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Isotopic Effects on the Temperature of the Triple Point of Water

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Abstract An investigation into the effects of isotopic composition on the triple point temperature of water has been carried out at the National Institute of Metrology (NIM), China, since redefinition of the kelvin with respect to Vienna Standard Mean Ocean Water (V-SMOW) was officially proposed by the Consultative Committee for Thermometry (CCT) in 2005. In this paper, a comparison of four cells with isotopic analyses and relevant results corrected for isotopic composition, employing the isotope correction algorithm recommended by the CCT, is described. The results indicate that, after application of the corrections, the maximum temperature difference between the cells drops from 0.10 mK to 0.02 mK and that these cells are in good agreement within 0.02 mK. Also, temperature deviations arising from isotopic variations fall in the range from −55.9 μK to +40.7 μK. We consider that the distillation temperature and degassing time of the production procedure lead to isotopic variations.

Keywords Isotopic composition · Isotopic fractionation · Key comparison · Triple point of water · Vienna Standard Mean Ocean Water (V-SMOW)

1 Introduction

Over the last 10 years, considerable research has been conducted on the effects of isotopic composition on the triple-point temperature of water (TPW) [1–5]. Research has shown that it is necessary to correct for isotopic composition in order to reduce

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differences resulting from isotopic variations due to different water sources, distillation and degassing during the manufacture of TPW cells, and isotopic fractionation. In particular, in the CCT-K7 key comparison of water triple-point cells organized by the Bureau International des Poids et Mesures (BIPM) [6], most participating national metrology institutes (NMIs) were unaware of the isotopic compositions of their cells. Accordingly, some underestimated the level of uncertainty associated with isotope effects, while others perhaps overestimated it. Thus, views regarding the choice of the key comparison reference value (KCRV) diverged so greatly that voting was adopted to determine it. Also, the CCT-K7 comparison results provide convincing evidence of the importance of correcting for isotopic composition in order to reconcile present discrepancies. Through discussions during the comparison, all laboratories realized the necessity of redefining the kelvin with regard to V-SMOW and of employing the corresponding correction algorithm in order to improve the International Temperature Scale of 1990 (ITS-90) and guarantee the international equivalence of realizations of the kelvin. As a result, at the 23rd meeting of the Consultative Committee for Thermometry (CCT) in 2005, a *mise en pratique* for the definition of the kelvin was created, and adopted by the CCT [7,8]. At the same time, a corresponding correction algorithm with respect to isotopic composition was recommended. Moreover, the International Committee for Weights and Measures (CIPM) clarified the definition of the TPW by referring to the composition of V-SMOW in 2005 [9]. Consequently, increased concern has been concentrated on the isotopic correction and effects for NMIs.

In recent years, such a study has been carried out at NIM, China. In this paper, we report experimental results corrected for isotopic composition by means of the isotope correction algorithm proposed by the CCT.

2 Procedure

2.1 Triple Point of Water Cells

In order to investigate isotopic effects, four special TPW cells (s/n NIM-3, s/n NIM-5, s/n NIM-6, and s/n NIM-7) with glass ampoules containing the same water samples as the corresponding cells were fabricated using our usual production process during March, 2005 [10]. A schematic diagram of such a cell is shown in Fig. 1. Also, when testing for the "water hammer" effect, these cells gave very sharp clicking sounds, indicating very little residual air in the sealed cells. In addition, these cells have the same water sources (de-ionized water with high purity in Beijing), glass materials, dimensions, and production procedure as the NIM transfer cell and national references taking part in the CCT-K7 international key comparison of water triple-point cells.

2.2 Isotopic Analysis

After completion of the cells, ampoules filled with water samples from the completed cells were removed and sealed with a flame at a previously thickened and constricted section, as shown in Fig. 1. Next, the sealed ampoules containing approximately 20 ml

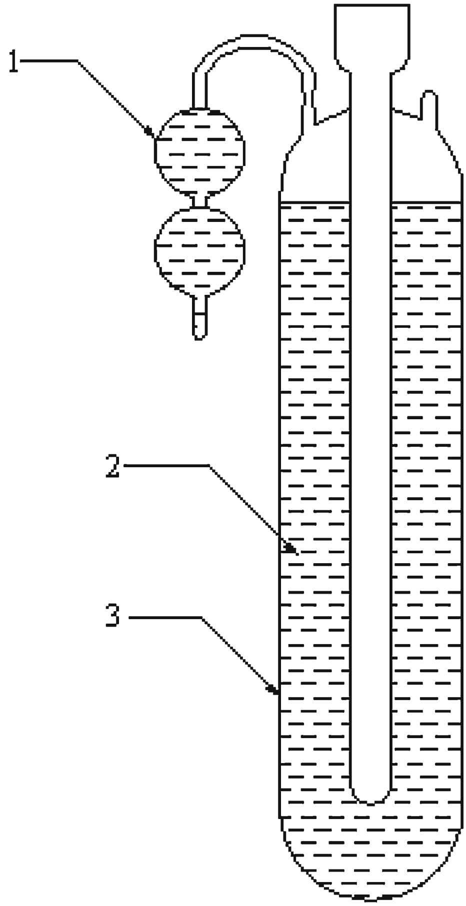

Fig. 1 Schematic diagram of a special TPW cell with a glass ampoule: 1—glass ampoule containing water sample; 2—air-free water; 3—TPW cell

Table 1 Isotopic analysis of water samples[a] and temperature differences with respect to Vienna Standard Mean Ocean Water (V-SMOW)

Sample name	δ^{18}O (‰)	δ^{2}H (‰)	δT (μK)
NIM-3	−10.70	−77.6	−55.9
NIM-5	−8.25	−65.5	−46.7
NIM-6	−0.24	−0.2	−0.3
NIM-7	6.34	58.0	40.7

[a] All measurements are with respect to V-SMOW, and have uncertainties of ±1.0 ‰ for δ^{2}H and ±0.1 ‰ for δ^{18}O

water samples, well packaged with bubble wrap in a crush-proof box, were sent to the Institute of Geological and Nuclear Sciences (GNS), Lower Hutt, New Zealand, for analysis of the isotopic composition. The water isotope report received from the institute is presented in Table 1.

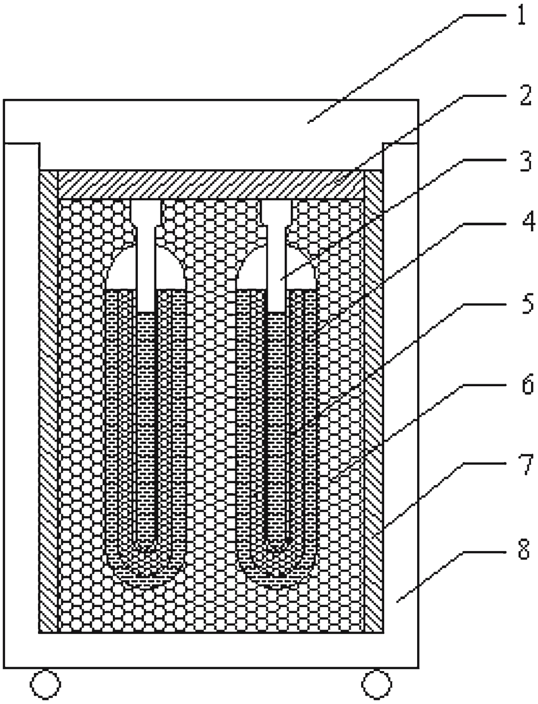

Fig. 2 Sketch of the storage apparatus: 1—cover of the enclosure; 2—sponge cover; 3—TPW cell; 4—ice mantle; 5—inner melt; 6—crushed ice; 7—plastic insulating layer; 8—container

2.3 Freezing Method

A liquid nitrogen technique, our usual freezing method at NIM, was used to simultaneously prepare ice mantles in the four cells. The detailed preparation procedure was described in a previously published paper [5].

2.4 Storage Apparatus

After forming the solid mantle of ice, these cells were kept in a refrigerator containing crushed ice, as shown in Fig. 2. After failing to obtain adequate temperature control in a refrigerator with a PT100 platinum thermometer, we were able to achieve excellent control using an uncontrolled refrigerator packed with ice that could store the cells for at least 30 days.

2.5 Measurement Apparatus and Procedure

One Guildline 9975 bridge with a nominal 10 Ω standard resistor (s/n 666427) and three standard platinum resistance thermometers (SPRTs) (s/n 400131, s/n 400150, and s/n 68804) were employed for the measurements. In order to eliminate stress effects, the measurements began 7 days after the mantles were aged to become stable

[11]. The corresponding measurement procedures are the same as presented in our published paper [5].

2.6 Correction for Isotopic Composition [12,13]

The effects of isotopic composition on the triple point temperature of water are expressed as

$$T_{\text{meas}} = T_{\text{V-SMOW}} + A_{\text{D}}\delta\text{D} + A_{^{17}\text{O}}\delta^{17}\text{O} + A_{^{18}\text{O}}\delta^{18}\text{O} \tag{1}$$

where $T_{\text{V-SMOW}}$ is the thermodynamic temperature of V-SMOW; δD, δ^{17}O, and δ^{18}O are the deviations of the isotope concentrations from that of V-SMOW for deuterium (D), ^{17}O, and ^{18}O, respectively; and A_{D} , $A_{^{17}\text{O}}$, and $A_{^{18}\text{O}}$ are depression constants for D, ^{17}O, and ^{18}O, respectively. Here, $A_{\text{D}} = 628\,\mu\text{K}$, $A_{^{17}\text{O}} = 57\,\mu\text{K}$, and $A_{^{18}\text{O}} = 641\,\mu\text{K}$. Moreover, δ^{17}O is obtained from the formula:

$$\delta^{17}\text{O} = (1 + \delta^{18}\text{O})^{0.528} - 1 \tag{2}$$

Thus, by using the data from the analysis report for isotopic composition in conjunction with Eqs. 1 and 2, the isotope effects on the triple points of the four cells were calculated. The corresponding values are reported in Table 1.

3 Results and Discussion

Based on the isotopic analysis supplied by GNS, it can be seen that the temperature deviations with respect to V-SMOW vary from $-55.9\,\mu$K to +40.7 μK. The mean temperature difference is $-16\,\mu$K with a standard uncertainty of 22 μK, which is representative of the variations in isotopic composition for the cells fabricated at NIM. Moreover, the isotopic composition of the cell s/n NIM-6 is closest to that of V-SMOW, with an equivalent deviation of only $-0.3\,\mu$K. Consequently, in the following comparison, cell s/n NIM-6 may be regarded as equivalent to V-SMOW, without taking its uncertainty into account.

Although these cells were produced using the same water sources and production procedure, they differ in isotopic composition. It is likely that these differences are associated with the distillation temperature and degassing time. On the one hand, distillation results in the depletion of heavy isotopes in the condensate relative to the source water when only a fraction of the source water is distilled (the remaining source water becomes enriched in heavy isotopes). On the other hand, degassing leads to the enrichment of heavy isotopes. In fact, the production procedures are such that it is difficult to ensure that the cells have uniform distillation temperatures and degassing times throughout the process of fabrication. Hence, due to these differences, isotopic variations among cells will always exist.

When commencing the CCT-K7 comparison, the protocol did not require the participating laboratories to provide isotopic analyses and corrections for isotopic compositions differing from V-SMOW. Accordingly, there was little information on

Table 2 Results of experimental results with SPRT (s/n 400131)

Date of measurement	R_{tpw}(NIM-3)[a] (Ω)	R_{tpw}(NIM-5) (Ω)	R_{tpw}(NIM-6) (Ω)	R_{tpw}(NIM-7) (Ω)
Sept. 4, 2006	25.038661	25.038663	25.038663	25.038666
Sept. 5, 2006	25.038662	25.038660	25.038664	25.038670
Sept. 6, 2006	25.038652	25.038653	25.038659	25.038661
Sept. 7, 2006	25.038654	25.038655	25.038661	25.038664
Sept. 8, 2006	25.038648	25.038648	25.038653	25.038659
Sept. 9, 2006	25.038651	25.038651	25.038660	25.038660
Sept. 10, 2006	25.038649	25.038648	25.038667	25.038663
Sept. 11, 2006	25.038650	25.038651	25.038663	25.038668
Mean of the R_{tpw}	25.038653	25.038653	25.038661	25.038664
Standard deviation of the mean (Ω)	0.000002	0.000002	0.000002	0.000001
SD of corresponding temperature (mK)	0.02	0.02	0.02	0.01

[a] Resistance of the SPRT at the TPW realized by cell NIM-3

Table 3 Results of experimental results with SPRT (s/n 400150)

Date of measurement	R_{tpw}(NIM-3) (Ω)	R_{tpw}(NIM-5) (Ω)	R_{tpw}(NIM-6) (Ω)	R_{tpw}(NIM-7) (Ω)
Sept. 4, 2006	24.621139	24.621140	24.621140	24.621144
Sept. 5, 2006	24.621137	24.621140	24.621144	24.621148
Sept. 6, 2006	24.621138	24.621136	24.621143	24.621146
Sept. 7, 2006	24.621135	24.621132	24.621146	24.621149
Sept. 8, 2006	24.621134	24.621126	24.621135	24.621137
Sept. 9, 2006	24.621137	24.621140	24.621139	24.621142
Sept. 10, 2006	24.621134	24.621140	24.621136	24.621145
Sept. 11, 2006	24.621135	24.621139	24.621143	24.621144
Mean of the R_{tpw}	24.621136	24.621137	24.621141	24.621144
Standard deviation of the mean (Ω)	0.000001	0.000002	0.000001	0.000001
SD of corresponding temperature (mK)	0.01	0.02	0.01	0.01

isotopic composition at most labs, except for reports from the Measurement Standards Laboratories of New Zealand (MSL) and the National Research Council of Canada (NRC). Also, the transfer cell (s/n NIM-1-08) and reference cells at NIM did not undergo isotopic analysis. Thus, in order to apply these corrections to them, they must be compared against those cells for which isotopic analysis exists.

The results of the measurements obtained with three SPRTs (s/n 400131, s/n 400150, and s/n 68804) are given in Tables 2, 3, and 4, respectively. All data in these tables were corrected for self-heating, the temperature of the standard resistor, and the hydrostatic head.

In addition, the correction algorithm proposed by the CCT was applied to the comparison results, as shown in Table 5. Note that the maximum difference between the cells drops by 0.08 mK after application of the correction, and the corrected triple-point temperatures of these cells are consistent within 0.02 mK.

Table 4 Results of experimental results with SPRT (s/n 68804)

Date of measurement	R_{tpw}(NIM-3) (Ω)	R_{tpw}(NIM-5) (Ω)	R_{tpw}(NIM-6) (Ω)	R_{tpw}(NIM-7) (Ω)
Sept. 5, 2006	25.331513	25.331515	25.331517	25.331522
Sept. 6, 2006	25.331509	25.331506	25.331512	25.331516
Sept. 7, 2006	25.331509	25.331511	25.331519	25.331520
Sept. 8, 2006	25.331503	25.331502	25.331513	25.331512
Sept. 9, 2006	25.331506	25.331505	25.331516	25.331517
Sept. 10, 2006	25.331506	25.331507	25.331518	25.331521
Sept. 11, 2006	25.331506	25.331507	25.331518	25.331515
Mean of the R_{tpw}	25.331507	25.331507	25.331516	25.331518
Standard deviation of the mean (Ω)	0.000001	0.000002	0.000001	0.000001
SD of corresponding temperature (mK)	0.01	0.02	0.01	0.01

Table 5 Summary of comparison results

$\delta T(x)^a$	SPRT (s/n 400131)	SPRT (s/n 400150)	SPRT (s/n 68804)	δT^b (mK)	δT^c (mK)
δT (NIM-3) (mK)	−0.08	−0.05	−0.09	−0.07	−0.01
δT (NIM-5) (mK)	−0.08	−0.04	−0.09	−0.07	−0.02
δT (NIM-7) (mK)	0.03	0.04	0.02	0.03	−0.01

[a] Temperature difference between cell *x* and the reference cell (s/n NIM-6)
[b] Mean of temperature difference before correcting for isotopic composition differences between cell *x* and the reference cell (s/n NIM-6)
[c] Mean of temperature difference after correcting for the isotopic composition difference between cell *x* and the reference cell (s/n NIM-6)

Strictly speaking, the isotopic composition of the inner melt is an important influencing factor on the realized TPW temperature. However, even though the isotopic compositions of the water are measured before forming an ice mantle, it is very difficult to measure accurately the isotopic composition in the inner melt, since the isotopic composition can change with different freezing methods.

On the other hand, there are many other factors affecting the triple-point temperature, such as impurities in the water, residual air, buoyancy, and long-term drift, in addition to the isotopic composition. It is possible that these other effects have the same magnitude as that of variations in isotopic composition, so the remaining differences among the cells include all of these effects. Accordingly, it is not appropriate to attribute these differences solely to isotopic effects. Further research is needed to understand and characterize these problems.

4 Conclusions

On the basis of the above-mentioned comparison results, we conclude that it is necessary to apply isotopic corrections to reduce the temperature differences stemming from isotopic variations attributable to differences in distillation temperature and degassing time during the production procedure. After application of the isotope correction, the maximum temperature difference among the four NIM cells drops from 0.10 mK to 0.02 mK. Thus, when comparing TPW cells, the corresponding corrections for isotopic composition may be made with a small degree of uncertainty, provided an isotopic analysis is available; otherwise, the relevant uncertainty component in the overall uncertainty budget for the realization of the triple point of water should take into account the possible range of isotopic variations.

An ad hoc CCT Task Group on the TPW concluded that most TPW cells made from continental fresh water can be expected to be within $-110\,\mu$K and $+10\,\mu$K of V-SMOW [12]. However, according to our data, the temperature deviations with respect to V-SMOW fall in the range of $-55.9\,\mu$K to $+40.7\,\mu$K. Therefore, it is more reasonable that the upper limit in their conclusion should extend to $+40.7\,\mu$K to cover the full range observed in practice.

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