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Intercomparison of Copper Fixed-Point Cells by Using Pt/Pd Thermocouples

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Abstract The objective of the EUROMET Project No. 844 in the field of thermometry was the intercomparison of the freezing temperatures of the copper fixed-point cells ($t_{90} = 1084.62°\text{C}$) of the participating laboratories by using Pt/Pd thermocouples. For most of the 13 participating laboratories, agreement of the freezing temperatures of the different copper fixed points within ±0.06 K was found. Furthermore, the results

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of the intercomparison show that Pt/Pd thermocouples are suitable for use as transfer standards for the dissemination of temperatures and to approximate the ITS-90, at least up to the freezing point of copper.

Keywords Copper freezing point · Intercomparison · Platinum/palladium thermocouple

1 Introduction

The EUROMET Project No. 844 was intended to establish the equivalence of calibrations at the freezing point of copper ($t_{90} = 1084.62°\mathrm{C}$) and to assess the uncertainties associated with the calibration of thermocouples. Besides the pilot laboratory, Physikalisch-Technische Bundesanstalt (PTB), 12 laboratories of European Metrological Institutes participated in this project. The measurements were organized in two loops. The participants of Loop A and Loop B are listed in Table 1. The order of the measurements can be seen from Table 1. PTB, as the pilot laboratory, circulated two stable Pt/Pd thermocouples, one in each loop. The two thermocouples (Pt/Pd 01/03—Loop A and Pt/Pd 03/03—Loop B) had been annealed and calibrated previously at PTB at fixed points of the International Temperature Scale of 1990 (ITS90). The intercomparison lasted from August 2005 to August 2006. The measurements were performed according to previously agreed procedures to assure their uniformity and to facilitate the analysis of the results. At the end of the comparison, the Pt/Pd thermocouples were calibrated at the freezing point of copper, again at PTB.

2 Instrumentation

2.1 Thermocouples

Two Pt/Pd thermocouples (Pt/Pd 01/03 and Pt/Pd 03/03) were constructed from pure platinum (99.999%) and palladium (99.9%) wires of 0.5 mm diameter from the same batches as those used to construct the Pt/Pd thermocouples 9/90, 11/90, and 12/90 used to establish a provisional reference function for Pt/Pd thermocouples [1]. The thermoelements were cleaned using ethyl alcohol and distilled water. After a bare wire electrical anneal at 1,300°C for 10 h, the 2 m long wires were mounted in twin-bore capillary tubes (outer diameter, 3.5 mm; bores, 1 mm; length, 740 mm) protected by ceramic tubes (diameter, 6 × 4 mm; length, 725 mm) closed at one end, both made of pure alumina (Al_2O_3, 99.7%). The measuring junctions were prepared using Pt coils of 0.2 mm diameter wire.

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Table 1 Participants of the intercomparison and sequence of the measurements

Loop A—Pt/Pd 01/03		Loop B—Pt/Pd 03/03	
Laboratory	Country	Laboratory	Country
PTB	Germany	PTB	Germany
SP	Sweden	EIM	Greece
JV	Norway	BEV	Austria
MIKES	Finland	CEM	Spain
CMI	Czech Republic	INM	Romania
PTB[a]	Germany	MIRS/FE-LMK	Slovenia
VMT/PFI	Lithuania	LPM	Croatia
GUM	Poland	PTB	Germany
PTB	Germany		

[a] Pd thermoelement of the thermocouple Pt/Pd 01/03 broke close to the measuring junction after the measurements at CMI were finished. It was repaired and recalibrated at the freezing points of copper and silver at PTB

Before starting the intercomparison, the assembled Pt/Pd thermocouples were annealed several times at 1,100°C for 150 h to remove any physical defects, which might have been introduced during the assembly and to improve the stability and homogeneity of the thermoelements. The thermoelectric stability was proven by repeated measurements at the freezing point of copper. The results presented in Fig. 1 shows that, after a maximum of 100 h annealing at a temperature of 1,100°C, the Pt/Pd thermocouples reached metallurgically stable conditions. The differences of the measured emfs between the last two measurements were within a temperature equivalent of less than a few mK. Therefore, the thermocouples were considered to be stable enough for the comparison. Their homogeneities were checked at the freezing point of silver over a length of about 10 cm by withdrawing them in 2 cm increments from the silver cell during a freeze. The immersion profiles (shown in Fig. 2) measured at PTB before and after the intercomparison indicate an almost unchanged inhomogeneity characteristic of thermocouple Pt/Pd 01/03, with a maximum emf difference (at immersion depths unaffected by environmental influeneces) of about 1.3 μV (before the intercomparison) and of 0.9 μV (after the intercomparison). For thermocouple Pt/Pd 03/03, a change in the characteristic was observed, but the maximum emf difference of about 1 μV measured during the immersion profile at the freezing point of Ag was maintained over the course of the intercomparison.

Thermocouple Pt/Pd 01/03 (Loop A) had to be repaired and recalibrated at PTB at the freezing points of copper and silver after the measurements of the fourth participant (CMI) were carried out, due to a breakage of the Pd thermoelement near the measuring junction. The recalibration at PTB showed no changes in the thermoelectric properties of this thermocouple in spite of its temporary failure.

2.2 Fixed Points and Voltmeters of the Participants

The details of the fixed-point cells and the types of the voltmeters used by the participants are summarized in Table 2. Most of the participants used sealed copper fixed-point cells provided by Isotech (UK) and Hart Scientific/Fluke (US) and voltmeters manufactured by Keithley and Hewlett Packard (HP).

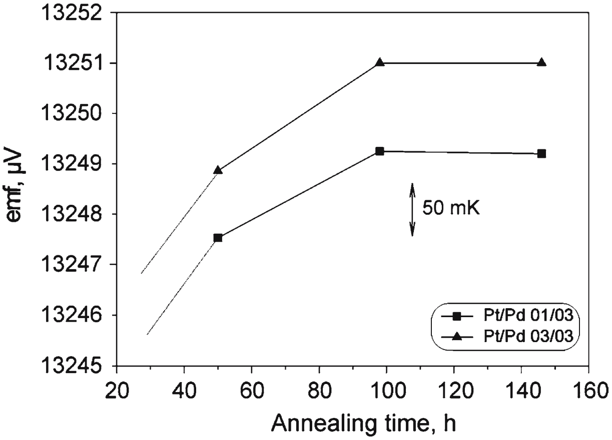

Fig. 1 Thermoelectric stability of the Pt/Pd thermocouples 01/03 and 03/03: measured emfs at the freezing point of copper

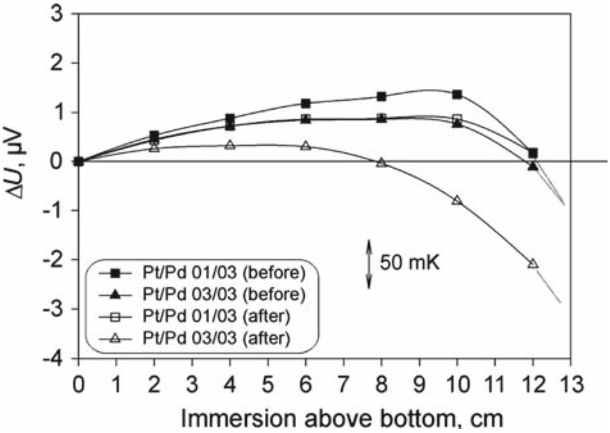

Fig. 2 Immersion profiles of the Pt/Pd thermocouples 01/03 and 03/03, measured at the freezing point of silver (before starting and after finishing the intercomparison)

3 Measuring Program

According to the agreed measurement procedures, the Pt/Pd thermocouples were calibrated thrice at the freezing point of copper in independent realizations with an intermediate annealing (see Sect. 3.1). Afterward, the Pt/Pd thermocouples were calibrated once at the freezing point of silver. Immersion profiles were measured during the realization of this plateau to estimate the uncertainty contribution caused by the inhomogeneity of the thermoelements.

Table 2 Fixed-point cells and voltmeters used for the comparison

Laboratory	Copper cell	Silver cell	Voltmeter
PTB	Open cell, home-made, purity: 5N–6N	Open cell, Isotech, purity 6N	HP 3458A
SP	Sealed cell, Isotech, ITL-M-17674S, purity: 6N	Sealed cell, Engelhard Pyro-Controle, purity: 5N	Keithley 182
JV	Sealed cell, Hart Scientific, Model 5919A	Sealed cell, Engelhard Pyro-Controle	Keithley 182
MIKES	Open cell, Isotech, Cu 32	Open cell, Leeds &Northrup/8411	Keithley 182
CMI	Sealed cell, Isotech, ITL-M Cu17, purity: 6N	Sealed cell, Isotech, ITL-M Ag39, purity: 6N	Datron 1281
VMT/PFI	Sealed cell, Isotech, ITL-M-17674, purity: 6N	Sealed cell, Isotech, ITL-M-17673, purity: 6N	Fluke 8508A
GUM	Sealed cell, ITME[a], Cu 2, purity: 6N	Open cell, home-made, purity: 5N5	Wavetek 1281
EIM	Sealed cell, Hart Scientific, 5909 Cu-7005, purity: 6N	Sealed cell, Isotech, ITL-M-17673, purity: 6N	Keithley 2001
BEV	Sealed cell, Isotech, ITL-M-17674, purity: 6N	Sealed cell, Hart Scientific, “5908 Ag-8028”	Keithley 182
CEM	Sealed cell, Hart Scientific, Model 5919A	Sealed cell, Isotech, ITL-M-17673, purity: 6N	HP 3458A
INM	Open cell, home-made, purity: 4N8	Sealed cell, Isotech, purity: 6N	Keithley 2182A
MIRS/FE-LMK	Sealed cell, Hart Scientific 5909, purity 6N	Sealed cell, Isotech, ITL-M-17673, purity: 6N	HP 34420A HP3458A
LPM	Open cell, Isotech, ITL-M-17674, Cu026	–	Keithley 2002

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3.1 Annealing Procedure

The objective of the annealing at 1,000°C (4 h) was to remove, by dissociation, any Pd oxide which might have formed during the calibration of the thermocouples, on the portion of the Pd wires exposed to temperatures between about 550 and 800°C [2,3]. The annealing temperature was chosen to be high enough to decompose the Pd oxide and to be low enough to avoid changing the thermoelectric properties of the thermocouples, and thereby affect the measurements at the freezing point of copper. The immersion depth of the thermocouples in the annealing furnace should exceed the immersion depths in the fixed point furnaces during the calibration of thermocouples at both fixed points.

3.2 Fixed-Point Realization

In order to maintain their thermoelectric stability, the Pt/Pd thermocouples were exposed to high temperatures for as short a period of time as possible. Therefore, they were not immersed in the fixed-point cell until the copper was completely molten, as registered by an auxiliary thermocouple, i.e., when the molten copper and the furnace reached an equilibrium temperature about 5–10 K higher than the expected freezing temperature. The freezing of the silver point was performed by means of the standard procedure of the participating laboratories.

4 Measurement Uncertainties

The emf at the freezing point of copper generated by the Pt/Pd thermocouple, E_{Cu}, can be written as

$$\begin{aligned} E_{\mathrm{Cu}} = {} & E_X(\mathrm{Cu}) + (\delta t_{\mathrm{F}} + \delta t_{\mathrm{DF}} + \delta t_{\mathrm{HF}})C_{\mathrm{F}X} \\ & + \delta E_{X1} + \delta E_{X2} + \delta E_{X3} + \delta E_{X4} + \delta t_{0X} C_{0X} + \delta E_{\mathrm{Hom}} E_{\mathrm{Cu}}/E_{\mathrm{Ag}} \end{aligned} \tag{1}$$

with $E_X(\mathrm{Cu})$ as the emf indicated by the voltmeter. The combined uncertainty of E_{Cu} includes uncertainty contributions due to the unknown fixed-point temperature, δt_{F}, the drift of the fixed-point temperature, δt_{DF}, heat flux effects, δt_{HF}, the calibration, resolution, and drift of the voltmeter used, δE_{X1}, δE_{X2}, and δE_{X3}, respectively, the influence of ambient parameters and connecting leads, δE_{X4}, the reference temperature, δt_{0X}, and the inhomogeneity, δE_{Hom}, of the thermocouples. C_{FX} and C_{0X} are the Seebeck coefficients of the Pt/Pd thermocouple at the freezing point of copper and at the reference temperature, and E_{Ag} is the emf at the freezing point of silver.

The component uncertainty contributions according to Eq. 1, the repeatability of the measurements at the freezing point of copper, E_{RP}, and the combined uncertainties u for $k = 1$ of the calibration of the thermocouples at the freezing point of copper, as provided by the participating laboratories, are summarized in Table 3. The expanded uncertainties ($k = 2$) cover a range between 1.5 and 6.4 μV (0.07 and 0.3 K).

The majority of the participants found the uncertainties of the freezing temperature of the copper cells and their drifts to be the most significant uncertainty contributions, because of the lack of suitable thermometers to check the freezing temperature. If these two uncertainty contributions are disregarded (which is justified because the aim was a comparison of the freezing temperatures of different fixed-point cells), the combined uncertainties are significantly lower. In this case, the most important uncertainty contribution is the inhomogeneity of the thermocouples. The wide variation in the estimates of this uncertainty contribution probably result from different approaches by the participants in calculating this component from the immersion profile measurements at the freezing point of silver. The other uncertainty contributions specified by the participants are of the same order of magnitude, which argues in favor of a standard value for these uncertainty components for all of the participants.

5 Results

The measured emfs and their combined uncertainties for $k = 1$ at the freezing point of copper are summarized in Figs. 3 (Loop A) and 4 (Loop B). The simple mean of the emfs for each loop are indicated by straight lines. The emfs measured by six out of the

Table 3 Uncertainty contributions and combined uncertainties at the freezing point of copper in μV (k = 1), dominant contribution in bold characters

	E_{RP}	δt_{F}	δt_{FD}	δt_{HF}	δE_{X1}	δE_{X2}	δE_{X3}	δE_{X4}	$\delta t_{0\mathrm{X}}$	δE_{Hom}	u
PTB^{a}	0.2	**0.63**	0.63	0.13	0.3	0.03	0.17	0.3	0.05	0.46	1.13
SP^{a}	0.06	0.21	0.6	0.06	0.03	0.003	0.12	0.29	0.03	0.29	0.77
JV^{a}	0.09	0.4	0.03	0.09	0.04	0.003	0.23	0.29	0.07	**1.2**	1.33
MIKES^{a}	0.21	0.21	0.1	0.08	0.77	0.03	0.06	**3.0**	0.0	0.24	3.12
CMI^{a}	0.2	0.2	**1**	0.1	0.1	0.1	0.5	0.7	0.5	**1**	1.76
VMT^{a}	0.3	**1.25**	**1.25**	0.21	0.3	0.0	0.2	0.4	0.15	0.49	1.95
GUM^{a}	0.02	0.15	**0.6**	0.07	0.04	0.003	0.11	0.58	0.03	0.39	0.94
PTB^{b}	0.2	**0.63**	0.63	0.13	0.3	0.03	0.17	0.3	0.05	0.35	1.09
EIM^{b}	0.32	**1.04**	0.06	0.06	0.6	0.003	0.3	0.3	0.03	0.37	1.37
CEM^{b}	0.1	**1.21**	–	0.24	0.28	0.03	0.06	0.29	0.15	0.69	1.48
BEV^{b}	0.09	**1.25**	0.13	0	0.02	0.003	0.12	0.58	0.05	**1.9**	2.36
INM^{b}	0.23	**2.3**	**2.1**	0.21	0.2	0.003	0.23	0.29	0.03	0.39	3.18
LMK^{b}	0.35	**1.04**	0.1	0.06	0.47	0.03	–	0.3	0.06	0.37	1.29
LPM^{b}	0.45	**1.04**	0.23	0.21	0.9	0.52	0.03	0.3	0.03	0.2	1.61

[a] Pt/Pd thermocouple 01/03, Loop A
[b] Pt/Pd thermocouple 03/03, Loop B

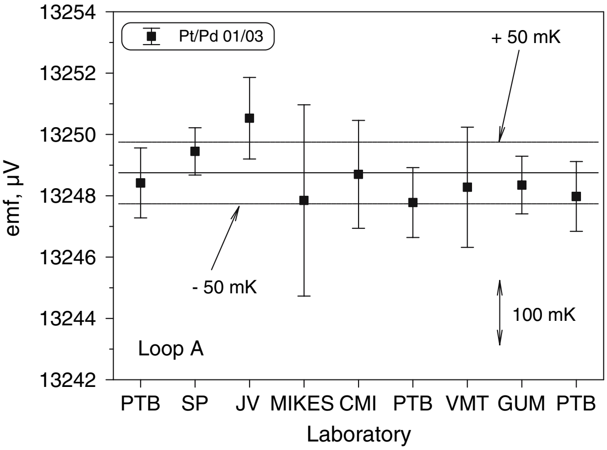

Fig. 3 Measured emfs and their combined uncertainties for $k = 1$ at the freezing point of copper (Loop A)

seven participants of Loop A agree within a temperature equivalent of ±50 mK of the simple mean and all emfs agree within the combined uncertainties of the calibrations, even for $k = 1$. Furthermore, the initial, the intermediate, and the final measurements at the freezing point of copper at PTB agree within a temperature equivalent of about 30 mK, indicating high thermoelectric stability of Pt/Pd thermocouple 01/03.

In Loop B, the measured emfs at the freezing point of copper show more scatter than in Loop A, as indicated by the standard deviation of the mean emf of about 0.7 μV, compared to the value of 0.4 μV obtained in Loop A. Nevertheless, most of the emfs agree within the combined uncertainties ($k = 1$), and all emfs agree within the expanded uncertainty of $k = 2$. Notable is the emf measured at INM, which is

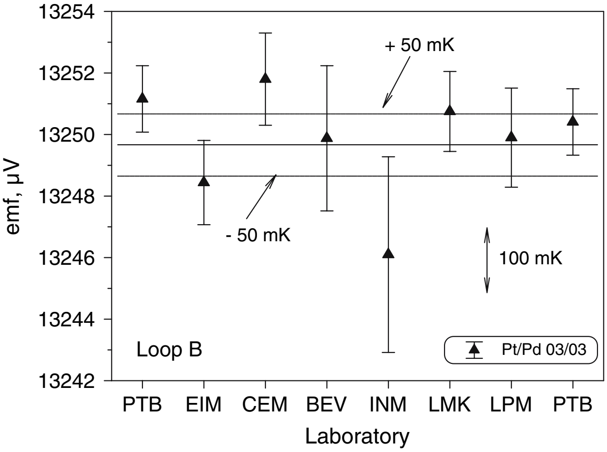

Fig. 4 Measured emfs and their combined uncertainties for $k = 1$ at the freezing point of copper (Loop B)

lower by about 4 μV, perhaps attributable to lower purity of the copper (see Table 2). By rejecting this measurement as an outlier, the mean emf increases by 0.6 μV and the corresponding standard deviation of the mean decreases to about 0.5 μV, which is comparable to the results obtained in Loop A. In this case, the emfs measured by four out of the six remaining laboratories agree within a temperature equivalent of ±50 mK of the simple mean. The initial and final measurements at the freezing point of copper at PTB, which agree within a temperature equivalent of about 40 mK, indicate high thermoelectric stability of Pt/Pd thermocouple 03/03.

The differences in the measured emfs at the freezing points of copper and silver can reveal the reason for a higher or lower emf measured at the freezing point of copper, assuming that an accurately known silver freezing point temperature is used. In general, this is a reasonable assumption because the freezing temperatures of silver are well known with low uncertainties (10–20 mK). Figure 5 shows the emf-differences between the freezing points of copper and silver and the combined uncertainties for $k = 1$, calculated from the uncertainties of both fixed points. These differences were found to be consistent, confirming the emfs measured at the freezing point of copper, with the exception of the measurement at INM. This significantly smaller emf difference confirms the lower freezing temperature of the INM Cu cell—by about 4 μV (0.2 K), see Fig. 4—because the emf measured at the freezing point of silver at INM agrees with the emfs measured at the freezing points of silver by the other participants.

The results of the two loops can be linked on the basis of emf differences with respect to the PTB copper freezing point cell. The simple mean (+0.15 μV), weighted mean (+0.33 μV), and median (+0.22 μV) differences from the PTB cell were calculated. The differences between these three values are negligible. Thus, the mean of these three values was selected as the reference value to compare the results of the two loops. Figure 6 shows the deviations of the emfs measured at the fixed-point cells of copper from the reference value and their combined uncertainties for $k = 2$, but without considering the uncertainty contributions of the fixed-point temperatures and their

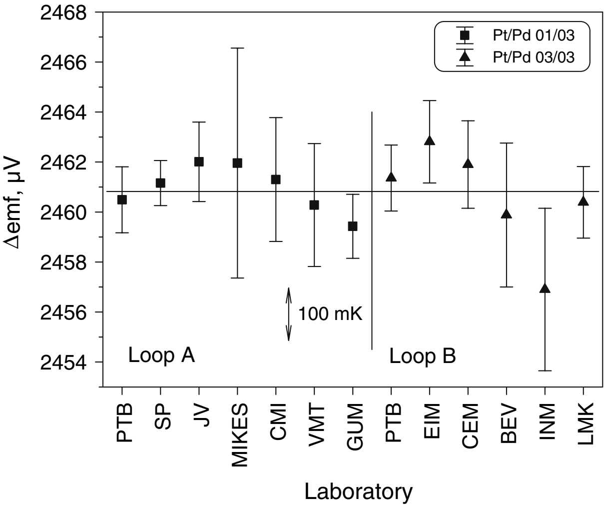

Fig. 5 Differences between the measured emfs at the freezing points of copper and silver with the combined uncertainties for $k = 1$

drifts, δt_{F} and δt_{FD}. (The INM measurement (Loop B) was rejected in this calculation). The results confirm that the freezing temperatures of the copper fixed-point cells of 10 out of the 13 participating laboratories agree within a temperature equivalent of about ±60 mK with respect to the reference value. From this good agreement, it follows that the uncertainty of the freezing temperature (Table 3) seems to be overestimated in most cases. As a result of the intercomparison, the uncertainty of the freezing temperature of the copper cells of most participants can be reduced to a temperature equivalent of about 50 mK. Furthermore, INM can correct its copper cell by +0.2 K and JV by –0.1 K, with an uncertainty of about ±50 mK. A correction of the EIM copper fixed-point temperature is not recommended as its measurement at the freezing point of Ag is also discrepant.

6 Conclusions

The reproducibility of the calibration of Pt/Pd thermocouples at the copper freezing point in different laboratories was demonstrated. The agreement of the measured emfs, within a temperature equivalent of ±0.06 K, along with the high thermoelectric stability (±0.02 K) of the Pt/Pd thermocouples used, allows the reduction of the estimated uncertainty contribution due to the uncertainty and drift of the fixed-point temperatures of the copper cells by most of the participants, with the remaining ones able to correct the freezing temperature based on the comparison results, excepting EIM. Furthermore, it was shown that, due to their stability at temperatures up to the freezing point of copper, Pt/Pd thermocouples are suitable for use as transfer standards for the dissemination of temperatures and to approximate the ITS-90. The results obtained in this intercomparison are consistent with the results of the EUROMET Project 624 [4],

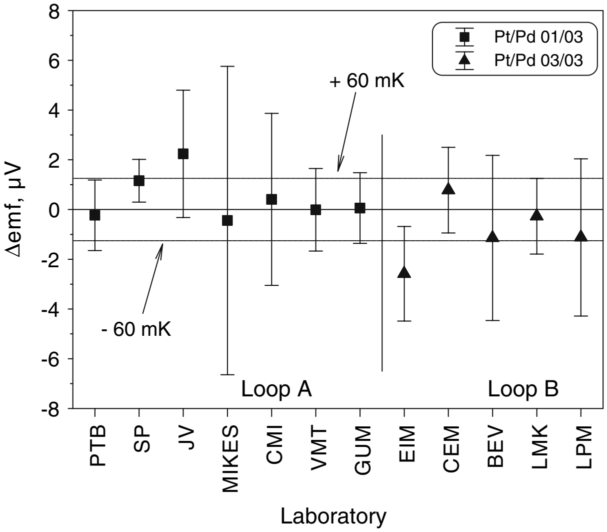

Fig. 6 Emf deviations and their combined uncertainties for $k = 2$ at the freezing point of copper from the mean deviation from the PTB Cu-cell (without the uncertainty contributions δt_F and δt_FD)

where an agreement of the measured emfs at different copper freezing points within a temperature equivalent of ±50 mK was found.

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