Int. J. Metrol. Qual. Eng. **2**, 13–17 (2011)

DOI: 10.1051/ijmqe/2011003

Uncertainty evaluation in the calibration of Pt/Pd thermocouples up to copper freezing point at NIS-Egypt

F.M. Megahed and Y.A. Abdelaziz*

National Institute for Standards NIS, Thermal Measurements Lab, Tersa St. Elharam, El-Giza, P.O. 136 Giza, 12211 Egypt

Received: 4 February 2011 / Accepted: 21 February 2011

Abstract. The dissemination of traceability to the International Temperature Scale of 1990 (ITS-90) through comparison calibration of thermocouples, is playing an important role in metrology institutes, secondary laboratories and industrial measurements. The previous studies of the Pt/Pd thermocouples at NIS-Egypt, shows promise of achieving significant improvements uncertainty of temperature measurements up to 960 °C. In this paper we describe the uncertainty assessment on the measurements of the calibration of Pt/Pd thermocouples at fixed point cells up to the freezing point of copper and by the comparison technique following a defined heat treatment at 1100 °C. All the measurements on Pt/Pd thermocouples were carried out using NIS facilities.

Keywords: Copper freezing point; Pt/Pd thermocouples; incertainty

1 Introduction

Thermocouples prepared from pure elements do not suffer from oxidation and evaporation problems [1–3] than alloys thermocouples. They are more thermoelectrically homogeneous and their thermoelectric stability is not limited by changes in alloy composition caused by oxidation.

In order to establish the Egyptian calibration service system for high-temperature thermocouple thermometry, NIS has started calibration service of Pt/Pd thermocouples by fixed points up to the freezing points of copper and by comparison technique. As the primary standard of the Cu point, a new three zone furnace was used and its uncertainty in realizing the fixed point was evaluated. The emf changes of Pt/Pd thermocouples up to the Cu point have been studied.

In a previous works [1, 4–7] thermal measurement lab, NIS-Egypt and other laboratories studied the stability and calibration uncertainty of Pt/Pd thermocouple following heat treatment up to 960 °C.

In the present work, the stability characteristics and sources of uncertainty of Pt/Pd thermocouple calibration concerning the reference junction, the change of the thermocouple emf, and the thermocouple inhomogeneity up to the freezing point of copper have been taken into consideration, and the overall uncertainty is evaluated.

2 Preparation of the thermocouple

The Pt/Pd thermocouple has been assembled at NIS-Egypt using reference grade platinum of 99.999% purity and palladium of 99.997% purity wires of 0.5 mm diameter and 150 cm length supplied by Johnson Matthey, England.

The wires were annealed electrically in air for l0 h at about 1300 °C for palladium wire and 1100 °C for platinum after cleaning them with alcohol [8] then cooled to ambient temperature by switching off the current. We applied this rapid cooling to prevent oxidation of the Pd wire in the temperature range 500 °C up to 800 °C [7].

Twin bore alumina tube 600 mm length, 3.5 mm outer diameter and 0.8 mm bore, was used to insert the wires. Expansion coil constructed from 0.2 mm Platinum each wire wounded into a coil of four turns of 1 mm diameter each were connected at the measuring junction of the Pt and Pd thermoelements [8]. Closed end alumina tube was used as thermocouple protection cover during the annealing of the thermocouple [9]. A pair of insulated Cu wires was soldered to the other ends of the thermoelements to form the reference junction.

3 Measurements equipment and procedure

For calibration and evaluation of the Pt/Pd thermocouple in the temperature range from 420 °C to 1100 °C, the freezing points of Zn, Ag and Cu were used in this study.

For the freezing points measurements, sealed cells containing high purity (99.9999%) metals Zn, Ag or Cu were used. The immersion of the measuring junction of the thermocouple inside the cell was 18 cm below the surface of Zn, Ag or Cu at full immersion into the thermometer well during measurements.

Zn, Ag and Cu cells were supplied by NPL. The furnace used for Zn and Ag freezing point cells was made

---

* Correspondence: yasserabdelfatah@yahoo.com

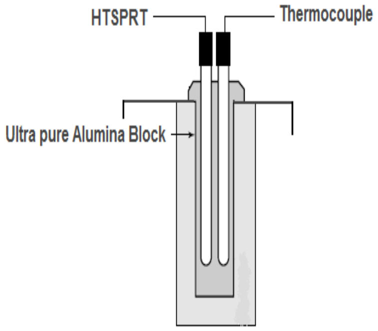

Fig. 1. Alumina block used for calibration of thermocouple.

by carbolite-UK its maximum temperature 1000 °C and utilized double walled sealed sodium heat pipe, the temperature of the furnace was controlled by a controller unit at 1 °C below the freezing point has a set point resolution 0.1 °C and ±3 °C set point accuracy at Ag freezing point. The temperature stability of Zn and Ag freezing point furnaces was ±0.03 °C and ±0.3 °C respectively.

The furnace used for Cu freezing point was three-zone furnace made by ISOTECH – UK, its max temperature 1200 °C. It has separate temperature controller with 0.1 °C resolution and two addition controllers to adjust temperature gradient along the upper and lower heater.

The reference junction of the thermocouple was maintained at 0 °C in a dewar filled with distilled water and crushed ice (ice bath). The reference junction was inserted into closed end glass tube and was immersed 20 cm in the ice bath.

Digital Nanovoltmeter with internal resistance higher than $10^9\,\Omega$ was used to measure emf, its resolution corresponds to temperature resolution of 1 mK and 48 nV accuracy.

Calibrations of the thermocouple were also performed from 800 to 960 °C by comparison with a high temperature standard platinum resistance thermometer (HTSPRT) calibrated according to ITS-90 at fixed points. The alumina block in which the thermocouple and HTSPRT were compared is made of ultra pure alumina with 50 mm outer diameter and 55 cm length as shown in Figure 1.

The thermocouple was placed very close to the centre of the resistance thermometer coil. To prevent heat losses by convection, the furnace tube was closed with an alumina cover with a central hole through which the insert was inserted inside the furnace. The temperature gradient along the furnace was about 0.05 °C over the length of 20 cm. Resistance measurements of the HTSPRT were made with a model F-18 AC Bridge manufactured by Automatic Systems Laboratories Inc.

4 Results and discussion

The aim of this work is to study the emf stability and repeatability as sources of uncertainty budget of Pt/Pd thermocouples, in the temperature range from 420 °C up to 1100 °C comparing the calibration with a reference function of emf versus temperature, as proposed by Burns et al. [8].

At first the Pt/Pd thermocouple was thermally treated in air for 10 h at about 1300 °C for palladium wire and at 1100 °C for platinum wire, then it was calibrated at freezing points of Zn, Ag and Cu. Three freezing sets were carried out; each set consists of five freezing experiments.

Pt/Pd thermocouple was heated for different periods of 70, 100, 150, 200 h in three-zone furnace at 1100 °C to check the thermal stability.

Table 1 shows the improvement of emf repeatability at Zn, Ag and Cu freezing points after being thermally treated at 1100 °C for a period of 70 h. The results also show that there is an increase in emf at the freezing points of Zn, Ag and Cu as a result of the 70 h heat treatment at about 1100 °C. This has been also found by Burns et al. [8].

They mentioned that the source of drift in Pt/Pd thermocouple is intrinsic to the Pd wire. The thermocouple stability after second heating period was of the same order as the standard deviation of the third set of measurements, ±0.01 μV for Zn, ±0.01 μV for Ag and ±0.04 μV for Cu freezing points.

The results of the stability test for the thermocouple are illustrated in Figure 2, in which the deviations with respect to the initial emf values at the freezing points of Zn, Ag and Cu are plotted as a function of heating time in hours.

Figure 3 shows the effect of heat treatment on the repeatability of the thermocouple expressed as standard deviation in microvolt of each set of freezing experiments against time of thermal heating.

At Zn freezing point (419.527 °C), the repeatability has been improved from (0.1 μV) to (0.01 μV) after heat treatment for 200 h as given in Table 1 but at Ag freezing point (961.78 °C), the repeatability has been improved from (0.07 μV) to (0.01 μV) also at the Cu freezing point (1084.62 °C), the repeatability has been improved from (0.05 μV) to (0.04 μV).

For calibration and interpolation between measured data we have used the standard reference function suggested by Burns et al. [8].

$$E_{\text{ref}} = b_o + \sum_{i=1}^{n} b_i t_{90}^i. \tag{1}$$

In the following the coefficients values b_i of the reference function for Pt/Pd thermocouples [8],

	Temperature range	
	0 °C to 660.323 °C	660.323 °C to 1500 °C
$b_0 =$	0.000000	4.9771370×10^{2}
$b_1 =$	5.296958	1.0182545×10^{1}
$b_2 =$	4.610494×10^{-3}	$-1.5793515 \times 10^{-2}$
$b_3 =$	-9.602271×10^{-6}	3.6361700×10^{-5}
$b_4 =$	$-2.6901509 \times 10^{-8}$	$-2.690150\,9 \times 10^{-8}$
$b_5 =$	$-2.012523 \times 10^{-11}$	$9.5627366 \times 10^{-12}$
$b_6 =$	$-1.268514 \times 10^{-14}$	$-1.3570737 \times 10^{-15}$
$b_7 =$	2.257823×10^{-17}	
$b_8 =$	$-8.510068 \times 10^{-21}$	

Table 1. Short term stability of Pt/Pd thermocouple by heat treatment at 1100 °C, expressed as standard deviation, using Cu, Ag and Zn freezing points.

	Standard deviation of results $\pm\mu$v				
Freezing point	Before eat treat.	After 70 h heat treat.	After 100 h heat treat.	After 150 h heat treat.	After 200 h heat treat.
Cu	0.05	0.04	0.04	0.04	0.04
Ag	0.07	0.07	0.01	0.01	0.01
Zn	0.10	0.01	0.01	0.01	0.01

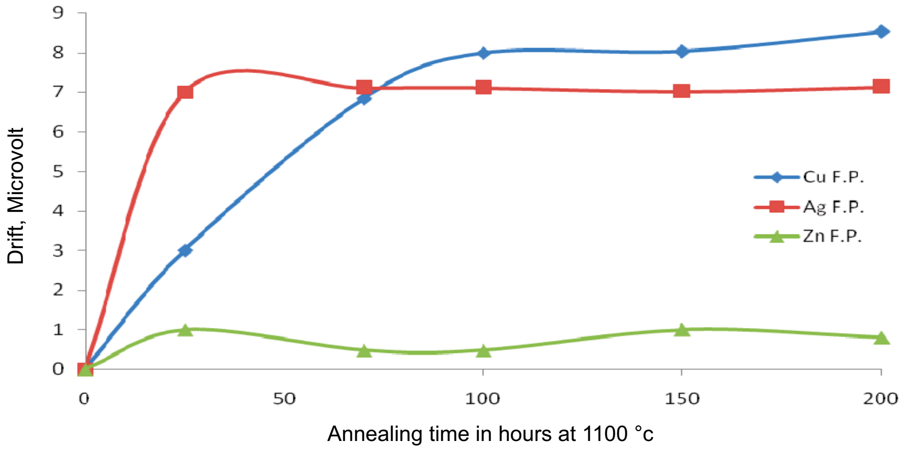

Fig. 2. The Pt/Pd thermocouple stability at Zn, Ag and Cu freezing points after different heat treatments.

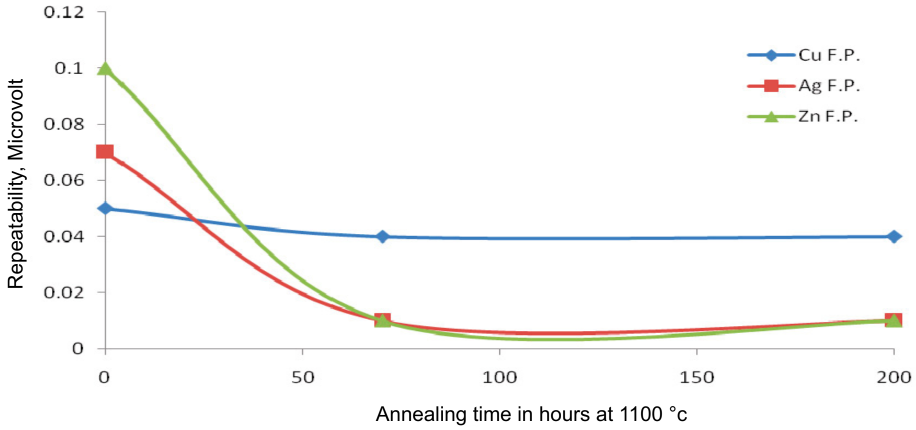

Fig. 3. Repeatability Pt/Pd thermocouple at Zn, Ag and Cu freezing points after different heat treatments.

Calibrations were also performed from 420 °C to 960 °C by comparison with high temperature standard platinum resistance thermometers (HTSPRT) and type R thermocouple using variable temperature heat pipe furnace and three zoon furnace. The data are given in Table 2.

5 Uncertainty components

Uncertainties of measurement shall be calculated in accordance with EA publication EA-4/02 "Expression of the Uncertainty of Measurement in Calibration" [10]. The uncertainty budget of Pt/Pd thermocouple at freezing points of Zinc, Silver and Copper incorporating the various contributory factors is shown in Table 3.

The uncertainties for the items labeled repeatability are typically evaluated as type A uncertainties, using statistical methods. The other items are primarily evaluated using type B methods. The major contribution to the uncertainty is attributed by inhomogeneity of thermocouple it has been estimated from the immersion/withdrawal thermo-emf profile of thermocouples in fixed point cells,

Table 2. Experimental values for temperature, t_{90}, thermoelectric voltage, and related standard deviation. A freezing point is denoted as FP.

Temperature $T_{90}/°\text{C}$	$\Delta E = E_{\text{calc}} - E_{\text{exp}}$ (μV)	Standard deviation (μV)	dE/dt (μV/°C)
419.527 (FP)	0.0	0.06	9.45
843.07	–1.8	0.21	17.14
926.00	–2.0	0.23	18.63
961.78 (FP)	0.0	0.06	19.29
1009.40	–2.0	0.40	20.17
1073.67	–2.1	0.44	21.33
1084.62 (FP)	0.01	0.82	21.55

* E_{exp} given in the above table is the experimental value obtained in the present work and E_{calc} are the calculated emf values using Burns et al. simple polynomial [8].

Table 3. The combined uncertainty U_c expressed in the form of 95% confidence level for the calibration of Pt/Pd thermocouples in Zn and Ag and Cu freezing points is estimated.

Expected components of uncertainty	At Zn freezing point (mK)	At Ag freezing point (mK)	At Cu freezing point (mK)
Repeatability (type A)	10.5	3.6	2.4
Uncertainty of fixed point	1.5	1.5	1.5
Uncertainty due to T/C inhomogeneity	52.0	52.0	52.0
Uncertainty due to interpolation formula	50.0	50.0	50.0
Uncertainty due to drift of thermocouple	10.0	10.0	10.0
Uncertainty of digital voltmeter	20.0	20.0	20.0
Uncertainty of ice point	5.0	5.0	5.0
Combined standard uncertainty, U_c	76.5	75.8	75.7
Expanded uncertainty U, $k = 2$	153.0	151.6	151.5

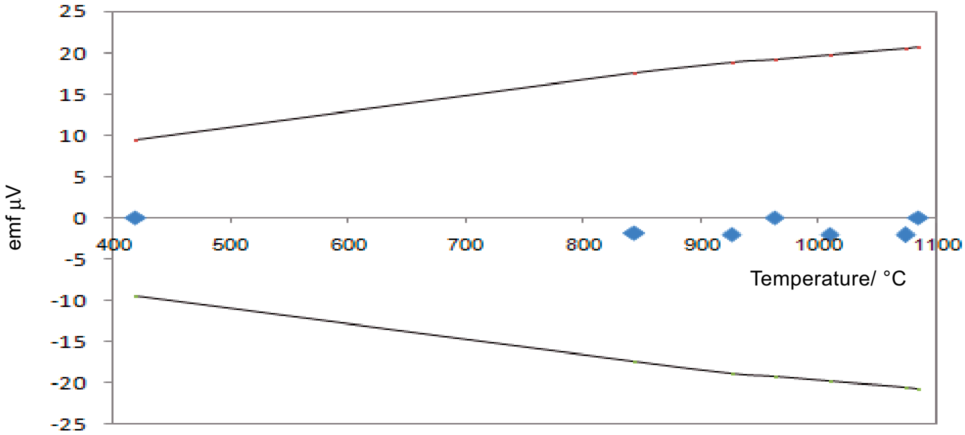

Fig. 4. Difference between the measured emf in range from 420 to 1100 °C and the corresponding values calculated using the reference function by Burns et al.

as described in detail before by the authors in other article [4]. The uncertainty due to purity of ingots was evaluated from the manufacturer's certificate stating that for 6/N purity, a repeatable plateau of 1.5 mK can be produced at freezing points [11]. The drift caused in the thermocouple is another component of uncertainty, which was estimated from the earlier fixed point measurements and included in the uncertainty budget. Other uncertainty sources, related electrical measuring system, are included in the total uncertainty budget as digital voltmeter and reference junction.

Table 4 provides a list of the possible uncertainty components for the calibration of thermocouples at specified test temperatures by comparison technique.

The uncertainties for the items labeled repeatability are typically evaluated as type A uncertainties, using statistical methods. The other items are primarily evaluated using type B methods. The standard deviation

Table 4. The combined Uncertainty U_c expressed in the form of 95% confidence level for the calibration of Pt/Pd thermocouple by comparison in the temperature range from 420 °C to 960 °C with HTSPRT is estimated.

Expected components of uncertainty	mK
Repeatability (type A)	40.0
Uncertainty due to T/C	52.0
Uncertainty due to interpolation formula	50.0
Uncertainty due to drift of thermocouple	10.0
Furnace homogeneity	30.0
Uncertainty of voltmeter	20.0
Uncertainty of ice point	5.0
HTSPRT calibration	10.0
Combined standard uncertainty U_c	81.3
Expanded uncertainty $U, K = 2$	182.6

is a type A measure of both bath stability and short-term repeatability of the measurement systems for the test and reference thermometer.

In Table 4, repeatability of the complete calibration process may be evaluated by taking the standard deviation, at each test temperature, of a set of emf values measured on check-standard thermocouples. The calibration uncertainty of the reference thermometer can generally be obtained from the calibration certificate. For an SPRT, this uncertainty should also include the drift of the resistance-temperature relation with time and the uncertainty of measuring the resistance ratio which may be that are small relative to other uncertainties for thermocouple calibrations.

The calibration uncertainty of the digital voltmeter as thermocouple readout can generally be obtained from the calibration certificate. Also the uncertainty contribution from the inhomogeneity of the tested thermocouples can be evaluated by insertion/withdrawal test of the thermocouple at fixed point as shown before in Table 3. Thermocouple drift at elevated temperatures is well documented and estimated from the earlier fixed point measurements and included in the uncertainty budget.

Some uncertainty sources, such as the bath non-uniformity and bath stability, are naturally expressed in units of temperature. Other terms, such as the extraneous emf, are conveniently expressed in units of voltage. The general conversion between an uncertainty in emf and the equivalent temperature uncertainty is given by $u(E) = u(t)/Sn(t)$, where $Sn(t)$ is the Seebeck coefficient of a thermocouple, at temperature t.

A detailed analysis of the different components of measurements uncertainty had been estimated as given in Tables 3, and 4.

6 Conclusions

The Pt/Pd thermocouple inhomogeneity was the most dominant component of uncertainty in this work. After good heat treatment of the thermocouple the emf drift became very small typically 0.03 °C at 1100 °C.

Accordingly a small number of calibration points should be necessary to calibrate a Pt/Pd thermocouple within a temperature range from 420 °C to 1100 °C. So, it is important to evaluate the deviation of the reference table (Δemf) versus temperature to determine other points to the calibration. It will modify also the degree of the fitting curve degree to calculate interpolated values.

The good stability and repeatability exhibited by Pt/Pd thermocouples when thermally treated at 1100 °C, suggest that such a thermocouple type can be recommended for use as transfer standards for the dissemination of temperatures and to approximate the ITS-90 at NIS.

References

1. Y.A. Abdelaziz, F.M. Megahed, M.M. Halawa, Stability and calibration of platinum/palladium thermocouples following heat treatment, Measurement Journal IMEKO-UK **35**, 413–420 (2004)
2. E.H. McLaren, E.G. Murdock, H.H. Plumb, New Considerations on the Preparation, Properties, and Limitations of the Standard Thermocouple for Thermometry, in *Temperature: its Measurement and Control in Science and Industry* (1972) Vol. 4, pp. 1543–1560
3. E.H. McLaren, E.G. Murdock, *The Pt/Au Thermocouple*, NRC Report NRCC/27703 Monograph (Canada Publ., 1987), pp. 15–30
4. A.Y. Abdelaziz, F.M. Megahed, M.M. Halawa, M.M. Ammar, Performance, Thermoelectric Homogeneity and Stability of Au/Pt and Pt–10Rh/Pt Thermocouples, in *Temperature: its Measurement and Control in Science and Industry* (2003) Vol. 7, pp. 475–480
5. F. Edle, H.J. Jung, H. Maas, J.Y. Le Pommele, CCT/93-5, A provisional reference function for platinum vs. palladium thermocouples in the range 0 °C until 1084 °C (1993), Vol. 1, pp. 1–3
6. L. Crovini, A. Ctis, V. Fernicola, R. Galleano, CCT/93-17, On the behavior of platinum palladium thermocouples from 600 °C to 1100 °C (1993), pp. 1–5
7. E. Renaot, M. Elgourdou, E. Devin, M. Liedberg, Contribution to a reference function for Pt/Pd thermocouples from 0 °C to 960 °C, in *EUROMET Workshop Temperature, Paris, France, 1998*, pp. 113–118
8. G.W. Burns, D.C. Ripple, M. Battuello, Platinum versus palladium thermocouples: an emf-temperature reference function for the 0 °C to 1500 °C, Metrologia **35**, 761–780 (1998)
9. *Manual on the Use Thermocouples in Temperature Measurements*, ASTM Manual Series MNL (1993), Vol. 12, pp 289–290
10. *Expression of the Uncertainty of Measurement in Calibration*, EURAMET publication EA-4/02 (1999), pp. 25–30
11. D. Ripple, K. Garrity, Uncertainty Budgets for Comparison Calibrations of Thermocouples, in *NCSL Int. Workshop and Symp. 2006*, Vol. 1, pp. 28–35