

IMPROVED UNCERTAINTY OF PALLADIUM WIRE BRIDGE METHOD***M.Gotoh¹, M.Ogawa², and J.Ode³***¹Division of Engineering, Tamagawa University
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Abstract: Wire method of calibration for R type thermocouple has reevaluated. Four kinds of source material of Pd wire was distributed and R type thermocouples from the same spool of wire were used among 7 members of the study group to equalize the experimental condition. More than 140 runs of the palladium point were performed. To avoid ambiguity in assigning Emf to the palladium melting point a data analysis program was developed which can determine a unique Emf from the data and can reject low quality plateau. Reproducibility expressed in terms of standard deviation is 0.18K which is better than the previous results.

Keywords: Palladium wire bridge method, Uncertainty, unambiguous determination

1 INTRODUCTION

In the contact thermometry Type K, R and S thermocouples are the major temperature sensor for higher temperature above 1000 °C. Especially Type R or S is used as a reference thermometer of the calibration in the temperature region. Since no proper fixed-point cell is available above copper point, they have to be calibrated either by radiation thermometer or by comparison with the other calibrated thermocouple. Although one cannot expect highest accuracy calibrations for alloy thermocouple at high temperature due to the metallurgical instability, wire method or wire-bridge method is one of the alternatives of the calibration. In this technique melting temperature of a small piece of metal (wire, disk, or rod) that is fastened (welded or mechanically clamped) to the thermocouple tip or between the thermocouple legs are measured. To calibrate Type S or Type R thermocouples palladium wire bridge method has been practiced for a long time. Especially in the steel industry temperature of the molten steel is measured with immersion type thermocouple (mainly Type R). So the wire bridge method is applied as the routine production test for the immersion thermocouple. The wire bridge method of calibration began to be investigated in 1960^{(1), (2), (3), (4)}. In these days Emf (Electromotive force) was measured with potentiometers which did not enable one to acquire the precise data in a short time interval. So the expanded uncertainty (k=2) of the palladium point calibration has been believed to be from 1K to 2K. In order to improve the accuracy of the calibration with the wire bridge method by making use of the modern electronic measurement technology, cooperative study was performed by a Forum which 21 organization take part in.

2 WIRE BRIDGE MATERIALS AND EXPERIMENTAL THECHNIQUE

In the 7 laboratories (Lab. A to Lab. G) actual measurement was done with Type R thermocouples fabricated from a single spool of reference grade wires. Four kinds of palladium wires are tested which came from 3 different sources. They are summarized in the table 1.

Table 1. Pd wires

Wires	Purity(%)	Sources(Company)
Wi re1	99.995	A
Wi re2	99.99	A
Wi re3	99.98	G
Wi re4	99.97	B

To apply the method, short length (5 to 10 mm) of 0.5 mm diameter Pd wire of high purity is used to form the junction between the two elements of the thermocouple by mechanically fastening, wrapping, or welding. Various mode of realization of the melting was tested. One of them is raising the temperature with a program temperature controller. And the other is manual stepwise temperature control. In every laboratory Emf was measured by a digital voltmeter and the data were acquired periodically by a personal computer connected online. All the digital voltmeters are calibrated and traceable to the national standards. All the melting of Pd are performed in the air.

3 JUDGING THE MELTING PLATEAU

In the case of wire bridge method alloying process between the bridge wire (Pd wire in this case) and thermocouple wire may take place. Quantity of the substance to give the melting plateau is very small. Therefore melting plateau is not always clear. Judging the melting point temperature might be dependent on the operator's subjective point of view. Evaluation of uncertainty of this cause is very difficult. However this uncertainty can be predominant. This has been one of the problems, which degrade the precision of the calibration by the wire bridge method. To avoid the ambiguity we have developed a computer program to determine unique Emf to assign to the palladium melting point. That is, the melting point Emf should be determined by the two criteria; Emf should be steady within 0.2 $\mu\text{V/s}$ and the steady state should last at least 30 second. Emf is determined by averaging the data set within this 30 seconds time "window". In the case that the window period which fulfill the two criteria lasts more than 30 seconds, one of the 30 seconds data sets, which has the least standard deviation is to be chosen.

4 RESULTS AND DISCUSSION

Each laboratory performs wire bridge calibration with its own facility. Five realizations of melting were done for a kind of Pd wire and each time Emf was determined with the method described above. Five data were averaged to determine the Emf for a specific Pd wire. In the figure 1 comparison of the Emf for the Pd wires is shown. All of the determined Emf data(30 data) are averaged for each different kind of wire. Standard deviation of all of the Emf data is 0.00088 mV, which corresponds to 63mK. Comparing the graph to the table 1, the result is interpreted as follows. Higher the purity, higher the melting point is. Temperature equivalent difference between the highest and lowest melting point is 0.13 K.

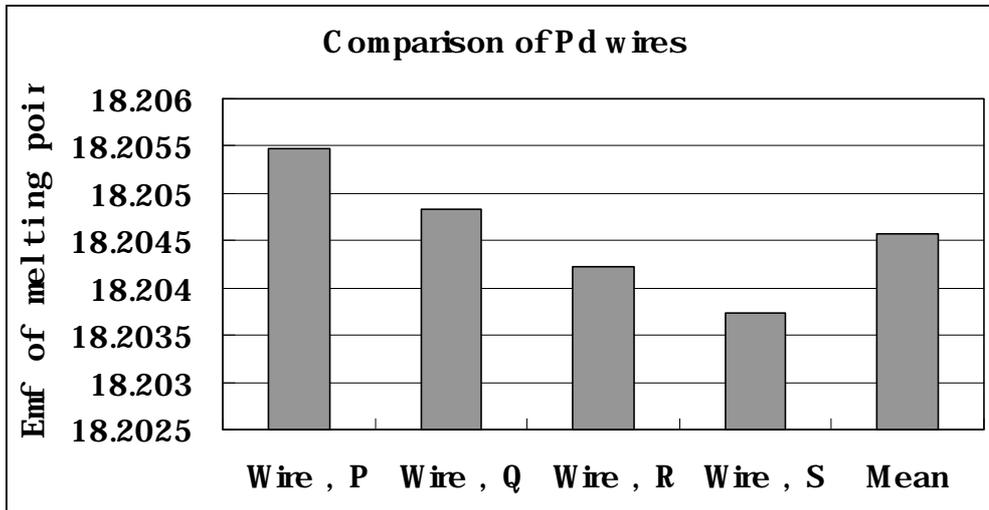


Figure 1 Comparison of the Emf given by different sample wire. Standard deviation is 0.00088mV.

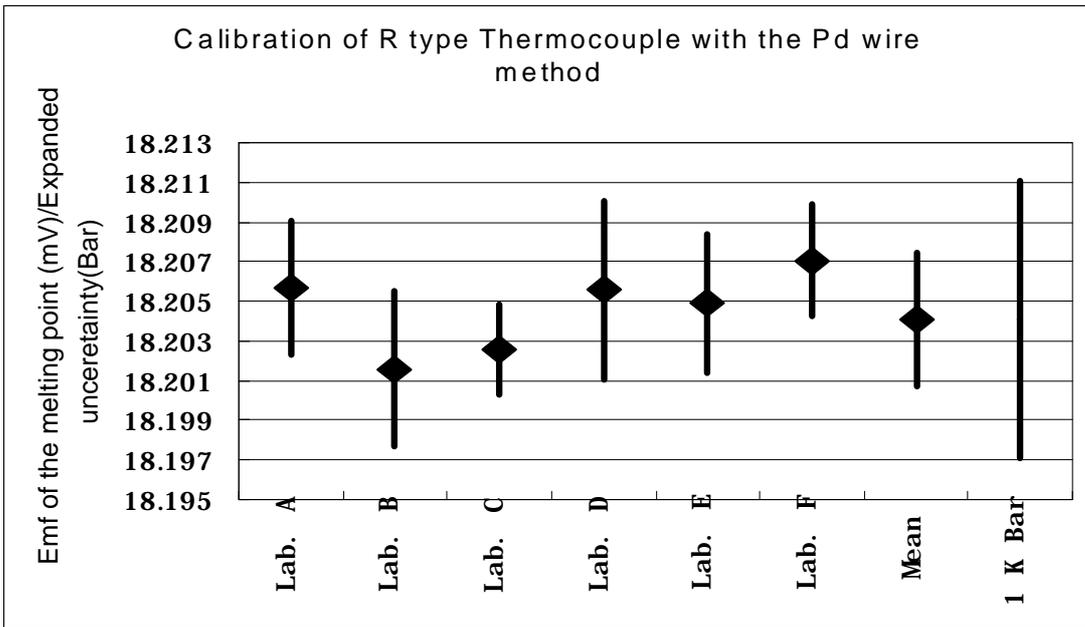


Figure 2 Results of the calibration by wire bridge method of each laboratory (Dots). Bar is the expanded uncertainty of the calibration. 1K Bar shows the measure of the temperature.

In the figure 2 variations of the Emf measured by each laboratory are shown. Bars associated with square dots give expanded uncertainty (k=2) of the measurement by each laboratory. Compared to the

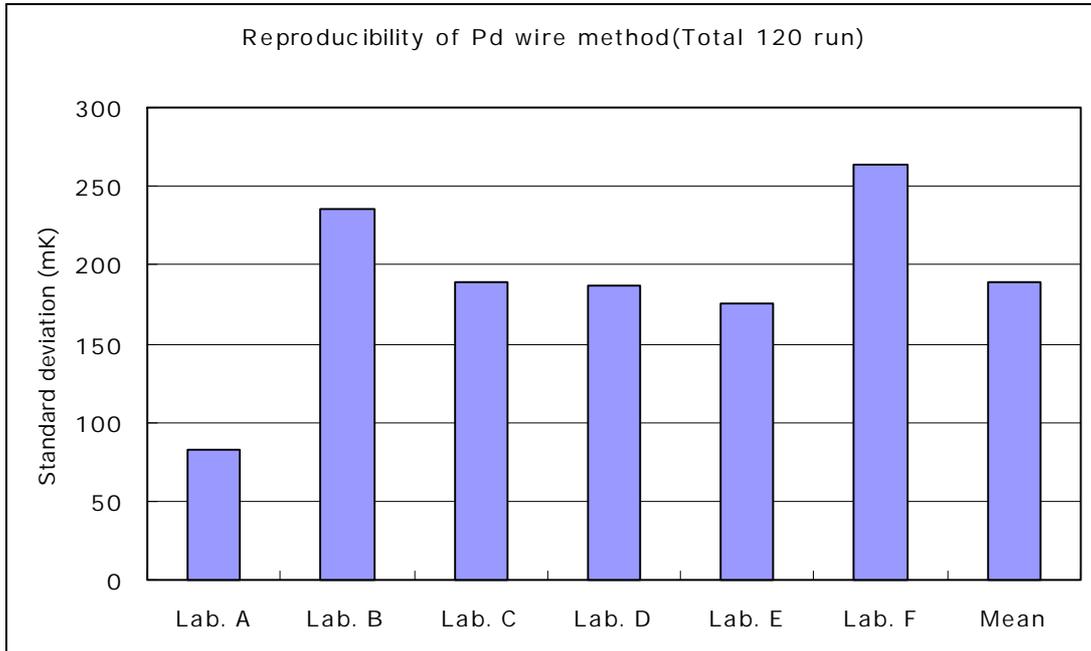


Figure 3 Reproducibility of calibration by Pd wire bridge method performed in many laboratories

1 K Bar index in the right end of the graph, discrepancies of the determined Pd point Emf are very small. In the figure 3 standard deviation of the determination of the melting point Emf of the wire bridge method is shown. Mean value of the standard deviation among the laboratories is 0.17 K. If the data is averaged for a single kind of wire it is slightly small (0.15K for the wire 1). This is interpreted as the index of the reproducibility of plateau determination. According to the results illustrated in this figure, reproducibility is smaller than the expanded uncertainty 0.48 K that is averaged among all the laboratories.

5 CONCLUSIONS

As is mentioned above, in this research project the same and newly built Type R thermocouples are used in order to homogenize the experimental conditions and to isolate reproducibility of the wire bridge method and Pd wire quality from the other effect. Since the experiment is performed by more than 6 laboratories the results reported here also represent differences in technical skills and measurement systems of the laboratories. However by averaging these data some of the conclusions can be drawn.

- (1) The melting point is judged by analyzing data acquired with computer. This method avoids operator's misjudge and reduces scattering of the determination of the melting point. Standard deviation of the scattering for total 120 runs is 0.18K.
- (2) Melting point measured by the wire bridge method depends on the purity of the Pd wire. The difference in this experiment is 0.13K while purity of the Pd wire varies from 99.995% to 99.97%.
- (3) Emf of Measured Pd point is 18.2041mV in average. Equivalent temperature is 1553.76°C. Scattering of the data is 0.15K expressed by standard deviation. The expanded uncertainty of the measurement is 0.49K in average, which is larger than the irreproducibility of the Pd wire melting point determination.

ACKNOWLEDGEMENTS

The authors very much appreciate important contributions given by M.Kazaoka(Okazaki Manufacturing Co. Ltd.), S.Miyashita(Ishifuku Metal Ind.Co.Ltd.), Y.Mizuma(Yamari Ind.), M.Ohya(Tokurikihonten Co.), K.Sinyashiki(Asahi Ind.), Y.Suyama(Tanaka Kikinzoku Kougyou K.K.) and T.Suzuki(Chino Co.). They performed parts of experiments or collected the data. K.Takahasi(Tamagawa Univ.) contributed by authoring the data analyzing computer program.

REFERENCES

- [1] R.E.Bedford, Reference tables for Platinum 20% Rhodium/Platinum 5% Rhodium thermocouples: *Rev. Sci. Instr.* **36**, (1964) 1571-1580
- [2] T.P.Jones, K.C.Hall: The melting point of palladium and its dependence on oxygen, *Metrologia* **15**,(1979),161-163
- [3] P.B.Coats, T.R.D Chandler, J.W. Andrew: A new determination of the freezing point of palladium: *High temperatures –high pressures* **15**,(1983) 573-582
- [4] L.Crovini et.al. ,Intercomparison of platinum thermocouple calibrations: *High temperatures –high pressures* **19**,(1987) 179-194

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