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Reliability of High-Temperature Fixed-Point Installations over 8 Years

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Abstract At NPL, high-temperature metal-carbon eutectic fixed points have been set up for thermocouple calibration purposes since 2006, for realising reference temperatures above the highest point specified in the International Temperature Scale of 1990 for contact thermometer calibrations. Additionally, cells of the same design have been provided by NPL to other national measurement institutes (NMIs) and calibration laboratories over this period, creating traceable and ISO 17025 accredited facilities around the world for calibrating noble metal thermocouples at 1324 °C (Co–C) and 1492 °C (Pd–C). This paper shows collections of thermocouple calibration results obtained during use of the high-temperature fixed-point cells at NPL and, as further examples, the use of cells installed at CCPI Europe (UK) and NIMT (Thailand). The lifetime of the cells can now be shown to be in excess of 7 years, whether used on a weekly or monthly basis, and whether used in an NMI or industrial calibration laboratory.

Keywords Calibration · Eutectic fixed-point cells · High-temperature fixed points · Lifetime · Thermocouple

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1 Introduction

Since the discovery of repeatable high-temperature fixed points (HTFPs) using a eutectic composition of metal with carbon, in 2000 [1], graphite cells containing Co–C (1324 °C), Pd–C (1492 °C) and many other eutectics have been studied and used across the world to extend the range of contact and noncontact temperature calibration artefacts [2].

In 2006, the first ISO 17025 accredited thermocouple calibration service using HTFPs was set up at NPL using a Co–C cell. In 2008 this was followed by the Pd–C cell. In addition, NPL have installed several duplicate systems, including at CCPI Europe and NIMT. The arrangement of the system is illustrated in Fig. 1.

These capabilities have enabled noninvasive thermocouple calibration at high temperatures, with improved measurement uncertainties [3–5], and in turn, have enabled Pt/Pd thermocouples to be used in industry [6,7]. Pt/Pd thermocouples have the main advantage of being significantly more stable than the standardised, and commonly available, Pt–Rh thermocouples (Types R, S and B) [8]. Prior to the availability of the Pd–C eutectic reference point, the only direct calibration method available was the wire-bridge technique, which melts a bridge of pure metal (e.g., Pd 1554.8 °C in air) between the thermocouple wires at the hot junction [9]. This is clearly an inappropriate technique for use with Pt/Pd thermocouples, and rendered the combination impossible to calibrate with low uncertainty.

HTFPs have been widely used and studied in many NMIs, and found to be both stable and reliable [10–15]. Their use in industrial calibration laboratories is significantly more strenuous and has not, until now, been reported.

This paper presents an overview of the performance of HTFPs at NPL, CCPI Europe and NIMT through the calibration results of thermocouples used over the years of operation. The data presented show the frequency of use for each cell and infers the stability of both the cell and thermocouple over the intervening years. This demonstrates the operational reliability of the HTFPs over 7 years.

2 Installation and Usage

Table 1 summarises the HTFPs used, and their duration of installation. The cells each have the same design and material purity, as described in previous work [10,16,17] – with a length of 125 mm and diameter of 37 mm. Figure 1 includes a diagram, photo of the installed system at NIMT and a typical thermal profile of the cell (measured with a Pt/Pd thermocouple and at approximately 5 °C below the melting plateau). The cell is designed to be operated under these conditions, to reduce the impact of thermal expansion on the graphite crucible.

At NPL, the Pd–C cell (1491.50 °C ± 0.65 °C) has been installed since Jun 2008 and is still in operation. A Co–C cell was installed from Dec 2006 to Nov 2014 (1324.29 °C ± 0.44 °C), lasting almost 8 years until the graphite thermowell failed. This cell was then replaced with a nominally identical, newly constructed, cell (whose assigned temperature is 1324.09 °C ± 0.44 °C), and the replacement is still in good working order. The temperature of these cells has been determined by radiation

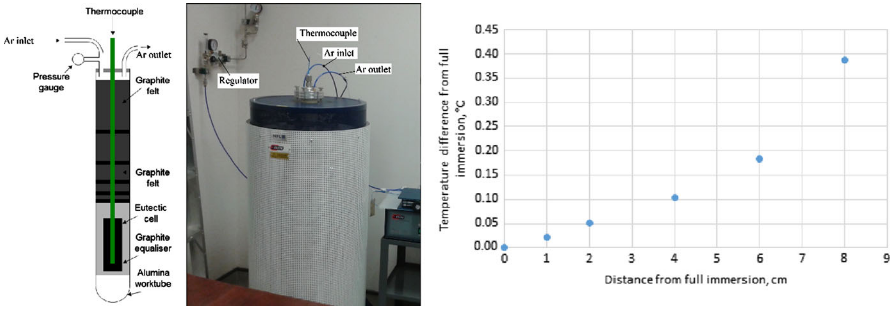

Fig. 1 From left: an illustration of the NPL HTFP set up; a HTFP calibration facility at NIMT; a typical thermal profile

Table 1 Summary of the HTFPs in use at NPL, CCPI Europe and NIMT

	HTFP	Installation	Failure	Pt/Pd	B	R	S
NPL	Pd–C	Jun 2008	–	✓	✓	✓	✓
	Co–C	Dec 2006	Nov 2014	✓		✓	✓
	Co–C	Dec 2014	–	✓		✓	✓
CCPI Europe	Pd–C	Jun 2012	–			✓	
	Co–C	Jan 2007	Oct 2014			✓	
	Co–C	Nov 2014	–			✓	
NIMT	Co–C	Feb 2015	–	✓	✓		✓

thermometry, directly traceable to the UK's national realisation of ITS-90 above the freezing point of silver (962 °C), using ISO 17025 accredited procedures. Many Pt/Pd and Type B, R and S thermocouples have been calibrated in these cells over the years. These all were constructed with alumina sheathes (OD = 7 mm) and twin-bores, and with high-quality thermoelements (OD = 0.5 mm).

The cells are set up for operation inside a Carbolite or Elite three-zone, high-temperature furnace, with a protective argon atmosphere. Furnace controllers have been chosen to offer programming ability, such that consecutive melt and freeze cycles can be automated. Each 'calibration operation' consists of three consecutive melts and freezes, with the furnace being reduced to just below the freezing plateau between each cycle. The furnace is then, typically, cooled to room temperature before starting calibration of the next thermocouple. Heating and cooling rates of between 2 $K \cdot min^{-1}$ and 5 $K \cdot min^{-1}$ are used through the phase transitions. Furnace temperature set points, offset from the phase transition plateau of between 3 K and 10 K, are typically used for both the melt and freeze transitions. The settings used are always consistent throughout each operation (including the preceding freeze). The thermovoltage is measured using a Keithley 2182A nanovoltmeter. Typically, the cold junction of the thermocouple is immersed into a Fluke 9101 Zero-Point Dry-Well.

At CCPI Europe, a Pd–C cell was installed in Jun 2012 (1491.16 °C $\pm$ 0.73 °C); is still in good working order and has been operated 27 times. A Co–C cell was installed from Jan 2007 to Oct 2014 (1324.29 °C ± 0.44 °C); it was operated 318 times over 7 years, before being replaced as the graphite crucible failed. Operation of the cells at CCPI Europe follows a modified version of the procedure used at NPL, but is typically performed with Type R thermocouples. The thermovoltage is measured using a Datron Wavetek 1281 multimeter.

At NIMT, a Co–C facility has been in operation since Feb 2015 (1324.06 °C ± 0.44 °C). Again typical usage follows a modified version of that used at NPL, and has been used most with Pt/Pd and Type S thermocouples. The thermovoltage is measured using an Agilent 3458A multimeter.

3 Thermocouple Calibration Data

For both the Co–C and Pd–C reference cells, the melting temperature has been found to be more reliable than the freezing temperature, and therefore is used as the calibration point. The melting temperature is taken to be the inflection point of a third-order polynomial fit to the melting plateau.

Over the period of use, each thermocouple has been calibrated once. For calibration purposes, the average thermovoltage of three consecutive measurements is assigned to the cell temperature, and an uncertainty is calculated (including contributions from local calibration methods, thermocouple inhomogeneity and repeatability). These calibration temperature values are not presented here as all thermocouples would simply report the cell temperature. Instead, to remove the influence of the cell performance, the calibration thermovoltage is reported; this is presented in temperature units to allow different thermocouple types (measured within each cell) to be displayed on a single graph. The thermovoltage has been converted to temperature using the respective published reference function to provide a constant baseline [18,19]. The influence of the thermocouple reproducibility (including the inhomogeneity and purity) and cell drift on the presented results cannot be deconvoluted, but rather, the presented results indicate the overall performance.

For each institute, the difference between the assigned temperature of the cell in use and the thermovoltage measurement (in temperature units) is shown, in Fig. 2, against the date of the thermocouple calibration. For NPL and CCPI Europe results, only the ISO 17025 accredited calibrations performed with these cells are shown (other measurements have also been made since installation for research purposes). For NIMT results, all results are shown (ISO 17025 accreditation is pending assessment). The left-hand column of graphs contain the Co–C results, and the right-hand column contain the Pd–C results. Each row contains the results from NPL, CCPI Europe and NIMT.

Since each thermocouple has performed to the published, locally achievable thermocouple calibration uncertainty, only this value is given; and as this uncertainty is different for each laboratory, a bar is shown in the top left of each graph to indicate it's magnitude at the given temperature. In each case, the cell temperature assignment uncertainty contribution (the gray bar) is the dominant factor.

All quoted uncertainties are multiplied by a coverage factor k (where, $k = 2$), corresponding to an approximate coverage probability of 95 %.

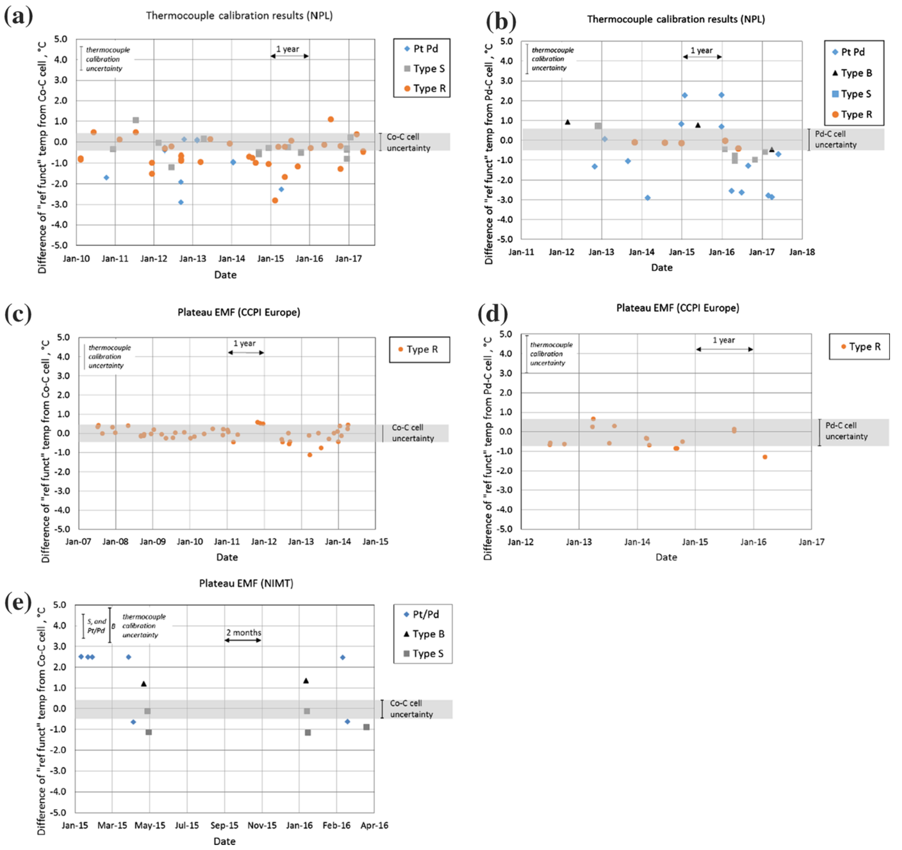

Fig. 2 Showing calibration results using Co–C and Pd–C HTFP reference cells at NPL (a, b), CCPI Europe (c, d) and NIMT (Co–C only, e)

Blind sampling has been used in the case of CCPI Europe and NPL to scale down the analysis, and therefore not every operation of the cells are shown. In the cases of NPL's Co–C and Pd–C cells, and CCPI Europe's Pd–C cell, more than half the operations are shown.

4 Discussion and Conclusions

There is generally no specific trend in the datasets, indicating contamination is very unlikely to have occurred to the cell over the years. The distribution of the results is dominated by the deviations from the corresponding reference temperature-voltage relationship of available thermoelements [18,19]. This is especially true for pure metal thermocouples where the thermovoltage generated is sensitive to the purity of the wires, and it is often not possible to source the same purity as the thermocouples which were used to determine the reference function [6,20,21].

The HTFP cells are robust and reliable, with no performance issues, until the graphite fails. The lifetime of the Co–C cell is found to be approximately 7–8 years, whether used weekly or monthly. The Pd–C cells are still operational after longer than 5 years (eight in NPL's case) but do show continual permeation of palladium into the thermowell. This is observed by the formation of small droplets of metal on the inside of the thermowell and outside of the thermocouple alumina sheath. Over time, this may bond the alumina sheath into the thermowell. This can be mitigated by periodically replacing the alumina sheath. This permeation of the palladium has not otherwise caused any operational issues.

Given that the eutectic ingot has a different thermal expansion to the graphite, and is also continually in contact with (and reacting with) the graphite crucible walls; this is an excellent lifetime, comparable with the pure metal, graphite encased, fixed-point cells of the ITS-90, which are (in NPL's experience) typically also reliable to 8 years, often showing drift or damage after this period.

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