Int J Thermophys (2007) 28:1923–1930
DOI 10.1007/s10765-007-0246-3

VSMOW Triple Point of Water Cells: Borosilicate versus Fused-Quartz

M. Zhao · G. F. Strouse

Abstract To investigate an ideal container material for the triple point of water (TPW) cell and to reduce the influence to the triple-point temperature, due to the deviation of the isotopic composition of the water, both borosilicate and fused-quartz glass shelled TPW cells with isotopic composition substantially matching that of Vienna Standard Mean Ocean Water (VSMOW) were developed and tested. Through a specially designed manufacturing system, the isotopic composition, δD and δ^{18}O, of the water in the TPW cell could be controlled within $\pm 10^0/_{00}$ (per mil) and $\pm 1.5^0/_{00}$, respectively, resulting in control of the isotopic temperature correction to better than $\pm 8\,\mu$K. Through an ampoule attached to the cell, the isotopic composition of the water in the cell could be individually analyzed . After manufacture, the initial triple-point temperatures of the two types of cell were measured and compared to assess the quality of the cells and manufacturing process. Cells fabricated with the new system agree within $50\,\mu$K. Two innovatively designed borosilicate and fused-quartz TPW cells were made, each with six attached ampoules. One ampoule was removed every 6 months to track any changes in purity of the water over time.

Keywords Isotopic composition · ITS-90, TPW cell · Vienna standard mean ocean water · VSMOW · Water impurities · Water triple point

1 Introduction

In 1999, National Research Council Canada (NRC) data suggested that the triple-point temperatures of "well-behaved" triple point of water (TPW) cells decrease approxi-

---

M. Zhao (✉)
Fluke Corporation, Hart Scientific Division, American Fork, UT 84003, USA
e-mail: mingjian.zhao@hartscientific.com

G. F. Strouse
National Institute of Standards and Technology,
100 Bureau Drive, MS 8363, Gaithersburg, MD 20899, USA

mately 14 μK per year, due to impurities leaching from the borosilicate glass envelope into the water [1]. A more recent and intensive study by Hill (NRC) [2] gives a decrease of 4 μK per year. The study identified boron, sodium, aluminum, and silicon as the dominant impurities in the TPW cells. These results suggest that the borosilicate glass is a less-than-ideal container, as it is a probable source of an increasing amount of contaminating elements, as a function of time. In order to determine if fused-quartz is a better container material for TPW cells, the National Institute of Standards and Technology (NIST) and Fluke Corporation, Hart Scientific Division ("Hart Scientific")[1] began a cooperative study in 2005.

The TPW realization temperature depends on the isotopic composition of the water, as well as the chemical impurities that may be present. The results of an international comparison of TPW cells [Consultative Committee for Thermometry Key Comparison 7, (CCT-K7)] for 21 participating national metrology institutes (NMIs) showed a disagreement of about ±85 μK, with only two NMIs making corrections for isotopic composition [3]. In 2005, the isotopic composition of the TPW was defined to be the isotopic equivalent of Vienna Standard Mean Ocean Water (VSMOW) for the purpose of defining the kelvin [4].

For this study, four TPW cells were fabricated with fused-quartz envelopes and two TPW cells with borosilicate glass envelopes. These TPW cells were sent to NIST for intercomparison. In order to reduce the uncertainty due to the deviation of the isotopic composition of the water in the cell from VSMOW, we have used ocean water as the source for all TPW cells in this cooperative study. During manufacture of the TPW cells, the isotopic composition of the water was well controlled to substantially match that of VSMOW. The six TPW cells were intercompared against NIST standards every 6 months from June 2005 to October 2006. Additionally, two innovatively designed TPW cells (one borosilicate envelope and one fused-quartz envelope) were made, each with six attached ampoules. One ampoule was removed for every 6 months (method of removal described in Sect. 2.3), providing a means to analyze the water periodically and track the purity of the water over time. All ampoules were sent to NIST for impurity analysis. The results of the impurity analysis were compared with the temperature intercomparison results in an attempt to quantify the impact of impurities present during manufacture and the effect of the time-dependent leaching of impurities from the different types of glass on the TPW realization temperature. We report these results in a separate article [5].

2 Manufacture of TPW Cells

2.1 Cleaning Process

Meticulous cleaning of all parts, including the cell envelope, ampoules, and borosilicate glass tubes in the distillation and vacuum system, is extremely important in the

---

[1] Certain commercial equipment, instruments, and materials are identified in this article in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the NIST.

manufacture of TPW cells. All parts are soaked in a proprietary detergent solution for a few days to remove organic impurities, and then flushed with deionized water. The parts are cleaned with a proprietary acid mixture to remove all metallic contaminants, and then flushed with high-purity water (with resistivity higher than 17.8 MΩ· cm). Finally, all parts are steam cleaned for two days. The cleaning procedures for borosilicate glass and fused-quartz are the same with the exception of the acid mixtures, which are different.

2.2 Water Purification and Vacuum System

For this study, a borosilicate glass system was designed that allowed for ocean water purification by triple distillation, water filling (into the cell), degassing, and sealing of the TPW cells. With this system, the isotopic composition of each step in the process can be controlled, so that the isotopic composition of the water contained in the sealed TPW cell substantially matches that of VSMOW. As shown in the schematic drawing in Fig. 1, this system is designed so that TPW cells with either borosilicate glass or fused-quartz envelopes can be readily manufactured.

On the vacuum system side of the TPW cell manufacturing system, the vacuum system is composed of a four-inch glass diffusion pump backed by a mechanical pump. The pumping speed of the system is 300 $\text{l}\cdot\text{s}^{-1}$, and the ultimate pressure is lower than 1.3×10^{-5} Pa (1×10^{-7} Torr). There are three liquid-nitrogen traps and one water-cooled condenser. The traps prevent oil vapor from the pumps from reaching the TPW cell and the condenser prevents water vapor from the cell from getting into the pumps.

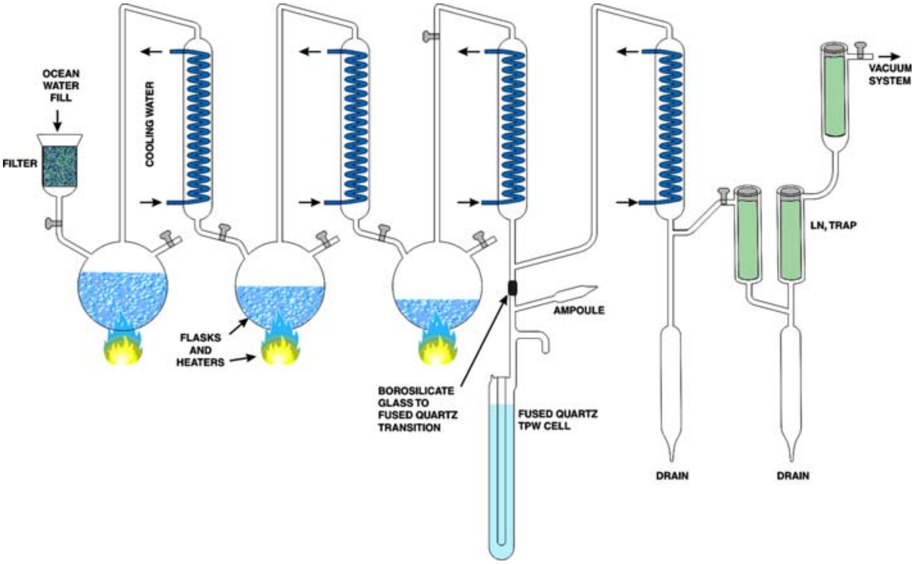

Fig. 1 Schematic drawing of the TPW cell manufacturing system

Prior to filling the TPW cell, the ocean water is filtered and then purified through a triple-distillation process. In order to avoid any possible contamination of the pure water, the system was constructed, so that there are no valves between the final condenser and the TPW cell, since valves are a potential source of contaminants for the pure liquid water. Once the water condenses after the final distillation stage, it flows directly into the TPW cell through clean glass tubes.

In order to allow both fused-quartz and borosilicate-glass TPW cells to be produced with this TPW cell manufacturing system, a special glass transition tube with varying thermal expansion coefficient along its length is used to attach a fused-quartz envelope cell.

2.3 Isotopic Composition Control

Even with VSMOW-equivalent ocean water, as the source water, the manufacturing process can impact the isotopic composition of the water contained in the manufactured TPW cell (e.g., isotopic fractionation), with a corresponding impact on the cell realization temperature. Table 1 shows how the isotopic composition, and subsequently the TPW realization temperature correction with respect to VSMOW-equivalent water, changes during the manufacturing stages. The isotopic compositions of the test cells were tested at the Stable Isotope Ratio Facility for Environmental Research (SIRFER), University of Utah. All SIRFER measurements are traceable to NIST. Measurement uncertainties ($k=1$) vary slightly, but average about $\pm 1{}^0\!/_{00}$ for δD, and $\pm 0.1{}^0\!/_{00}$ for δ^{18}O. Water isotopic compositions are usually reported as per mil (${}^0\!/_{00}$) deviations (δD and δ^{18}O for deuterium and ^{18}O, respectively) from VSMOW.

Filtering the source ocean water to remove particulate matter does not significantly affect the isotopic composition of the water. However, distillation depletes the water of heavy isotopes and degassing enriches the water. The net enrichment or depletion depends on the number of stages and temperatures of the distillations, and the period and temperature of degassing. It is apparent that, even if the source water is VSMOW-equivalent, the isotopic composition of water contained in TPW cells can vary if the manufacturing process is not well controlled or understood. Ideally, the isotopic composition of the water contained in every manufactured TPW cell should

Table 1 Water isotopic compositions [per mil (${}^0\!/_{00}$) deviations from VSMOW] and impact on the TPW realization temperatures incurred during the TPW cell manufacturing process

Isotopic compositions	Ocean water	After filter	After distillation			After degassing
			First	Second	Third	
δD(${}^0\!/_{00}$)	2.9	0.7	−12	−22	−31	−18
δ^{18}O(${}^0\!/_{00}$)	0.3	0.4	−1.8	−3.6	−4.9	−3.2
$\Delta T(\mu\text{K})$[a]	1.3	−0.3	−9.3	−16.5	−22.9	−13.6

[a] Calculation of ΔT is based on the δD value only

be individually analyzed. This would allow the user to make a temperature correction based on the unique isotopic composition of the water in their TPW cell.

The water sample used for isotopic analysis should be taken directly from the TPW cell after manufacturing so that the isotopic composition of the water sample is the same as that of the water in the TPW cell. As shown in Fig. 1, the method for doing this is to attach one or more 20 ml ampoules by fusing an extension to the TPW cell. After the TPW cell is manufactured, an ampoule is then filled with about 10 ml of water, flame sealed, and separated from the TPW cell, and then sent to SIRFER for analysis.

It is desirable for NMIs and some primary standard laboratories to have the isotopic composition of every newly manufactured TPW cell, individually analyzed, but this can be difficult and expensive. For other applications where the control of uncertainties is less critical, analysis of individual TPW cells is not required. In either case, an uncertainty component characterizing the state of knowledge of the isotopic composition of the water, based on either the uncertainty of the isotopic analysis or the uncertainty of the estimate, must be included within the overall uncertainty of the TPW cell realization temperature. The isotopic temperature correction, and the corresponding uncertainty of a TPW cell of unknown isotopic content, may be estimated using the method described in [5].

In order to control the isotopic composition of the water in the TPW cell, it is important to pay attention not only to the isotopic composition of the original water, but also the manufacturing technique. As evidenced in Table 1, the TPW cell manufacturing system systematically controls the isotopic composition at each step of the process so that the manufactured TPW cells contain nominally VSMOW-equivalent water. As of January 2007, the TPW cell manufacturing system has been used to produce over 200 TPW cells. Before May 2005, the isotopic compositions were not very well controlled. After a few months of experience with the new TPW cell manufacturing system, the isotopic composition in terms of δD and δ^{18}O could be controlled to within a tolerance

Table 2 TPW cell water isotopic compositions [per mil ($^0/_{00}$) deviations from VSMOW] and corresponding TPW realization temperature corrections for TPW cells manufactured from August 2005 to January 2007

TPW Cell	δD($^0/_{00}$)	δ^{18}O($^0/_{00}$)	ΔT (μK)[a]	TPW Cell	δD($^0/_{00}$)	δ^{18}O($^0/_{00}$)	ΔT (μK)[a]
G5028	−2.0	−0.2	−2.2	Q1027	−1.0	−0.3	−1.5
G5035	−1.0	−0.5	−1.5	Q1028	2.0	0.2	0.6
G5036	1.0	−0.1	−0.1	Q1030	2.0	0.4	0.6
G5037	1.0	−0.2	−0.1	Q1031	−3.0	−0.9	−2.9
Q1008	2.0	−0.3	0.6	Q1035	−3.0	−1.0	−2.9
Q1012	1.8	−0.3	0.5	Q1039	−1.0	−0.3	−1.5
Q1019	−1.0	0.0	−1.5	Q5012	2.0	−0.1	0.6
Q1021	−0.2	0.3	−0.9	Q5015	5.0	−0.7	2.8
Q1022	−0.2	−0.3	−0.9	Q5016	1.0	0.2	−0.1
Q1025	−0.7	−0.1	−1.3	Q5017	−2.0	−0.7	−2.2

[a] Calculation of ΔT is based on the δD value only

of $\pm 10\,^{0}/_{00}$ and $\pm 1.5\,^{0}/_{00}$, respectively, which translates to a TPW cell realization temperature within $\pm 8\,\mu\mathrm{K}$ of VSMOW-equivalent water. As shown in Table 2, based on the isotopic composition analysis, the isotopic temperature correction for the 20 TPW cells manufactured from August 2005 to January 2007 is within $\pm 3\,\mu\mathrm{K}$.

2.4 Special TPW Cells for Isotopic Composition and Impurity Analysis

In order to track the rate at which impurities leach from the containment envelope to the water sample and to determine whether fused-quartz might be a better material for TPW cells, specially designed TPW cells (one with borosilicate glass and one with fused-quartz envelopes) were manufactured in 2005. Each cell had six attached ampoules. We removed one ampoule every 6 months, providing a means to analyze the water periodically and track the purity of the water over time. Figure 2 shows this uniquely designed TPW cell. Two ampoules from each cell were removed immediately

Fig. 2 TPW cell for isotopic composition and impurity analysis. The ampoules that were removed periodically for water testing are shown

following manufacture. One ampoule from each cell was sent to SIRFER for isotopic composition water analysis, and the other was sent to NIST for water impurity analysis. Afterward, we removed one ampoule from each cell every 6 months and sent it to NIST for water impurity analysis. This allowed us to compare the rate of elemental leaching from the borosilicate glass and fused-quartz envelopes into the respective water samples. The results of impurity analysis over two years are reported in [5].

3 Initial Test Results

After developing the VSMOW-equivalent TPW cells with borosilicate glass and fused-quartz envelopes, the initial triple-point temperatures of the two types of cells were measured at Hart Scientific to assess the quality of the cells and manufacturing process. The Hart Scientific direct-comparison measurement uncertainties ($k = 2$) are estimated to be 50 μK. A total of 18 cells were intercompared at the Hart Scientific primary standard laboratory. Three TPW cells, S/N 1200, S/N 1430, and S/N 1457, were made with the original TPW cell manufacturing system built in 1994. The water source for these three cells was continental surface water. The isotopic compositions were not tested

Table 3 Initial intercomparison results of various TPW cells in 2005

Cell S/N	Year made	Container material	Water sources	ΔD $(^0/_{00})$	$\delta^{18}O$ $(^0/_{00})$	ΔT (μK) measured[a]	ΔT (μK) after correction[b,c]
Q1001	2005	Fused-quartz	Ocean	5.0	0.5		15
1200[d]	2000	Borosilicate	Continental	−99	−12	−149	−80
1430[d]	2005	Borosilicate	Continental	−99	−12	−91	−22
1457[d]	2005	Borosilicate	Continental	−99	−12	−100	−31
G1001	2005	Borosilicate	Ocean	10.0	1.3	4	−5
G1003	2005	Borosilicate	Ocean	5.0	0.8	21	15
G5002	2005	Borosilicate	Ocean	5.0	0.3	−6	−12
G5003	2005	Borosilicate	Ocean	0.0	−0.5	4	2
Q1002	2005	Fused-quartz	Ocean	14.0	1.9	28	16
Q5004	2005	Fused-quartz	Ocean	7.0	0.6	−27	−34
Q5005	2005	Fused-quartz	Ocean	0.3	−0.5	10	8
Q5006	2005	Fused-quartz	Ocean	−3.0	−0.5	−23	−23
Q5007	2005	Fused-quartz	Ocean	−3.0	−0.5	13	13
Q5008	2005	Fused-quartz	Ocean	2.0	−0.3	−13	−16
Q5009	2005	Fused-quartz	Ocean	7.0	0.6	−1	−8
Q5010	2005	Fused-quartz	Ocean	−6.0	−1.4	−7	−5
Q5011	2005	Fused-quartz	Ocean	−7.0	−1.6	9	12

[a] TPW cell Q1001 is set as the standard to which the other cells are compared

[b] Temperature corrected for isotopic composition. Isotopic composition of cell Q1001 is also considered

[c] Uncertainty ($k = 2$) of the ΔT measurement is 50 μK

[d] Isotopic compositions are estimated

individually, but we sampled the water used to fill the cells. Cell S/N 1200 was made in 2000, and the other two cells were made in 2005. The inter-comparison results are shown in Table 3. The results show that the temperature differences among the TPW cells made in 2005 are within the 50 μK expanded uncertainty ($k = 2$) of the comparison tests. However, the TPW realization temperature of S/N 1200 cell made in 2000 differed by −80 μK from those made in 2005. The drift in realization temperature of the borosilicate TPW cell (S/N 1200) is estimated to be −13 μK per year, which agrees to within measurement uncertainties with the results found in [1,5].

4 Conclusions

A new borosilicate glass TPW cell manufacturing system was developed so that both fused-quartz and borosilicate glass TPW cells can be produced with this system. The quality of the cells and the manufacturing process were assessed through initial intercomparison testing. The isotopic composition of the water in the cells could be individually tested through a 20 ml ampoule attached on the cell. Using ocean water as the water source, the isotopic composition of the water in the TPW cells substantially matches that of VSMOW. The isotopic composition, δD and δ^{18}O, of the water in these manufactured TPW cells can be well controlled within $\pm 10^0/_{00}$ and $\pm 1.5^0/_{00}$, respectively. For TPW cells without an individual isotopic composition analysis, the temperature realization deviation from VSMOW-equivalent water is within ±8 μK. Specially designed TPW cells made from borosilicate glass and fused-quartz were manufactured with six ampoules attached to each cell that allowed the water in the cell to be analyzed periodically and the rate of impurity leaching from the envelope to be evaluated. We report results of the impurity analysis and the inter-comparison results performed over two years at NIST in a separate article [5].

Acknowledgments The authors would like to acknowledge the assistance of Hart Scientific Staff: Deming Chen, Rong Ding, and Rick Walker for their considerate advice, and also thank Wayne Newland for his assistance with the illustrations and publishing of this article. The authors would also like to express their gratitude for the contributions made to this project by many other professionals at NIST and Fluke Corporation, Hart Scientific Division.

References

1. K.D. Hill, in *Proc. TEMPMEKO 1999*, ed. by M. de Groot, (Edauw and Johannissen bV, The Netherlands, 1999), pp. 68–73
2. K.D. Hill, Metrologia **38**, 79 (2001)
3. M. Stock, S. Solve, D. del Campo, V. Chimenti, E. Méndez-Lango, H. Liedberg, P.P.M. Steur, P. Marcarino, R. Dematteis, E. Filipe, I. Lobo, K.H. Kang, K.S. Gam, Y.-G. Kim, E. Renaot, G. Bonnier, M. Valin, R. White, T.D. Dransfield, Y. Duan, Y. Xiaoke, G. Strouse, M. Ballico, D. Sukkar, M. Arai, A. Mans, M. de Groot, O. Kerkhof, R. Rusby, J. Gray, D. Head, K. Hill, E. Tegeler, U. Noatsch, S. Duris, H.Y. Kho, S. Ugur, A. Pokhodun, S.F. Gerasimov, Metrologia, Tech. Suppl. **43**, 03001 (2006)
4. Technical Annex for the International Temperature Scale of 1990 (ITS–90), Consultative Committee for Thermometry (2005), available at http://www.bipm.org/utils/en/pdf/MeP_K_Technical_Annex.pdf
5. G.F. Strouse, M. Zhao, in *Proc. TEMPMEKO 2007, Int. J. Thermophys.*, DOI 10.1007/s10765-007-0240-9 (2007)