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# Metal–Carbon Eutectics to Extend the Use of the Fixed-Point Technique in Precision IR Thermometry

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**Abstract** The high-temperature extension of the fixed-point technique for primary calibration of precision infrared (IR) thermometers was investigated both through mathematical simulations and laboratory investigations. Simulations were performed with Co–C (1,324°C) and Pd–C (1, 492°C) eutectic fixed points, and a precision IR thermometer was calibrated from the In point (156.5985°C) up to the Co–C point. Mathematical simulations suggested the possibility of directly deriving the transition temperature of the Co–C and Pd–C points by extrapolating the calibration derived from fixed-point measurements from In to the Cu point. Both temperatures, as a result of the low uncertainty associated with the In–Cu calibration and the high number of fixed points involved in the calibration process, can be derived with an uncertainty of 0.11°C for Co–C and 0.18°C for Pd–C. A transition temperature of 1,324.3°C for Co–C was determined from the experimental verification, a value higher than, but compatible with, the one proposed by the thermometry community for inclusion as a secondary reference point for ITS-90 dissemination, i.e., 1,324.0°C.

**Keywords** Co–C · Eutectics · Fixed points · Infrared thermometry

## 1 Introduction

A scheme based on the use of a number of fixed-point temperatures and a specified interpolation equation may be conveniently used to calibrate precision IR thermometers with low-level uncertainties. The method, originally proposed by Sakuma and Hattori [1] and further investigated at IMGC (now INRIM) [2], has been successfully

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applied in various laboratories throughout the world to cover the interval from the indium point (156.5985°C) to the copper point (1,084.62°C), the latter being the highest available with suitable repeatability and reproducibility. This fixed-point technique may now be extended to higher temperatures by taking advantage of the eutectic metal–carbon fixed points that have been developed in recent years.

At present, a proposal has been put forward to define the temperatures of four new secondary points [3], i.e., Co–C (1,324.0°C), Pd–C (1,491.7°C), Pt–C (1,737.9°C), and Re–C (2,474.2°C), but no definite temperature values have been assigned to the various eutectic fixed points. This causes a problem when implementing the fixed-point technique, since the temperature values to be used are not well defined. At INRIM, mathematical simulations and experiments were carried out with the aim of determining the applicability of the technique and the temperature values to be used. Mathematical simulations were carried out based on the uncertainty estimates of measurements at INRIM, the extension up to the Co–C and Pd–C points was analyzed, and the possibility of directly deriving the temperatures of the Co–C and Pd–C points as an extrapolation of the calibration from In to the Cu point was investigated. Such an approach can be followed because of the low uncertainties of the measurements, ranging from 0.02°C at the In point to 0.05°C at the Cu point, and of the large number of fixed points used for the calibration, i.e., six points.

The paper will describe the mathematical simulations, the setup for the experimental verification, and the results of the measurements carried out with both contact and radiation thermometers. Finally, the results will be compared with the proposed temperature value for the Co–C eutectic fixed point, $T_{\mathrm{Co–C}}$.

## 2 Mathematical Simulations

The fixed-point technique is a typical interpolation approach, and it is commonly understood that such approaches may be used within the interpolation points, but that extrapolation beyond these points is highly risky and may give rise to large errors. This is true, in general, but we will show, as a result of mathematical simulations (alternatively, a different approach based on the Lagrange polynomials could be used [4]) that when a large number of calibration points are used and low-level uncertainties are achieved, an extrapolation process can be used safely. This demonstration turns out to be particularly interesting as it may allow us to independently derive the temperature of a fixed point from measurements at a sufficient number of other points.

A set of ideal pairs of data, $S_i = f(T_i)$, was obtained where the $T_i$'s are the fixed-point temperatures of In, Sn, Zn, Al, Ag, and Cu points as defined by the ITS-90, the $S_i$'s are the respective normalized signals obtained from the radiances calculated according to Planck's law, and the subscript $i$ identifies the fixed point. The value of 1,324.0°C, as proposed in [3], was assumed when calculating the corresponding signal $S_{\mathrm{Co–C}}$ for the transition temperature of the Co–C fixed point.

To make the simulation resemble a real situation, radiances were calculated at wavelengths derived from the following empirical equation that relates the limiting effective wavelength to temperature:

$$1/\lambda = a + b/T \tag{1}$$

where $\lambda$ is the wavelength, $T$ is the temperature in kelvin, and $a$ and $b$ are the calibration coefficients of the INRIM thermometer that will be described later.

A temperature uncertainty ($k = 1$) was associated with each data point from In to Cu, namely, 0.021, 0.021, 0.022, 0.035, 0.045, and 0.05°C for In, Sn, Zn, Al, Ag, and Cu, respectively, as estimated for the INRIM calibration and reported in [2] and [5].

One thousand data sets were generated from a Gaussian distribution to simulate the possible calibration data. Each data set was then used with Eq. 2 to relate signals to temperatures:

$$S(T) = C/(\exp(c_2/(AT + B)) - 1) \tag{2}$$

where $S(T)$ is the output voltage; $T$ is the temperature in kelvin; $c_2$ is the second radiation constant; and $A$, $B$, and $C$ are constants. Equation 2 was proposed by Sakuma and Kobayashi [6] to overcome the limitations of the original Sakuma and Hattori equation [1] which was based on Wien's approximation. It can be easily verified that the latter is adequate up to the Ag or Cu point, but for higher temperatures an equation based on Planck's law must be used.

Coefficients $A$, $B$, and $C$ of Eq. 2 were calculated for each of the 1,000 data sets and the temperatures corresponding to the $S_{Co–C}$ were then derived by solving the inverse of Eq. 2. The 1,000 calculated $T_{Co–C}$ values were located within a band of ±0.25°C about the value 1,324.0°C and with an associated standard deviation of 0.09°C. Similar simulations were carried out for the Pd–C point for which the value of 1,491.7°C was assumed, and a standard deviation of 0.14°C was found. To also include the propagation of the uncertainty related to the nonlinearity of the thermometer response, the characteristics of the INRIM thermometer were assumed to calculate, according to the approach described in Sect. 3.1.3, the uncertainty due to nonlinearity at $T_{Co–C}$ and $T_{Pd–C}$. The resulting uncertainty components are 0.06 and 0.10°C, respectively.

The uncertainties summarized in Table 1 were derived by combining in quadrature the two components for the mathematical extrapolation and the nonlinearity; different simulations made by changing the lower interpolation limit, namely, for In–Cu, Sn–Cu, Zn–Cu, and Al–Cu interpolation ranges, are presented. Table 1 shows that $T_{Co–C}$ and $T_{Pd–C}$ can be derived with very low uncertainty, namely 0.11 and 0.18°C, respectively, when the full In–Cu interval is used. It may be helpful to compare the uncertainty of this extrapolated temperature determination with that achievable with a scale realized by extrapolation from a single fixed point, as in the ITS-90 definition. A

**Table 1** Results of mathematical simulations with different interpolation ranges

| Interpolation range | Standard uncertainty in the extrapolated $T_{Pd–C}$ and $T_{Co–C}$ temperatures (°C) | |
|---|---|---|
| | $T_{Pd–C}$ | $T_{Co–C}$ |
| In to Cu | 0.18 | 0.11 |
| Sn to Cu | 0.19 | 0.12 |
| Zn to Cu | 0.25 | 0.15 |
| Al to Cu | 0.63 | 0.33 |

"normal accuracy" realization of the ITS-90, i.e., one normally obtainable at present in national metrology institutes, has standard deviations of 0.22 and 0.32°C at $T_{Co–C}$ and $T_{Pd–C}$, respectively, values higher than those attained here through a much simpler procedure [7]. A "best accuracy" realization, i.e., one that can be obtained with considerable effort by the small number of leading workers in the field, is a little better than the multiple fixed-point technique, being 0.05 and 0.06°C at $T_{Co–C}$ and $T_{Pd–C}$, respectively.

A linear increase in the standard uncertainty is observed up to the Zn point, but there is a sudden increase when the calibration interval is limited to the Al–Cu interval, i.e., when only three calibration points are used. Such a result is not surprising and confirms the importance of using a large number of calibration points. Checks were also done with reduced sets of data, e.g., 500 and 250 data sets. The results in terms of average extrapolated temperature and standard deviation are substantially the same as with 1,000 data sets, thus confirming the significance of the simulation.

The results of the mathematical simulations show that the temperature of fixed points above the upper interpolation limit may be independently derived with an uncertainty limited in extent and closely related to the uncertainty of the other calibration points. In the following section, an experiment carried out at INRIM to confirm the results of the simulations will be described.

## 3 Experimental Verification

The aim of the experiment was to test the viability of the fixed-point technique at higher temperatures and to verify the results of the mathematical simulations. When the measurements were made, the Pd–C point was not yet available, so only the Co–C point was investigated. The absolute calibration of a precision IR thermometer was performed by the multiple fixed-point technique; namely, the thermometer was calibrated against blackbodies at the freezing temperatures of In, Sn, Zn, Al, Ag, and Cu and at the melting temperature of Co–C. The measured signals were then used to derive the coefficients of the interpolation equation (Eq. 2). A check was then made by using the measurement results up to the Cu point to derive the temperature of the Co–C point. The following sub-sections describe the experimental arrangement (the fixed-point cells, the furnaces, and the thermometer) and present the measurement results.

### 3.1 Experimental Arrangement

#### *3.1.1 Fixed-Point Cells*

Seven different fixed-point cells were used for this experiment. The In, Sn, Zn, Al, Ag, and Cu cells were of the same design described in [2] and [5]. The available volume inside the crucible was 48 $cm^3$. The blackbody was a cylindrical cavity 9 mm in diameter and 61.5 mm in length terminated with a cone of 120° included angle. The effective normal emissivity of the cavity was calculated to be 0.99957, assuming a value of 0.9 for the emissivity of the graphite.

The In, Sn, and Zn cells were filled with 6N pure metals, while 5N pure metals were used for the Al, Ag, and Cu cells.

The Co–C cell was described in [8] and identified there as *Co_4N8_small*. The available inside volume was about 10 $cm^3$; the blackbody was a cylindrical cavity, 8.5 mm in diameter and 88-mm long. An effective normal emissivity of 0.99974 was calculated. The cell was filled with a mixture at approximately the eutectic composition of 4N8 pure cobalt powder and 6N pure graphite powder (carbon mass fraction of 2.6%).

### *3.1.2 Furnaces*

Three different furnaces were used to cover the full temperature range from In to the Co–C point. A detailed description of the blackbody furnace used for the In, Sn, and Zn points, and its performance may be found in [5]. The furnace allows freezing plateaux to be obtained with a repeatability better than 0.02°C when the precision thermometer to be described later is used for the measurements. A furnace provided with three independent heaters was used for the Al and Ag points. The Cu and Co–C points were realized in a single-zone furnace equipped with six heating elements made from silicon carbide for operation up to 1,600°C. The furnace can be operated both horizontally and vertically, and for the present investigation it was arranged in a horizontal configuration. The heated chamber was 450 mm in length and a zone uniform in temperature within 5°C was assured over a length of 350 mm. An $Al_2O_3$ tube, 43 mm in diameter, was used to accommodate the crucibles.

### *3.1.3 Radiation Thermometer*

The radiation thermometer was the improved version [9] of the precision transfer standard developed for the EC-funded project TRIRAT ("TRaceability in Infrared RAdiation Thermometry") and used in the European comparison of the local realization of temperature scales [10]. The instrument, originally designed for the realization of temperature scales from In to the Cu point, was further modified for the present experiment and its electronics was adapted to increase the input signal dynamic range. The thermometer, based on an InGaAs photodetector with a sensing area 5 mm in diameter (Hamamatsu Model G5832-15) and cooled down to −10°C by means of a thermoelectric cooler, works in a narrow spectral band centered near 1.6μm. By replacing the previous 2-mm-diameter detector with a larger one of 5-mm diameter to ensure underfilling of the sensing area, the nonlinearity was completely suppressed [9]. Nonlinearity was measured at INRIM up to photocurrents corresponding approximately to the Ag point and, consequently, an assumption was made that the response is linear also in the extrapolated region. This assumption can be supported by the results in [11] where InGaAs detectors were investigated and found to exhibit a linear response at higher photocurrent levels. To calculate the propagated uncertainty component related to nonlinearity, the approaches described in [12] and [13] were followed and additional values of 0.05 and 0.08°C at $T_{Co–C}$ and $T_{Pd–C}$, respectively, were included to take into account possible departure by linearity of the response.

Combined standard uncertainty components due to nonlinearity of 0.06 and 0.10°C at $T_{Co–C}$ and $T_{Pd–C}$, respectively, were calculated.

Other features of the thermometer, specifically its high-temperature resolution at the lowest temperatures (4 mK at the In point, 0.6 mK at the Sn point, and 0.3 mK at the Zn point, in terms of noise-equivalent temperature), low size-of-source effect, and high long-term stability, make it suitable for calibration with fixed-point blackbodies to realize temperature scales with low uncertainty.

### 3.2 Uncertainty in Fixed-Point Calibration

The uncertainties obtained by combining in quadrature the various uncertainty components (impurities, emissivity, temperature drop, size-of-source effect, identification of the plateau, repeatability) were already given in Sect. 2 for the points from In to Cu. Regarding the Co–C point, the results of the experimental investigations described in [8], particularly the reproducibility between different cells and the effects of the melting rate, pre-freezing rate, and annealing time on the melting behavior, were analyzed and included in the uncertainty budget to give a combined standard uncertainty of 0.08°C.

### 3.3 Measurements and Results

The thermometer was calibrated at all the fixed points from In to Co–C. The measured signals were adjusted for the different gain ratios used during the calibration (from $10^9$ at the In point to $10^4$ at the Co–C) and corrected for the emissivity of the different blackbody cavities and for the size-of-source effect for the different measuring configurations. Even though the thermometer was compensated for internal temperature variations, a small residual temperature coefficient $(\mathrm{d}S/S)/\mathrm{d}t = 0.01073\%/°\mathrm{C}$ remained. All the signals were corrected and referred to a reference internal temperature of 28.5°C. As a first step in validating the mathematical simulations, the experimental data from In to Cu were fitted with Eq. 2. The fit produced residuals within a range of about 0.02°C. The calculated constants $A$, $B$, and $C$ were used to derive $T_{Co–C}$ and a value of 1,324.32°C was found, compatible with the value of 1,324.0°C proposed in [3]. It is worth noting that the proposed value is the simple mean of widely dispersed determinations, as indicated by its associated uncertainty (0.6°C, $k = 2$).

An alternative analysis consisted of fitting Eq. 2 with all the experimental results from In to Co–C, and by assigning the value of 1,324.0°C to the Co–C point. Figure 1 shows the residuals compared to those for the calibration from In to Cu. The calculated rms residuals are 0.01 and 0.05°C for calibration up to the Cu and Co–C points, respectively. The deterioration in the quality of the fit may be the consequence of (a) an erroneous signal associated with the Co–C calibration point or (b) an incorrect temperature assigned to Co–C. Regarding possibility (a), it is worth mentioning that the cell we used was investigated in [8] and produced results in very good agreement with other cells, without any evidence of possible depression of the transition temperature. Furthermore, because the results are in perfect agreement with the estimated

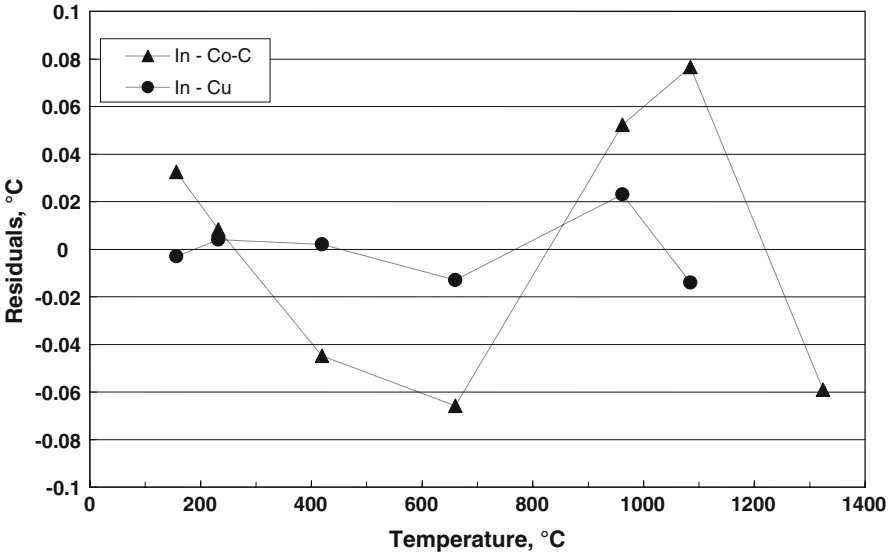


**Fig. 1** Residuals from fitting the calibration data for two different temperature intervals: from In to Cu and from In to Co–C

uncertainties at all the other points, there are no apparent reasons to expect different behavior when including the Co–C point in the fixed-point technique. Possibility (b) was then investigated by fitting the data with different values for $T_{\mathrm{Co–C}}$ and by analyzing the residuals. Figure 2 shows the residuals obtained with different values of $T_{\mathrm{Co–C}}$.

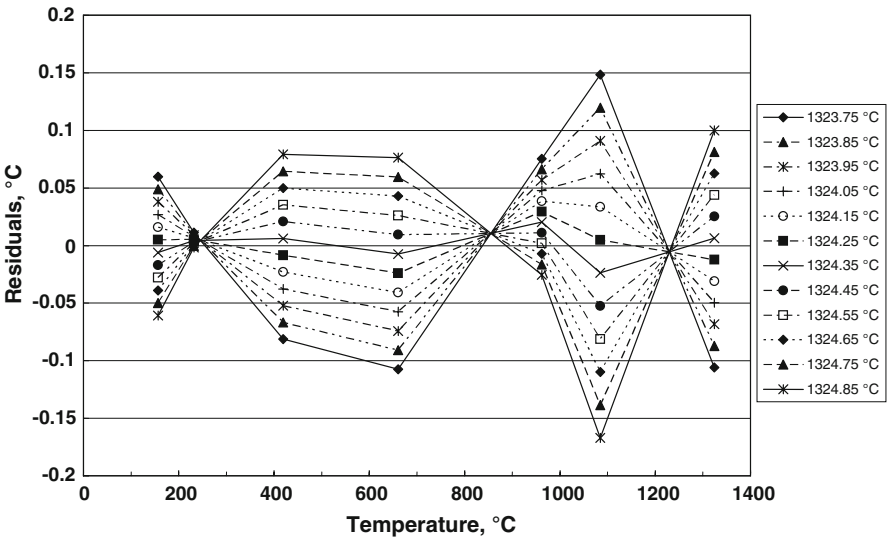


**Fig. 2** Dependence of the residuals on the value of $T_{\mathrm{Co–C}}$ assumed for fitting the calibration data from In to Co–C

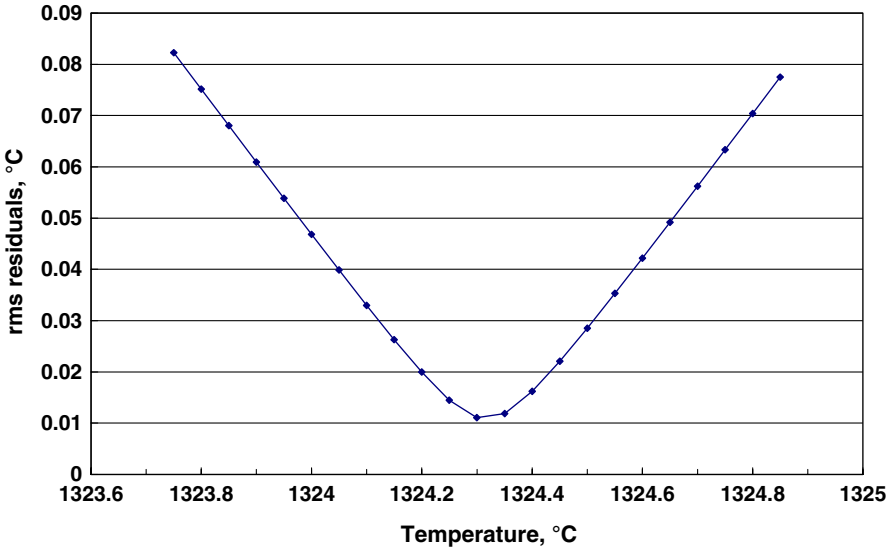


**Fig. 3** rms Residuals as a function of the assumed value for $T_{\mathrm{Co–C}}$

The dependence of the residuals on the value of $T_{\mathrm{Co–C}}$ is evident and, clearly, the assumed value 1,324.0°C does not correspond to the lowest residuals. The rms residuals of the fit are shown in Fig. 3 where the minimum corresponds to $T_{\mathrm{Co–C}} = 1{,}324.3$°C.

## 4 Summary

Investigations, including both mathematical simulations and experimental verifications, were carried out at INRIM which allowed interesting results to be achieved to extend the fixed-point calibration technique. Laboratory investigations demonstrated that a precision IR radiation thermometer can be calibrated from In (156.5985°C) to the Co–C point (1,324°C) with low uncertainties. In this phase of investigating metal–carbon eutectic points, definitive results cannot be stated because the transition temperatures for such points are not yet available and formally defined. The low uncertainties with the "fixed-point technique" at INRIM and the large number of fixed points involved in the calibration process allowed the temperature of the Co–C eutectic to be derived by extrapolating the calibration beyond the Cu point. A value of 1,324.3°C was found, and a standard uncertainty of 0.14°C was estimated by combining in quadrature the uncertainty of the extrapolation, 0.11°C, with the uncertainty in the realization of the Co–C point, 0.08°C. This result was obtained with a completely different approach with respect to other determinations by radiometric methods and, consequently, it represents a valuable verification of the methods and the respective uncertainty estimates. Our determination is compatible with the value of 1,324.0°C proposed for Co–C to be included as a secondary reference point of the ITS-90 [3]. The planned extension of the experimental verification to the Pd–C point would allow useful results to be derived for this point too.

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