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Use of Different Furnaces to Study Repeatability and Reproducibility of Three Pd-C Cells

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Abstract Three different Pd-C eutectic fixed-point cells were prepared and investigated at INRIM. Several tens of phase transition runs were carried out and recorded with both a Si-based radiation thermometer at 950 nm and a precision InGaAs-based thermometer at 1.6 µm. Two of the cells were of the same design with an inner volume of 12 cm^3. The third one was smaller with a useful inner volume of 3.6 cm^3. The three cells were filled with palladium powder 4N5 or 4N8 pure and graphite powder 6N pure. The repeatability and stability of the inflection point were investigated over a period of 1 year. The noticeably different external dimensions of the two cells, namely, 110 mm and 40 mm in length, allowed the influence of the longitudinal temperature distribution to be investigated. For this purpose, two different furnaces, a single-zone with SiC heaters and a three-zone with $MoSi_2$ heaters, were used. Different operative conditions, namely, temperature steps, melting rate, longitudinal temperature distributions, and position of cells within the furnace, were tested to investigate the reproducibility of the cells. Effects on the duration and shape of the plateaux were also studied. This article gives details of the measurement setup and analyses of the melting plateaux obtained with the different conditions.

Keywords Fixed points · Metal–carbon eutectics · Palladium–carbon · Radiation thermometry

1 Introduction

Because of the quite recent introduction and the large number of high-temperature eutectic fixed points [1], although a huge amount of activities has been already carried

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out by investigators in several national metrology institutes [2], not all the issues potentially affecting the quality of these fixed points have been fully investigated. The Pd-C point is one of the nine metal–carbon eutectic points which potentially can be used to realize high-temperature scales by interpolation up to about 2750 K. Its transition temperature, i.e., 1765 K, is about 400 K above that of the copper point, namely, the highest pure metal point, and makes it a particularly suitable point for the realization of scales by interpolation extending up to the Ru-C (2227 K) or Re-C (2747 K) points.

At INRIM, investigations on the Pd-C point started in 2007, and since then, cells of different designs for both radiation and contact thermometry applications have been constructed and investigated with different heating furnaces. From time to time, and according to the specific issues in which we were interested, different investigations were performed and consequently a large amount of data has been collected, even if sometimes randomly obtained. The measurements covered a period of more than two years, and a large part of the possible influencing factors were investigated thus providing useful data for an estimate of the reproducibility of the Pd-C point.

2 Preparation of Cells

Three fixed-point cells were prepared and investigated. Two cells were of the same design already adopted for Co–C cells and described in detail in [3] and the third one of smaller dimensions and compatible with the design also adopted by other investigators [4]. Details of the three cells, in the following referred to as PdC_1, PdC_3, and PdC_small, are summarized in Table 1, and a picture of the two typologies is presented in Fig. 1.

A graphite sleeve which reduces the effective inner volume to about 12 cm^3 and mechanically improves the robustness of the cells was inserted into PdC_1 and PdC_3.

Table 1 Details of PdC_1, PdC_3, and PdC_small cells

	PdC_1	PdC_3	PdC_small
Date of preparation	March 2007	April 2008	July 2008
Dimensions of cells			
Outer diameter	42 mm		24 mm
Length	110 mm		40 mm
Blackbody aperture—diameter	8.5 mm		3 mm
Cavity length	88 mm		28 mm
Inner sleeve	Yes		Yes
Effective inner volume	12 cm^3		3.64 cm^3
Crucible graphite	Ringsdorff R7510P5 (ash content < 5 ppm)		Ringsdorff R7510P5 (ash content < 5 ppm)
Palladium powder specs[a]	Alfa Aesar 99.995 %	Alfa Aesar 99.998 %	Alfa Aesar 99.998 %
Graphite powder specs[a]	Alfa Aesar 99.9999 %	Alfa Aesar 99.9999 %	Alfa Aesar 99.9999 %
Graphite powder contents	≈2.7 %	≈1.7 %	≈1.7 %

[a] Purity values as claimed by the supplier

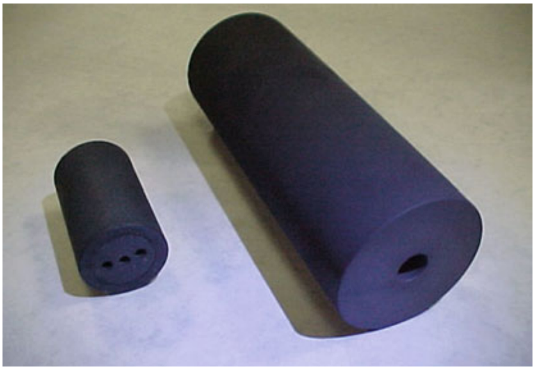

Fig. 1 Schematic of the cells

The three cells were prepared with different mixtures of palladium and graphite powders: an approximately eutectic composition, namely, about 2.7 % (in mass) of graphite was used for PdC_1. Cells PdC_3 and PdC_small were filled with a mixture with only 1.7 % of graphite. Slightly purer palladium was used for cells PdC_3 and PdC_small.

All the crucible components, which are made from high-purity graphite with <5 ppm ash content, were first washed in an ultrasound bath and then baked for 1 h in a furnace at a temperature of 1500 K. A vertical furnace provided with silicon carbide heaters was used for the filling.

Different filling procedures were adopted. With regard to cells PdC_1 and PdC_3, a funnel designed to contain approximately half of the powder mixture was connected to the cell. The crucible was heated for 2 h to a temperature about 10 K above the eutectic melting temperature and then cooled to room temperature. A furnace temperature rate of $4\ \mathrm{K \cdot min^{-1}}$ was used for the melting process; a $1\ \mathrm{K \cdot min^{-1}}$ rate was set for going down to 12 K below the freezing point and then a rate of $3\ \mathrm{K \cdot min^{-1}}$ was set to cool to room temperature. After the first run, part of the powder solidified into the funnel. It was then filled with the remaining powder, and several additional runs were necessary to allow for the complete filling of the crucible.

A different filling procedures were adopted for the cell PdC_small. It was filled with the mixture and then heated with the same rates and set points used for PdC_1 and PdC_3. After each run, an additional charge of powder was made and the cycle repeated. Approximately 20 repeated runs were necessary to completely fill the cell.

3 Instrumentation

Two different furnaces, namely, a single- and a three-zone apparatus, were used to realize the phase transitions with the three cells. The former is equipped with six heating elements made from silicon carbide to heat a chamber 450 mm in length. An Al_2O_3 tube of 43 mm in diameter was used to accommodate the crucible and graphite insulators. To allow a direct measurement of the temperature profile, a setup with a dummy crucible and graphite insulators specifically designed to allow scans with a thermocouple was arranged. The longitudinal temperature profile inside the

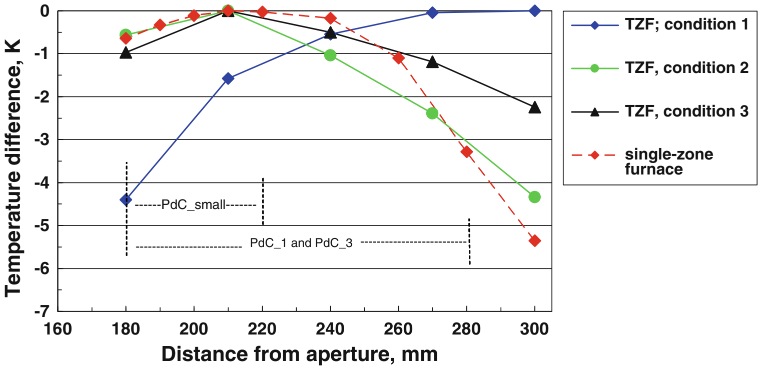

Fig. 2 Longitudinal temperature profile of the two furnaces used for the measurements

furnace tube was measured with a Pt/Pd thermocouple. It can be seen from Fig. 2 that where cells PdC_1 and PdC_3 were placed, the temperature was uniform within approximately 3 K.

The second was a high-temperature GERO furnace. It consists of three independent heating zones and is equipped with eight heating elements made from molybdenum disilicide ($MoSi_2$) for operation up to 1800 °C; the ceramic working tube inside the furnace is 900 mm long with an inner diameter of 70 mm and with a heated length of 600 mm. The short working distance of the INRIM thermometer, namely, 460 mm, in conjunction with the length of the furnace tube did not allow the cells to be positioned, as normal, at the middle of the furnace. Checks were made which showed that for safe operation of the thermometer and to avoid overheating of the objective lens, a minimum distance of about 170 mm between the thermometer lens and the aperture of the furnaces should be defined. With such an arrangement, the aperture of the cells was 180 mm from the middle of the furnace. The possibility of adjusting independently the temperature of the heating zones allowed different temperature distributions to be obtained, even if, due to the off-centered positioning, the potential best uniformity cannot be attained. The same "simulation set-up" already used with the single-zone furnace was utilized with the three-zone furnace. Figure 2 shows different temperature distributions obtained with both the single- and the three-zone furnaces.

Two different radiation thermometers, namely, a Si- and an InGaAs-based instrument, were used to record the melting plateaux. The latter was only employed in the earlier phases of the work to investigate cell PdC_1. It is a high-precision transfer standard instrument based on an InGaAs photo-detector with a 5 mm in diameter sensing area (Hamamatsu Model. G5832-15) that was cooled to −10 °C by means of a thermoelectric cooler and works in a 70 nm wide spectral band centered near 1.6 μm [5].

The former is basically the primary standard radiation thermometer of INRIM based on a silicon photodiode and used for the realization of the ITS-90. A Hamamatsu S2592-03 silicon photodiode operated in an unbiased mode with a built-in Peltier element allowing the temperature of the detector to be controlled at +10 °C was used.

A recently introduced channel with a filter centered at 950 nm with a bandpass of about 70 nm was used for the measurements [6].

4 Measurements and Results

The measurements consisted of the realization of 65 phase transition runs and took place at INRIM over a period of more than Two years from June 2007 to October 2009.

4.1 Measurements with the Single-Zone Furnace

The furnace was used to realize 55 phase transition runs from June 2007 to October 2008. All the melting curves are shown in Figs. 2, 3, 4, and 5, and a summary of the measurement results and details is given in Table 1. Both first derivative and melting histogram approaches were used to derive the transition signals of the melting curves [3]. The former was applied to the six curves derived with the InGaAs thermometer, with the melting histogram approach applied to all other curves derived with the Si thermometer. In the melting histogram procedure, the melting signal is identified with the average signal of the flattest part of the plateau. Signal steps of 0.5 mV, corresponding to temperature steps of about 0.04 K, were adopted to generate the histograms. The time scale on axis *X* was normalized to the time corresponding to the melting signal.

4.1.1 Measurements with PdC_1 Cell

A first set of six transition runs was performed with the InGaAs thermometer to check possible effects of the melting rate. Figure 3 shows the six melting curves obtained

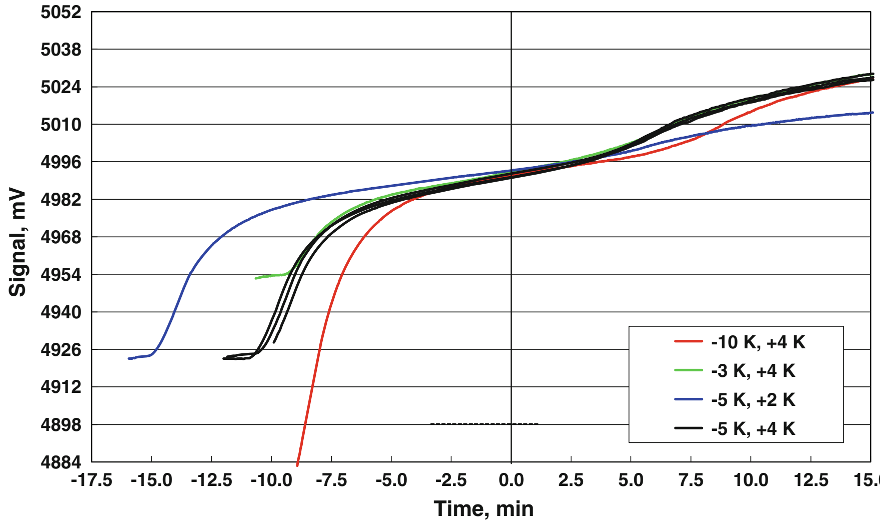

Fig. 3 PdC_1 cell: summary of the melts with the single-zone furnace and the InGaAs thermometer. *Y*-axis: 1 K/division

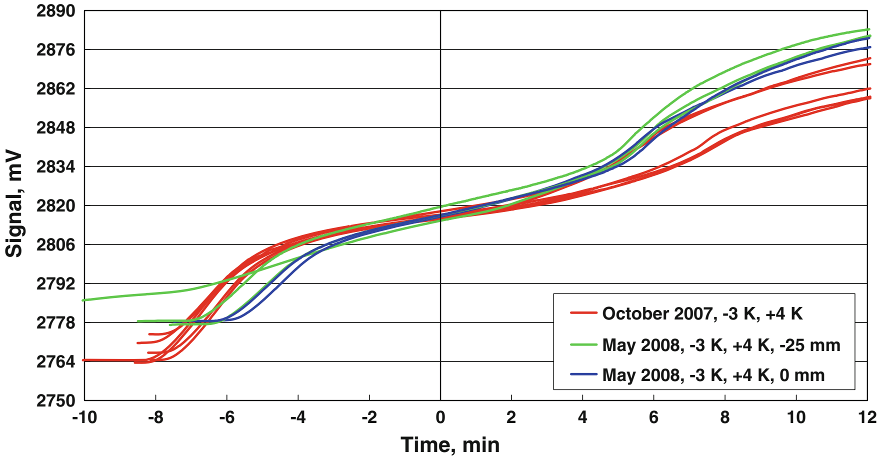

Fig. 4 PdC_1 cell: summary of the melts with the single-zone furnace and the Si thermometer. *Y*-axis: 1 K/division

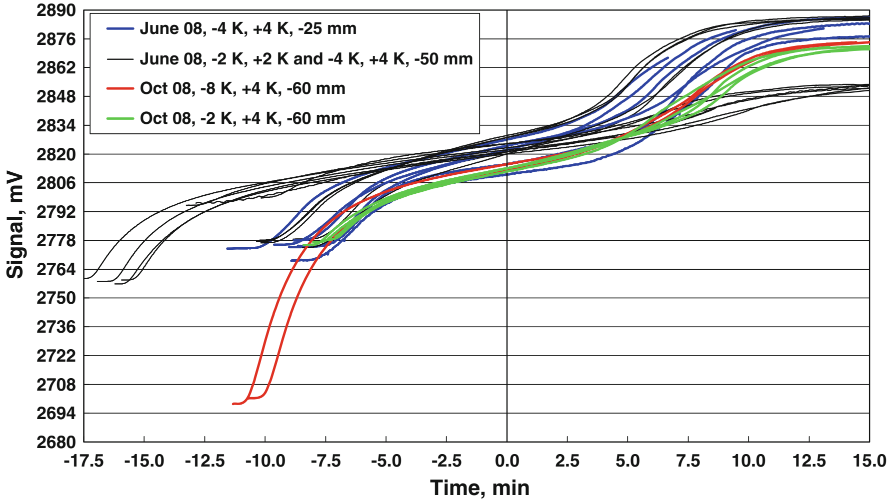

Fig. 5 PdC_3 cell: summary of the melts with the single-zone furnace. *Y*-axis: 1 K/division

with different offsets of the furnace temperature setting (+2 K and +4 K with respect to the melting temperature) following freezes induced with offsets of −10 K, −5 K, and −3 K. All the melting signals were included within a band of 0.23 K with a standard deviation of 0.08 K. The difference between the two outermost conditions, namely, those with −3 K and −10 K offsets, is 0.10 K, namely, the same order as the repeatability of three curves obtained with −5 K and +4 K offsets.

Two further sets of measurements with cell PdC_1 were performed using the Si-based thermometer (see Fig. 4). The first one consisting of six phase transition runs was essentially a repeatability test carried out with the same temperature offsets, i.e., −3 K and +4 K. The six melting signals were included within a band of 0.20 K

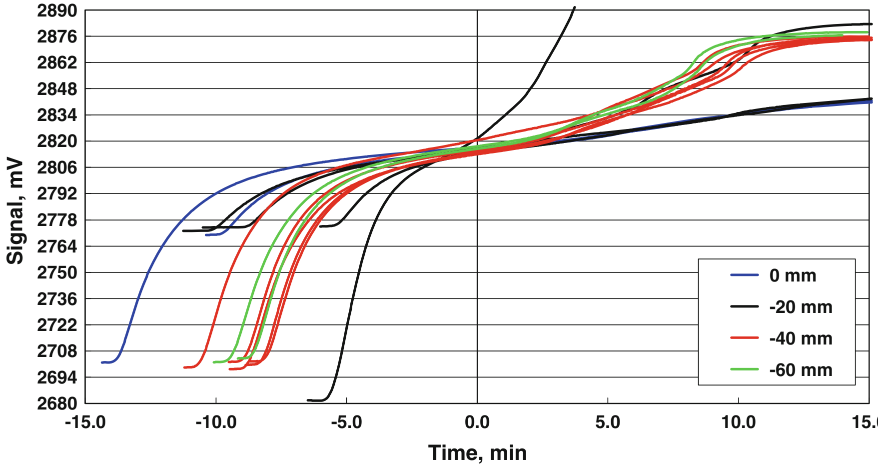

Fig. 6 PdC_small cell: summary of the melts with the single-zone furnace. *Y*-axis: 1 K/division

with a standard deviation of 0.07 K, namely, a result similar to that found with the InGaAs thermometer.

The second set of measurements took place 6 months later and was aimed to investigate the effects of the cell positioning inside the furnace. The cell was measured in its original position and then moved backwards 25 mm. The dispersion was higher than during the repeatability tests, i.e., 0.13 K, thus suggesting a real, even if slight, effect.

4.1.2 Measurements with PdC_3 Cell

The 24 melting curves obtained with cell PdC_3 are reported in Fig. 5. The first set of 18 melting runs performed in a period of about one month in June 2008 was aimed to investigate the effect of different positioning of the cell inside the furnace. The cell was moved 25 mm and 50 mm backwards toward the middle of the furnace. Differences as large as 1.36 K were found, but a direct relation with the position of the cell was difficult to find. A further set of six runs was carried out in October 2008 with the cell positioned 60 mm backwards. Different melting offsets, namely, −8 K, +4 K, and −2 K, +4 K, were tested.

4.1.3 Measurements with PdC_Small Cell

The 13 melting curves are shown in Fig. 6. As for cell PdC_3, the effect of positioning of the cell inside the furnace was investigated by moving the cell backwards up to 60 mm, but considerably smaller variations have been found.

4.2 Measurements with the Three-Zone Furnace

A summary of measurement results and details is given in Table 3. The measurements were carried out with cells PdC_3 and PdC_small in October 2009. The ten melting

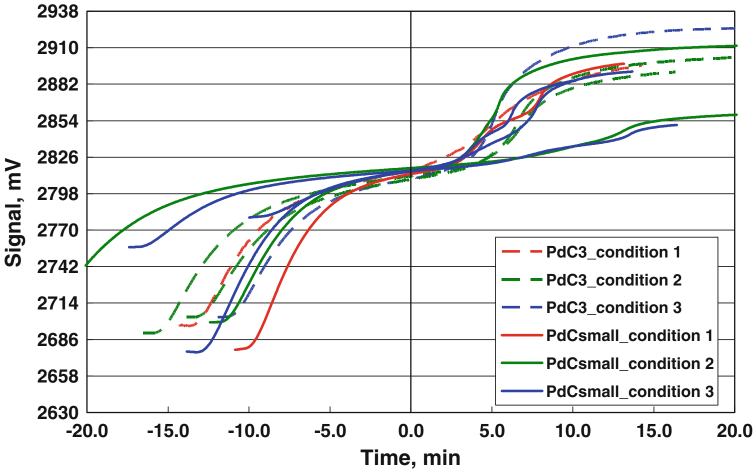

Fig. 7 Summary of the melts with the three-zone furnace. Y-axis: 2 K/division

curves are shown in Fig. 7. Three different temperature distributions, namely, those referred to as conditions 1, 2, and 3 in Fig. 2, were tested with both cells.

5 Discussion of the Results

The results summarized in Tables 2 and 3 and graphically presented in Figs. 3, 4, 5, 6, and 7 allow some conclusions to be reached.

Table 2 Summary of measurement cycles with single-zone furnace

Cell	Thermometer	Date of measurement	Average melting signal (mV)	SD (K)	Max – Min (K)	No. of meltings
PdC_1	InGaAs	June 2007	4991.4	0.08	0.23	6
PdC_1	Si	October 2007	2816.2	0.07	0.20	6
PdC_1	Si	May 2008	2816.9	0.13	0.36	6
PdC_3	Si	June 2008	2822.4	0.33	1.36	18
PdC_3	Si	October 2008	2812.8	0.09	0.25	6
PdC_small	Si	October 2008	2815.9	0.20	0.64	13

Table 3 Summary of measurement cycles with three-zone furnace

Cell	Thermometer	Date of measurement	Average melting signal (mV)	SD (K)	Max – Min (K)	No. of meltings
PdC_3	Si	October 2009	2811.3	0.23	0.48	4
PdC_small	Si	October 2009	2815.3	0.10	0.33	6

(1) *Repeatability*: Results may be derived for all the three cells and are typically within 0.10 K, independent of the measurement conditions.
(2) *Plateau shape*: Results obtained with the three-zone furnace showed an improvement with respect to the single-zone furnace and particularly when best temperature distributions are used.
(3) *Effect of the melting rate*: Different melting rates were tested with PdC_1 and PdG_3, and no systematic effects were found. All the variations were of the same order as the repeatability.
(4) *Effect of temperature distribution*: Measurements with the three-zone furnace allowed three different temperature distributions to be tested. As expected, PdC_small was less influenced than PdC_3: standard deviations of the melting signals of 0.10 °C and 0.23 °C were found with the two cells, respectively. The results obtained with PdC_small and summarized in Fig. 7 show that, even if better temperature distributions, namely, those referred to as conditions 4 and 5, may improve flatness and duration of the plateaux, a worse temperature distribution, i.e., condition 1, produce plateaux which may be of poorer quality, but with a close transition temperature.
(5) *Effect of the cell positioning*: PdC_small and PdC_3 were moved inside the single-zone furnace backwards up to 60 mm with respect to the normal measuring position: standard deviations of the melting signals of 0.20 °C and 0.33 °C resulted for PdC_small and PdC_3, respectively. The effect is similar to that found testing different temperature distributions with the three-zone furnace, i.e., the small cell was less influenced than the bigger one.
(6) *Differences among the three cells*: Figure 8 shows the differences of each set of measurements with respect to the arithmetic mean of all the sets. A substantially constant difference of approximately 0.25 K was found between cells PdC_small and PdC_3, measured with single- and three-zone furnaces. On the other hand, first measurements with PdC_3 provided values higher than both PdC_1 and PdC_small.

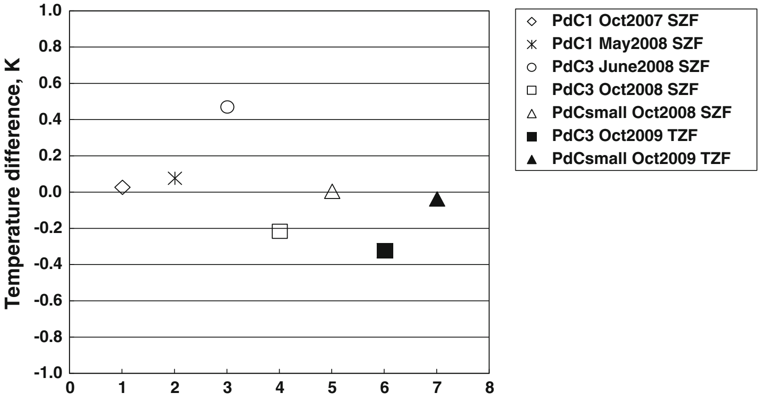

Fig. 8 Differences of each set of measurements with respect to the arithmetic mean of all the seven sets

Table 4 Different elaborations of the 59 melting signals

Elaboration	Average signal (mV)	SD (K)
Mean of all determinations	2817.3	0.34
Mean of the three cells	2815.9	0.04
Mean of all the seven cycles	2815.8	0.25
Mean of the single-zone furnace cycles	2816.8	0.25
Mean of the three-zone furnace cycles	2813.3	0.20

(7) *Reproducibility of the melting signal*: The amount of data at our disposal, namely, 59 melting curves obtained with the same thermometer, allows some data on the reproducibility to be derived.

The 59 melting signals were analyzed in different ways, and the results of the calculations are reported in Table 4. All the calculated means agree within <0.3 K with a standard deviation of 0.1 K. It must be noted that no correction of the measured signals has been done to take into account possible drift of the thermometer. It could be presumed that, because of the long time duration of the measurements, i.e., more than two years, part of the dispersion of the results could originate from signal variations of the thermometer.

In any case, it is an interesting result which shows a quite limited effect of possible influencing parameters like the design of the cell, the different filling procedures, the furnaces, the positioning inside the furnace, and the melting rate.

6 Conclusion

Three Pd-C cells manufactured at INRIM have been measured over a period of two years. The considerably different external dimensions of the cells, namely, 40 mm and 110 mm in length, and the use of two different furnaces, namely, single- and three-zone furnaces, allowed many different conditions to be tested. A large number of phase transitions were performed with different temperature steps, melting rates, longitudinal temperature distributions, and positions of cells. As expected, the smaller cell was less influenced by the temperature distribution and positioning than the bigger ones. It was also shown that the use of a multi-zone furnace may improve the quality of the melting plateaux by increasing their flatness and duration, and such a result is a confirmation of previous findings with Co–C cells [7]. The large number of the plateaux realized, namely, 59, and the different conditions tested, allowed reproducibility figures to be derived. It was found that whatever condition was tested, the standard deviation of the measured signals was always within 0.3 K.

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