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Indirect Determination of the Thermodynamic Temperature of a Gold Fixed-Point Cell

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Abstract Since the value $T_{90}(\mathrm{Au})$ was fixed on the ITS-90, some determinations of the thermodynamic temperature of the gold point have been performed which form, with other renormalized results of previous measurements by radiation thermometry, the basis for the current best estimates of $(T - T_{90})_{\mathrm{Au}} = 39.9\,\mathrm{mK}$ as elaborated by the CCT-WG4. Such a value, even if consistent with the behavior of $T - T_{90}$ differences at lower temperatures, is quite influenced by the low values of T_{Au} as determined with few radiometric measurements. At INRIM, an independent indirect determination of the thermodynamic temperature of gold was performed by means of a radiation thermometry approach. A fixed-point technique was used to realize approximated thermodynamic scales from the Zn point up to the Cu point. A Si-based standard radiation thermometer working at 900 nm and 950 nm was used. The low uncertainty presently associated to the thermodynamic temperature of fixed points and the accuracy of INRIM realizations, allowed scales with an uncertainty lower than 0.03 K in terms of the thermodynamic temperature to be realized. A fixed-point cell filled with gold, 99.999 % in purity, was measured, and its freezing temperature was determined by both interpolation and extrapolation. An average $T_{\mathrm{Au}} = 1337.395\,\mathrm{K}$ was found with a combined standard uncertainty of 23 mK. Such a value is 25 mK higher than the presently available value as derived by the CCT-WG4 value of $(T - T_{90})_{\mathrm{Au}} = 39.9\,\mathrm{mK}$.

Keywords Gold fixed point · Radiation thermometry · Thermodynamic temperatures

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1 Introduction

The ITS-90 above the freezing point of silver is defined in terms of the ratio of Plank's radiances with respect to a reference point to be chosen among silver, gold, or copper [1]. Any inconsistency in the temperatures assigned to the three points cause inconsistencies in T_{90} at higher temperatures, that is to say, that the scales could be dependent upon the choice of the reference point. Recently, the CCT-WG4 on thermodynamic determinations produced revised and improved values of $(T - T_{90})$ and their associated uncertainties [2]. They highlighted a lack of reliable determinations of the thermodynamic temperature of both gold and copper points. When the ITS-90 was formulated, no direct determinations of these temperatures were available with an uncertainty comparable to determinations by indirect spectral radiation thermometry, i.e., obtained with reference to a lower temperature [3]. In the successive years, a few radiometric determinations were made which gave rather contradictory results. Fox et al. [4] made an absolute spectral radiometric determination of T_{Au} with $(T - T_{90})_{\mathrm{Au}} = -0.03\,\mathrm{K}$ and a standard uncertainty of 0.05 K. More recently, an "absolute pyrometer," i.e., one with an absolutely calibrated detector, was used by Yoon et al. [5] and a $(T - T_{90})_{\mathrm{Au}}$ value of 0.014 K with a standard uncertainty of 0.06 K was found. The two determinations agree within their combined uncertainty but are quite far from the results derived by previous renormalized measurements of the Au–Ag interval [6–8] which provided $(T - T_{90})_{\mathrm{Au}}$ values of 72 mK, 60 mK, and 63 mK with standard uncertainties of 12 mK, 22 mK, and 60 mK, respectively.

A similar situation occurs for the copper point. Two determinations by absolute radiation thermometry [9] and by noise thermometry [10] produced results 148 mK above and 80 mK below the ITS-90 value with standard uncertainties of 77 mK and 60 mK, respectively. The difference of 228 mK was found between the two determinations, namely, a very large difference, well outside of the combined uncertainties of the two experiments. A recent determination at INRIM by a multi-fixed-point approach produced a $(T - T_{90})_{\mathrm{Cu}}$ value of 70 mK with a standard uncertainty of 47 mK [11]. It is worthwhile to remember that the presently available $(T - T_{90})$ differences at the Au and Cu points, as elaborated by the CCT-WG4, are 39.9 mK and 52.1 mK, respectively. A summary of the figures discussed above is reported in Fig. 1, where $(T - T_{90})$ values have been drawn from the last CCT-WG4 document [2] and from [11]. The CCT-WG4, considering the weaknesses discussed above, recommends and encourages new measurements to be undertaken urgently.

Both primary radiometry methods and indirect relative spectral-band thermometry methods can be employed to realize thermodynamic temperatures. It is noteworthy that indirect determinations, even if they give uncertainties slightly higher than primary radiometry methods, are considerably easier to implement.

However, one of the most critical points of classical spectral radiation thermometry, i.e., the approach consisting of the measurement of spectral ratios at a defined wavelength, is represented by the uncertainty connected to the spectral characterization of the thermometer. The uncertainty in the measurement of the spectral responsivity propagates as $(T/\lambda)(T/T_{\mathrm{ref}} - 1)$, thus becoming a dominant contribution at high temperature. At INRIM a multi-fixed-point technique which does not need the spectral characterization of the thermometer, has been applied to the calibration of precision IR

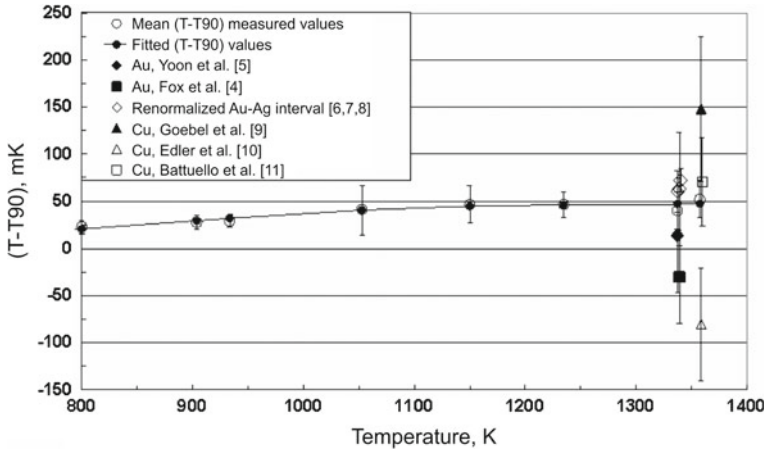

Fig. 1 Overview of $(T - T_{90})$ values. Fitted values are those calculated with the fifth-order polynomial recommended by the CCT-WG4 [2]. Recent Au and Cu determinations are those cited in the paper. *Error bars* associated to the mean measured values represent uncertainties with $k = 1$ as reported in [2]

thermometers for many years. Recently, the technique has been improved and already used for the indirect determination of the thermodynamic temperature of the copper point [11] and of the transition temperature of the Co–C eutectic fixed point [12]. In the present exercise the technique has been implemented for deriving T_{Au} both by interpolation and extrapolation of a thermodynamic scale.

This paper briefly describes the approach and the experimental arrangement and presents the results obtained by measuring a gold fixed-point cell with the standard radiation thermometer of INRIM.

2 Multi-Fixed-Point Approach

A spectral radiation thermometer can be used as a relative thermodynamic instrument, i.e., one that allows thermodynamic temperatures to be derived by measuring radiance ratios and applying the Planck law provided that the temperature of the reference point is known. Such an approach requires the spectral characterization of the thermometer, i.e., the process that determines the value of λ to be included in the Planck formula. An alternative approach exists which does not need the spectral response to be measured and consists of calibrating the thermometer at three or more fixed points and using a Planck-related equation to interpolate the data. Sakuma and Kobayashi [13] proposed an equation which relates the output signals to the temperature:

$$S(T) = C/(\exp(c_2/(AT + B)) - 1) \tag{1}$$

where $S(T)$ is the output signal, T is the thermodynamic temperature in kelvin, c_2 is the second radiation constant, and A, B, and C are calibration constants. The adequacy of Eq. 1 has been established in [14], where it was found that when a primary standard

thermometer is used, the interpolation errors are less than 1 mK, i.e., a figure which does not affect significantly the uncertainty.

It is generally accepted that such an approach may be safely used within the extreme end points and that extrapolation beyond these points is not recommended. However, it has been proved that in some circumstances, namely, when a low uncertainty can be associated to the fixed-point realizations and when the temperature difference between the highest calibration point and the extrapolated point is relatively small, the uncertainty in the extrapolated temperature can be kept reasonably low [11,12].

In the present exercise the multi-fixed-point technique will be used for both interpolation and extrapolation.

3 Experimental Arrangement

The measurement setup was part of that already described in [12] and used for the determination of the thermodynamic temperature of the copper point. Essentially it is based on a standard radiation thermometer, a set of fixed-point cells, and the furnaces for realizing the fixed points.

All used cells, namely, for Zn, Al, Ag, Au, and Cu points, were of the same design [15,16]. The available inside volume was about 48 cm^3, and a cylindrical blackbody was used with a cavity 9 mm in diameter and 61.5 mm in length and terminated with a cone of 120° included angle. The aperture of the cavities was reduced to 5 mm by means of an additional diaphragm holder.

The effective normal emissivity of the cavity was calculated assuming a value of 0.9 for the emissivity of the graphite walls, and a value of 0.99987 with an estimated uncertainty of 0.00009 was found. The Zn cell was filled with 6N pure metals, having used 5N pure metals for Al and Ag. Importantly, all individual cells were previously compared with similar ones and proved to be either better or equivalent to the others.

The Cu point, a 6N cell used for T_{Cu} determination and designated as GF, was used for realizing the scale between the Al and Cu points. The Au cell was the INRIM standard, i.e., a cell filled many years ago with 99.999 % in purity gold supplied by Leico Industries and only occasionally used. Unfortunately, a second working cell was set aside because of a temperature depression of about 0.04 K, probably due to contamination.

The radiation thermometer was basically the primary standard of INRIM based on a silicon photodiode and used for realization of the ITS-90. An Hamamatsu S2592-03 silicon photodiode operated in an unbiased mode with a built-in Peltier element allowing the temperature of the detector to be controlled at +10 °C was used. The instrument was used in two different spectral configurations, namely, in its original configuration with a filter centered at 900 nm with a bandpass of 12.7 nm for operation above the Al point and with a new channel at 950 nm with a larger bandpass of about 70 nm for operation down to the Zn point.

The two furnaces used for this exercise were those already described in [12]. The compact fixed-point furnace, for which constructional details may be found in Ref. [16], was used for the Zn point. A furnace with three independent heaters was utilized for the Al, Ag, Au, and Cu points. Typically a freezing plateau obtained with

the Au cell can be identified with an uncertainty of approximately 2 mK with signals comprised within a band of 10 mK for approximately 20 min.

With the three-zone furnace, a water-cooled flange was placed in front of the furnace to avoid both overheating and stray radiation outside a diameter of 55 mm reaching the thermometer. As for the stray radiation between the target and the 55 mm diameter baffle, corrections were made according to the SSE characteristics of the thermometer taking into account the measured radial temperature distributions.

4 Measurements and Results

The measurements covered the period from April 2009 to February 2010. Table 1 summarizes the four different measurement cycles. In cycles 1 and 2 complete calibrations of the thermometer were performed at the Zn, Al, and Ag points, and the respective temperature scales were used to derive T_{Au} by extrapolation. In cycles 3 and 4 the thermometer was used in the configurations at 900 nm and 950 nm, respectively, to realize scales from Al to Cu and consequently to derive T_{Au} by interpolation.

Different from the measurements for deriving T_{Cu} which involved more than 50 realizations of the Cu point with four different cells, in the present exercise only 12 determinations of the Au point were performed. On the other hand, the temperature scales realized with the Si standard thermometer proved to be more repeatable and reproducible than those with the InGaAs thermometer which was used to derive T_{Cu} [12]. The 12 freezing temperatures obtained during the four measurement cycles are summarized in Table 2.

With regard to cycles 3 and 4, different T_{Au} values can be obtained depending on the thermodynamic temperature associated with the Cu point. Values in Table 2 are obtained assuming $T_{Cu} = 1357.840$ K, i.e., the value determined by INRIM [11].

Table 1 Summary of the four measurement cycles

Cycle	Date of measurements	Thermometer configuration	Scale	No. of Au determinations
1	April 2009	950/70	Zn–Al–Ag	3
2	May–June 2009	950/70	Zn–Al–Ag	2
3	January 2010	900/12.7	Al–Ag–Cu	5
4	February 2010	950/70	Al–Ag–Cu	2

Table 2 Summary of the different T_{Au} determinations

Cycle	Scale	T_{Au} (K)				
1	Zn–Al–Ag	1337.392	1337.405	1337.406		
2	Zn–Al–Ag	1337.381	1337.387			
3	Al–Ag–Cu	1337.415	1337.411	1337.41	1337.406	1337.408
4	Al–Ag–Cu	1337.385	1337.387			

Table 3 Average values of T_{Au} derived by extrapolation and by interpolation

	T_{Au} (K)	St. dev. (K)
T_{Au} derived by extrapolation	1337.394	0.011
T_{Au} derived by interpolation (with $(T - T_{90})_{Cu} = 70$ mK (INRIM))	1337.403	0.012
T_{Au} derived by interpolation (with $(T - T_{90})_{Cu} = 52$ mK (CCT-WG4))	1337.389	0.012

Values lower by 14 mK would be obtained assuming the current thermodynamic temperature as derived by the official $(T - T_{90})_{Cu} = 52.1$ mK.

Average values of T_{Au} derived by interpolation and by extrapolation are reported in Table 3. The extrapolated estimate for $T_{Au} = 1337.394$ K is within the interpolated values obtained assuming the two T_{Cu} values, as described before.

5 Uncertainties

The method described in [17,18] was used to derive two different uncertainty budgets for T_{Au} depending on whether the extrapolation or interpolation approach has been used. Uncertainty components used in [11] for the determination of the budget for T_{Cu} also apply for the present exercise. An uncertainty component related to the possible drift of the thermometer signal has been added. Experimental evidence from measurements in [11] allows an estimate of 10 mK for this component. Table 4 summarizes the combined standard uncertainties for both extrapolated and interpolated values.

Such figures can be used to derive a weighted mean from the T_{Au} values reported in Table 3. A weighted mean value of 1337.395 K with an expanded uncertainty of about 0.05 K ($k = 2$) was found.

6 Conclusions

The thermodynamic temperature of the freezing point of gold has been determined at INRIM measuring the local standard fixed-point cell. Different thermodynamic scales were realized from Zn to Cu using the standard radiation thermometer in two different spectral configurations at 900 nm and 950 nm. Both interpolation and extrapolation approaches were used, and a mean value of $T_{Au} = 1337.395$ K with an expanded uncer-

Table 4 Standard uncertainty components in T_{Au} determination

Uncertainty contribution	Extrapolation (mK)	Interpolation (mK)
Uncertainty in the extrapolated T_{Au}	39	
Uncertainty in the interpolated T_{Au}		26
Uncertainty due to the drift of the thermometer	10	10
Combined standard uncertainty	40	28

tainty of about 0.05 K ($k = 2$) was found. Such a value gives a $(T - T_{90})_{\mathrm{Au}} = 65$ mK, namely, 25 mK higher than the CCT-WG4 value of 39.9 mK.

Even if consistent with the CCT-WG4 value, the noteworthy agreement of the INRIM result with the old indirect determinations at PTB and CSIRO [6–8], i.e., 72 mK, 60 mK, and 63 mK, could suggest the present $(T - T_{90})_{\mathrm{Au}}$ being low, as also confirmed by the results at the Cu point [11].

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