EURAMET-1071: Bilateral Comparison of Copper Fixed-Point Cells by Using Pt/Pd Thermocouples

O. Kerkhof[1], F. Edler[2]

[1] O. Kerkhof
VSL, Thijsseweg 11, 2629 JA Delft, the Netherlands
Email: okerkhof@vsl.nl

[2] F. Edler
PTB, Abbestrasse 2-12, 10587 Berlin, Germany

Abstract. A bilateral comparison between VSL and PTB of copper fixed points is reported as a supplementary to the earlier reported [1] intercomparison EUROMET-844. Agreement of the freezing temperatures of the fixed points within ± 0.03 K was found.

1. Introduction

PTB served as the pilot laboratory for the EUROMET-844 intercomparison whose results were published in 2008 [1]. VSL was not able to complete the measurements in that project for which reason a bilateral comparison between VSL and PTB was agreed afterwards.

2. Experimental details

2.1 Experimental setup

Two Pt/Pd thermocouples were used as transfer standards to compare the freezing temperatures of the fixed point cells. The first thermocouple (NPL-PtPd-2008-1), manufactured by NPL and owned by VSL, was calibrated at the fixed points of Cu and Ag by VSL, then by PTB and checked by VSL afterwards for the occurrence of any drift in the thermocouple. The second thermocouple (PTB PtPd 01/03), manufactured and owned by PTB, was first calibrated by PTB, then by VSL and again by PTB. The calibration included a homogeneity test at the freezing point of silver. The laboratories passed the thermocouples through the following measurement procedure:

- Annealing at 1030 °C for a duration of 4 hours followed up by slowly withdrawing from the furnace.
- 1st Cu freezing point plateau realization
- 2nd Cu freezing point plateau realization
- 3rd Cu freezing point plateau realization
- Ag freezing point plateau realization and immersion profile

In contrast with the procedure in EURAMET-844 the annealing steps in between each Cu freezing point measurements to remove oxidation were skipped in this bilateral comparison. It appeared from homogeneity checks at the Cu plateaus and by comparing the thermal voltage at subsequent plateau realizations that the oxidation effect is negligible.

The open cell Cu freezing point at VSL is used in combination with a multi-zone furnace of their own design. The furnace consists of two auxiliary heaters at the top and bottom and two main heating elements. The main heater is temperature controlled. The auxiliary heater controllers are connected to a differential thermocouple to keep a fixed temperature difference between the top and bottom

zones with respect to the main zone. The resulting temperature profile in the furnace is shown in Fig. 1

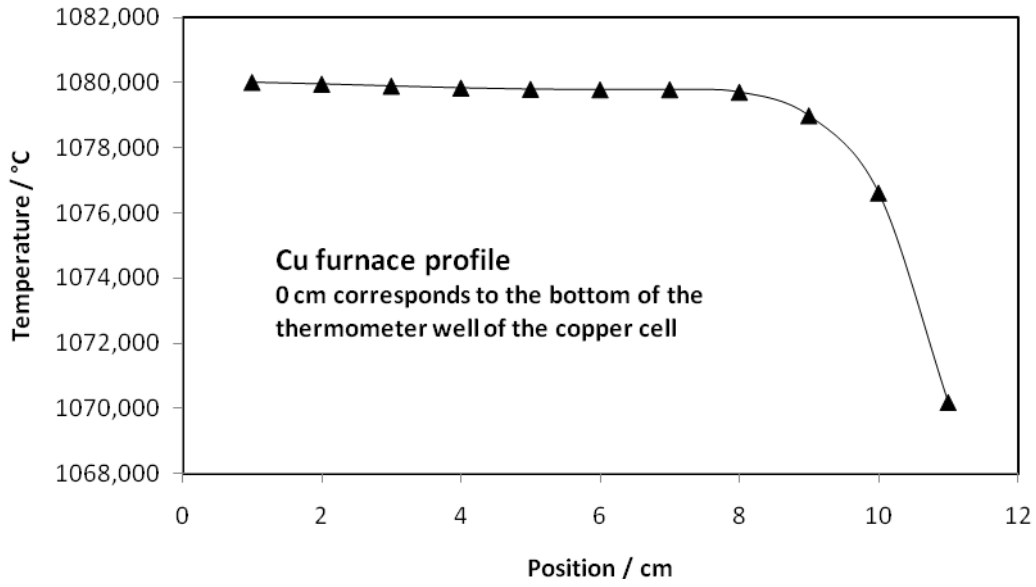

Figure 1. Vertical copper furnace (VSL) at about 1080 °C.

The Cu freezing point of PTB was a homemade open cell inserted in a ceramic tube of 470 mm in length and 50 mm inner diameter. Additional nine caps made of graphite (diameter 48 mm) were placed above the copper cell to prevent an oxidation of the copper. The resulting temperature profile in the furnace is shown in Fig. 2

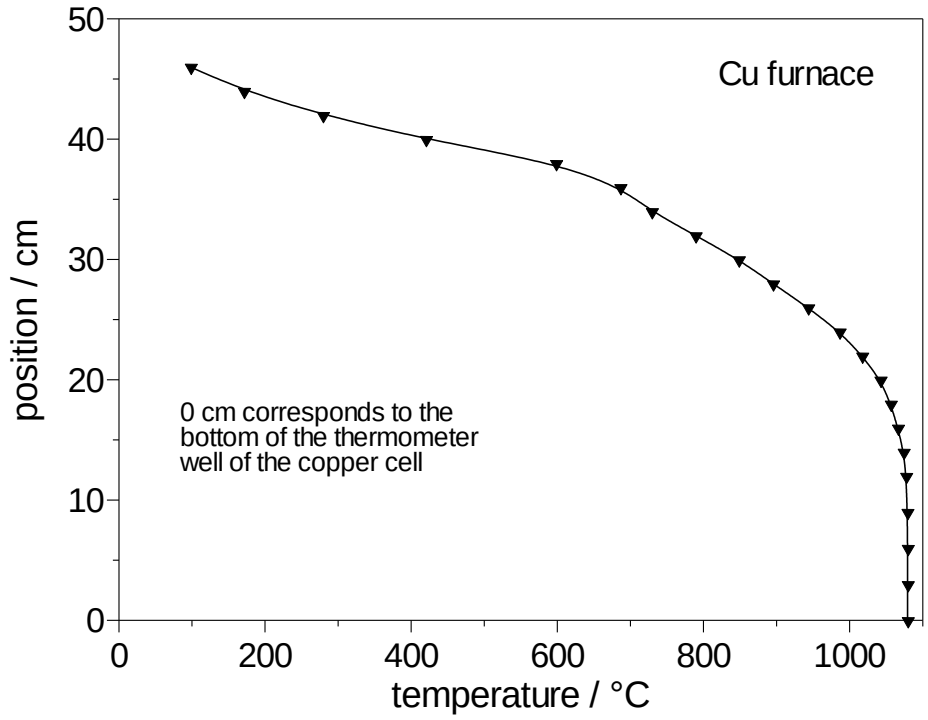

Figure 2. Vertical copper furnace (PTB) at about 1080 °C.

2.2 Voltage measurements

The equipment used to measure the thermal voltage of the thermocouples at VSL consisted of a HP nanovolt meter, type 34420A. PTB used an Agilent voltmeter 3458A.

3. Results

3.1 electromotive force measurements

Tables 1 and 2 include the measured electromotive force (emf) voltages given by VSL and PTB for the two thermocouples.

Table 1. Comparison data for the freezing temperatures of the Cu fixed-point cell plateau realizations measured with the NPL-PtPd-2008-01 thermocouple.

	E_{VSL} / µV	E_{PTB} / µV	E_{VSL} - E_{PTB} / µV
1st plateau	13279.07	13278.48	
2nd plateau	13279.00	13278.44	
3rd plateau	13278.91	13278.58	
Average	13278.99	13278.50	0.49

The return measurements by VSL at three independently realized Cu freezing plateaus had an average value of 13278.98 µV indicating that no significant drift had occurred.

The emf measured by VSL at the Ag freezing point was: 10814.65 µV
The emf measured by PTB at the Ag freezing point was: 10814.27 µV

Table 2. Comparison data for the freezing temperatures of the Cu fixed-point cell plateau realizations measured with the PTB-PtPd-01/03 thermocouple.

	E_{PTB} / µV	E_{VSL} / µV	E_{VSL} - E_{PTB} / µV
1st plateau	13248.25	13248.02	
2nd plateau	13248.05	13248.20	
3rd plateau	13248.16	13248.33	
Average	13248.15	13248.18	0.03

The return measurement by PTB at a single realized Cu freezing plateau resulted in a value of 13247.68 µV indicating that the drift remained well within the limits of the measurement uncertainty (see paragraph 3.2)

The emf measured by VSL at the Ag freezing point was: 10786.88 µV
The emf measured by PTB at the Ag freezing point was: 10787.56 µV

3.2 uncertainty analysis

The electromotive force (emf) $E_X(t_X)$ of the thermocouple under calibration at a fixed point indicated by the voltmeter can be written as:

$$E_X(t_X) = E_X(t_F) + (\delta t_F + \delta t_{DF} + \delta t_{HF}) \cdot C_{FX} + \delta E_{X1} + \delta E_{X2} + \delta E_{X3} + \delta E_{X4} + \delta t_{0X} \cdot C_{0X} + \delta E_{Hom} \cdot E_X(t_{Cu}) \Big/ E_{Ag}$$

where:

$E_X(t_F)$ emf at the fixed point temperature t_F
δt_F correction on basis of the calibration of the fixed point
δt_{DF} correction on basis of the drift of the fixed point temperature
δt_{HF} correction on basis of a heat flux along the thermocouple
C_{FX} sensitivity of the thermocouple at the fixed point temperature
δE_{X1} correction on basis of the voltmeter calibration
δE_{X2} correction on basis of the voltmeter resolution
δE_{X3} correction on basis of the voltmeter drift
δE_{X4} correction due to the influence on ambient parameters and connection leads
δt_{0X} temperature correction due to the reference temperature
C_{0X} sensitivity of the thermocouple at the reference temperature of 0 °C
δE_{Hom} correction due to the influence of inhomogeneous thermocouple wires at the freezing point of copper
E_{Ag} emf at the freezing point of silver

Due to the lack of calibration information no uncertainty estimate could be made by VSL for δt_F and δt_{DF}. Instead of this an estimate was made for:

δt_{imp} correction on basis of the purity of the fixed point material
δt_{plat} correction on basis of the plateau progress

The estimated uncertainties for the measurements are stated in tables 3-10.

Table 3. Estimated uncertainty by PTB for the measurements at the freezing point of Cu using the NPL-PtPd-2008-01 thermocouple.

Quantity	Estimation	Standard uncertainty	Probability distribution	Sensitivity coefficient	Uncertainty contribution / µV
$E_x(t_F)$	13278,5 µV	0,2 µV	normal	1	0,2
δt_F	0 K	0,03 K	rectangular	20.89 µV/K	0,63
δt_{DF}	0 K	0,03 K	rectangular	20.89 µV/K	0,63
δt_{HF}	0 K	0,006 K	rectangular	20.89 µV/K	0,13
δE_{X1}	0 K	0,3 µV	normal	1	0,3
δE_{X2}	0 µV	0,03 µV	rectangular	1	0,03
δE_{X3}	0 µV	0,17 µV	rectangular	1	0,17
δE_{X4}	0 µV	0,3 µV	rectangular	1	0,3
δt_{0X}	0 K	0,01 K	normal	5.3 µV/K	0,05
δE_{Hom}	0 µV	0,7 µV	rectangular	1,23	0,86
				combined uncertainty:	1,34

Table 4. Estimated uncertainty by PTB for the measurements at the freezing point of Ag using the NPL-PtPd-2008-01 thermocouple.

Quantity	Estimation	Standard uncertainty	Probability distribution	Sensitivity coefficient	Uncertainty contribution / µV
$E_x(t_F)$	10814,27 µV	0,2 µV	normal	1	0,2
δt_F	0 K	0,006 K	rectangular	19.2 µV/K	0,12
δt_{DF}	0 K	0,006 K	rectangular	19.2 µV/K	0,12
δt_{HF}	0 K	0,006 K	rectangular	19.2 µV/K	0,12
δE_{X1}	0 K	0,3 µV	normal	1	0,3
δE_{X2}	0 µV	0,03 µV	rectangular	1	0,03
δE_{X3}	0 µV	0,17 µV	rectangular	1	0,17
δE_{X4}	0 µV	0,3 µV	rectangular	1	0,3
δt_{0X}	0 K	0,01 K	normal	5.3 µV/K	0,05
δE_{Hom}	0 µV	0,7 µV	rectangular	1	0,7
				combined uncertainty:	0,89

The uncertainty associated with the homogeneity is based on the immersion profile at Ag and dividing the maximum deviation by $\sqrt{3}$.

Position	Δemf/µV
0 cm	0
2 cm	+0,29
4 cm	+0,62
6 cm	+0,85
8 cm	+1,09
10 cm	+1,21
12 cm	+0,55

Table 5. Estimated uncertainty by PTB for the measurements at the freezing point of Cu using the PTB-PtPd-01/03 thermocouple.

Quantity	Estimation	Standard uncertainty	Probability distribution	Sensitivity coefficient	Uncertainty contribution / µV
$E_x(t_F)$	13248,15 µV	0,2 µV	normal	1	0,2
δt_F	0 K	0,03 K	rectangular	20.89 µV/K	0,63
δt_{DF}	0 K	0,03 K	rectangular	20.89 µV/K	0,63
δt_{HF}	0 K	0,006 K	rectangular	20.89 µV/K	0,13
δE_{X1}	0 K	0,3 µV	normal	1	0,3
δE_{X2}	0 µV	0,03 µV	rectangular	1	0,03
δE_{X3}	0 µV	0,17 µV	rectangular	1	0,17
δE_{X4}	0 µV	0,3 µV	rectangular	1	0,3
δt_{0X}	0 K	0,01 K	normal	5.3 µV/K	0,05
δE_{Hom}	0 µV	0,4 µV	rectangular	1,23	0,49
				combined uncertainty:	1,14

Table 6. Estimated uncertainty by PTB for the measurements at the freezing point of Ag using the PTB-PtPd-01/03 thermocouple.

Quantity	Estimation	Standard uncertainty	Probability distribution	Sensitivity coefficient	Uncertainty contribution / µV
$E_x(t_F)$	10787,56 µV	0,2 µV	normal	1	0,2
δt_F	0 K	0,006 K	rectangular	19.2 µV/K	0,12
δt_{DF}	0 K	0,006 K	rectangular	19.2 µV/K	0,12
δt_{HF}	0 K	0,006 K	rectangular	19.2 µV/K	0,12
δE_{X1}	0 K	0,3 µV	normal	1	0,3
δE_{X2}	0 µV	0,03 µV	rectangular	1	0,03
δE_{X3}	0 µV	0,17 µV	rectangular	1	0,17
δE_{X4}	0 µV	0,3 µV	rectangular	1	0,3
δt_{0X}	0 K	0,01 K	normal	5.3 µV/K	0,05
δE_{Hom}	0 µV	0,4 µV	rectangular	1	0,4
				combined uncertainty:	0,67

The uncertainty associated with the homogeneity is based on the immersion profile at Ag and dividing the maximum deviation by $\sqrt{3}$.

Position	Δemf/µV
0 cm	0
2 cm	+0,39
4 cm	+0,62
6 cm	+0,7
8 cm	+0,7
10 cm	+0,31

Table 7. Estimated uncertainty by VSL for the measurements at the freezing point of Cu using the NPL-PtPd-2008-01 thermocouple.

Quantity	Estimation	Standard uncertainty	Probability distribution	Sensitivity coefficient	Uncertainty contribution / µV
$E_x(t_F)$	13278.98 µV	0.15 µV	normal	1	0.15
δt_{imp}	0 K	0.0012 K		20.89 µV/K	0.025068
δt_{plat}	0 K	0.1 K	rectangular	20.89 µV/K	2.089
δt_{HF}	0 K	0.005 K	rectangular	20.89 µV/K	0.10445
δE_{X1}	0 µV	0.25 µV	normal	1	0.25
δE_{X2}	0 µV	0.058 µV	rectangular	1	0.03
δE_{X3}	0 µV	0.06 µV	rectangular	1	0.06
δE_{X4}	0 µV	0.29 µV	rectangular	1	0.29
δt_{0X}	0 K	0.005 K	normal	5.3 µV/K	0.026
δE_{Hom}	0 µV	0.8 µV	rectangular	1.23	0.98
				combined uncertainty:	2.13

Table 8. Estimated uncertainty by VSL for the measurements at the freezing point of Ag using the NPL-PtPd-2008-01 thermocouple.

Quantity	Estimation	Standard uncertainty	Probability distribution	Sensitivity coefficient	Uncertainty contribution / µV
$E_x(t_F)$	10814.27 µV	0.0005 µV	normal	1	0.0005
δt_{imp}	0 K	0.312 mK	rectangular	19.2 µV/K	0.0059904
δt_{plat}	0 K	0.115 mK	rectangular	19.2 µV/K	0.002208
δt_{HF}	0 K	0.005 K	rectangular	19.2 µV/K	0.096
δE_{X1}	0 K	0.25 µV	normal	1	0.25
δE_{X2}	0 µV	0.058 µV	rectangular	1	0.03
δE_{X3}	0 µV	0.06 µV	rectangular	1	0.06
δE_{X4}	0 µV	0.29 µV	rectangular	1	0.29
δt_{0X}	0 K	0.005	normal	5.3 µV/K	0.026
δE_{Hom}	0 µV	0.8 µV	rectangular	1	0.8
				combined uncertainty:	0.90

The uncertainty associated with the homogeneity is based on the immersion profile at Ag and dividing the maximum deviation by √3.

Position	Δemf/µV
0 cm	0
2 cm	+0,34
4 cm	+0,67
6 cm	+0,97
8 cm	+1,2
10 cm	+1,4

Table 9. Estimated uncertainty by VSL for the measurements at the freezing point of Cu using the PTB-PtPd-01/31 thermocouple.

Quantity	Estimation	Standard uncertainty	Probability distribution	Sensitivity coefficient	Uncertainty contribution / µV
$E_x(t_F)$	13248.18 µV	0.05 µV	normal	1	0.05
δt_{imp}	0 K	0.0012 K		20.89 µV/K	0.025068
δt_{plat}	0 K	0.1 K	rectangular	20.89 µV/K	2.089
δt_{HF}	0 K	0.005 K	rectangular	20.89 µV/K	0.10445
δE_{X1}	0 µV	0.25 µV	normal	1	0.25
δE_{X2}	0 µV	0.058 µV	rectangular	1	0.03
δE_{X3}	0 µV	0.06 µV	rectangular	1	0.06
δE_{X4}	0 µV	0.29 µV	rectangular	1	0.29
δt_{0X}	0 K	0.005 K	normal	5.3 µV/K	0.026
δE_{Hom}	0 µV	0.7 µV	rectangular	1,23	0.86
				combined uncertainty:	2.30

Table 10. Estimated uncertainty by VSL for the measurements at the freezing point of Ag using the PTB-PtPd-01/03 thermocouple.

Quantity	Estimation	Standard uncertainty	Probability distribution	Sensitivity coefficient	Uncertainty contribution / µV
$E_x(t_F)$	10786.88 µV	0.0007 µV	normal	1	0.0007
δt_{imp}	0 K	0.312 mK	rectangular	19.2 µV/K	0.0059904
δt_{plat}	0 K	0.115 mK	rectangular	19.2 µV/K	0.002208
δt_{HF}	0 K	0.005 K	rectangular	19.2 µV/K	0.096
δE_{X1}	0 K	0.25 µV	normal	1	0.25
δE_{X2}	0 µV	0.058 µV	rectangular	1	0.03
δE_{X3}	0 µV	0.06 µV	rectangular	1	0.06
δE_{X4}	0 µV	0.29 µV	rectangular	1	0.29
δt_{0X}	0 K	0.005	normal	5.3 µV/K	0.026
δE_{Hom}	0 µV	0.7 µV	rectangular	1	0.7
				combined uncertainty:	0.81

The uncertainty associated with the homogeneity is based on the immersion profile at Ag and dividing the maximum deviation by $\sqrt{3}$.

Position	Δemf/µV
0 cm	0
2 cm	+0,33
4 cm	+0,69
6 cm	+1,04
8 cm	+1,18
10 cm	+1,17
12 cm	+0.89

3.3 Comparison of results

The difference in the measured emf at the Cu fixed-point cells at VSL and PTB and the associated combined uncertainty (k=1) is:

	$E_{VSL} - E_{PTB}$	$U(E_{VSL} - E_{PTB})$
NPL-PtPd-2008-01	0.5 µV	2.5 µV
PTB-PtPd-01/03	0.0 µV	2.6 µV

The difference in the measured emf at the Ag fixed-point cells at VSL and PTB and the associated combined uncertainty (k=1) is:

	$E_{VSL} - E_{PTB}$	$U(E_{VSL} - E_{PTB})$
NPL-PtPd-2008-01	0.4 µV	1.3 µV
PTB-PtPd-01/03	-0.7 µV	1.1 µV

The PTB-PtPd-01/03 was used as transfer standard for loop A of the EUROMET-844 intercomparison [1]. The reported simple average of the measured emfs was 13248.8 ± 1,0 µV (k=1).

It is not possible to establish the VSL degree of equivalence with respect to the EUROMET-844 intercomparison directly because the copper cell used for that comparison was broken and not used in the bilateral comparison reported here. The emf of the copper cell used in this bilateral comparison is reported to be about 0.3 or 0.4 µV higher than the old cell of EUROMET-844.

4. Conclusion

The VSL/PTB bilateral comparison of Pt/Pd thermocouple measurements at the freezing temperature of Cu has revealed calibrations at VSL to be in agreement with the calibrations at PTB within the expanded uncertainty.

References

[1] F. Edler et al, Int J Thermophys (2008) 29:171–180