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### Water enriched in the rare stable isotopes

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## Chapter 6

### Accurate experimental determination of the isotope effects on the triple point temperature of water. I. Dependence on the $^2\text{H}$ abundance

#### Abstract

Variation in the isotopic composition of water is one of the major contributors to uncertainty in the realization of the triple point of water (TPW). Although the dependence of the TPW on the isotopic composition of the water has been known for years, there is still a lack of a detailed and accurate experimental determination of the values for the correction constants. This chapter is the first of two chapters (Part I and Part II) that address quantification of isotope abundance effects on the triple point temperature of water. In this chapter, we describe our experimental assessment of the  $^2\text{H}$  isotope effect. We manufactured five triple point cells with prepared water mixtures with a range of  $^2\text{H}$  isotopic abundances encompassing widely the natural abundance range, while the  $^{18}\text{O}$  and  $^{17}\text{O}$  isotopic abundance were kept approximately constant and the  $^{18}\text{O}$ - $^{17}\text{O}$  ratio was close to the Meijer-Li relationship for natural waters. The selected range of  $^2\text{H}$  isotopic abundances led to cells that realised TPW temperatures between approximately -140  $\mu\text{K}$  to +2500  $\mu\text{K}$  with respect to the TPW temperature as realized by VSMOW (Vienna Standard Mean Ocean Water). Our experiment led to determination of the value for the  $\delta^2\text{H}$  correction parameter of  $A_{2\text{H}} = 673 \mu\text{K} / (\text{‰ deviation of } \delta^2\text{H} \text{ from VSMOW})$  with a combined uncertainty of 4  $\mu\text{K}$  ( $k=1$ , or  $1-\sigma$ ).

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## 6.1 Introduction

The triple point of water (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 TPW is also the most important fixed point for the practical realization of the International Temperature Scale of 1990 (ITS-90) [1]. Any ITS-90 temperature,  $T_{90}$ , in the range between 13.8033 K and 1234.93 K is defined in terms of the ratio of the resistance of a standard platinum resistance thermometer (SPRT) at a temperature  $T_{90}$  and the resistance of the same SPRT at the TPW temperature. As a consequence, any uncertainty in the realization of the TPW is therefore propagated to any temperature  $T_{90}$  over this range.

To assess the uncertainties in the realization of the TPW, international comparisons of cells were carried out among various metrology laboratories. One such international comparison, organized by the BIPM (Bureau International des Poids et Mesures, Paris), carried out between 1994 and 1996 [2] showed surprisingly large dispersion of the results. Following this, Nicholas et al. [3] demonstrated the larger than expected influence of isotope effects on the TPW. This knowledge motivated the Consultative Committee for Thermometry (CCT) to organize another international comparison (the CCT-K7). In 2005, the results of the CCT-K7 showed that the different isotopic composition of the water used in the TPW cells by 21 metrology institutes all over the world was indeed one of the major sources of variability in the realized TPW temperature [4]. Prompted by the results of this international comparison, the CCT clarified the definition of the kelvin by requiring the water to have the same isotopic composition of VSMOW [5] and recommended the use of the following algorithm to correct the TPW temperature realized by non-VSMOW water [6]:

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

where the  $A_{2H} = (628 \pm 20) \mu\text{K}$ ,  $A_{18O} = (641 \pm 50) \mu\text{K}$ , and  $A_{17O} = (57 \pm 5) \mu\text{K}$  are the recommended isotopic correction constants, and the  $\delta^2H$ ,  $\delta^{18}O$ , and  $\delta^{17}O$  are the isotopic deviations from VSMOW expressed in terms of abundance ratios as:

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

and similarly for oxygen isotopes ( $^{17}\text{O}$  and  $^{18}\text{O}$ ). The data are then normalized to the international VSMOW-SLAP scale [7]. Since these  $\delta$ -values are small numbers for natural substances, they are usually expressed in ‰ (per mille, or per thousand). However, in equation (1) they should be inserted as they are, namely small numbers. The values for the isotope correction constants at that time were determined based on the measured data obtained from the freezing point of mixtures of  ${}^2\text{H}$  and  $^{18}\text{O}$  enriched waters by Kiyosawa [8], and the reported values by White et al. on the triple point temperature measurements for a set of five TPW cells; four containing waters with natural isotope abundances and one containing highly depleted water [9].

Kiyosawa used waters with 10-100 fold higher  ${}^2\text{H}/{}^1\text{H}$  ratio and 4-40 fold higher  $^{18}\text{O}/^{16}\text{O}$  than VSMOW, and the CCT had to extrapolate the results back to the natural range. Furthermore, he apparently relied on the manufacturer's specifications of the heavy waters used in the measurements (both for the enrichment levels of the enriched isotopes, and –most likely- the statement by the manufacturer that the other isotopes had been "renormalized"), and did not provide the uncertainties in measurements. Four of the five waters used in the work by White et al. were natural waters, while the fifth was a highly  ${}^2\text{H}$ -depleted water. The evaluation of the parameters of equation (1) thus was severely limited due to the high correlation of the  ${}^2\text{H}$ ,  $^{18}\text{O}$  and  $^{17}\text{O}$  concentrations (the  ${}^2\text{H}$  depleted water was also much depleted in  $^{17}\text{O}$  and  $^{18}\text{O}$ ) which makes the individual isotope effects indistinguishable. Furthermore, the range of triple point temperatures for the four natural waters was very small. These limitations resulted in large uncertainties in the fitted values for the parameters of equation (1). 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 based on data from isotopic fractionation measurements, enthalpies of fusion and freezing points of the water isotopologues [10]. The values derived by White and Tew were  $A_{2\text{H}} = (671 \pm 10) \mu\text{K}$ ,  $A_{18\text{O}} = (603 \pm 3) \mu\text{K}$  and  $A_{17\text{O}} = (60 \pm 1) \mu\text{K}$ , which are the values currently recommended for use with the ITS-90.

However, a thorough and accurate empirical investigation of the isotope dependence of the TPW temperature, with proper quantitative control over the isotopic composition of the waters, is 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 this chapter (Part I) we present the results of our determination of the  $^2\text{H}$  dependence of the TPW temperature. We manufactured a set of five TPW cells containing waters with different  $\delta^2\text{H}$  values (ranging from  $\approx -220$  ‰ to  $\approx 3800$  ‰, equivalent to a  $^2\text{H}$  abundance range from 0.8 to 4.8 times the  $^2\text{H}$  abundance in VSMOW), having nearly identical  $^{18}\text{O}$  and  $^{17}\text{O}$  abundances close to VSMOW, and the  $^{18}\text{O}$ - $^{17}\text{O}$  ratio according to the Meijer-Li relationship for natural waters [11]. The TPW temperature of the five cells was then measured following well established thermometric procedures. In the following, we first describe the production of water mixtures by gravimetric mixing of waters with well-known isotopic compositions. Then, the manufacturing of the TPW cells containing the prepared water mixtures, and the impact of the manufacturing process on the isotopic composition of the waters are described. Finally, we report and discuss the determined correction parameter for the  $^2\text{H}$  dependence of the TPW temperature and its uncertainty.

## 6.2 Gravimetric preparation of water mixtures

A set of five water mixtures, 1.5 liters each, four enriched and one depleted in  $^2\text{H}$  content, were prepared gravimetrically by mixing two or more parent waters: distilled natural water (typical  $\delta^2\text{H} = -43.5$  ‰ and  $\delta^{18}\text{O} = -6.3$  ‰), isotopically pure  $^2\text{H}$  water (specified  $^2\text{H}$  fraction = 99.993 %, Sigma Aldrich, Zwijndrecht, The Netherlands), highly  $^{18}\text{O}$ -enriched water (specified  $^{18}\text{O}$  fraction = 97.6 % and  $^{17}\text{O}$  fraction = 0.7 %, Cortecnet, Voisins-Le-Bretonneux, France), highly  $^{17}\text{O}$ -enriched water (specified  $^{17}\text{O}$  fraction = 41.1 % and  $^{18}\text{O}$  fraction = 43 %, Rotem, Leipzig, Germany), and  $^2\text{H}$ -depleted water ( specified  $\leq 1$ ppm  $^2\text{H}$ , Sigma Aldrich, Zwijndrecht, The Netherlands).

These parent waters have been thoroughly assessed for their isotopic compositions. For this we made use of specific, gravimetric dilution schemes, and a variety of analysis techniques:

continuous flow IRMS (Isoprime 10) combined with either high temperature pyrolysis (Hekatech) for  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  analysis [12], or chromium reduction (Europa PyrOH) for only  $\delta^2\text{H}$  analysis [13], dual inlet IRMS (SIRA10) combined with a home-built  $\text{CO}_2\text{-H}_2\text{O}$  equilibration system for  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  analysis (the latter with limited precision) [14], and finally a prototype laser gas analyzer based on OF-CEAS (optical feedback cavity enhanced absorption spectroscopy) for measurement of all three isotopes simultaneously, which we have developed newly for water liquid samples [15,16]. We benefitted from our experience in a previous study, in which we produced new isotope-enriched reference waters for the isotope community [17]. The  $^2\text{H}$  and the  $^{18}\text{O}$  enriched waters were from the same batch of waters as used in this previous study. It turned out that the supplier's statements of oxygen isotopic abundances for the  $^{18}\text{O}$  enriched water were not accurate (enough) and the isotopic abundances of the non-specified side of these highly enriched waters ( $^2\text{H}$  in  $^{18}\text{O}$  water and  $^{17,18}\text{O}$  in  $^2\text{H}$  water) were also substantially enriched. We checked the purity of the  $^2\text{H}$  water with the isotope dilution method, and it corroborated the stated value by the supplier, but with less precision. Therefore, we relied on the stated purity, but used a conservative uncertainty estimate of  $\pm 0.005\%$  in this value. Similarly, the dilution testing of the  $^2\text{H}$ -depleted water would also lead to a result with limited accuracy. Therefore, we used a value based on the information by the manufacturer and attributed a relatively large uncertainty, namely  $0.5 \pm 0.5$  ppm for the  $^2\text{H}$  abundance. This is equivalent to  $(-997 \pm 3) \text{‰}$  for  $\delta^2\text{H}$ . This  $^2\text{H}$ -depleted water appeared to be considerably depleted in its oxygen isotopes as well (actually in a very similar way as the  $^2\text{H}$  depleted water used in White et al. [9]). The abundances as provided by the supplier for the  $^{17}\text{O}$ -enriched water were in reasonable agreement with our measurements, but also for those we used our own determinations for  $^{17}\text{O}$  and  $^{18}\text{O}$ . For  $^2\text{H}$ , we assumed it to be in the natural range ( $\approx 0.015\%$ ), but with a large uncertainty. This uncertainty, however, is totally negligible in the combined uncertainty calculations due to the small amount of  $^{17}\text{O}$ -enriched water that will be added. Table 1 provides the isotopic specifications of the parent waters as determined in our precise quantifications.

Table1. Isotopic compositions of the parent waters used for the preparation of the water mixtures, expressed in delta values or isotopic abundances, with their combined uncertainties ( $k = 1$ ). The isotope delta values are expressed in ‰ as defined by equation (2).

Components	Isotopic Abundances (%) or Isotope delta Values (‰)		
	$^2\text{H}$	$^{18}\text{O}$	$^{17}\text{O}$
distilled natural water ( $\delta$ )	$(-44.0 \pm 1.0) \text{‰}$	$(-6.26 \pm 0.06) \text{‰}$	$(-3.3 \pm 0.4) \text{‰}$
$^2\text{H}$ -enriched water	$(99.993 \pm 0.005) \%$	$(0.8998 \pm 0.0010) \%$	$(0.0874 \pm 0.0004) \%$
$^{18}\text{O}$ -enriched water	$(0.1791 \pm 0.0014) \%$	$(96.05 \pm 0.12) \%$	$(1.176 \pm 0.020) \%$
$^{17}\text{O}$ -enriched water	$(0-0.05) \%$	$(44.5 \pm 0.4) \%$	$(39.42 \pm 0.03) \%$
$^2\text{H}$ -depleted water ( $\delta$ )	$(-997 \pm 3) \text{‰}$	$(-623.4 \pm 0.5) \text{‰}$	$(-391.5 \pm 1.0) \text{‰}$

Using the parent waters in Table 1, we calculated "recipes" for water mixtures that would cover a wide range of  $\delta^2\text{H}$  values, while the  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  values should be identical for all waters as much as possible, and also correspond to the natural  $^{17}\text{O}$ - $^{18}\text{O}$  relationship. For these calculations, we used a thoroughly tested spreadsheet that we developed for the calculation of isotopic abundances for water mixtures [18]. We chose to make four mixtures enriched in  $^2\text{H}$ , and for those addition of only the  $^2\text{H}$  enriched water to the natural water sufficed. However, for the fifth one, that we chose to be substantially depleted in  $^2\text{H}$ , the mixture had to be made from four parent waters.

For preparation and storage of these five waters, we used 2 liters glass bottles and filled each of the five bottles with the calculated quantities of demineralized local tap water (Elix 10, Millipore, Amsterdam, The Netherlands) and weighed them to a precision of 0.01 g using a precision balance (KERN 572-39, Balingen, Germany). For the four mixtures with enriched  $^2\text{H}$  amounts, the  $^2\text{H}$  enriched isotope water additions, that were 1 gram or less, were served in small vials such that the quantities could be weighed to 0.01 mg precision with a precision analytical balance (CPA225D, Sartorius, Göttingen, Germany) and then immersed into their glass bottles for thorough mixing with the demineralized waters. For the fifth mixture, we first added the  $^2\text{H}$ -depleted water to the glass bottle filled with the demineralized water, and as the amount of

depleted water added was substantial ( $\approx 300$  gram) weighing the bottle before and after the addition produced an accurate enough estimate for the amount of  $^2\text{H}$  depleted water. Next, small amounts of  $^{18}\text{O}$  enriched and  $^{17}\text{O}$  enriched water were added in vials, as described above. After adding the vials, the bottles were tightly capped (and caps again wrapped with parafilm), and regularly shaken for two-three days to ensure complete mixing.

Given the desired accuracy of the weighing process, we had to take the slight influence of the different densities of the waters on the buoyancy effect into account, so correction for the buoyancy effect differences had to be applied. At 1013 hPa (the Groningen laboratory is at sea level) and at 21 °C, and relative humidity of 60%, air has a density of 1.19 kg/m<sup>3</sup>. With densities (at 21 °C) of 998 kg/m<sup>3</sup> for natural water, 1105 kg/m<sup>3</sup> for pure  $^2\text{H}_2\text{O}$ , and 1106 kg/m<sup>3</sup> for highly enriched, but not pure  $^{18}\text{O}$  water [19-22], the buoyancy effect leads to a systematic relative difference of slightly above  $10^{-4}$  in their mass ratios. That influence is significant, and we correct for this effect. The same holds for the enriched  $^{17}\text{O}$  water (which is also enriched in  $^{18}\text{O}$ ), for which we calculate a density of 1067 kg/m<sup>3</sup>. The  $^2\text{H}$ -depleted water has a density (at 21 °C) of 998 kg/m<sup>3</sup> [23], which is so close to the density of natural water, that the difference in the buoyancy effect is negligible. (See for more details on the buoyancy correction [17]).

Using the developed spreadsheet, the isotopic composition of the parent waters from Table 1, and the exact masses of the constituents of the mixtures, we could calculate the isotope values of the water mixtures. Table 2 summarizes information on the mass contents of the water mixtures and the calculated isotope values with their combined uncertainties. The latter have been deduced from the uncertainties given in Table 1 and the weighing uncertainties.



Table 2. Masses of the parent waters used for the water mixtures and the calculated isotope values of water mixtures with respect to VSMOW, with their combined uncertainties (k=1). The uncertainties in the masses at and below 1 gram are  $\pm 0.00001$  g, and are  $\pm 0.01$  g for the amounts of the natural water and  $^2\text{H}$  depleted water.

Sample	Mass of contents (g)					Calculated delta values (‰)		
	Natural water	$^2\text{H}$ depleted water	$^{18}\text{O}$ -enriched water	pure $^2\text{H}$ water	$^{17}\text{O}$ -enriched water	$\delta^2\text{H}$	$\delta^{18}\text{O}$	$\delta^{17}\text{O}$
	(buoyancy ratio corrected)							
mixture 1	1505.04	-	-	1.00071	-	( 3793.4 $\pm$ 1.0 )	(-4.16 $\pm$ 0.06)	(-2.5 $\pm$ 0.4)
mixture 2	1505.93	-	-	0.60129	-	( 2260.4 $\pm$ 1.0 )	(-5.00 $\pm$ 0.06)	(-2.8 $\pm$ 0.4)
mixture 3	1509.08	-	-	0.20066	-	( 723.4 $\pm$ 1.0 )	(-5.84 $\pm$ 0.06)	(-3.2 $\pm$ 0.4)
mixture 4	1509.09	-	-	0.08062	-	( 264.3 $\pm$ 1.0 )	(-6.09 $\pm$ 0.06)	(-3.2 $\pm$ 0.4)
mixture 5	1299.67	299.88	0.37560	-	0.10341	( -219.6 $\pm$ 1.0 )	(-6.9 $\pm$ 0.2)	(-6.8 $\pm$ 0.5)

As can be seen, all five water mixtures have approximately the same  $^{17,18}\text{O}$  isotopic composition such that the effect of only  $^2\text{H}$  isotopes on water triple point temperatures can be assessed.

### 6.3 Manufacture of TPW cells and triple point temperature measurements

Five TPW cells were manufactured by VSL with the above-mentioned mixtures using the usual production process described in [24]. A schematic drawing of the TPW cell manufacturing system is shown in Figure 1. It is basically a two stage distillation system. The original water starts in boiling flask B1, which is connected to condenser C1 that continuously condenses the larger part of the vapour produced back into the boiling flask. Condenser C2 condenses the water vapour into the second boiling flask B2, which is in its turn connected to condenser C3. The water is then distilled into a cooled receiver flask. Finally, the receiver finishes the double distillation and condenses the water into a conductivity testing system. If the purification through the distillation procedure is entirely satisfactory, this water can be subsequently filled into the evacuated triple point cell. Each condenser has its own individual cooling water system. The entire distillation process is performed in vacuum and temperatures are maintained at 12 °C, so

residual gas contents of the water with higher condensation point are effectively removed by pumping. Of course, in this process also some water vapour is removed, and since water vapour is depleted in its light isotopes compared to the liquid water it originates from, this gives rise to isotope enrichment of the remaining water that is collected in the receiver. After transferring the water from the receiver to the cell, the cell is vacuum-pumped for some hours by a higher capacity vacuum pump to ensure the water is entirely degassed. Also this step leads to a change in the isotopic composition of the remaining water. Finally, the filled cell is flame-sealed from the system. The production of each cell requires about two weeks, one for cleaning and pre-conditioning the cell and the other one for distilling the water and degassing the cell. As described, the distillation of the water and the degassing of the cell have impact on the isotopic composition of the water due to isotope fractionation processes, which implies that the isotopic composition of the final water sealed in the cell is not that of the original source water.

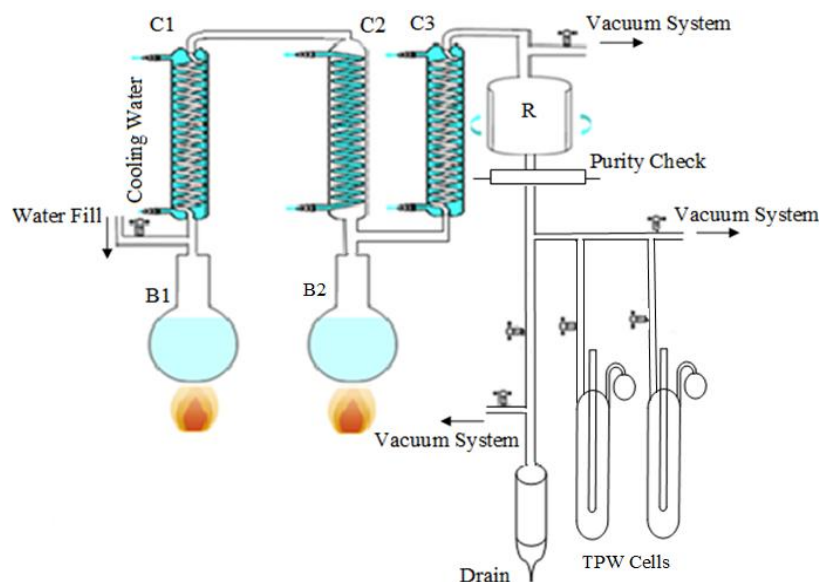


Figure 1. Schematic drawing of the TPW cell water purification system; B1, boiler 1; B2, boiler 2; C1, condenser 1; C2, condenser 2; C3, condenser 3; R, receiver.

To quantify the isotopic fractionation processes, and mostly to accurately determine the isotopic composition of the water actually sealed within the cells, samples at three stages of the production process were taken: the water used to fill the first boiler of the double distillation

system (source water, this is the water delivered with its composition given in Table 2), the water at the end of double distillation before degassing (receiver water), and the water from the sealed triple point cell itself (cell water). To sample the latter, the triple point cell has a special design such that, after flame-sealing the cell, a "quartz bulb" connected to the cell could be filled with the cell water and subsequently flamed off without breaking the vacuum on either side (see Figure 2). For each cell there were thus three water samples, which were analyzed for their isotopic composition (see next section).

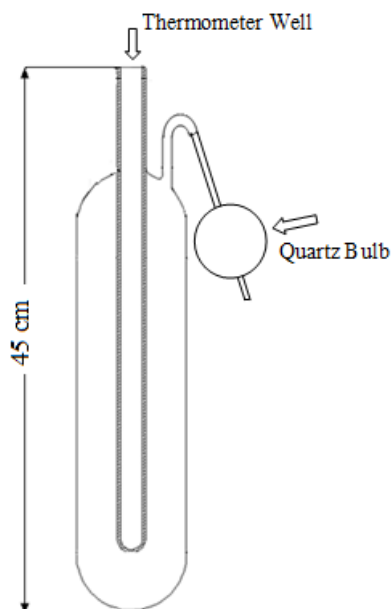


Figure 2. Schematic drawing of a VSL TPW cell.

The temperature differences between each manufactured cell and the VSL national reference cell of 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. All measurements were performed as ratios of the resistance of a calibrated Standard Platinum Resistance Thermometer (SPRT), inserted in the well of the TPW cell, to the resistance of a 25  $\Omega$  calibrated reference resistor with temperature coefficient of about 1 ppm/ $^{\circ}\text{C}$ , maintained in a temperature-controlled oil bath at  $(28.000 \pm 0.002) \text{ }^{\circ}\text{C}$ . The measured resistances were corrected for self-heating and hydrostatic pressure. For each manufactured cell, the SPRT resistance difference from the VSL national reference cell was then transformed into a temperature difference, using the sensitivity coefficient of the SPRT. We performed measurements for each

cell with two different ice mantles. The measurements on each cell were taken over two weeks for each ice mantle starting at least four days after the preparation of the ice mantle. The mean of the temperatures obtained for each cell is attributed to the realized temperature by the cell. The uncertainty budget in measuring the temperature difference between each cell and the VSL national reference cell is reported in Table 3.

Table 3. Uncertainty budget for the temperature difference measurements between an arbitrary cell and the VSL reference cell.

Uncertainty source	Contribution ( $\mu\text{K}$ )
Repeatability for a single ice mantle	7
Reproducibility for different ice mantles and SPRTs	12
SPRT self-heating	8
Stray thermal exchanges	7
Hydrostatic head correction	4
Resistance bridge non-linearity	6
<b>Combined uncertainty (<math>k = 1</math>)</b>	<b>19</b>

Although we focus here on the isotope effects on the triple point temperature of water, an attempt has been done to quantify the impact of impurities on the measured TPW temperatures. The waters were investigated using Inductively-Coupled Plasma Mass Spectrometry (ICPMS). The results showed that the impurities will affect the triple point temperatures by 10  $\mu\text{K}$  at most. The impurity influence is thus small (although not entirely negligible) compared to the combined uncertainty given in Table 3.

## 6.4 Results and discussion

The  $\delta^2\text{H}$  measurements of the 3 x 5 samples were performed using our OF-CEAS laser spectrometer. For the calibration of our scales in this measurement range, far outside the natural range, we made use of the newly produced isotope-enriched reference waters from our previous project [17]. Although the laser spectrometer in principle also gives  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  values, the strong absorption line of the  $^2\text{H}^1\text{H}^{16}\text{O}$  isotopologue of the water mixtures (for water mixtures 1 to 4) affects the accuracy and precision of laser spectroscopic measurements for  $^{18}\text{O}$  and  $^{17}\text{O}$ , and this effect had not quantitatively been dealt with at the moment these measurements took place. Therefore, we had to rely on the classical  $\text{H}_2\text{O}-\text{CO}_2$  equilibrium-IRMS technique which gives high quality  $\delta^{18}\text{O}$  results and in addition  $\delta^{17}\text{O}$ , but the latter with only limited accuracy. Table 4 shows the measured isotopic compositions for the water samples with their combined measurement uncertainties, which incorporate contributions from the precision of repeated measurements, the uncertainties in delta values of reference waters used to normalize the  $\delta$ -scale and experimental biases. The measured delta values of Table 4 for the source waters confirm the gravimetrically calculated ones presented in Table 2 (although the  $\delta^2\text{H}$  values for water mixtures 3 and 4 differ by 2 to 2.5 times the measurement uncertainty), which ensures that all involved procedures in preparation of the water sources went properly. 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 and the triple point temperature deviations of the water cells with their combined uncertainties ( $k = 1$ ) are given in the rightmost columns of Table 4. The uncertainty in the final delta values of the cell waters is calculated based on the uncertainty in the difference of the measured delta values for source and cell waters (this difference is known with lower uncertainty than the values themselves) and the uncertainty in the gravimetric delta value of the source waters.

Table 4. 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 filling ("Cell water"). The rightmost columns give the final values for the isotopic composition of the cell waters, and the registered temperature deviations from the VSL national reference cell. For further explanation see text.

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			$\delta^2\text{H}$	$\delta^{18}\text{O}$	$\delta^{17}\text{O}$	$\Delta T$ ( $\mu\text{K}$ )
	$\delta^2\text{H}$	$\delta^{18}\text{O}$	$\delta^{17}\text{O}$	$\delta^2\text{H}$	$\delta^{18}\text{O}$	$\delta^{17}\text{O}$	$\delta^2\text{H}$	$\delta^{18}\text{O}$	$\delta^{17}\text{O}$	$\delta^2\text{H}$	$\delta^{18}\text{O}$	$\delta^{17}\text{O}$	
1	(3805 ± 23)	(-4.09 ± 0.06)	(-2.5 ± 0.4)	(4030 ± 23)	(1.20 ± 0.06)	(-0.4 ± 0.4)	(3686 ± 22)	(-6.79 ± 0.06)	(-3.6 ± 0.4)	(3675 ± 5)	(-6.86 ± 0.07)	(-3.7 ± 0.4)	(2479 ± 19)
2	(2270 ± 13)	(-5.00 ± 0.06)	(-2.9 ± 0.4)	(2386 ± 14)	(-1.08 ± 0.06)	(-1.1 ± 0.4)	(2202 ± 12)	(-6.83 ± 0.06)	(-3.7 ± 0.4)	(2192 ± 2)	(-6.83 ± 0.07)	(-3.7 ± 0.4)	(1496 ± 19)
3	(715 ± 4)	(-5.87 ± 0.06)	(-2.9 ± 0.4)	(905 ± 6)	(5.73 ± 0.06)	(2.5 ± 0.4)	(698 ± 12)	(-6.88 ± 0.06)	(-3.6 ± 0.4)	(706 ± 9)	(-6.86 ± 0.07)	(-3.9 ± 0.4)	(474 ± 19)
4	(272 ± 3)	(-5.89 ± 0.06)	(-3.3 ± 0.4)	(349 ± 3)	(0.99 ± 0.06)	(1.3 ± 0.4)	(249 ± 3)	(-7.65 ± 0.06)	(-3.0 ± 0.4)	(242 ± 2)	(-7.85 ± 0.07)	(-3.0 ± 0.4)	(182 ± 19)
5	(-216 ± 3)	(-6.11 ± 0.06)	(-6.6 ± 0.4)	(-209 ± 2)	(-5.48 ± 0.06)	(-6.2 ± 0.4)	(-209 ± 2)	(-5.11 ± 0.06)	(-6.3 ± 0.4)	(-213 ± 2)	(-5.9 ± 0.2)	(-6.5 ± 0.5)	(-136 ± 19)

The results, as shown in Table 4, show that both the distillation and the degassing process change the isotopic composition of the water. Normally, both processes would lead to isotopic enrichment: as explained earlier, water molecules containing the light isotopes have lower binding energies which cause them to evaporate more readily than the water molecules containing the heavy isotopes. When evaporation takes place, the resulting water vapour that is removed by the vacuum pump will be depleted in the heavy isotopes. As a result, the remaining reservoir water will be enriched in the heavy isotopes. This in fact happens during both the distillation and the degassing processes. However, in the production of the triple point cells, the distilled receiver water is often already extracted from the receiver when the distillation process is incomplete. At that stage of the process, the distilled water is still depleted compared to the original source water, as the "heavy" water only gets distilled at the end of the process. Therefore the cell water is depleted compared to the original source water, in spite of the degassing process. The distillation process continues after the extraction of water from the receiver, and eventually leads to enrichment of the receiver water, both due to the loss of depleted water vapour, and because depleted water has been taken out of the process. Enrichment of receiver water, and depletion of cell water with respect to the source water is indeed clearly observed.

The four enriched waters all follow the same pattern in the qualitative sense, but there is considerable spread in the fractionation effects between the cells. This must be caused by the variation in timing of extraction of the water from the receiver. In contrast, the results for cell 5 hardly show any fractionation at all.

In summary, it is clear that the isotopic composition of the water in the TPW cells depends on not only the isotopic composition of the source waters, but also the manufacturing techniques. Duration of the distillation and degassing processes, and the timing of the moment in the distillation process when water is extracted from the receiver might be different among cells in the fabrication process. In this regard it is vital to not only determine the isotopic composition of the source water, but also (or even only) that of the cell water.

Table 4 also contains the triple point temperature difference measurements. The  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  values for cells 4 and 5 are slightly different from those for the other cells. Using equation (1) we can estimate a temperature deviation of  $< \pm 1 \mu\text{K}$  in the realized triple point temperatures by these

two cells. As this is very small compared to the uncertainty in the measured temperatures, we have neglected this influence on the  $\delta^2\text{H}$ -triple point temperatures.

The uncertainty in each individual triple point temperature difference is 19  $\mu\text{K}$  according to Table 2. However, several of the error contributions are shared by all five temperature difference measurements, making their results correlated. We calculated the covariance matrix according to the guidelines in [25], and concluded that we expect a random uncertainty of 11  $\mu\text{K}$  in the linear regression of  $\Delta T$  with  $\delta^2\text{H}$ . Furthermore, in this regression, the uncertainties in the  $\delta^2\text{H}$  values are negligible compared to those in  $\Delta T$ .

The linear regression is shown in Figure 3, and this figure thus embodies the main result of this work: the relation between the  $^2\text{H}$  content (expressed as  $\delta^2\text{H}$ ) and the triple point temperature deviation relative to the VSL cell.

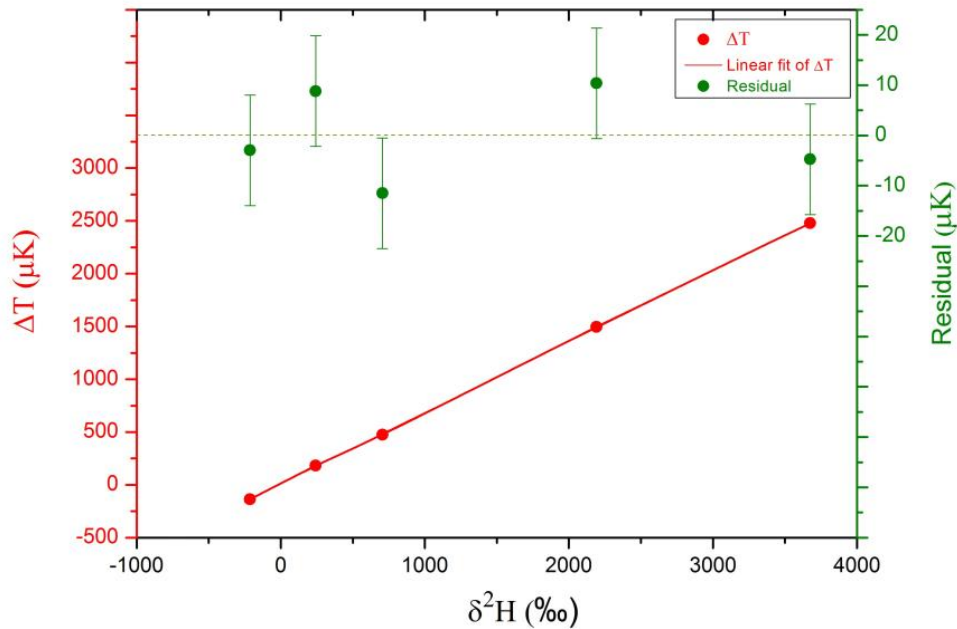


Figure 3. Triple point temperature differences between the five cells and the VSL reference cell against the corresponding  $\delta^2\text{H}$  values of the cells, with a linear fit line (left-hand scale, in red) and residuals of the linear fit (right-hand scale, in green).



The slope of the fit is the  $^2\text{H}$  isotopic correction constant,  $A_{2\text{H}}$ , for which we find the value of 673  $\mu\text{K}$  with a standard uncertainty of 4  $\mu\text{K}$ . The fit curve crosses the  $\Delta T = 0$   $\mu\text{K}$  point at  $\delta^2\text{H} = (-15 \pm 15)$  ‰. This value agrees with the  $\delta^2\text{H}$  value of -20.5 ‰ for the content of the VSL reference cell. Figure 3 shows also the residuals of the fit. The uncertainties indicated,  $\pm 11$   $\mu\text{K}$ , agree well with the observed scattering around the fit.

The  $A_{2\text{H}}$  correction constant derived from our accurate experiment disagrees with the previously recommended value  $A_{2\text{H}} = (628 \pm 20)$   $\mu\text{K}$  by the CCT in 2005 (based on the work by Kiosawa [8] and White et al. [9]). Probably the manufacturer's specifications of the enriched waters that Kiosawa relied on were not accurate. Our present study shows that careful characterization of the enriched waters is a crucial aspect of the measurement process. Furthermore, as noted before, the limited isotopic range of water samples, and the strong correlation between the abundances of the three isotopes in the experimental design of the earlier study by White et al. made their results inaccurate.

Our finding does agree very well, however, with the currently recommended value of  $(671 \pm 10)$   $\mu\text{K}$  from the more recent study of White and Tew [10]. The total uncertainty has been improved by a factor of 2.5. Perhaps even more important, the value is now based on a straightforward experiment that resembles the actual situation for which corrections have to be made, and with waters of which the full isotopic composition is accurately known.

## 6.5 Conclusions

In a collaborative project of VSL and CIO, we have succeeded in determining the  $^2\text{H}$  isotope effect on the triple point temperature of water unambiguously, and with higher accuracy than before. Five water mixtures were prepared using gravimetric mixing of well characterized parent waters. This resulted in accurate values for all stable isotopes (especially not dependent on data from the enriched water manufacturers). The accuracy in the  $\delta^2\text{H}$  values was such that its influence was negligible compared to the uncertainties in the triple point temperature differences. Our experimental design furthermore allowed us to keep the isotopic composition of the oxygen side of the water virtually constant.

This robust, straightforward experiment resulted in an excellent linear correlation between the measured triple point temperature differences and the  $\delta^2\text{H}$  values. This resulted in the  $^2\text{H}$

correction constant the  $A_{2H} = (673 \pm 4) \mu\text{K}$  ( $k=1$ ), which is consistent with the currently recommended value for use with the ITS-90, but improved in terms of uncertainty. In particular, the uncertainty induced by correction for non-VSMOW  $\delta^2\text{H}$  values in a triple point cell will be negligible from now on, compared to other uncertainties, even for cells filled with very depleted natural waters (even for a cell with  $\delta^2\text{H} = -200 \text{ ‰}$  the uncertainty in the correction will be  $< 1 \mu\text{K}$ ). Perhaps even more important, the value is now based on a straightforward experiment that resembles the actual situation for which corrections have to be made, and with waters of which the full isotopic composition is accurately known.

This work will be continued by measurements along the same line, but now aimed at the oxygen isotope effect on the triple point temperature of water. Together, this work will provide a complete, detailed, and accurate experimental study of isotope effects on the TPW temperature.

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### **References**

- [1] Preston-Thomas H 1990 *Metrologia* **27** 3
- [2] Pello R, Goebel R and Kohler R 1997 *Metrologia* **34** 292
- [3] Nicholas J V, Dransfield T D and White D R 1996 *Metrologia* **33** 265
- [4] Stock M *et al* 2006 *Metrologia* **43** 03001 *Tech. Suppl*
- [5] Consultative Committee for Thermometry, Recommendation T1 2005 to the CIPM.  
[http://www.bipm.org/cc/CCT/Allowed/23/CCT\\_05\\_30\\_rev.pdf](http://www.bipm.org/cc/CCT/Allowed/23/CCT_05_30_rev.pdf)
- [6] Ripple D C, Gam K S, Hermier Y, Hill K D, Rusby R L, Steele A G, Steur P P M, Stock M, Strouse G F and White D R 2005 *Summary of Facts Relating to Isotopic Effects and the Triple Point of Water: Report of the Ad Hoc Task Group on the Triple Point of Water CCT/05-07*
- [7] Gonfiantini R 1984 Report on an advisory group meeting on stable isotope reference samples for geochemical and hydrochemical investigations *IAEA Report to the DirectorGeneral*

- [8] Kiyosawa K 1991 *J. Solution Chem.* **20**, 583
- [9] White D R, Dransfield T D, Strouse G F, Tew W L, Rusby R L and Gray J 2003 *Temp. Its Meas. Control Sci. Ind.* **7** 221
- [10] White D R and Tew W L 2010 *Int. J. Thermophys.* **31** 1644
- [11] Meijer H A J and Li W 1998 *J. Isot. Environ. Health Stud.* **34** 349
- [12] Gehre M and Strauch G 2003 *Rapid Commun Mass Spectrom.* **17** 1497
- [13] Gehre M, Hofling R, Kowski P and Strauch G 1996 *Anal. Chem.* **68** 4414
- [14] Epstein S and Mayada T K 1953 *Geochim. Cosmochim. Acta* **4** 213
- [15] Morville J, Kassi S, Chenevier M and Romanini D 2005 *Appl. Phys. B: Lasers Opt.* **80** 1027
- [16] Romanini D, Chenevier M, Kassi S, Schmidt M, Valant C, Ramonet M, Lopez J and Jost H J 2006 *Appl. Phys. B: Lasers Opt.* **83** 659
- [17] Faghihi V, Verstappen-Dumoulin B M A A, Jansen H G, van Dijk G, Aerts-Bijma A T, Kerstel E R T, Groening M and Meijer H A J 2015 *Rapid Commun. Mass Spectrom.* **29** 311
- [18] Faghihi V, Meijer H A J and Groening M 2015 *Rapid Commun. Mass Spectrom* **29** 1351
- [19] Steckel F and Szapiro S 1963 *Trans. Faraday Soc.* **59** 331
- [20] Kell G S 1977 *J. Phys. Chem. Ref. Data.* **6** 1109
- [21] Nakamura M, Tamura K and Murakami S 1995 *Thermochim. Acta.* **253** 127
- [22] Chaplin M 2013 *Water Structure and Science*  
[http://www1.lsbu.ac.uk/water/water\\_structure\\_science.html](http://www1.lsbu.ac.uk/water/water_structure_science.html)
- [23] Goncharuk V V, Kavitskaya A A, Romanyukina I Y and Loboda O A 2013 *Chem. Cent. J.* **7** 103
- [24] De Groot M J, Lacroes N and Dubbeldam J F 2001 *Proc. TEMPMEKO* **1** 459
- [25] Evaluation of measurement data – Guide to the expression of uncertainty in measurement JCGM 100:2008 (GUM 1995 with minor corrections) 2008, Paris: BIPM Joint Committee for Guides in Metrology.