, slight mechanical strains of the thermoelements in the reference-junction probe, and differences in the annealed state of the thermoelements at the reference and measuring-junction ends of the thermocouple.

A reference function for Au/Pt thermocouples on the ITS-90 has been measured at NIST [4]. The calibration function for each thermocouple was obtained by fitting a quadratic function to the deviation of the measured emf from the fixed-point emf values of the reference function.

The effects of inhomogeneity of the thermocouple were determined by measuring its emf during insertion into and withdrawal from aluminum and silver freezing-point cells during a freeze. The insertion and withdrawal process took 150 min to complete. At immersions greater than 8 cm, the thermocouple measuring junction was in thermal equilibrium with the freezing metal, and the emf for an ideal thermocouple would be constant, to within the equivalent of 1 mK. In practice, the emf generated by an inhomogeneous thermocouple will vary with depth of immersion into a fixed-point cell because different sections of the thermoelements will be exposed to the regions of thermal gradients in the furnace. Thus, in the measured immersion curves, any deviation from a constant value of emf was taken as an indication of inhomogeneity or drift of the thermocouple.

3. UNCERTAINTY OF THE THERMOCOUPLE CALIBRATION

We have included in the uncertainty budget for the SRM 1749 both the uncertainties of the calibration process and uncertainties intrinsic to the thermocouple itself, such as reproducibility and inhomogeneity. Figure 1 shows the components of calibration uncertainty of the SRM 1749 thermocouples. Except for the component "Thermocouple reproducibility," all components are Type B uncertainties.

In previous work using the same techniques and emf-measuring system [4], we determined in fixed-point cells the reproducibility of a set of Au/Pt thermocouples with construction very similar to the SRM 1749 thermocouples. This reproducibility was taken as the Type A uncertainty for the calibration at the metal freezing points. At the ice point, the Type A uncertainty was determined from repeated measurements on several thermocouples in the SRM 1749 lot. The value found was u_A(ice) = 1.74 mK. This uncertainty is termed the "Reproducibility of Au/Pt TCs," but more accurately can be considered to include effects of the reproducibility of the emf measurements, the reproducibility of the reference junction bath, the thermoelectric instability of the thermocouples over the course of the calibration measurements, and the reproducibility of the fixed-point realizations.

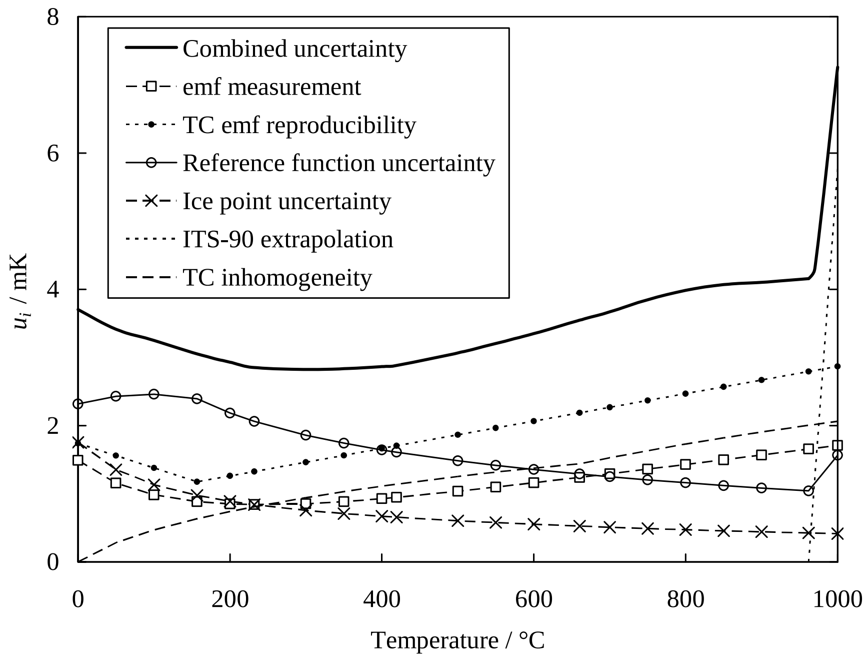


Figure 1: Calibration standard uncertainties (*k*=1) and subcomponent uncertainties for the SRM 1749 thermocouples. Only subcomponents that are significant within the temperature range are shown.

Uncertainties of the emf measurements not covered in the Type A uncertainty were determined by independent measurements of the variation of the thermal emfs from the scanner relays and wiring, measurement of the voltmeter non-linearity, measurements of the gain stability of the multimeter over extended periods of time, and by intercomparison of the multimeter with other multimeters of the same and a different manufacturer.

For measurements at each fixed point, a Type B uncertainty was included to account for deviations of our cells from an ideal fixed point of a pure material. These deviations were determined by measurements of freezing plateaus with an SPRT or a high temperature SPRT, by comparison with the reference standard cells maintained by the Platinum Resistance Thermometry Laboratory at NIST, and by estimation of uncertainty from known impurities.

Referring to the sample immersion profile in Fig. 2, thermoelectric inhomogeneity will cause variations in the output emf of a thermocouple with changes in immersion depth even if the temperature of the measuring junction is fixed. Since it is unlikely that the SRM 1749 thermocouple will be used in a thermal environment identical to its calibration environment, an additional uncertainty u_i must be included to account for inhomogeneity. At the aluminum and silver fixed points, we have taken the standard uncertainty for this effect to be equal to the rms deviation of the measured emf values from the emf value at full immersion, for all immersions greater than 8 cm into the fixed-point cell. At other temperatures, we have estimated the inhomogeneity using linear interpolation and assuming that there is no inhomogeneity uncertainty at 0 °C. When used at immersion depths shorter than the minimum immersion depth of the NIST calibration furnaces (8 cm below the metal surface), the inhomogeneity uncertainty must be increased, as described in Ref. [1].

In the calibration procedure, the emf-temperature relation of the thermocouple is modeled as the reference function for Au/Pt thermocouples plus a quadratic function. This model is an approximation with an associated uncertainty. Any errors in the reference function that can be modeled with a quadratic function have no effect on the uncertainty of the combined model of reference function plus quadratic function. Errors that could be modeled with higher-order terms

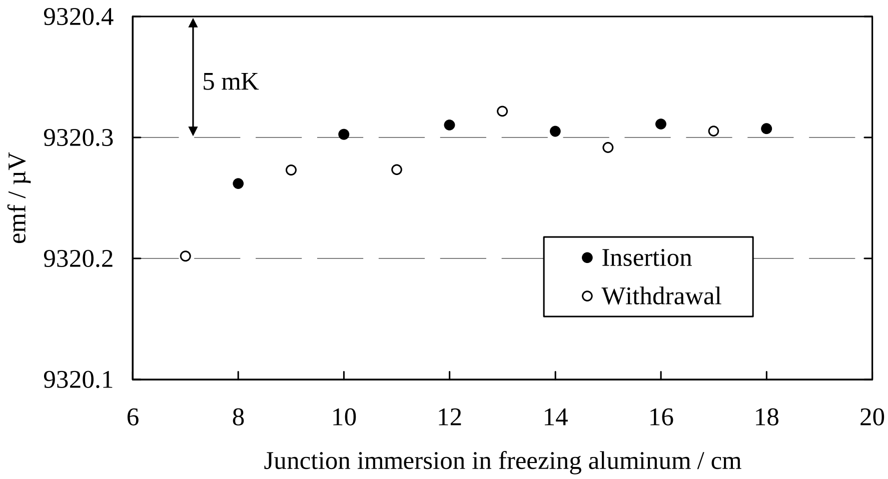


Figure 2: Values of emf measured for an SRM 1749 thermocouple on insertion into and withdrawal from the aluminum freezing-point cell during a freeze.

must be included in the uncertainty budget. We take the systematic discrepancy between data obtained by fixed-point measurements and data obtained by comparison with an SPRT at nearby temperatures (see Ref. [4]) as an estimate of this uncertainty. This uncertainty is 0.04 μV at 1000 °C, 0.026 μV from 962 °C to 157 °C, and decreases to approximately 0.014 μV near 10 °C.

No uncertainty term has been added to account for the reproducibility of the ice point, since the Type A uncertainty for the reproducibility of the thermocouple emf at the various fixed points already incorporates any effects of variations in the ice point. However, we have added an uncertainty to account for any systematic errors in the NIST ice-point realization caused by impurities in the distilled water used for the preparation of the ice and ice baths. Because of slight variations in the physical or chemical characteristics of the wires inside the reference-junction probe, the emf generated by the SRM 1749 thermocouples between room temperature and the reference junctions will vary slightly depending on the depth of immersion of the probe into the ice, even if the reference junctions remain at 0 °C. An uncertainty for this effect has been included.

As seen in Fig. 1, no single component dominates the combined uncertainty over the entire temperature range. At low temperatures, the uncertainty of the reference function dominates. Above 962 °C, the reference function is based on an extrapolation of the ITS-90, which is poorly known, and this becomes the dominant uncertainty. For intermediate temperatures, thermocouple reproducibility, uncertainty of the emf measurements, and thermocouple inhomogeneity are all significant.

4. PROPERTIES OF THERMOCOUPLES PREPARED FOR SRM 1749

The emf versus temperature responses of the SRM 1749 thermocouples deviate from the reference function by no more than 16 mK. The results of the least squares fitting of the quadratic model to the data gave values of the reduced chi-squared statistic of 0.60±0.37, less than the expected value of one. We believe that this is primarily because the reproducibilities had been evaluated for data including multiple thermal cycles over a period of many months, but the SRM 1749 data included thermal excursions to only one round of fixed-point temperatures over a briefer period of time.

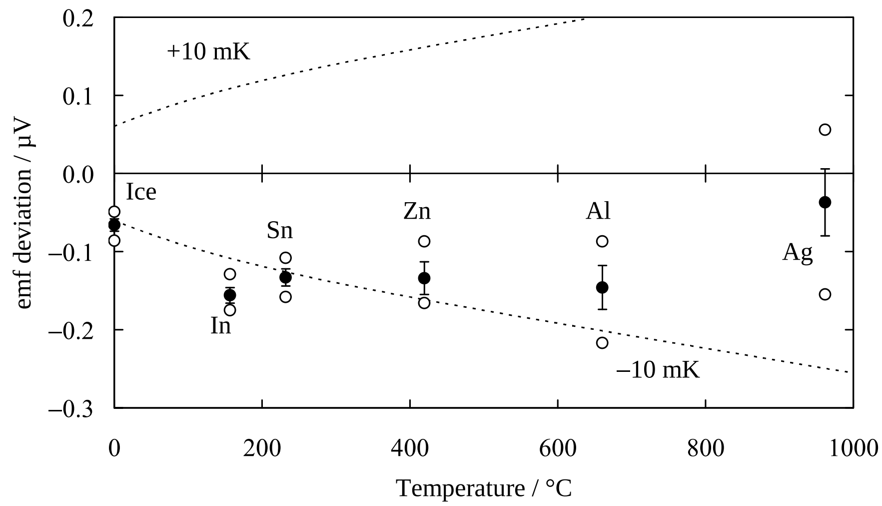
Figure 3 shows the average, maximum, and minimum deviation of the measured emf from the reference function, for all 18 selected SRM 1749 thermocouples. The maximum deviation from the reference function in the lot, in equivalent temperature, is 0.18 μV at the indium freezing point, equivalent to 16 mK. The maximum spread in the emf values at any of the fixed points is 0.21 μV at the silver freezing point, equivalent to 8.5 mK, which is approximately a factor of 10 smaller than we observe with platinum-rhodium alloy thermocouples fabricated from a single pair of wire lots. The small spread in the emf values is an indication that the gold and platinum wires were chemically homogeneous, and that the annealing procedures were highly reproducible.

The scatter at each fixed-point temperature shown in Fig. 3 is not random. Correlation plots of the emf deviation at one fixed-point temperature versus the deviation at another fixed point show a high degree of correlation, as seen in Fig. 4. The average correlation coefficient for emf readings between adjacent fixed points (e.g., indium and ice) is 0.71 for the 18 selected thermocouples and 0.58 for the complete set of 21, with a standard deviation of 0.13 in both cases. This result confirms that there are statistically significant differences in the emf-temperature relationships of the SRM thermocouples.

The representative immersion profile into an aluminum fixed-point cell shown in Fig. 2 is typical of high-quality Au/Pt thermocouples, showing little variation in emf values beyond an immersion of 8 cm of the measuring junction below the surface of the freezing metal. At the silver freezing point, there is hysteresis of approximately 2 mK between measurements taken on insertion of the thermocouple into the cell, compared to measurements taken on withdrawal. This is a result of reversible metallurgical changes, such as changes in the number of lattice vacancies in the thermoelements, incurred during measurement of the immersion profile. Each of the SRM 1749 thermocouples had a total spread in emf values for immersions greater than 8 cm of less than 0.19 μV (7 mK) at the silver freezing point, and less than 0.13 μV (6 mK) at the aluminum point. These values are extreme limits; the pooled rms values for inhomogeneity for the SRM 1749 thermocouples are 0.050 μV (2 mK) and 0.029 μV (1.4 mK) at the silver and aluminum freezing points, respectively. Three of the SRM 1749 thermocouples were reannealed or were modified by rearrangement of wire segments (see fabrication in Ref. [1]) to reduce the inhomogeneity to acceptable levels.

Although the level of effort expended in the fabrication, annealing, and testing of these SRM thermocouples was quite high, the effort was rewarded with performance that is quite remarkable for a thermocouple and that is consistent for a high fraction of the lot of fabricated probes (18 of 21).

Figure 3: Differences between the measured emf values for the 18 SRM 1749 thermocouples and the reference function for all 18 Au/Pt thermocouples. Solid circles indicate the average values for all thermocouples, the open circles indicate maximum and minimum values, and the error bars indicate one standard deviation variations in the emf values.



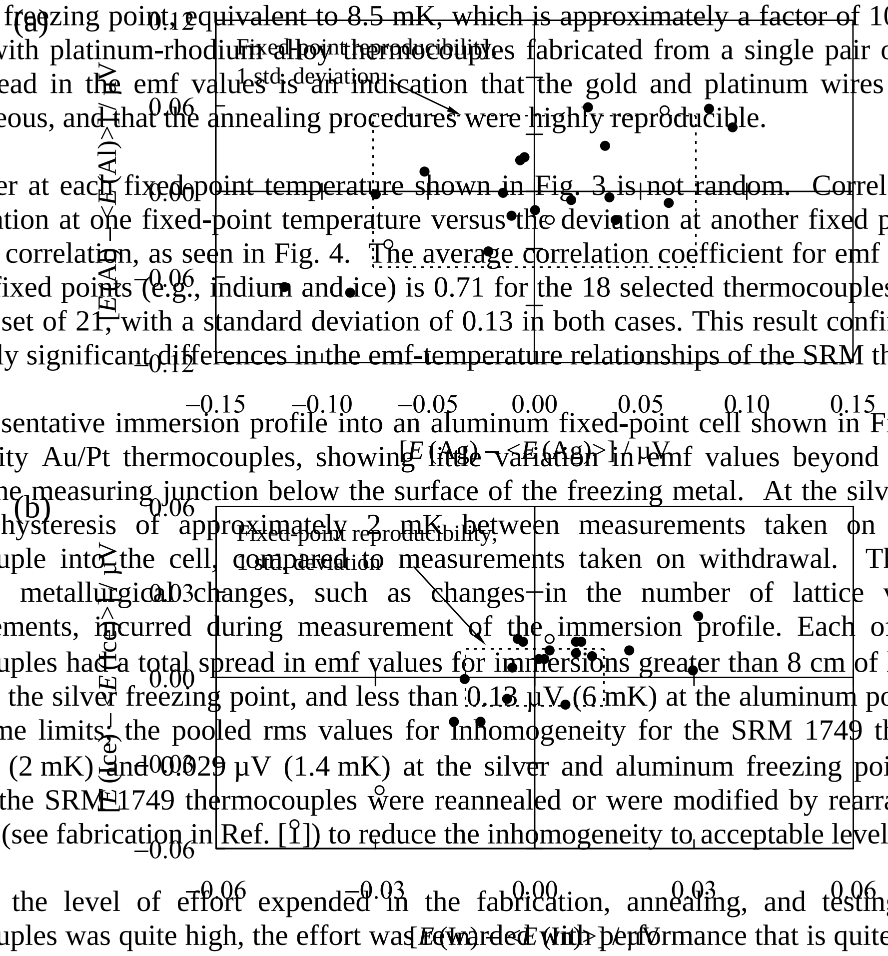


Figure 4: (a) Correlation of emf values at the aluminum point, *E*(Al), with emf values at the silver point, *E*(Ag); (b) correlation of emf values at the ice point, *E*(Ice), with emf values at the indium point, *E*(In). Solid circles are for the SRM 1749 thermocouples. Open circles are for additional thermocouples fabricated from the same wire lots as the SRM 1749 thermocouples.

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