



PERFORMANCE EVALUATION OF AN OPEN TIN CELL CONSTRUCTED AT INMETRO

R.N. Teixeira¹, R. da Silva²

¹Inmetro, Rio de Janeiro, Brazil, rnteixeira@inmetro.gov.br

²Inmetro, Rio de Janeiro, Brazil, rdsilva@inmetro.gov.br

Abstract – The Inmetro Thermometry Laboratory uses fixed-points cells defined in the International Temperature Scale of 1990 (ITS-90) to calibrate thermocouples and standard platinum resistance thermometers. In order to meet this, the laboratory counts on reference fixed-point cells from the Argon triple point (-189,3442 °C) to the Copper fixed-point (1084,62 °C). In a quest to improve its best measurement capability and to disseminate this, the laboratory has been investing in the manufacture of its own primary standards. This process was started with water triple point cells, mercury triple point cells and pure noble metal thermocouples which have results validated through comparisons and are part of the laboratory standards regularly used in calibrations. The following step came to be an open metal cell. Zinc was chosen for being relatively inexpensive. The methodology and the corresponding results achieved were published in 2006 and 2008. Going on with this task, the laboratory constructed a Tin cell in 2010. All Inmetro cells are open, and they were compared to the three commercially available cells the laboratory previously had. The materials, methodology, uncertainty evaluation (impurity effect estimates) and results are discussed in the present paper.

Keywords: tin cell, fixed-point, thermometry

1. INTRODUCTION

In the past few years, NMIs all over the world have been struggling in order to improve or develop new measurement procedures, equipment and standards, aiming at even better measurement and calibration capabilities. Following the avant-garde researches in the field, Inmetro Thermometry Laboratory has been developing its own primary standards. Inmetro owns a total of 10 defining fixed-points so as to cover the International Temperature Scale of 1990, the ITS-90, in the range from -189,3442 °C to 1084,62 °C [1]. Except for the Water Triple-Point and Mercury TP cells (manufactured in the Laboratory), all of them were purchased, i.e. commercially available. Especially for their measurement practicability, most of the cells were chosen to be sealed. The reference material applied is certified by their supplier to present nominal purity greater than or equal to 99,999 %.

The cells were compared to other NMIs cells and they presented temperatures lower than 2 mK [2]. Later, when the laboratory started using open cells, these differences also occurred in the internal comparisons realised involving them. One of the most substantial differences had been found in the tin freezing point, a tin FP cell was chosen to be the starting point. It is also worth mentioning that most of SPRT calibrations performed at the lab fall within the WTP to Zn FP temperature range, where the tin point is located.

This is the first tin cell produced and it presented results as expected, which followed the procedure and design used for the last zinc cell constructed at Inmetro.

At present, apart from manufacturing these cells, the concern is also investigating how (much) impurities in the metal interfere the cells final results. Much has been said but it is still some space for discussion on methods for determining chemical impurities of the materials as well as metal filling procedures.

2. MATERIALS

The metal employed in the cell was supplied by Alfa Aesar (Johnson Matthey Company). The metal was in teardrop form for both ease of use and minimisation of contamination [2]. The nominal purity of the metal is declared to be 99,9999 %, although the supplier assay detected none impurities, i.e. they were below the method detection limits (0,1 ppm for most elements). This analysis was realised through ICP-OES – Inductively Coupled Plasma Optical Emission Spectrometry.

The graphite parts were purchased from Carbono Lorena Ltda, a subsidiary of Groupe Carbone Lorraine in Brazil. The material nominal purity is 99,999 % (10 ppm of ash content). As for the gas employed when an inert atmosphere was necessary, in both manufacture procedure and use of the cell, Argon with nominal purity of 99,999 % was used.

3. CELL DESIGN

The tin cell Sn-2010 follows the design applied in NIST [3], with a few adaptations, as seen in [4]. Basically, it consists of the metal, contained within a high-purity graphite assembly (crucible, cap and re-entrant well) which was then inserted into a precision-bore borosilicate-glass envelope. Above the graphite cap, there was a matte-finished

borosilicate-glass guide tube, washed-ceramic fiber disks and three heat shunts adequately positioned. A silicone rubber stopper was used as a cap in the top of the glass envelope. This had two holes: a central one for the glass tube leading to the re-entrant well and a small hole for inserting a stainless steel gas filling tube for evacuating and backfilling the cell with inert gas (Ar).

4. FILLING OF THE CELL

Prior to filling the graphite crucible with tin, the graphite parts were baked at 650 °C under vacuum for 4 hours. This was done in order to remove hydrocarbons and other possible contaminants that might have been present from the fabrication process. Whenever handling the material (graphite parts, tin shots and other material that would be in contact with the metal), disposable polyethylene gloves were worn so as not to degrade the purity neither of the metal nor of the fixed-point cell components.

In total, 1100 g of tin were used to fill the cell Sn-2010. However, two fillings were required in order to introduce the metal into the crucible and insert the graphite re-entrant well. The first “fill” consisted of approximately 700 g of tin shots, as it was the most that could be poured directly into the crucible at once.

Pouring the metal shots was done under an Argon atmosphere to prevent metal oxidation. Furthermore, the metal lot was opened and the metal portion needed was handled under an Ar atmosphere, as well, all inside a glove box.

The graphite crucible with the metal shots and the graphite cap were placed into the silica-glass furnace tube and then in the furnace. The system was evacuated for 1 hour and then back-filled with argon to a pressure of nearly 34 kPa. This process – pumping and flushing – was done three times. When complete the last cycle, the system was then back filled with argon to a pressure of 34 kPa. After this, the furnace temperature was set up to 237 °C in order to melt the metal sample. After nearly 3 hours, the metal was totally molten and the furnace was then turned off so as to cool down to room temperature before the removal of the graphite crucible from the glass tube.

After cooling down, the remaining metal was added to complete the total 1100 g of tin. The graphite re-entrant well was inserted in the crucible through the hole in the graphite cap. The assembly was then placed in the furnace tube. The process of pumping and flushing, as described above, was repeated. In order to slowly push the re-entrant well into the melted metal, a silica-glass push rod (weighing ~ 100 g) was used together with a T-shaped metal piece (weighing ~ 220 g) to fight buoyancy. When the graphite re-entrant well was totally inserted, the furnace was switched off and the system allowed to cool down to room temperature. After that, the graphite crucible assembly was inserted into its borosilicate-glass envelope and fixed-point cell assembly.

5. EQUIPMENT

The furnace used for the realization of the tin freezing point in this work was a three zone Hart Scientific model 9114. It was previously tuned in order to have the best temperature profile in the three zones. For the water triple point it was used a cell constructed at Inmetro, usually maintained in a dewar flask with ice. All the measurements were performed using an ASL F18 thermometry bridge, connected to 100 ohm Wilkins type standard resistor from Tinsley, kept at 20 °C in a temperature controlled oil bath. As for the bridge, it was selected a very narrow bandwidth (0,02 Hz) for the measurements at the tin freezing point, in order to have the minimum noise influence.

During all the measurements, two different quartz standard platinum resistance thermometers were used: one from Rosemount Aerospace, model 162 CG, and the other from Hart Scientific, model 5683. Both SPRTs showed adequate stability throughout the measurement period. It is possible to see in fig.1 the stability of one of these SPRTs at the WTP, during the period that the cell was measured.

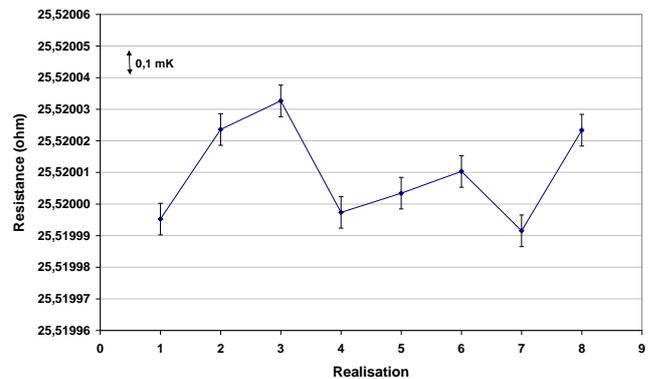


Fig. 1. Drift of one of the SPRTs used in the measurements in 4 months. Resistance in the Water Triple Point.

6. RESULTS

Using the Certificate of Analysis provided by Alfa Aesar, the supplier of the Tin, it was calculated the influence of the impurity concentrations in the temperature of the cell. This value can be estimated by the use of Raoult's Law of dilute solutions, where the temperature difference is obtained by dividing the mole fraction impurity concentration (x_2) by the first cryoscopic constant (A) [5].

$$\Delta T = T_0 - T = \frac{x_2}{A} \quad (1)$$

where T_0 is the freezing point temperature of the 100% pure sample and T is the observed realisation temperature.

According to the Certificate of Analysis of the lot used for manufacturing the cell, no impurities were detected by the method employed (ICP). So, it was decided to base its estimate on the most common impurities present in tin [6] considering half of the detection limits of each element.

However, as there were many elements listed, the calculations seemed to be out of reality, once the sum of the impurities based on this would correspond to a 5N tin sample (a total of 10 ppm of impurities), which is not the case, specially for the “prior to handling” condition of the metal (table 1).

Table 1. Impurity uncertainty component evaluation based on the list of the most common impurities in tin. Elements that were not determined in the ICP-OES analysis are marked as ND.

Assay element	Atomic weight g/mol	Detection limit ppm	Influence ppm	Number of atoms	Mole fraction %
Ag	107,87	0,1	5,0E-08	4,64E-10	5,50E-08
Al	26,98	0,1	5,0E-08	1,85E-09	2,20E-07
As	74,92	5,0	2,5E-06	3,34E-10	3,96E-06
Bi	208,98	0,1	5,0E-08	2,39E-10	2,84E-08
Ca	40,08	0,1	5,0E-08	1,25E-09	1,48E-07
Cl	35,45	ND	ND	ND	ND
Co	58,93	0,5	2,5E-07	4,24E-09	5,04E-07
Cu	63,55	0,5	2,5E-07	3,93E-09	4,67E-07
Fe	55,85	0,1	5,0E-08	8,95E-10	1,06E-07
Ge	72,61	0,1	5,0E-08	6,89E-10	8,17E-08
In	114,82	0,2	1,0E-07	8,71E-10	1,03E-07
Mg	24,31	0,1	5,0E-08	2,06E-09	2,44E-07
Mn	54,94	0,1	3,5E-08	6,37E-10	7,56E-08
Na	22,99	ND	ND	ND	ND
Ni	58,69	0,5	2,5E-07	4,26E-09	5,06E07
P	30,97	ND	ND	ND	ND
Pb	207,20	0,3	1,5E-07	7,24E-10	8,59E-08
S	32,07	ND	ND	ND	ND
Sb	121,76	0,3	1,5E-07	1,23E-09	1,46E-07
Si	28,09	0,1	5,0E-08	1,78E-09	2,11E-07
Ti	47,87	1,0	5,0E-07	1,04E-08	1,24E-06
Mole fraction sum of impurity concentrations					8,18E-06
1 st cryoscopic constant for Sn, K ⁻¹					0,003377
Estimated impurity uncertainty component value, mK					2,42

Again, if checked the consistency of this prediction based on the theoretical list with the other methods described in [5], it is possible to verify it is rather underestimating the metal purity. Then, it was decided to try to determine the impurities of the sample through other types of analysis. The only type available was XRF (X-ray Fluorescence) in the Materials Metrology Division at Inmetro. The results pointed out the following impurities: aluminium, calcium, chromium, iron, indium, nickel, silicon and strontium. As this analysis was qualitative, the calculations were made using the elements detected by this technique and applying the correspondent detection limits of the ICP-OES. This estimate resulted in an impurity concentration of 1,6E-06, corresponding to 0,46 mK. Although not the best estimate, once it was not quantitative on its own, it provided a more realistic estimate of the metal sample.

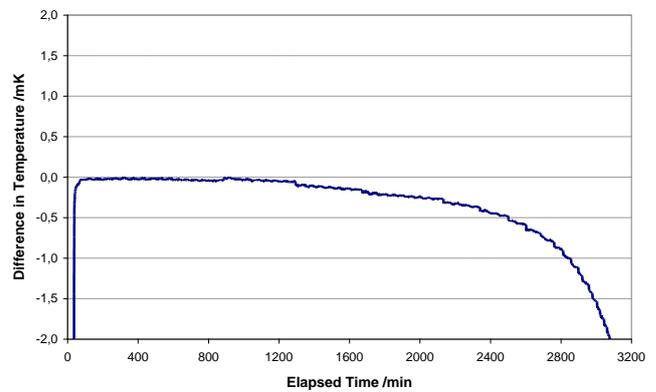


Fig. 2. First slow Freeze of Sn-2010. Duration of ~ 40 hours.

Using the freezing curve method it is possible to check the consistency of the previous method (pre-fabrication of the cell). In this case, the value achieved for the impurity concentration was 1,4 ppm, which represents 0,42 mK. This fact suggests that the effects of possible contamination during the manufacturing process were minimal, which can be seen in fig. 2, where half of the freezing plateau occurs within 0,05 mK. These values were calculated through a linear regression from the values representing 20% ($F_{0,2}$) and 70% ($F_{0,7}$) of the sample frozen. After that, it was mirrored from 50% to 0% ($\Delta T = F_{0,5} - F_0$), to determine the slope and the impurity concentration.

The freezing curve shown in fig. 2 had a duration of 40 hours, with the temperature of the furnace set to 0,3 °C below the freezing point of Tin.

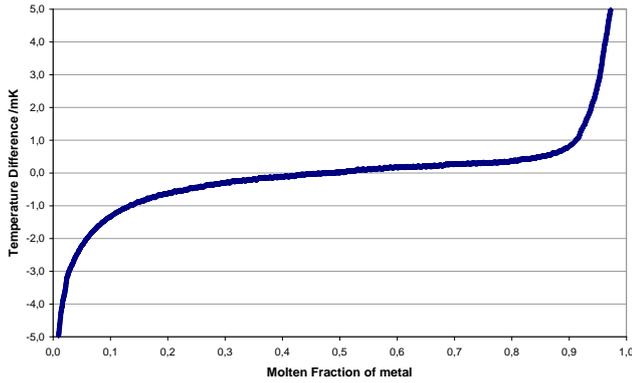


Fig. 3. First slow melt of the cell Sn-2010. Duration of ~ 52 hours.

Similarly, the melting point was realised with the temperature of the furnace set to 0,3 °C above Tin melting point, as shown in fig. 3. The melting point was used as another alternative to estimate the mole fraction impurity concentration in the cell. In order to do this, a linear regression from the correspondent value of $1/F_{1,5}$ to $1/F_5$ was used to determine the slope of the $1/F$ plot. After that, this regression made it possible to calculate the difference in temperature from $1/F_1$ to $1/F_0$, denoted $\Delta T(1/F_1 - 1/F_0)$. This was done for both melting and freezing curves, plotted as difference in Temperature ΔT as a function of the reciprocal fraction frozen or molten.

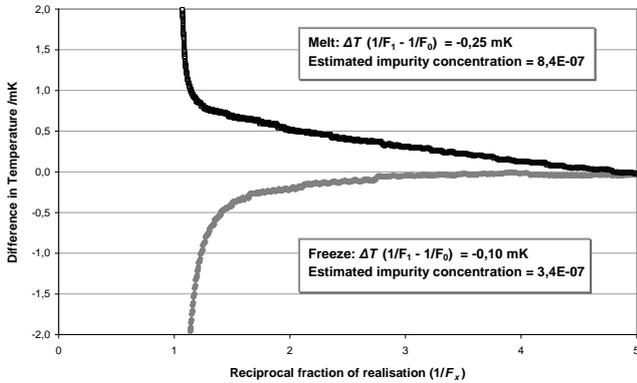


Fig. 4. $1/F$ realization-curve method for Sn-2010-01.

It is worth mentioning the fact that the values obtained from the mole fraction sum of impurities and the freezing curve method were compatible. However, when it comes to the $1/F$ melting curve realization, the linear regression $\Delta T(1/F_1 - 1/F_0)$ resulted in a value more than three times greater than the ones related to the freezing curves (post-fabrication evaluation). Besides, this was greater than the value calculated for the metal prior to the fabrication of the cell (pre-fabrication evaluation), as shown in detail in table 1.

Table 2. Summary of the different methods of evaluating the impurity uncertainty component

Method, in order of priority	Estimated impurity concentration	Estimated impurity uncertainty component, mK
mole fraction sum of impurities	1,6 E-06	0,46
freezing curve	1,4 E-06	0,42
$1/F$ (freeze)	3,4 E-07	0,10
$1/F$ (melt)	8,4 E-07	0,25

It is important to stress that table 2 presents the results in order of priority (confidence, supposedly), according to NIST. Hence, the $1/F$ melting curve would be the least reliable value utilized and recommended by them. Reference [4] states that there is a limitation in using the melting curve to estimate the purity of the metal using the $1/F$ realization curve method due to the fact that the slope of a melting curve depends on the previous freezing of the cell: a slow freeze (> 10 h) causes the impurities to be segregated by zone refining, which causes the slope of the following melting curve to be maximized. On the other hand, a quick freeze (< 30 min) causes a homogeneous mixture of the impurities within the ingot, providing a minimized slope.

On account of these facts, prior to all melting point realizations, a *reset* in the cell was carried out in order to guarantee that the results would present the minimum slope due to impurity segregation. This *reset* was made by a fast cycle of melting and freezing, having the furnace adjusted 5 °C above the melting point, and then, after at least 10 h of wait so that impurities could be well distributed in the ingot, 5 °C below the freezing point. Despite this, as shown in figs. 3 and 4, the slope reached about 1,0 mK ($\Delta T = F_{0,7} - F_{0,2}$), hence amplifying the linear regression result. As for the freezing point, this process was satisfactory.

Table 3. Summary of the comparison between the cells Sn-2010 and the reference cell from Leeds & Northrup

#	Ref cell Ω	Test cell Ω	Difference Ref - Test mK
1 st	48,299 230	48,299 225	0,045
2 nd	48,299 206	48,299 211	-0,046
3 rd	48,299 203	48,299 200	0,047
	Average difference /mK		0,015
	Hydrostatic Head Correction /mK		-0,053
	Result of Comparison (Ref - Test) /mK		-0,037

When compared to the laboratory reference cell, a Leeds & Northrup open cell, the Sn-2010 tin cell presented an equivalent freezing temperature. The hydrostatic head correction is due to the difference between the immersions

of the cells, being the reference cell 24 mm longer than the test cell. This difference means that the reference cell would read 0,053 mK higher than the test cell. After all corrections due to the differences in the design of the cell (SPRT self-heating effect and hydrostatic head), the cell Sn-2010 presented a temperature value of 0,04 mK higher than the reference cell, with an uncertainty of $\pm 0,60$ mK ($k=2$).

It is important to notice that it is not a method for estimating the impurity uncertainty component as described in [5], which compares 2 or 3 cells made from the same metal lot, in the same period of time, using the same procedure. This method is based on the assumption that the difference between them ($A \times B$; $B \times C$, etc) can reveal their impurity concentration. Theoretically, this difference should be null, but it takes into account that a possible contamination occurred during the fabrication of one or more cells, or even the fact that non-homogeneity due to impurity segregation during the fabrication of the metal lot (indicating that a certain portion of shots could have a greater amount of impurities concentrated on them) would result in cells with different behaviours. This can represent differences of more than 0,1 mK for a 6N Indium cell [5].

For the purpose of this investigation it is not applicable due to the fact that we only produced a single Sn cell. Then, as a means of comparison, a direct comparison with a reference cell (commercially available) took place.

It is also worth mentioning that the Leeds & Northrup cell was compared, indirectly, to the Tin cells from NIST and PTB, the first one through a comparison within the Inter-American Metrology System - SIM, still not published.

7. CONCLUSIONS

Despite the encouraging results, there is still space for further improvements in the construction process as well as in the qualification procedure itself. This can be done, for instance, by using more advanced filling techniques such as the one by Yamazawa et al. [7].

One possibility to better qualify the cell is to analyse the pure material by a different chemical process, like instead of ICP provided by the metal supplier, the Glow Discharge Mass Spectrometry – GDMS – which presents much lower detection limits, achieving ppb resolution. This will be particularly helpful to validate the results from the thermal analysis (freezing curve method).

Another possibility of cell qualification is to take a sample from the assembled Tin cell, in order to check if the construction procedure did not add impurities in detectable levels. Unfortunately, this possibility is only achievable if the cell was disassembled and not used as a temperature reference anymore.

The Sn FP cell constructed at Inmetro shows a performance at least equivalent to the laboratory reference cell. The results available point to metal purity of more than 6N. These results compare favourably to those from the chemical assay. This motivates the construction of other cells from different metals, In being the next candidate.

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