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INMETRO ZINC FIXED-POINT OPEN CELL

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Abstract: A zinc fixed-point open cell (419.527 °C) was manufactured by the Thermal Metrology Division of Inmetro for the realisation of the International Temperature Scale of 1990 (ITS-90). This paper presents the fixed-point cell design, fabrication method, results of the cell evaluation and the estimated uncertainty assigned to the temperature of the cell.

Keywords: Zinc point, fixed-point, temperature.

1. INTRODUCTION

Fixed-point cells are reference standards of the International Temperature Scale of 1990 [1,2]. Within this scale, 17 fixed-points are defined, covering the temperature range from 3 K to 1084.62 °C. It is important for a National Metrology Institute (NMI) to realise them with the lowest possible uncertainty, in order to disseminate temperature standards according to the International Temperature Scale of 1990.

Inmetro has 10 defining fixed-points in the range of –189.3442 °C (Ar) to 1084.62 °C (Cu). All the cells are (or were) commercially available and most of them are sealed cells using reference materials with nominal purity of at least 99.999 %. In some previous comparisons with other metrology institutes [3,4], using Zn and Sn sealed cells, the results presented differences higher than 2 mK in the realisation of these fixed-points. This behaviour was also confirmed in internal comparisons when these cells were compared to the Zn and Sn open cells. The largest difference was found at the zinc freezing point, which motivated the construction of an open zinc freezing point cell at Inmetro.

2. CELL DESIGN AND MATERIALS

2.1 Cell Design

The manufactured open cell from Inmetro (named Inm Zn 01) follows a standard design and consists basically of a graphite crucible containing a zinc metal ingot (approximately 960 g). This graphite crucible is kept in a borosilicate glass tube 460 mm long (fig.1).

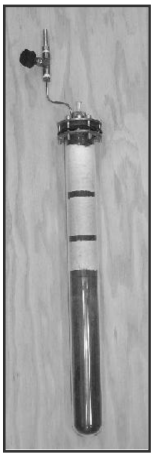

Fig. 1. The Inm Zn 01 zinc open cell

The graphite crucible is 230 mm long and its diameter is 45 mm. The immersion of the graphite thermometric well in the metal ingot is approximately 170 mm. These details are shown in figure 2.

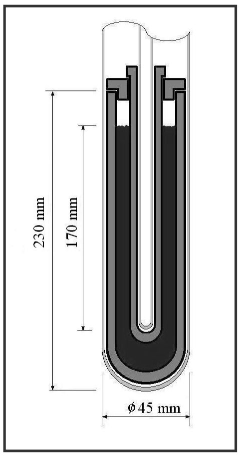

Fig. 2. Internal details of the Inm Zn 01 open cell

2.2 Zinc sample and inert gas

The material used to fill the cell was zinc with nominal purity of 99.9999 % in the form of small shots, supplied by Alfa Aesar (Johnson & Matthey Co). The material was analysed at the manufacturer, showing an impurity content below the level of detection, i.e., 0.1 p.p.m for most materials.

In all fabrication steps whenever an inert atmosphere was necessary, argon with nominal purity of 99.999 % was used.

3. FABRICATION METHOD

Initially, before the filling of the graphite crucible with the metal sample, the graphite crucible assembly was placed in a glass tube and baked at 430 °C under vacuum over night. After that, the assembly was cooled down to ambient temperature under vacuum and the glass tube was purged with argon gas and the graphite pieces removed for storage — a similar procedure is described in [5].

Two fillings were required to complete the filling of the graphite crucible — approximately 3/4 of the sample was poured directly in the first filling. The graphite crucible containing the metal sample was mounted in the glass tube and placed in the furnace.

The system was evacuated for 1 hour at 230 °C and for 15 minutes at 310 °C. It was then back-filled with purified argon to a pressure slightly above the ambient. The process was repeated three times (pumping and flushing) and kept finally in overpressure.

In the first melt of the zinc sample, the temperature set point of the furnace was 430 °C — the melting was realised with the metal sample in an argon atmosphere. The furnace was turned-off and a second filling was realised at ambient temperature. In the second melt, the set-point temperature was 445 °C. To freeze the sample, the "set-point" was reduced to 415 °C and after the supercool, the furnace temperature was set to 414 °C.

4. CELL EVALUATION

The cell evaluation method used was a direct comparison with the zinc reference open cell from Inmetro Thermometry Laboratory. This reference cell (named LN), was manufactured by Leeds & Northrup (s/n 742879) and was compared with other NMIs, having shown a temperature difference of -0.86 ±2.56 mK[4].

Two similar furnaces were used at the same time for the realisation of the freezing points, both having three heating zones controlled electronically.

The furnaces were previously tuned in order to present the lowest temperature difference among the three heating zones (over the metal ingot length). A value of less than 0.2°C was achieved for both furnaces.

A 25 Ω check SPRT (Hart model 5681) measured the freezing plateaux for both cells, following the sequence: reference cell, test cell and reference cell. All measurements were performed using a F18 AC bridge, operating at 1 mA and 1.414 mA, in order to calculate the SPRT resistance value at zero power dissipation.

The AC bridge was operated at low frequency (30 Hz) with a 100 Ω standard resistor kept at 20 °C. Before and after every comparison at the zinc freezing point, the resistance at the triple point of water was also measured.

4.1 Melting-point realisation

The temperature furnace is set at about 2 °C above the freezing-point temperature to slowly melt the metal over a period of time of approximately 7.5 hours. During the realization of the melting-point, all measurements with the SPRT were realised using a current of 1 mA.

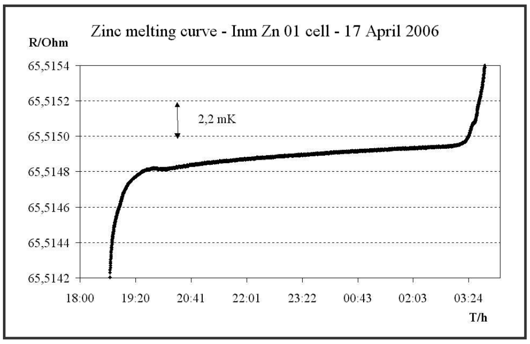

Fig. 3. Zinc melting curve of the Inm Zn 01 cell

4.2 Freezing-point realisation

After the melting realisation, the temperature is set at 5 °C below the freezing temperature value. The temperature is monitored using a check thermometer. When the supercool of the metal and the subsequent recalescence occurs the SPRT is removed and two ceramic rods (at ambient temperature) are inserted three minutes each into the reentrant well of the cell to induce an inner solid-liquid interface.

During the thermal chocks with ceramic rods, the temperature of the furnace is set to 0.5 °C below the freezing point. The SPRT is reinserted into the cell and the measurements begin after the equilibrium. The measurements were performed using an excitation current of 1 mA. For a setting furnace temperature of 0.5 °C below the freezing-point, the freezing is realised over a period of time of approximately 15 hours.

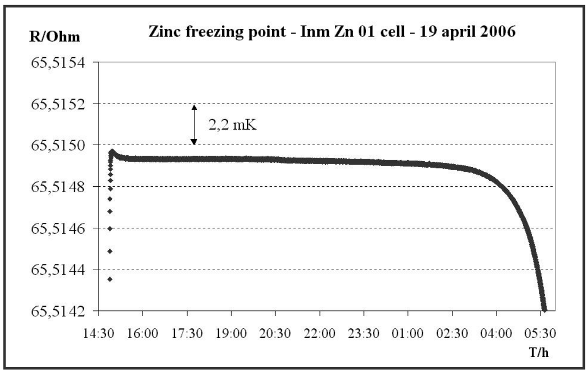

Fig. 4. Zinc freezing curve of the Inm Zn 01 cell – 19 April 2006

5. RESULTS

As described in the cell evaluation procedure, simultaneous zinc freezing plateaux were realised and the temperature differences between Zn test cell and Zn reference cell were calculated. These results are shown in Table 1.

Table 1. Temperature differences between the Zn cells. Diff = Temp [Inm Zn 01] – Temp [LN]

Date	Diff / mK
21 -June - 05	-1.24
23 - June - 05	-0.78
24 - June - 05	-0.83
28 - June - 05	-1.02
29 - June - 05	-1.02
01 - July - 05	-0.75
Average/mK =	-0.94
Std.dev./mK =	0.19

The results indicate that, after six series of measurements, the mean freezing temperature of the test cell is 0.94 mK lower than mean freezing temperature of the reference cell.

After the direct comparison between the cells, another SPRT Hart model 5681 was measured in the zinc point using both Zn open cells (test and the reference cell) and in the triple point of water. The difference between W_{Zn} (R_{Zn} / R_{tpw}) measured in both cells was calculated and the result is in agreement with the result obtained in Table 1 (-0.66 mK).

Table 2. Measured W_{Zn} for the Zn reference cell and Zn test cell.

Date	W_{Zn} (LN)	W_{Zn} (Inm Zn 01)
13-March-06	2.568 740 2	
17-March-06	2.568 738 7	
20-March-06	2.568 741 0	
23-March-06	2.568 737 9	
30-March-06		2.568 738 0
03-April-06		2.568 736 3
Average =	2.568 739 4	2.568 737 1
Std. dev =	0.0000014	0.0000012
Std.dev./ mK =	0.40	0.36
W difference =	- 0.000 002 3	
Diff / mK =	- 0.66	

The equivalent temperature difference in W value is calculated as: W_{Zn}[Inm Zn 01] - W_{Zn}[LN] with zero power dissipation (0 mA). The disadvantage of this procedure is that the temperature difference between the cells depends of the SPRT stability along all the time of the comparison.

A freezing curve obtained in March 2006 (figure 5) shows that the plateau was performed in approximately six hours with the furnace temperature set two degrees bellow the freezing temperature. The temperature stability during the freezing was better than 0.20 mK for at least 3 hours.

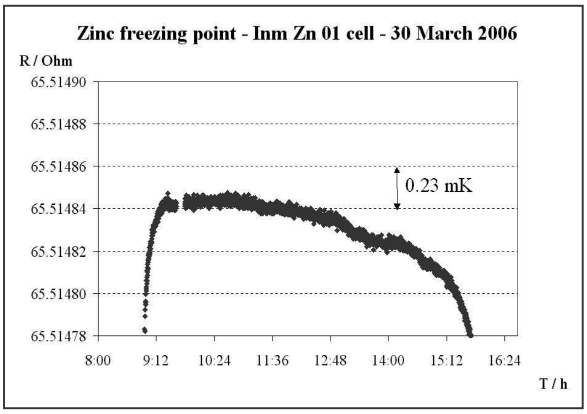

Fig. 5. Zinc freezing curve of the Inm Zn 01 cell – 30 March 2006

According the analysis procedure described in [5], "impurities present in the high-purity samples will cause a depression in the temperature of a freezing point". In that case, "the total mole fraction impurity level of the metal sample and the Raoult's Law of dilute solutions gives a calculated estimation of the depression in temperature over the first 50% of a freezing curve." The zinc freezing point curves (figures 4 and 5) show depressions less than 0.3 mK over the first 50% of the freezing curves. These results are of the same order as that obtained in [5] (0.1 mK).

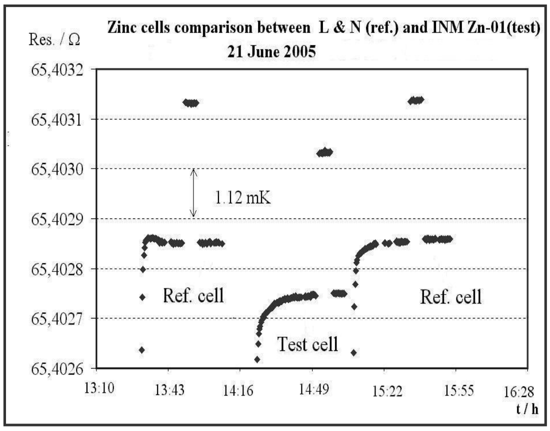

Fig. 6. Zinc cells comparison – 21 June 2005

Figures 6 and 7 are graphs of the direct comparisons between zinc reference cell and zinc test cell realised in June 2005. The comparisons were performed using a 25 Ω SPRT Hart model 5681 driven with currents of 1 mA and 1.414 mA. The AC bridge measured the ratios (Rx/Rs), where Rx is the thermometer resistance and Rs is the resistance of a 100 Ω standard resistor. On June 21th 2005 the difference was - 1.24 mK (figure 6) and on June 23th 2005 the difference was - 0.78 mK (figure 7).

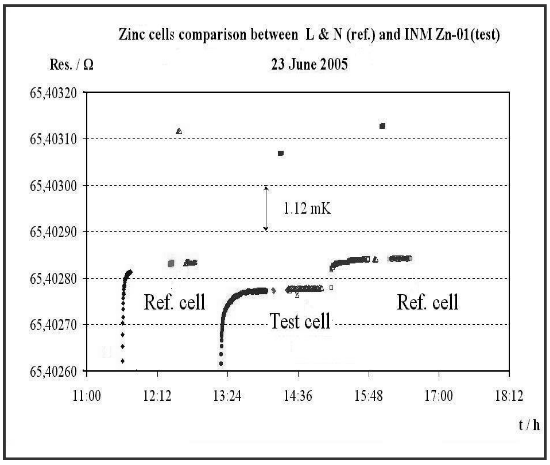

Fig. 7. Zinc cells comparison – 23 June 2005

6. UNCERTAINTY EVALUATION

The Inmetro uncertainty budget for the Inm Zn 01 cell is presented in the Table 3. The main component is due to the uncertainty of the reference cell. This uncertainty was estimated based on comparisons of cells involving Inmetro and other NMIs.

Table 3 - Measurement uncertainties of Inmetro for the Zn cell comparison. All values are in mK.

Fixed-point	**Zn**
Type B uncertainty components	
1. Uncertainty of reference cell	1.1
2. Hydrostatic head -- Ref. Cell	0.02
3. Heat-flux -- Ref. Cell	0.09
4. Self-heating -- Ref. Cell	0.06
5. Hydrostatic head -- Test. Cell	0.02
6. Heat-flux -- Test. Cell	0.09
7. Self-heating -- Test. Cell	0.06
8. Measurement system stability	0.02
9. Reproducibility of the cells difference	0.19
10. Standard resistor	0.01
Type B combined	1.12
Type A uncertainty for Refer.cell	0.02
Type A uncertainty for the Test cell	0.03
Combined uncertainty	1.13
Expanded uncertainty, $k = 2$	2.3

7. CONCLUSION

The results of the direct comparison between Inmetro zinc open cell (Inm Zn 01) and Inmetro reference cell (LN) presented, in the freezing plateaux, temperatures about 0.9 mK below the reference cell temperature. Linking this result with the others obtained using Zn sealed cells, it is possible to conclude that the temperature of the Inm Zn 01 cell is closer to the defined temperature than those obtained with sealed cells.

If a correction of 1 mK is applied, it can also be used as a reference cell, because the repeatability of the temperature of the cell is similar to the Inmetro reference open cell.

So, the Inm Zn 01 cell can be used in the calibration of SPRTs and thermocouples in the same way as the sealed Zn cells of Inmetro. This is an encouraging result for the construction of fixed point cells with other metals.

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