Int J Thermophys (2008) 29:815–824
DOI 10.1007/s10765-008-0392-2

The Long-Term Drift of Triple-Point-of-Water Cells

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Published online: 4 March 2008

Abstract As the triple point of water is of great importance for the International Temperature Scale of 1990 (ITS-90) and for the definition of the unit of thermodynamic temperature, its long-term stability has attracted a great deal of attention. In a study of long-term stability, a mystery has been uncovered. Some triple-point-of-water cells remain stable for many decades, while others decrease with increasing age of the cells, which is called long-term drift. To investigate this mystery, we used cells with different manufacture dates ranging from 1974 to 2002 and compared their analyses, which were done in 1984 and 2003. Using the same model of long-term drift as that used by Hill, the long-term drift rates of the two data sets are $-4.7\,\mu K \cdot year^{-1}$ and $-9.2\,\mu K \cdot year^{-1}$, respectively. One is consistent with the observed depression of about $-4\,\mu K \cdot year^{-1}$ measured by Hill, whereas the other differs greatly from Hill's result. In addition, corresponding factors influencing long-term drift are discussed in this paper.

Keywords International Temperature Scale of 1990 (ITS-90) · Long-term drift · Residual air · Solubility of borosilicate glass · Triple point of water

1 Introduction

Over approximately the last decade, the long-term stability of triple-point-of-water (TPW) cells has attracted a great deal of attention in the thermometry field, since

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the TPW plays an important role in realizing and disseminating the International Temperature Scale of 1990 (ITS-90) [1] and in defining the unit of thermodynamic temperature.

To study the long-term stability, research has been carried out at several national metrology institutes (NMIs) such as the National Research Council of Canada (NRC). In 1997, Hill [2] compared cells that had been fabricated between 1954 and 1997. Some cells appeared to remain stable for decades while others decreased with increasing age of the cells, a phenomenon called long-term drift. To find an answer to this problem, inductively coupled plasma mass spectrometry (ICPMS) [3] was used to analyze the water purities. According to this chemical analysis, the relative concentrations of the predominant elements in water were very similar to those in borosilicate glass. As a result, Hill concluded that the long-term drift was mainly caused by the solubility of borosilicate glass. Based on the assumption that the equilibrium temperature changes in the cells are continuous and linear with time, Hill proposed a simple model to predict the behavior of cells with time. According to these assumptions and experimental results, Hill suggested that it should be appropriate to use a decrease of 4 μK per year to describe the average behavior of TPW cells [4].

Since cells made of glass are breakable, it is rather difficult for NMIs to possess many old cells to keep track of their behavior. Therefore, few NMIs other than NRC have undertaken such investigations. Fortunately, the National Institute of Metrology (NIM) has continued to investigate four old cells as well as many new cells, so that relevant experiments could be performed to investigate the long-term drift. This paper will describe our research results.

2 Experiment

Seven TPW cells with different manufacture dates ranging from 1974 to 2002 were used, as listed in Table 1.

Comparison experiments were performed in 1984 and again in 2003. Four cells (s/n 69, s/n72, s/n 92, and s/n 83-1) were compared against the reference cell (s/n 148) in 1984, and the four old cells (s/n 69, s/n 72, s/n 92, and 148) with two new reference cells (s/n 2002-011 and s/n 2002-021) in 2003. In these comparisons, two Guildline 9975 resistance bridges were employed to measure the resistances of stan-

Table 1 Description of triple-point-of-water cells

Identification	Year of fabrication	Inner diameter of the thermometer well (mm)	Outside diameter (mm)	Overall length (mm)
69	1974	12	60	340
72	1976	12	60	340
92	1978	12	60	340
83-1	1983	12	60	340
148	1984	12	60	340
2002-011	2002	12	60	400
2002-021	2002	12	60	400

Table 2 Uncertainty budget

Component	Type	Standard uncertainty (mK)
Reproducibility	A	0.017
Isotopic compositions	A	0.022
Impurities	B	0.017
SPRT Self-heating	A	0.021
Residual gas pressure	B	0.003
Perturbing heat exchanges	B	0.014
Non-linearity and precision of the bridge	B	0.035
Temperature variation of the bath	B	0.002
Different SPRTs	B	0.002
Combined standard uncertainty	0.054 mK	
Expanded uncertainty	0.108 mK ($k = 2$)	

dard platinum resistance thermometers (SPRTs) at the TPW. In the first experiment, one SPRT (s/n 149417) was utilized, and two SPRTs (s/n 400131 and s/n 400150) in the second. Moreover, our usual freezing method, the liquid-nitrogen technique [5,6], was applied to form ice mantles, and an ice bath [6] was used to store them. Measurements began 7 days after forming the ice mantles.

The expanded uncertainty in measuring the temperature differences between pairs of cells is evaluated as 0.108 mK. The detailed uncertainty budget is shown in Table 2. Unfortunately, we have no knowledge regarding the isotopic compositions and chemical impurities of the water in the old and new cells. However, effects of isotopic composition on the triple-point temperature of water have been investigated using similar new cells with known isotopic compositions, and the results have been published [7].

3 Results and Discussion

Comparison results obtained with the SPRT (s/n 149417) are shown in Table 3. Note that there are no apparent discrepancies between the cells. According to the simple model of long-term drift rate adopted by Hill [4], the average drift rate is −4.7 µK per year. The linear relationship for this drift rate is shown in Fig. 1 with our comparison results from 1984.

However, based on the comparison results given in Table 4 from 2003, we arrived at a different average drift rate of −9.2 µK per year, after omitting an abnormal cell (s/n 92) because it contains excess air as indicated by the water hammer test. Strangely, the mean temperature of the oldest cell (s/n 69) was the lowest in the comparison undertaken in 1984, whereas it was the hottest among the old cells in the 2003 comparison. It was 0.19 mK lower than the reference cells (s/n 2002-011 and s/n 2002-021) in 2003 (Table 4).

The measured differences cannot be attributed solely to the solubility of borosilicate glass since the old cells and the new cells were fabricated using different production processes at NIM. In the first comparison, the five cells were constructed according to our old production procedure [8], while the new cells used in 2003 were made

Table 3 Comparison results with SPRT (s/n 149417) in 1984

Measurement date	R_{TPW}[a] (s/n 69) (Ω)	R_{TPW} (s/n 72) (Ω)	R_{TPW} (s/n 83-1) (Ω)	R_{TPW} (s/n 92) (Ω)	R_{TPW} (s/n 148) (Ω)
Oct. 26, 1984	24.283379	24.283377	24.283372	24.283380	24.283379
	24.283378	24.283376	24.283382	24.283374	24.283383
Oct. 27, 1984	24.283382	24.283381	24.283385	24.283381	24.283383
	24.283380	24.283379	24.283386	24.283379	24.283383
Oct. 29, 1984	24.283383	24.283386	24.283385	24.283383	24.283384
Oct. 30, 1984	24.283377	24.283379	24.283386	24.283381	24.283383
	24.283374	24.283375	24.283386	24.283375	24.283381
Oct. 31, 1984	24.283379	24.283383	24.283386	24.283384	24.283385
	24.283381	24.283386	24.283389	24.283383	24.283386
Mean of R_{TPW}	24.283379	24.283380	24.283384	24.283380	24.283383
ΔT[b] (mK)	−0.04	−0.03	0.01	−0.03	0.00

[a] Resistance of the SPRT at the TPW
[b] Mean temperature difference between cell × and the reference cell (s/n 148)

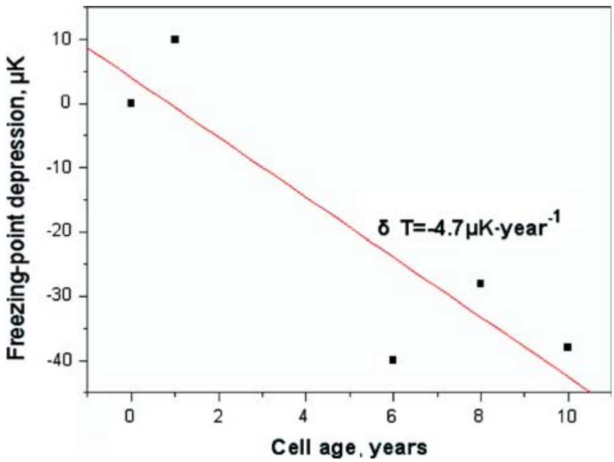

Fig. 1 Freezing-point depression of five old triple-point-of-water cells measured at NIM in 1984, as a function of cell age

according to our new procedure [9]. The new cells are of better quality than the old cells, as indicated by a sharper 'click' when performing a water hammer test.

The cell (s/n NIM 255) made in 1984 using the old production procedure took part in the comparison organized by the Bureau International des Poids et Mesures (BIPM) in 1998. The comparison results [10,11] showed that it was 0.14 mK lower than the average value of two BIPM reference cells (KRISS-1 and ASMW-131). The NIM national reference consisting of three new cells that were compared to the NIM transfer cell (NIM-1-08) used in the CCT-K7 key comparison of water triple-point cells was shown to realize a mean temperature 0.03 mK higher than that of the same BIPM reference cells [12]. Consequently, manufacturing processes could influence the realized temperature of the TPW. Since a comparison of the new cells (s/n 2002-011

Table 4 Comparison results with two SPRTs (s/n 400131 and s/n 400150) in 2003

Measurement date	R_{TPW}[a] (s/n 69) (Ω)	R_{TPW} (s/n 72) (Ω)	R_{TPW} (s/n 92) (Ω)	R_{TPW} (s/n 148) (Ω)	R_{TPW} (s/n 2002-011) (Ω)	R_{TPW} (s/n 2002-021) (Ω)
SPRT (s/n 400131)						
Jun. 11, 2003	25.038617	25.038609	25.038564	25.038608	25.038639	25.038641
Jun. 12, 2003	25.038616	25.038606	25.038565	25.038612	25.038639	25.038643
Jun. 13, 2003	25.038616	25.038603	25.038571	25.038607	25.038635	25.038638
Jun. 15, 2003	25.038621	25.038598	25.038570	25.038609	25.038634	25.038637
Jun. 16, 2003	25.038623	25.038604	25.038577	25.038611	25.038638	25.038639
Jun. 17, 2003	25.038619	25.038600	25.038579	25.038609	25.038631	25.038637
Mean of R_{TPW}	25.038619	25.038603	25.038571	25.038609	25.038634	25.038639
ΔT_1^{b} (mK)	−0.182	−0.333	−0.659	−0.277	−0.024	0.024
SPRT (400150)						
Jun. 11, 2003	24.621118	24.621108	24.621057	24.621102	24.621140	24.621137
Jun. 12, 2003	24.621110	24.621107	24.621052	24.621105	24.621137	24.621135
Jun. 13, 2003	24.621111	24.621095	24.621067	24.621106	24.621135	24.621134
Jun. 15, 2003	24.621120	24.621100	24.621068	24.621110	24.621132	24.621138
Jun. 16, 2003	24.621118	24.621098	24.621072	24.621112	24.621132	24.621131
Jun. 17, 2003	24.621117	24.621105	24.621079	24.621108	24.621135	24.621136
Mean of R_{TPW}	24.621116	24.621102	24.621066	24.621107	24.621135	24.621135
ΔT_2^{c} (mK)	−0.190	−0.327	−0.695	−0.276	0.002	0.002
ΔT_3^{d} (mK)	−0.19	−0.30	−0.68	−0.28	−0.01	0.01

[a] Resistance of the SPRT at the TPW
[b] Mean temperature difference obtained with the SPRT (s/n 400131) between cell×and the reference cells (s/n 2002-011 and s/n 2002-021)
[c] Mean temperature difference obtained with the SPRT (s/n 400150) between cell×and the reference cells (s/n 2002-011 and s/n 2002-021)
[d] Mean temperature difference obtained with the SPRTs (s/n 400131 and s/n 400150) between cell×and the reference cells (s/n 2002-011 and s/n 2002-021)

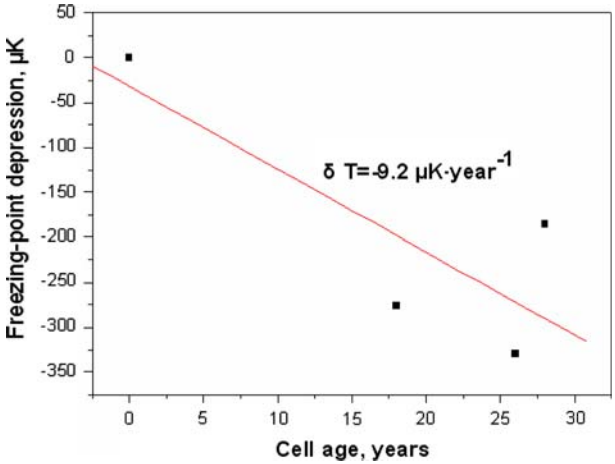

Fig. 2 Freezing-point depression of the triple-point-of-water cells measured at NIM in 2003, as a function of cell age

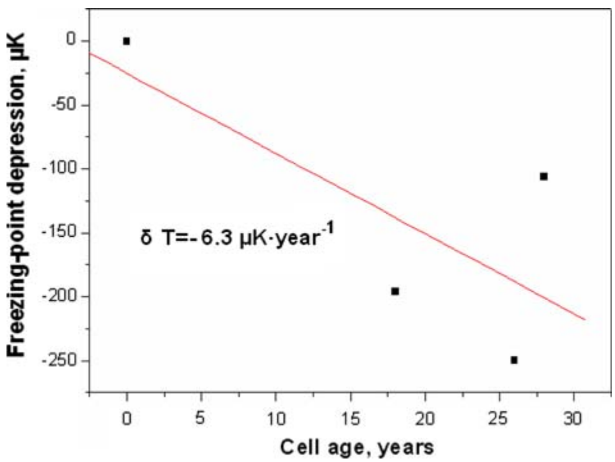

Fig. 3 Freezing-point depression of the triple-point-of-water cells measured at NIM in 2003, as a function of cell age after correcting for the difference arising from the production process

and s/n 2002-021) with the NIM cells participating in the CCT-K7 comparison could not be undertaken, it is difficult to link the comparison results to the CCT-K7 results.

We believe that it is more reasonable to compare the new ones with recently fabricated cells made using the old method as a means of determining an appropriate correction. Therefore, in March 2004, two new cells (s/n NIM-1-04 and s/n 2002-016) were compared against a cell (s/n 744) that had been manufactured using the old production procedure. The measured results indicate that this older cell is 0.08 mK colder than the new cells. If this correction is applied to the comparison results, the average long-term drift would be −6.3 μK per year, as shown in Fig. 3. This value may be a more suitable estimate of the long-term drift of the old cells at NIM.

Table 5 Summary of the data obtained for the 27 triple-point-of-water cells at NRC in 1997

Serial number	Date sealed	Age (years)	ΔT[a] (mK)	Serial number	Date sealed	Age (years)	ΔT[a] (mK)
201	1958	39	−0.84	1331	1985	12	−0.08
204	1958	39	−0.02	2053	1997	0	0.03
306	1959	38	−0.01	2061	1997	0	−0.03
387	1963	34	−0.30	T-224	1959	38	−0.10
463	1965	32	−0.24				
539	1966	31	−0.18	21	1954	43	−0.03
755	1975	22	−0.09	24	1954	43	−0.10
806	1978	19	−0.58	25	1954	43	−0.29
807	1976	21	−0.63	28	1954	43	−0.05
808	1978	19	−0.58	31	1954	43	−0.75
809	1978	19	−0.13	32	1954	43	−0.74
1199	1983	14	−0.09	26	1954	43	
1208	1983	14	−0.07	30	1954	43	

[a] Mean temperature difference between cell × and the reference cells (s/n2053 and s/n 2061)

In addition, the amount of residual gas in the sealed cell is also an important factor causing long-term drift. In general, the amount of gas in the sealed cell gradually increases with increasing age, since gases are released as a result of desorption or diffusion from the glass container with the gradual dissolution of the glass. An experiment was conducted to demonstrate this phenomenon. A newly fabricated cell (Type A) with an extension arm was used to entrap residual air to see the bubble diameter. At first, its diameter was less than one millimeter. Next, a spark leak detector was employed to emit sparks onto the extension arm. After about one minute, a larger entrapped bubble was observed after gases in the glass were released, resulting in much more residual gas accumulation in the cell. Furthermore, we observed that the bubble diameter increases with increasing age of the cell, indicating an increase of residual air in the cells. In conclusion, this observed phenomenon confirms that residual gases increase with increasing age.

Based on the above-mentioned inference, during investigations of long-term drift, those cells containing excessive air cannot be omitted, since accumulations of residual gases in the sealed cells are perhaps the result of increasing age. To evaluate Hill's conclusion without rejecting nine cells for various reasons, we considered Hill's experimental results obtained in 1997, as listed in Table 5. In that comparison, 19 cells were produced by the Jarrett Instrument Company and nine cells were made at NRC. Additionally, two cells (s/n 113 and s/n 744) without a manufacture date were omitted. To reduce the systematic differences between the two manufacturers, we first show comparison results of 17 cells from the same manufacturer and the corresponding fitted curve in Fig. 4. It can be seen that the average drift rate is −3.8 μK per year. Similarly, for all the cells, a separate average drift rate was calculated; it is about −4.0 μK per year, as shown in Fig. 5.

In addition, in this comparison, cells (s/n 26 and s/n 30) were opened once, pumped, and resealed to renew them to a satisfactory condition [2]. As this renewal cannot eliminate the dissolved air in the water when opening the cells, the residual gases in the

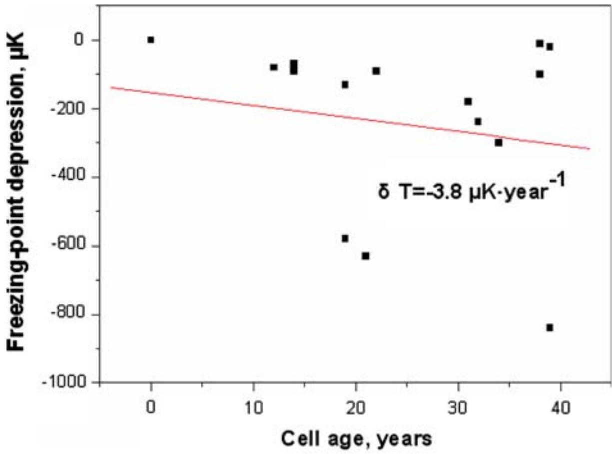

Fig. 4 Freezing-point depression of the cells manufactured by the Jarrett Instrument Company that were measured at NRC in 1997

cell could bring about the freezing-point depression. Thus, in our analysis, they were also omitted.

Another experiment at NIM on the freezing-point depression was carried out to investigate the effects of residual air in the sealed cell. Two cells (s/n NIM-1-185 and s/n NIM-1-70) were filled with distilled water, then pumped and sealed. The whole procedure is very similar to the one that Hill used. Also, when testing the "water hammer," they did not give a clicking sound, and a lot of bubbles were observed, indicating that a large amount of residual air was present in the cells. Then, these two cells were compared with cells (s/n 2002-007 and s/n 2002-009) made in accordance with the new production procedure [9]. A comparison of the results shows that cells (s/n NIM-1-185 and s/n NIM-1-70) are 0.13 mK colder than cells (s/n 2002-007 and s/n 2002-009). Since cells (s/n NIM-1-185 and s/n NIM-1-70) had the same water sources, manufacture date, and glass material as cells (s/n 2002-007 and s/n 2002-009), the temperature differences between them are hypothesized to have mostly resulted from residual air. Accordingly, if a similar method is used to restore the cell performance, the difference between the cell and reference cells consists of two main components; one is the solubility of borosilicate glass, while the other is the residual air in the cell. Consequently, it is not appropriate to use the results obtained from cells (s/n 26 and s/n 30) in drift investigations, so the comparison results of these cells are not used for the linear fit in Fig. 5.

As shown in Table 4, the depression of the oldest cell (s/n 69) is 0.19 mK over 28 years, while the depression of cell (s/n 92) is 0.68 mK over 24 years. As a result, the long-term drift varies from cell to cell, and a cell-to-cell variation is also very clear in the Hill data. There are three main factors affecting the apparent long-term drift: the solubility of borosilicate glass, residual air in the sealed cell, and isotopic composition. In addition, it is uncertain whether isotopic compositions change over a period of years. Therefore, it is more reasonable to establish a complicated model including all

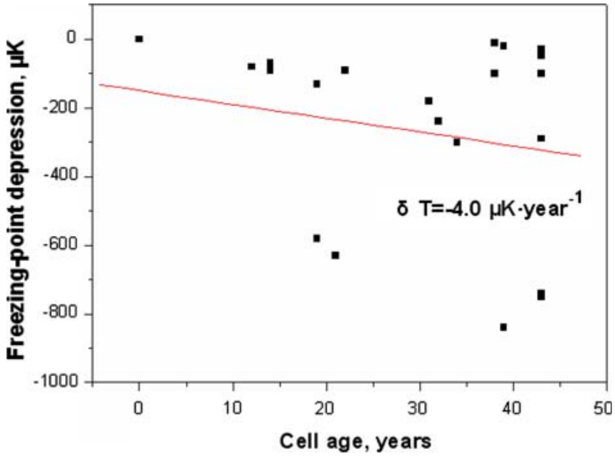

Fig. 5 Freezing-point depression of the cells manufactured by the Jarrett Instrument Company and NRC that were measured at NRC in 1997

three factors to comprehensively assess the long-term drift. To realize this objective, it is necessary to keep track of the cells using SPRTs with good long-term stability over many years and to obtain information on isotopic composition and residual air in the sealed cells.

4 Conclusions

Using the same model of long-term drift as that of Hill, the long-term drift rates of the two NIM data sets were $-4.7\,\mu\text{K}\cdot\text{year}^{-1}$ and $-9.2\,\mu\text{K}\cdot\text{year}^{-1}$. One is consistent with the observed depression of about $-4\,\mu\text{K}\cdot\text{year}^{-1}$ measured by Hill, while the other differs greatly from Hill's result. The main reasons appear to be the differences among cells arising from the production procedure, the isotopic composition, and the residual gases in the sealed cells. Moreover, it is reasonable to monitor cells with known isotopic compositions over many years to arrive at an accurate conclusion concerning the long-term drift rate in triple-point-of-water cells.

Acknowledgments The authors are grateful to Zhongyue Li for keeping the old cells for so many years. Also, we are indebted to Researcher Qi Zhao at NIM for her valuable discussions, suggestions, and modification of the paper. Additionally, we are indebted to Profs. Edmund Perozzi and Rhoda Perozzi for modification of the English in this paper.

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