9
Uncertainty evaluation

In this section the uncertainty associated with the measurements performed in this thesis are described. Essentially there are two quantities whose uncertainties need to be determined: the temperature (T) of the phase transition of the fixed-point cells and the concentration of the dopant in the eutectic alloy, the latter requires uncertainty in mass to be determined.

9.1. Uncertainty in the determination of the fixed point black body temperature

The uncertainty of the temperature obtained from the linear pyrometer LP3 has many individual components. Quantifying this is quite complex. Fortunately, the Working Group 5 of the Consultative Committee for Thermometry of the BIPM developed a document [64] which deals with this matter in detail. In this study, only the most important contributions are considered; the effect of the others is so small as to not influence the final temperature uncertainty.

The main influence quantities were:

i. Identification of the point of inflection of the melting curve of the M-C eutectic cell;
   This contribution was obtained through the analysis of the uncertainty of the curve fitting and first and second derivatives. The estimate was taken as the largest standard deviation of the fit, among all the melting curves of this study.

ii. Calibration of the linear pyrometer LP3;
   a. Uncertainty of the temperature of the silver fixed point cell; This uncertainty is declared in the calibration certificate of the silver fixed point cell, issued by NPL.

b. Uncertainty of the identification of the freezing plateau; The photocurrent relative to the freezing point of silver is a mean value of the first 15 minutes of readings obtained at the beginning of the plateau, after the occurrence of the recalescence. The uncertainty is the standard deviation of the mean of these readings.
c. Uncertainty in the responsivity calibration of the LP3 pyrometer; This uncertainty is taken from the calibration certificate of the spectral responsivity of the LP3 pyrometer, performed by the Radiometry and Photometry Laboratory of Inmetro.

iii. Linearity of the LP3 pyrometer;
This evaluation was performed in the pyrometry laboratory prior to the beginning of the measurements using the flux doubling method, using two high stability tungsten strip lamps and a cube beam splitter.

iv. Size-of-source of the LP3 pyrometer;
This evaluation also performed '*a priori*', using the indirect method utilizing an integrating sphere, a halogen lamp and multiple discs with diameters varying from 4 to 50 mm.

v. Stability of the photo current;
This component is obtained by the calculation of the standard deviation of the mean of measurement data for the freezing point of silver over the period of the measurement.

vi. Emissivity of the blackbody cavity;
This component is obtained from an estimate of the uncertainty of the surface emissivity of the graphite of the blackbody cavity as calculated by the method developed by Bedford and Ma [41].

vii. Drift in the wavelength of the interference filter;
This component was obtained by taking the difference between the last two calibrations of the spectral responsivity of the LP3 pyrometer.

Table 22: Uncertainty budget of the temperature determination.

Quantity X_i	Estimate x_i	Std. uncertainty $u(x_i)$	probability distribution	sensitivity coefficient c_i	uncertainty contribution $u_i(y)$, °C
Inflection point	1328,72 °C	0,007	normal	1	0,007
ε_{BB}	0,9997	0,0003	normal	$\lambda.T^2/c_2$	0,035
T_{Ag}	1234,93 K	0,05	normal	$(T/T_{Ag})^2$	0,084
Spec. resp./drift	650 nm	0,05	rectangular	$(T/\lambda)\cdot(T/T_{Ag} - 1)$	0,021
Non-linearity	1	0,0001	normal	$\lambda/c_2\cdot T^2\cdot u(S(T_{Ag})_L)/S(T_{Ag}))$	0,000
Stab.ref. photocurrent	2,01E-11 A	1,0E-14	normal	$(\lambda.T^2/c_2).u(I(T_{Ag}))/I(T_{Ag})$	0,057
				Combined Uncertainty	0,110
				Expanded Uncertainty k=2	0,22

T_{Ag} = Temperature of the reference cell (silver) = 1234,93 K; ε_{BB} = emissivity of the blackbody cavity of the Ni-C cell; c_2 = 0,014388 m K; T = 1602,15 K; λ = 650 nm; $u(S(T_{Ag})L)$ = uncertainty of the non-linearity correction; $S(T_{Ag})$ = signal measured at the Ag fixed point

9.2. Uncertainty in the determination of the concentration of dopants in the metal carbon alloy

In order to evaluate the uncertainty in the determination of the molar fraction of the dopants, first it is necessary to identify the uncertainty components:

i. Uncertainty due to the calibration of the Sartorius balance

ii. Uncertainty due to the resolution of the Sartorius balance

iii. Stability of the readings of the balance

The molar fraction is the number of moles, $n(D)$, of the dopant divided by the total number of moles of the mixture $n(Total)$:

$$X(D) = \frac{n(D)}{n(Total)} \qquad (28)$$

The number of moles is calculated by:

$$n(D) = \frac{m(D)}{M(D)} \tag{29}$$

Where *m*(*D*) stands for the mass, *M*(*D*) for the molecular weight and *D* is related to the dopant, Cu or Sn.

$$X(D) = \frac{\dfrac{m(D)}{M(D)}}{\dfrac{m(D)}{M(D)} + \dfrac{m(C)}{M(C)} + \dfrac{m(Ni)}{M(Ni)}} \tag{30}$$

So, applying the law of propagation of uncertainties [65], it is possible to obtain the uncertainty of the molar fraction:

$$u^2(X(D)) = \left(\frac{\partial X(D)}{\partial m(D)}\right)^2 \cdot u^2(m(D)) + \left(\frac{\partial X(D)}{\partial m(C)}\right)^2 \cdot u^2(m(C)) + \ldots$$

$$\ldots + \left(\frac{\partial X(D)}{\partial m(Ni)}\right)^2 \cdot u^2(m(Ni)) \tag{31}$$

It was considered that the uncertainties of the molecular weights of the elements were zero. For the other contributions to the uncertainty budget it was considered:

M(C) = 12,011 g/mol M(Ni) = 58,6934 g/mol M(Cu) = 63,54 g/mol

m(C) = 0,557754 g *m*(Ni) = 32,2513 g *m*(Cu) = 0,15849 g

u(*m*(C)) = *u*(*m*(Ni)) = *u*(*m*(Cu)) = 0,0001 g. In this value all the uncertainty contributions described in *i*, *ii* and *iii* were combined in quadrature.

The expanded uncertainty of the dopant concentrations was found to be very small, around 5 ppm for all the dopants. The effect of this uncertainty on the temperatures obtained with Thermo-Calc simulation is negligible.