PERFORMANCE OF A REPAIRED WATER TRIPLE POINT CELL IN BRAZIL

S. G. Petkovic, J. F. N. Santiago, M. S. Monteiro, R. N. Teixeira, and P. R. F. Santos

National Institute for Metrology , Standardisation and Industrial Quality, INMETRO
Rio de Janeiro, Brazil

ABSTRACT

The water triple point is the most important fixed point of ITS-90 and fundamental for measurements with resistance thermometers. The Thermometry Laboratory of the National Institute for Metrology, Standardisation and Industrial Quality, INMETRO, has been working with water triple point cells since 1981. In order to acquire the necessary technology to build a water triple point cell, it was decided to repair a broken one and to investigate the performance and stability of the repaired cell.

The cell had a small hole at the bottom of the thermometer well and was fixed in 1996 at the glass workshop of the Brazilian Physical Research Center, CBPF, by a skilled glassmaker. Afterwards, with the help of a chemist, the cell was submitted to chemical cleaning and filled with distilled water and then sealed.

This paper presents the comparison results of this repaired cell with others cells from different manufactures.

1. INTRODUCTION

The fundamental definition point of the Thermodynamic Scale of Temperature is the triple point of water (TPW). It is also the most important fixed point in International Temperature Scale of 1990 (ITS-90)[1] and it has the value of 0,01°C (273,16 K). It is suitable to calibrate primary gas thermometers that will determine the temperatures of the other fixed points of ITS-90. In the International Scale of Temperature, the interpolations equations based on Standard Platinum Resistance Thermometers (SPRT's) use the measurements in the triple point of water to obtain the resistance ratio (W) in each fixed point. As W = R(T)/R(0,01°C), in which R(T) is the resistance of the thermometer measured at a fixed point and R(0,01°C) is the measure of the resistance of the thermometer in the triple point of water, it is important to know the accuracy of the measurements in TPW and its reproducibility, because the uncertainties in R(0,01°C) are propagated in W.

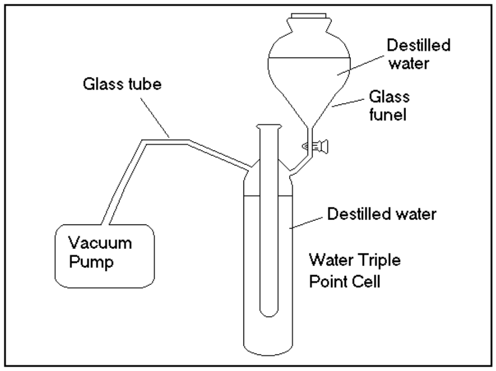
The uncertainties of the triple point of water cells are within 0,1mK (k=2) and the maximum difference found in the comparisons with the repaired cell (PTB s/n 10-77) was approximately –0,20mK (value found with respect to the cell PTB s/n 221).

The data shown refer, mainly, to the comparisons done between the cell PTB 10-77 and the cell PTB 221, the one which was compared at BIPM in 1996, when a difference of the order of 0,065 mK in relation to the reference of the Bureau was obtained [2]. The cells CENAM s/n 420-A-024, ISOTECH s/n 483 were also used, indicating similar results.

2. REPAIR OF THE CELL PTB 10-77

The cell had only a small hole at the bottom of the thermometric well, which made it easier to repair. The procedure used to the repair was: 1) to remove the water; 2) to divide the cell in two parts along the diameter at the bottom zone; 3) to weld the glass thermometric well; 4) to fasten the two separate parts of the cell, restoring its borosilicate glass structure; 5) to open the two short filling glass tubes at the cell top zone; 6) to wash the cell internal parts with chemical products; 7) to wash the cell internal parts with distilled water; 8) to immerse the cell in distilled water during seven days; 9) to empty the cell; 10) to fasten two borosilicate tubes (washed) with 5 cm long at two short filling glass tubes at the cell top zone; 11) to distil one litter water; 12) to put the distilled water into the borosilicate glass funnel (with valve); 13) to close the funnel with the glass stopper; 14) to weld the funnel glass tube at the cell filling glass tube; 15) to fix the cell and the funnel with two claws in vertical position; 16) to connect the high vacuum system at another filling glass tube to purge the air inside the cell with the vacuum pump (with 3 mbar vacuum); 17) to fill the cell with the distilled water, opening the funnel valve slowly (step by step until the air leave completely the water; 18) to finish the water filling operation when the level of water reaches approximately 5 cm bellow the top; 19) to cut and to weld the two filling glass tubes, sealing the cell; 20) to anneal the cell top zone to finish the repair, cooling the cell slowly. This procedure lasted approximately 6 hours (welding, air purging, water filling, cell sealing and annealing).

Figure 1 – Filling of the cell



3. MEASUREMENT EQUIPMENT

An AC Bridge from Automatic System Laboratory to perform the measurements, model F18 with standard resistor from H.Tinsley (100Ω s/n 236063 and 25Ω s/n 236233) immersed in a controlled oil bath Guildline model 9732 VT was used. During the measurements the oil temperature was 20,01°C ±0,01°C.

The main comparisons between cell PTB 10-77 and cell PTB 221 were performed by to 25Ω SPRT from H. Tinsley model 5187A s/n 238698 and it was also used SPRT's HART s/n 5680-5-1022 and Leeds & Northrup s/n 1720580.

A Guildline bridge model 9975, using standard resistors H.Tinsley (100Ω s/n 236063) and H.Tinsley (10Ω s/n 265973), maintained in a thermostatic enclosure with temperature controlled at 36°C, this last one was used in comparisons of the cell PTB 10-77 with the cells ISOTECH 483 and CENAM 420-A-024 (in 2001 these measurements were performed using the bridge F18 and standard resistor s/n 236233).

4. PROVENANCE OF THE CELLS

The cells PTB 10-77 and PTB 221 were donated to INMETRO by Physicalische-Technische Bundesanstalt (PTB) and the cell PTB 221 was certified with the uncertainty of ±0,2 mK in November 1978. The cell ISOTECH 483 was certified with the uncertainty of ±0,1 mK in December 14th, 1978, by NPL and the cell CENAM 420-A-024, was certified with ±0,02 mK in March 10th, 1997.

5. WTP STORAGE APPARATUS

The main comparisons between the cells PTB 221, CENAM 420-A-024 and PTB 10-77 were accomplished maintaining the cells in a DEWAR vase with ice. They were kept in that big vase, separated from the ice by PVC tubes. Its thermometric wells were half filled with distilled water and its extremities were protected to avoid the presence of particles of ice in its interior.

The cell ISOTECH 483 and was kept in a water triple point bath from ISOTECH. This bath contains about 34 litres of water, which is stirred with air bubbles supplied by a pump. The temperature of the water is maintained at 0,010°C by four thermoelectric cooling modules. The proportional controller controls the current through the cooling modules with high stability.

6. PROCEDURE TO BUILD THE MANTLE

The mantle of cells PTB 10-77, ISOTECH 483 and PTB 221 in the comparisons performed in 1997 were prepared inserting repeatedly a liquid nitrogen cooled rod into the well which contained alcohol. Once the mantle was ready and the well of the cell cleaned, the small amount of new pre-cooled water was poured into it to improve the thermal contact between the cell and the thermometer. The TPW cell was allowed to rest for about 24 hours before na acrylic rod was introduced into the cell in order to melt the thin layer of ice next to it.

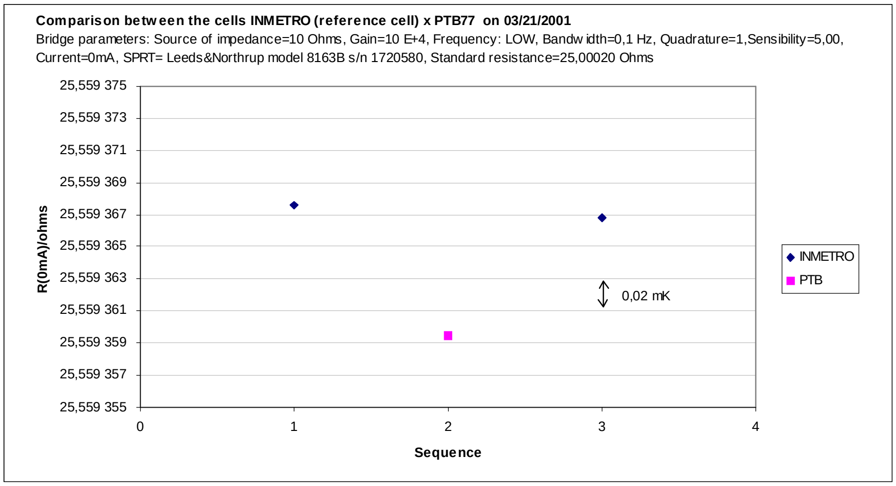
After 1997, the mantles of cells were prepared inserting crushed solid-CO_2 inside the well. Initially little piece of crushed solid-CO_2 were introduced into the well and pressed against the bottom by an acrylic rod. When an initial mantle was formed at the end of the thermometric well, more crushed solid-CO_2 was filled in to form the mantle and its size and growth were controlled with the aid of a copper stem. After prepared, the cell was kept in a big DEWAR vase with ice.

7. METHODOLOGY AND RESULTS

The comparisons performed in 1997 began in May 14th, approximately one year after the repair of the cell PTB 10-77. In that month another comparison was performed in our lab and in May 14th the cell PTB 10-77 was prepared in the morning and the first measurement against cell PTB 221 were obtained in the afternoon with SPRT HART s/n 5680-5-1022. The measurements were performed with the bridge ASL F18 and the same thermometer H.Tinsley 5187^{A} s/n 238698. The mantles of the cell were loosened as described in 6 and the thermometer was left in each cell by 30 minutes before the measurements started.

The values measured by bridge ASL F18 were taken automatically at regular intervals for a period of about 20 to 30 minutes for 1 mA, 1,41 mA and 1 mA currents. These values were taken by the computer and stored in a file. The program developed at INMETRO only takes into account the last of three successive measurements in equilibrium taken by the bridge. The total data were about 15 or more values measured for every current. One of these data can be seen in graph 1.

Graph 1: Comparison of cells INMETRO x PTB



The usual procedure to compare water triple point cells is to prepare them as the method described in item 6 and to start the measurements after 24 hours. Normally five days are enough to perform the comparison. But 7 days are recommended to detect problems related to the ageing of the mantles [3]. This was accomplished by the fact of the measurements be separated by more days, without the mantles had been melted. The cells PTB 10-77 and PTB 221 were conserved during months in DEWAR vases.

As there were other comparisons in course in the laboratory, the cells were conserved during the whole year of 1997 and some measurements were performed with other thermometers and other cells. This result is showed, but in order to calculate the uncertainties it was used four data groups: group 1 — 05/19/1997, 05/20/1997 and 05/28/1997; group 2 — 05/19/1997, 05/20/1997, 05/28/1997 and 09/10/97; group 3 — 07/06/98, 07/07/98 and 07/24/98 and group 4 — 03/06/01, 03/07/01, 03/12/01, 03/14/01 and 03/21/01. They are related in table 1.

Table 1: Results of Comparisons

Cell rep. – Cell ref.	DATE	SPRT	Bridge	dif./mK
PTB 10-77 – PTB 221	05/14/97	Hart	ASL F18	-0,06
PTB 10-77 – ISO 483	05/15/97	Tinsley	Guildline	-0,07
PTB 10-77 – PTB 221	05/19/97	Tinsley	ASL F18	-0,15
PTB 10-77 – PTB 221	05/20/97	Tinsley	ASL F18	-0,14
PTB 10-77 – PTB 221	05/28/97	Tinsley	ASL F18	-0,12
PTB 10-77 – PTB 221	06/23/97	Tinsley	Guildline	-0,12
PTB 10-77 – PTB 221	09/10/97	Tinsley	ASL F18	-0,19
PTB 10-77 – PTB 221	09/10/97	Tinsley	ASL F18	-0,17
PTB 10-77 – CENAM	02/11/98	Tinsley	Guildline	-0,09
PTB 10-77 – PTB 221	07/02/98	Leeds	ASL F18	-0,08
PTB 10-77 – PTB 221	07/06/98	Tinsley	ASL F18	-0,09
PTB 10-77 – PTB 221	07/06/98	Tinsley	ASL F18	-0,05
PTB 10-77 – PTB 221	07/07/98	Leeds	ASL F18	-0,11
PTB 10-77 – PTB 221	07/24/98	Tinsley	ASL F18	-0,09
PTB 10-77 – CENAM	03/06/01	Leeds	ASL F18	-0,07
PTB 10-77 – CENAM	03/07/01	Leeds	ASL F18	-0,08
PTB 10-77 – CENAM	03/12/01	Leeds	ASL F18	-0,08
PTB 10-77 – CENAM	03/14/01	Leeds	ASL F18	-0,09
PTB 10-77 – CENAM	03/21/01	Leeds	ASL F18	-0,08

The data presented in this paper refer to the zero-power dissipation values and also include corrections for the hydrostatic head of the cells.

8. UNCERTAINTIES OF THE RESULTS

The evaluation of the uncertainty was made for a sample of the measures (see paragraph 1 of the item 7). The comparisons between cell PTB 221 and cell PTB 10-77 and cell CENAM 420-A-024 and cell PTB 10-77 used the same SPRT and bridge to get the difference in temperature. The following uncertainty components were taken into account:

Type A:
This type of uncertainty consider the measurement results under the following conditions:
Same bridge, SPRT, standard resistor and isothermal enclosure with one ice mantle realisation.
s_{dev}(cnm24) and s_{dev}(ptb77) - Standard deviation of a single measurement to reference cell and testing cell.

Type B:
Considering that the measurements were taken with the same bridges, standard resistors and SPRT for both cells in a short period of time and the stability of standard resistors was about 1 ppm/yr, the uncertainty of the bridges was not taken into account in the evaluation of type B uncertainties. It was not considered also other type B uncertainties like: SPRT heat flux, SPRT equilibrium with TPW, SPRT resistance leakage, water purity, etc [4].

Uncertainty due to the stability of standard resistors during the comparison (u_{rs})
Uncertainty due to hydrostatic head (u_{cch})
Uncertainty due to self heating (u_{sh})
Uncertainty due to due to difference between the cells (u_{dif})
Uncertainty due to electrical measurement (u_{em})

Table 2: Results of the comparison between test cell and reference cells.

	(Test Cell – Reference Cell)	Average difference /mK	Uncertainty / mK (k=2)
Case A – Group 1	PTB 10 77 – PTB 221	-0,14	±0,20
Case B – Group 2	PTB 10 77 – PTB 221	-0,15	±0,20
Case C – Group 3	PTB 10 77 – PTB 221	-0,08	±0,20
Case D – Group 4	PTB 10 77 – CENAM 024	-0,08	±0,05

Table 3: Uncertainty budget of the difference between the cells CENAM 420-A-024 and PTB 10-77 Group 4

Symbol	**Value ±**	**Unit**	**Probability distribution**	**Divisor**	C_i	**Unit**	$u_i(Rx)$ **± mK**	ν_i **or** ν_{eff}	u_i^4/ν_i
s_{dev}(cnm24)	8,68E-07	Ω	normal	1	9,81E+03	MK/Ω	0,009	30	2,E-10
s_{dev}(ptb77)	6,00E-07	Ω	normal.	1	9,81E+03	MK/Ω	0,006	30	4,E-11
u_{rs}	2,50E-07	Ω	rectangular	1,732	9,81E+03	MK/Ω	0,001	inf.	0
u_{cch}	2,00E-02	mK	rectangular	1,732	1,00E+00		0,012	inf.	0
u_{sh}	2,91E-02	mK	rectangular	1,732	1,00E+00		0,017	inf.	0
u_{dif}	2,00E-02	mK	rectangular	3,464	1,00E+00		0,006	inf.	0
u_{em}	8,00E-03	mK	rectangular	1,732	1,00E+00		0,005	inf.	0
U_c	Comb.Uncert.		normal				**0,02**		
U_e	Exp. Uncert.	(k =2)	normal				**0,05**		

9. CONCLUSIONS

All the results show the temperature of the cell PTB 10-77 is lower than the reference cells — mainly the cell PTB 221. The average difference between the cell PTB 10-77 and the cell PTB 221 was –0,14 mK ±0,20 (k=2) considering 3 measurements in May, 1997, separated with maximum interval of 8 days. This difference (group 1) changed the value to –0,15 mK ±0,20 mK (k=2) (group 2), showing that the age of the mantles, in this case, did not have a positive influence.

In the measurements performed in 1998 (group 3), the difference assumed the value –0,08 mK ±0,20 mK (k=2). In this case, the difference in the methodology of the comparison was in the procedure to build the mantles (crushed solid CO_2), explained with details in [3].

The uncertainty ±0,20 mK obtained for groups 1, 2 and 3 were due to electrical measurements mainly. However, the cell PTB 221 showed slightly worse results than the other reference cells. So, the cell CENAM 420-A-024 was used as reference cell in 2001 and the difference between this cell and PTB 10-77 was –0,08 mK ±0,05 mK (k=2).

Although this cell (a Type B cell with moderate vacuum) has shown values lower than reference cells, we used it as reference for SPRT in comparison calibrations. It possible to use it in fixed-point calibrations, performed with uncertainties in the order of ±1 mK to ±4 mK (k=2) (in the range –39°C to 420°C), for example. Better results might be obtained in the future when the next triple point of water cell can be manufactured more carefully using the same method or another.

ACKNOWLEDGEMENTS

The authors thank Maurício Araújo Soares and Fernando Antonio L. Goulart for grammatical review and the chemist (Elena Mavropoulos) and the glassmaker from CBPF for technical support in the repair of the cell.

REFERENCES

1. Preston-Thomas H., Quinn T.J. and Bloembergen P., *Supplementary Information for the International Temperature Scale of 1990, BIPM*, 1990, 29-35
2. Pello R., Goebel R. and Koehler R., *Report on the International Comparison of Water Triple Point Cells*, BIPM, 1996
3. Furukawa G.T., Mangum B.W. and Strouse G.F, *Metrologia*, 1997, **34**, 215-233
4. Marcarino P., Dematteis R., Comparison of Triple Point of Water Cells (Report on IMGC measurements – BIPM comparison), 1995

Addresses of the Authors:

Slavolhub Garcia Petkovic – Instituto Nacional de Metrologia, Normalização e Qualidade Industrial, Divisão de Metrologia Térmica – Av. N. Sra. das Graças, 50 – Xerém – Duque de Caxias – RJ – Brasil – 25250-020
e-mail: sgpetkovic@inmetro.gov.br, Internet: http://www.inmetro.gov.br