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Water enriched in the rare stable isotopes

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Chapter 7

Accurate experimental determination of the isotope effects on the triple point temperature of water. II. Combined dependence on the ^{18}O and ^{17}O abundances

Abstract

This chapter is the second of two chapters on the quantification of isotope effects on the triple point temperature of water. In this second chapter, we address the combined effects of ^{18}O and ^{17}O isotopes. We manufactured five triple point cells with waters with ^{18}O and ^{17}O abundances exceeding widely the natural abundance range while maintaining their natural $^{18}\text{O}/^{17}\text{O}$ relationship. The ^2H isotopic abundance was kept close to that of VSMOW (Vienna Standard Mean Ocean Water). These cells realized triple point temperatures ranging between $-220\ \mu\text{K}$ to $1420\ \mu\text{K}$ with respect to the temperature realized by a triple point cell filled with VSMOW. Our experiment allowed us to determine an accurate and reliable value for the newly defined combined $^{18,17}\text{O}$ correction parameter of $A_{\text{O}} = 630\ \mu\text{K}$ with a combined uncertainty of $10\ \mu\text{K}$. To apply this correction, only the ^{18}O abundance of the TPW needs to be known (and the water needs to be of natural origin). Using the results of our two articles, we recommend a correction equation along with the coefficient values for isotopic compositions differing from that of VSMOW and compare the effect of this new equation on a number of triple point cells from the literature and from our own institute. Using our correction equation, the uncertainty in the isotope correction for triple point cell waters used around the world will be $< 1\ \mu\text{K}$.

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7.1 Introduction

This chapter is the second of the two-part joint study of the Centre for Isotope Research (CIO) of the University of Groningen and the VSL-Dutch Metrology Institute on accurate experimental determination of isotope effects on the triple point of water (TPW). The TPW is the physical state of water in which all the three phases coexist in thermodynamic equilibrium. This TPW defines a unique state in terms of pressure and temperature. The unit of the thermodynamic temperature scale, the kelvin, is defined based on the TPW as the 1/273.16 fraction of the TPW temperature. The Consultative Committee for Thermometry (CCT) clarified that such definition applies only to a triple point cell filled with water that has the isotopic composition of VSMOW [1]. For TPW containing non-VSMOW water, the CCT recommended the following correction algorithm [2]:

$$T_{\text{meas}} - T_{\text{VSMOW}} = A_{2\text{H}}\delta^2\text{H} + A_{18\text{O}}\delta^{18}\text{O} + A_{17\text{O}}\delta^{17}\text{O} \quad (1)$$

here the δ -values for the isotopes are defined in the conventional way:

$$\delta^{18}\text{O} = \frac{\left(\frac{[\text{H}_2^{18}\text{O}]}{[\text{H}_2^{16}\text{O}]}\right)_{\text{sample}}}{\left(\frac{[\text{H}_2^{18}\text{O}]}{[\text{H}_2^{16}\text{O}]}\right)_{\text{VSMOW}}} - 1 \quad (2)$$

and in the same fashion for the other isotopes. The data are then normalized to the international VSMOW-SLAP scale [3]. Although δ -values are usually expressed in ‰, in equation (1) they should be inserted as they are, namely small numbers. The coefficients in equation (1) have been determined predominantly using data based on triple point temperatures of the different isotopologues and related thermodynamic quantities, as well as on isotope fractionation factors between the solid and liquid phase. Our previous chapter gives some details [4]. In 2010, White and Tew made a critical review of the existing literature available at the time, and derived new values and standard uncertainties for the isotopic correction constants. This resulted in $A_{2\text{H}} = (671 \pm 10) \mu\text{K}$, $A_{18\text{O}} = (603 \pm 3) \mu\text{K}$ and $A_{17\text{O}} = (60 \pm 1) \mu\text{K}$, which are the values currently recommended for use with the ITS-90 [5].

However, a thorough and accurate empirical investigation of the isotope dependence of the TPW temperature itself, with proper quantitative control over the isotopic composition of the waters, was still lacking. Therefore the Centre for Isotope Research (CIO) of the University of

Groningen and the VSL Dutch Metrology Institute decided to join forces in a project aimed at improving the accuracy and reliability of the isotopic parameter values, using state-of-the-art instrumentation for the isotope analysis at CIO and for the triple point temperature measurements at VSL.

In the previous chapter, we described our assessment of the A_{2H} coefficient in equation (1), which led to $A_{2H} = (673 \pm 4) \mu\text{K}$ [4 and chapter 6 of this thesis]. Our finding was in good agreement with the value currently recommended by the CCT based on historical measurements and in part on values inferred from values of related thermophysical quantities [5]. However, our assessment gave a more accurate result, based on direct measurements of triple point temperatures of cells containing waters with well known isotopic compositions, but spanning a much greater range than had been measured previously [6]. In this chapter, we complete this work by presenting a similar direct determination of the combined ^{18}O and ^{17}O dependence of the TPW. For all natural waters on earth, the ^{17}O and ^{18}O abundances are very closely related. Expressed as delta values this relation is:

$$\delta^{17}\text{O} = (1 + \delta^{18}\text{O})^\lambda - 1 \quad (3)$$

as first was shown by Meijer and Li who also determined $\lambda = 0.528$ [7]. This relation holds irrespective of isotope fractionating processes like evaporation and freezing, which do of course change both the $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ themselves. As long as triple point cells are filled using fresh water with natural isotopic abundances, equation (3) holds for these cells, too. It is therefore easier, and less error-prone, to correct for the ^{17}O and ^{18}O isotope effects on the triple point temperature in a combined fashion:

$$T_{meas} - T_{\text{VSMOW}} = A_{2H}\delta^2\text{H} + A_O\delta^{18}\text{O} \quad (4)$$

In this way only the $\delta^{18}\text{O}$ for the cell water has to be determined (which is the common practice anyway).

We chose to base our experiments on water mixtures for which the ^{17}O - ^{18}O relationships follow equation (3) closely. Similar to the previous exercise, we manufactured a set of five TPW cells containing waters with different $\delta^{18}\text{O}$ values ranging from $\approx -300 \text{‰}$ to $\approx 2200 \text{‰}$ (equivalent to a ^{18}O abundance range from 0.7 to 3.2 times the ^{18}O abundance in VSMOW), while closely obeying equation (3) for their $\delta^{17}\text{O}$ values. The ^2H isotope abundances were approximately the same for all five waters, and were close to VSMOW.

This chapter has the same structure as the previous chapter. It starts with a description of the gravimetric mixing process by which the water mixtures were made, followed by a short description of the manufacture of water cells containing the water mixtures. Then the measurements of the TPW temperatures realized by the manufactured cells are reported. After that, we report and discuss the influences of the purification stages on isotopic compositions during the manufacturing of the cells and the determination of the A_O coefficient for the TPW temperature with its combined uncertainty. Finally, using the results of this chapter and chapter 6, we recommend a correction equation along with the coefficient values for isotopic compositions differing from that of VSMOW and compare the effect of this new equation on a number of triple point cells from the literature and from our own institute.

7.2 Gravimetric preparation of water mixtures

A set of five water mixtures, three enriched and two depleted in ^{18}O , in quantities of ~1.5 liters each, were prepared gravimetrically by mixing three to four well-characterized parent waters. A detailed description of our assessment of the full isotopic composition of the parent waters and employed measurement techniques was provided in chapter 6. Table 1 summarizes the isotopic specifications of the parent waters used for preparation of the present series of water mixtures. Since the amount of ^{18}O -enriched water we had available appeared to be insufficient, we characterized and used ^{18}O -enriched water from a different batch to make water mixture 4 in this series (See Table 2).

Table1. Isotopic compositions of the parent waters expressed in δ values (as isotope ratio deviations from VSMOW) or isotopic abundances, with their combined uncertainties (k=1).

Components	Isotopic Abundances (%) or Isotope delta Values (‰)		
	^2H	^{18}O	^{17}O
demineralized local tap water	$(-43.0 \pm 0.6) \text{‰}$	$(-6.10 \pm 0.06) \text{‰}$	$(-3.3 \pm 0.4) \text{‰}$
depleted natural water (Antarctica water)	$(-380.5 \pm 1.0) \text{‰}$	$(-45.97 \pm 0.06) \text{‰}$	$(-24.5 \pm 0.4) \text{‰}$
^2H -enriched water	$(99.993 \pm 0.005) \%$	$(0.8998 \pm 0.0010) \%$	$(0.0874 \pm 0.0004) \%$
^{18}O -enriched water	$(0.1791 \pm 0.0014) \%$	$(96.05 \pm 0.12) \%$	$(1.176 \pm 0.020) \%$
^{18}O -enriched water *	$(0.087 \pm 0.008) \%$	$(96.55 \pm 0.15) \%$	$(0.891 \pm 0.020) \%$
^{17}O -enriched water	$(0-0.05) \%$	$(44.5 \pm 0.4) \%$	$(39.42 \pm 0.03) \%$
^2H -depleted water	$(-997 \pm 3) \text{‰}$	$(-623.4 \pm 0.5) \text{‰}$	$(-391.5 \pm 1.0) \text{‰}$

* Only used for water mixture 4 in Table 2.

Using the isotopic specifications of the parent waters in Table 1, we calculated the "recipes" for the five water mixtures with our newly developed spread sheet [8]. For preparation and storage of these five waters, we used two liters glass bottles. The bottles were carefully washed and then dried in an oven (~ 100 °C) before filling. We first filled the bottles with the water with the largest quantity calculated (demineralized local tap water for mixtures 2-5 and depleted natural water for mixture 1, see Table 2), in which the quantity could be weighed to 0.01 g precision using a precision balance (KERN 572-39, Balingen, Germany). Then, the ^2H -depleted water was added to the glass bottles of the first and second mixtures. As the amount of this water added was substantial (700 and 200 g, respectively), weighing the bottle before and after the addition produced an accurate enough measure for the amount of the water added. The isotopically ^2H , ^{18}O and ^{17}O enriched parent waters, were served into small vials, such that the quantity could be weighed to a precision of 0.01 mg with a precision analytical balance (CPA225D, Sartorius, Göttingen, Germany). They were then immersed into the respective glass bottles to ensure that the entire quantity was indeed mixed with the large quantity of water. All weighing procedures were executed swiftly, and with covered bottles to minimize evaporation as much as possible.

Furthermore, we applied a correction for the buoyancy effect where applicable (See [4, 9] for more details). The bottles were tightly capped to avoid evaporation and contamination with water vapour from the atmosphere and gently shaken periodically during 2-3 days for complete mixing. The mass contents and the final isotope delta values of the water mixtures with their combined uncertainties are provided in Table 2. The latter have been derived (in a fashion similar to the description by Kragten [10]) from the uncertainties given in Table 1 and the weighing uncertainties.

Table 2. The calculated isotope values of water mixtures relative to VSMOW with their combined uncertainties (1σ , $k=1$), along with the masses of the parent waters used. The uncertainties in the masses are 0.00001 g for the ^2H , ^{17}O , and ^{18}O enriched waters, and 0.01 g for the amounts of the natural, depleted natural, and ^2H depleted water.

Sample	Mass of contents (g)						Calculated isotope values (‰)		
	Natural water (local tap water)	depleted natural water	^2H -depleted water	^{17}O -enriched water	^{18}O -enriched water	pure ^2H - water	$\delta^2\text{H}$	$\delta^{18}\text{O}$	$\delta^{17}\text{O}$
mixture 1	-	800.00	700.00	0.01466	-	0.16363	(-38.8 ± 0.5)	(-313.2 ± 0.3)	(-186.3 ± 0.5)
mixture 2	1500.01	-	200.00	0.00955	-	0.04376	(-6.7 ± 0.6)	(-77.6 ± 0.1)	(-43.5 ± 0.4)
mixture 3	1500.01	-	-	0.11399	0.51999	0.01124	(3.6 ± 0.6)	(160.0 ± 0.2)	(80.3 ± 0.4)
mixture 4	1500.01	-	-	0.70166	3.32420	0.00691	(-7.0 ± 1.4)	(1056.3 ± 1.6)	(497.7 ± 1.2)
mixture 5	1500.01	-	-	1.18068	7.24648	-	(3.2 ± 1.4)	(2251.0 ± 2.8)	(895.9 ± 2.4)

From the results in the table above, it can be seen that the water mixtures cover a wide range of ^{18}O abundances and that the ^{17}O abundances are such that they follow equation (3) closely. Only the $\delta^{17}\text{O}$ values for the cells 4 and 5 are about 30 % too high in that respect. Also, the $\delta^2\text{H}$ values show some variability. The realized triple point temperatures have been corrected for these small differences, as will be discussed in the results section.

7.3 Manufacture of TPW cells and triple point temperature measurements

Five TPW cells were manufactured by VSL with the above-mentioned mixtures, following the same procedure as described in chapter 6 [4]. Shortly, the water sample is double-distilled and

transferred into the cell, the filled cell is degassed by a vacuum pump for some hours and then is flame-sealed. After sealing off the cell from the manufacturing system, the cell is reversed and the glass bulb attached to the cell is filled with some of the cell water after which the bulb is sealed off. The entire filling and sealing process is performed under vacuum. To assess the impact of the distillation and degassing procedures on the isotopic composition of water mixtures, three samples of each water mixture were taken at three stages of the production process: the original water with the isotopic composition given in Table 2 (source water), the water after double distillation (receiver water), and the final cell water as sampled in the bulb. The temperature differences between each manufactured cell and the VSL national reference cell, which is filled with water with $\delta^{18}\text{O} = (-4.86 \pm 0.06) \text{‰}$ and $\delta^2\text{H} = (-20.5 \pm 0.4) \text{‰}$, were measured on two different ice mantles, each for two weeks, as explained in the first chapter. The realized triple point temperature difference of each cell is taken as the mean of the individual results on the two mantles. The detailed uncertainty budget and combined uncertainty of temperature differences ($\pm 19 \text{ }\mu\text{K}$) are as presented in chapter 6.

7.4 Isotope measurements

The ^{18}O and ^{17}O abundances of the 3 x 5 water samples were measured using our classical H_2O - CO_2 equilibrium-dual inlet Isotope Ratio Mass Spectrometry (IRMS) set-up. This installation, which can run up to 5 racks of each 16 samples automatically in a single run, is designed for accurate $\delta^{18}\text{O}$ measurements of natural waters. Each of the four racks we used for this exercise held two reference waters with two-three samples for each. The reference waters were chosen such that their $\delta^{18}\text{O}$ values span the expected isotope values of the water samples in the rack. The reference waters were selected from the set for the natural range and the isotope-enriched reference waters that we made for the isotope community recently [9]. The $\delta^{18}\text{O}$ values of samples were calibrated on a per rack basis, which required some extrapolation for the two most depleted water mixtures and the one with the highest ^{18}O enrichment. The system is able to produce $\delta^{17}\text{O}$ results as well, albeit with limited accuracy (see [9, 11]). The $\delta^{17}\text{O}$ values obtained were calibrated against the reference waters over the entire batch of 4 racks as a whole. The $\delta^2\text{H}$ measurements for the 3 x 5 water samples were performed by the high-temperature pyrolysis-IRMS continuous flow technique in a routine fashion, as all values were in the natural range.

Table 3 shows the measured isotopic compositions for the water samples with their combined measurement uncertainties. The experimental data for the source waters (the leftmost columns of Table 3) and the gravimetric results reported in Table 2 are in very good agreement, which ensures that all involved procedures in preparation of the water sources went properly. For $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$, the gravimetric values are considered as superior to the measured ones in terms of reliability and uncertainty. Therefore we determined the final delta values for the water inside the cells using those gravimetric values for the source water and the measured differences between source and cell waters. These final delta values with their combined uncertainties ($k = 1$) are also given in Table 3. For $\delta^2\text{H}$, the measured cell water values are more accurate than those based on the gravimetric values plus the differences. Therefore, the measured $\delta^2\text{H}$ values for the cells are taken as the final values for the cells.

Like in the previous work, the differences in isotope δ -values between the original, the receiver and the final cell water follow a general pattern of isotopic enrichment due to the distillation process and subsequent depletion again in the process of cell filling and evacuating. The latter effect, the depletion, is caused by the fact that water is already taken from the receiver while the distillation process is ongoing (see the previous chapter for a more detailed explanation). However, the scatter in the fractionation effects is rather large, which means that it is impossible to predict the cell water isotopic composition from the original water with sufficient accuracy. Therefore, always a sample from the final cell water should be taken and analyzed (or alternatively the water purification process needs to become fully standardized in terms of water quantities, pumping times, temperatures etc.). As expected the ^2H isotope fractionation is much larger (typically an order of magnitude) than that for the ^{18}O isotope, whereas the fractionation for ^{17}O is indeed about half that of ^{18}O (and equation (3) is obeyed throughout the process).

7.5 Results and discussion

The realized triple point temperature deviations of the cells must be corrected for two small effects: the deviation of $\delta^2\text{H}$ from that of the VSL cell (-20.5 ± 0.4) ‰, and the deviation of the $\delta^{17}\text{O}$ values from those based on $\delta^{18}\text{O}$ and equation (3). The $\delta^2\text{H}$ deviations can be corrected by using the $A_{2\text{H}}$ correction constant of $A_{2\text{H}} = (673 \pm 4)$ μK that we derived in chapter 6. The corrections range from +20 μK for cell 1, through 6, 1 and 0 μK for cells 2, 4, and 5 to -20 μK

for cell 3. The uncertainties in these corrections ($\leq 0.7 \mu\text{K}$) are all negligible compared to the uncertainty in the temperature difference measurements themselves.

The correction for the $\delta^{17}\text{O}$ deviations is very small: if we use the recommended $A_{17\text{O}}$ coefficient from equation (1), being $60 \mu\text{K}$ according to [5] to estimate this correction, we find for cells 4 and 5 about $-2 \mu\text{K}$, and for the other three only $0.1\text{-}0.3 \mu\text{K}$. All these numbers are truly negligible compared to the (random) uncertainty in the triple point temperature differences. The measured triple point temperature deviations, as well as the ones corrected for $\delta^2\text{H}$ differences, with their combined uncertainties ($k = 1$) are provided in the rightmost columns of Table 3.

Table 3. The measured delta values with respect to VSMOW (normalized on the VSMOW-SLAP scale) for water samples taken at the start of the process ("Source water"), after the distillation ("Receiver water") and after the degassing from the cell ("Cell water"). The next columns give the final delta values for the isotopic composition of the cell water. The rightmost columns give the measured temperature deviations from the VSL national reference cell ($\Delta T_{\text{measured}}$ (μK)), and the values corrected for the small offset in $\delta^2\text{H}$ of the cell water ($\Delta T_{\text{corrected}}$ (μK)). See text for further explanations.

Mixture No.	Measured delta values (‰)									Final values for the isotopic composition of the cell water			Triple point temperature deviation	
	Source water			Receiver water			Cell water			$\delta^2\text{H}$	$\delta^{18}\text{O}$	$\delta^{17}\text{O}$	$\Delta T_{\text{measured}}$ (μK)	$\Delta T_{\text{corrected}}$ (μK)
	$\delta^2\text{H}$	$\delta^{18}\text{O}$	$\delta^{17}\text{O}$	$\delta^2\text{H}$	$\delta^{18}\text{O}$	$\delta^{17}\text{O}$	$\delta^2\text{H}$	$\delta^{18}\text{O}$	$\delta^{17}\text{O}$					
1	(-39.1 ± 0.6)	(-313.1 ± 0.4)	(-186.5 ± 0.6)	(-8.6 ± 0.6)	(-309.9 ± 0.4)	(-184.5 ± 0.6)	(-50.0 ± 0.6)	(-313.8 ± 0.4)	(-186.4 ± 0.6)	(-50.0 ± 0.6)	(-313.9 ± 0.4)	(-186.2 ± 0.7)	(-217 ± 19)	(-197 ± 19)
2	(-6.8 ± 0.6)	(-77.73 ± 0.10)	(-42.5 ± 0.4)	(7.4 ± 0.6)	(-75.81 ± 0.10)	(-41.2 ± 0.4)	(-29.3 ± 0.6)	(-79.75 ± 0.10)	(-43.5 ± 0.4)	(-29.3 ± 0.6)	(-79.6 ± 0.2)	(-44.5 ± 0.6)	(-32 ± 19)	(-26 ± 19)
3	(4.1 ± 0.6)	(159.7 ± 0.3)	(79.9 ± 0.5)	(8.3 ± 0.6)	(160.3 ± 0.3)	(80.3 ± 0.5)	(9.7 ± 0.6)	(160.8 ± 0.3)	(80.6 ± 0.5)	(9.7 ± 0.6)	(161.1 ± 0.3)	(81.0 ± 0.6)	(126 ± 19)	(106 ± 19)
4	(-8.3 ± 0.6)	(1056.3 ± 1.6)	(498.0 ± 1.6)	(-17.9 ± 0.6)	(1052.5 ± 1.6)	(496.8 ± 1.6)	(-21.5 ± 0.6)	(1054.0 ± 1.6)	(497.6 ± 1.6)	(-21.5 ± 0.6)	(1054.0 ± 1.8)	(497.3 ± 1.5)	(696 ± 19)	(697 ± 19)
5	(2.1 ± 0.6)	(2251 ± 3)	(896.0 ± 1.9)	(76.3 ± 0.6)	(2276 ± 3)	(904.1 ± 1.9)	(-20.4 ± 0.6)	(2245 ± 3)	(894.3 ± 1.9)	(-20.4 ± 0.6)	(2245 ± 3)	(894.2 ± 2.6)	(1418 ± 19)	(1418 ± 19)

The linear regression between the corrected triple point temperature deviation of the cells ($\Delta T_{\text{corrected}}$ (μK)) and the $\delta^{18}\text{O}$ of the cell water is shown in Figure 1.

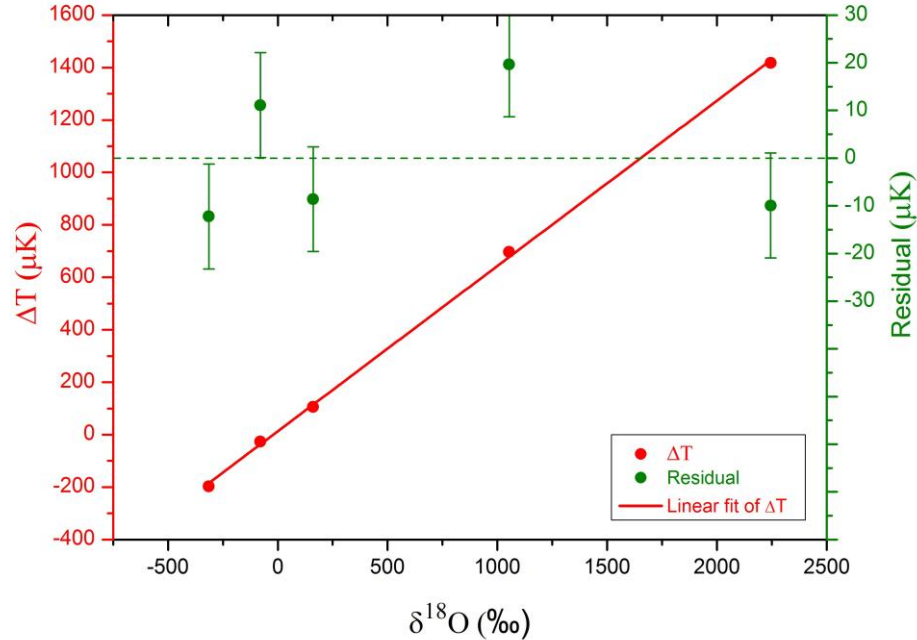


Figure 1. Triple point temperature differences between the five cells and the VSL reference cell, plotted against the corresponding $\delta^{18}\text{O}$ values, with a linear fit line (left-hand scale, in red) and residuals of the linear fit (right-hand scale, in green).

From the slope of the linear regression in Figure 1, we obtain the $^{18,17}\text{O}$ isotopic correction constant, $A_{\text{O}} = 630 \mu\text{K}$, with a standard uncertainty of $10 \mu\text{K}$. As in chapter 6, because some of the error contributions are shared by all five temperature difference measurements, we expect a random uncertainty of $11 \mu\text{K}$ using the GUM (The Guide to the Expression of Uncertainty in Measurement) approach [12]. The residuals of the fit, also shown in figure 1, are in good agreement with this expectation. Extrapolating to zero temperature difference leads to $\delta^{18}\text{O} = (-20 \pm 14) \text{‰}$. This agrees fairly with the $\delta^{18}\text{O}$ value of -4.86‰ for the content of the VSL reference cell.

Our newly derived A_{O} correction constant for equation (4), $A_{\text{O}} = (630 \pm 10) \mu\text{K}$, can be compared with the currently recommended values of $(603 \pm 3) \mu\text{K}$ for $A_{18\text{O}}$ and $(60 \pm 1) \mu\text{K}$ for $A_{17\text{O}}$ by the CCT in 2010 from the recent study of White et al. [5] The relation between the current equation

(1) and our newly proposed equation (4) can be derived through linearizing equation (3). We then obtain:

$$A_{\text{O}} = A_{18\text{O}} + \lambda A_{17\text{O}} \quad (5)$$

with $\lambda = 0.528$ [7]. The right-hand side of this equation, based on the current values, yields $(635 \pm 3) \mu\text{K}$, to which our newly found value compares favorably. The uncertainty attributed to the current values is smaller than that in our new value. It is primarily based on two deduced values for $A_{18\text{O}}$ (presented in Table 2 of [5]), one from work by Lehman and Siegenthaler [13] on isotope fractionation between ice and water, which resulted in a value for $A_{18\text{O}}$ of $(601 \pm 7) \mu\text{K}$, and the other based on triple point temperatures of pure water isotopologues and fusion enthalpies, which resulted in $(606 \pm 20) \mu\text{K}$. The un-weighted mean of these two, $603 \mu\text{K}$, with an uncertainty based solely on their consistency ($3 \mu\text{K}$) became the recommended value for $A_{18\text{O}}$. As there are no explicit fractionation factors measured for ^{17}O available, the value for $A_{17\text{O}} = (60 \pm 1) \mu\text{K}$ is only calculated, based on the information for ^{18}O and the ^{17}O - ^{18}O relation as in equation (3). To our opinion, the uncertainty of $3 \mu\text{K}$ claimed by White and Tew [5] for $A_{18\text{O}}$ is overly optimistic as it relies on the (probably coincidental) very good agreement between the two values quoted above. In that sense the uncertainty estimate in our present result is more reliable. As shown above, however, the values for the coefficients agree very well. To see our new correction formula (4) at work for real triple point cells containing waters with natural isotopic abundances, and to compare it to the currently recommended corrections, table 4 shows the isotope correction and uncertainty for a number of triple point of water cells reported in the literature by White et al., [6] along with a number owned by the VSL [14]. Four of the five cells used in the work by White et al. contained natural waters. White et al. measured the triple point temperature differences between three cells containing waters from Antarctica (Barne Glacier (96/2), Lake Vanda (96/3), and sea-ice (96/4)) and the one containing tap water (96/1) with $\delta^2\text{H} = (-95.8 \pm 1.0) \text{‰}$ and $\delta^{18}\text{O} = (-13.65 \pm 0.1) \text{‰}$. The first three rows of the table below present the results for White et al.'s data. The rest of the data in table 4 are for the VSL cells. The VSL measured the temperature differences between a total of fifteen triple point cells containing waters with natural isotopic abundances and the national reference cell. Here, we present the measured temperature differences between some selected cells (cells 2, 3, 4, 12 and 13 presented

in table 3 of [14]) and cell 1 (as a reference cell) having $\delta^{18}\text{O} = (-6.93 \pm 0.08) \text{‰}$ and $\delta^2\text{H} = (-51.1 \pm 0.8) \text{‰}$, along with their corrected values and the combined uncertainties.

Table 4. Comparison of isotope corrections and total uncertainties for a number of triple point cells filled with waters with natural isotopic abundances [6, 14]. The first columns give the measured isotope values for the cell waters. The $\delta^{17}\text{O}$ values were computed using equation (3) and not measured. The measurement uncertainties ($k=1$) of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ are, respectively, 1‰ and 0.1‰ for White's cells, 0.8‰ and 0.08‰, respectively, for the VSL cells. The second column presents the temperature deviations from the respective reference cells (see text), along with reported standard deviation of the differences for White's cells and combined uncertainties in the measured differences for the VSL cells. The rightmost columns are the total corrections calculated according to the CCT recommendations ($A_{2\text{H}} = (671 \pm 10) \mu\text{K}$, $A_{18\text{O}} = (603 \pm 3) \mu\text{K}$ and $A_{17\text{O}} = (60 \pm 1) \mu\text{K}$), and our new results ($A_{2\text{H}} = (673 \pm 4) \mu\text{K}$ and $A_{\text{O}} = (630 \pm 10) \mu\text{K}$). The calculated uncertainties in the corrections include terms due to the uncertainties in the isotope values and correction constants.

Cell	Isotopic composition of cell water			$\Delta T_{\text{measured}} (\mu\text{K})$	$\Delta T_{\text{corrected}} (\mu\text{K})$	
	$\delta^2\text{H}$	$\delta^{18}\text{O}$	$\delta^{17}\text{O}$		CCT values	present work
1	-0.271	-0.0351	-0.0187	(-145±7)	(-131.2 ± 2.0)	(-131.4 ± 1.2)
2	-0.307	-0.0398	-0.0212	(-165±5)	(-158.3 ± 2.3)	(-158.6 ± 1.3)
3	-0.040	-0.0041	-0.0022	(34±6)	(43.5 ± 1.1)	(43.6 ± 1.0)
4	-0.0455	-0.00630	-0.0033	(7±17)	(4.2 ± 0.8)	(4.2 ± 0.8)
5	-0.0669	-0.00860	-0.0045	(-3±17)	(-11.7 ± 1.0)	(-11.7 ± 0.8)
6	-0.0658	-0.00851	-0.0045	(2±17)	(-10.9 ± 1.0)	(-10.9 ± 0.8)
7	-0.0205	-0.00486	-0.0026	(28±17)	(21.8 ± 1.0)	(21.9 ± 0.8)
8	-0.0367	-0.00635	-0.0034	(23±17)	(10.0 ± 1.1)	(10.1 ± 0.8)

The corrected triple point temperatures using our new values are quite close, in fact almost identical, to the ones with CCT values. The uncertainties in our values, however, are smaller due to the lower uncertainty in our A_{2H} value compared to the CCT one. The uncertainties in the corrections for the oxygen isotopes have a small to negligible contribution. We have estimated the uncertainties in the isotope value determination conservatively; state-of-the-art measurements would give uncertainties of about 0.4 ‰ for δ^2H and 0.04 ‰ for $\delta^{18}O$. Using such uncertainties would even lower the minimum uncertainties in the correction further, from 0.8 to less than 0.5 μK .

7.6 Conclusions and recommendations

The joint study between VSL and CIO, as presented in this and the previous chapter, has resulted in an accurate and straightforward determination of the coefficients needed to correct realized triple point temperatures for the deviation of the isotope composition of the water from VSMOW. Contrary to the existing values, our ones are entirely based on the direct triple point temperature shift measurements as a function of the isotopic composition of the water, so directly comparable to the situation where the correction needs to be applied. Furthermore, for the 2H correction our result is considerably more accurate than the value that is presently in use. For the oxygen side, we propose an integrated $^{17}O, ^{18}O$ correction based on the isotope value for ^{18}O alone. As this is the isotope commonly measured this makes the correction more easily applicable (provided only natural water is used). Therefore, we recommend that the correction equation be changed to:

$$T_{\text{meas}} - T_{\text{VSMOW}} = A_{2H} \delta^2H + A_O \delta^{18}O \quad (6)$$

with $A_{2H} = (673 \pm 4) \mu K$ and $A_O = (630 \pm 10) \mu K$ and $\delta^2H, \delta^{18}O$ the isotopic ratio deviations from that of VSMOW (expressed as small numbers). As such corrections are usually significant, the cell water of all triple point cells should be measured for its isotopic content.

The low uncertainty in our coefficients, and the supporting evidence from previous measurements and values inferred from other thermophysical measurements, show that the uncertainty in the isotope correction for triple point cell waters used around the world will be $< 1 \mu K$ and thus negligible compared to the uncertainty in the temperature measurement. The

practice by some triple point cell manufacturers of adding unnatural, enriched waters to the initial source water, to compensate for isotope depletion during the purification process, is not recommended. After adding such enriched water, full isotope analysis ($\delta^2\text{H}$, $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$) is required (even when only adding fully deuterated water, since such water is also significantly enriched in the heavy oxygen isotopes, see Table 1), and the process will result in deviations from equation (3), such that our new A_{O} coefficient cannot be used. And even more important, since the corrections using equation (6) are now so accurate, there is no need to tune the water to values close to VSMOW. If, for other reasons, one still wants to achieve a triple point realization close to VSMOW, it is advisable to let the initial batch of water evaporate to the atmosphere under elevated temperatures (say 40 °C). If for instance one allows 50 % of the water to evaporate, typical enrichments of 40 ‰ and 7 ‰, for $\delta^2\text{H}$ and $\delta^{18}\text{O}$ respectively, will be achieved; for 75 % evaporation these numbers more than double (see the description of "Rayleigh fractionation", for example in [15]). This process is easy and cheap, and equation (3) remains valid as for all natural processes.

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