New Isotopic Correction Coefficients and Algorithms for the Triple Point of Water

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Document submitted to the CCT TG-K on the occasion of the 28th Meeting of the CCT
1-2 June 2017, Paris

Background

Variations in the isotopic composition of water are one of the major sources of uncertainty in the realization of the triple point of water (TPW). Natural water is a mixture of four main isotopologues ($^1H^1H^{16}O$, $^1H^2H^{16}O$, $^1H^1H^{17}O$ and $^1H^1H^{18}O$), each one of them having a different TPW temperature. As a consequence, each sample of natural water has a different TPW temperature, depending on the relative concentration of the four isotopologues.

For this reason, in 2005 the CCT clarified the definition of the kelvin [1] by emphasizing that the temperature of the TPW is exactly 273.16 K only for water having the following amount-of-substance ratios:

$^2H/^1H$ = 0.00015576(5)
$^{18}O/^{16}O$ = 0.00200520(5)
$^{17}O/^{16}O$ = 0.0003799(9)

which is the best available estimate for the isotope content of Vienna Standard Mean Ocean Water (V-SMOW) [2]. However, variations in isotopic composition of water can be measured much more accurately in relative mode (that is, relative to that of V-SMOW) than in absolute mode. This is the reason why the scale definition for isotope values of water is still based on the "artefact" V-SMOW.

Variations in amount-of-substance ratios are conventionally reported as deviations from V-SMOW, for example:

$$\delta^{18}O_{CAL} = \left[\frac{(^{18}O/^{16}O)_{sample} - (^{18}O/^{16}O)_{V-SMOW}}{(^{18}O/^{16}O)_{V-SMOW}} \right] \tag{1}$$

and similar expressions for the $\delta^{17}O$ and δ^2H (δD in the following). The subscript CAL emphasizes that the δ-value has been determined with respect to V-SMOW. The delta values of natural waters are usually in the parts-per-thousand range, so are expressed in ‰ (permil or per thousand).

Besides V-SMOW, to further improve the inter-laboratory reproducibility of the water isotopic composition measurements, Standard Light Antarctic Precipitation (SLAP) water is also used to define the scale. The δ-values of SLAP have been defined based on consensus between expert laboratories taking part in a large international intercomparison [3]. They are δD = -428 ‰ and $\delta^{18}O$ = -55.5 ‰ with respect to V-SMOW. These consensus values are used in the definition of the so-called normalized V-SMOW-SLAP scale:

$$\delta^{18}O(sample)_{NORM} = \left[\delta^{18}O(sample)_{CAL} \frac{(-0.0555)}{\delta^{18}O(SLAP)_{CAL}} \right]$$

and similarly for δD, with the value 0.428 in the nominator. All isotope laboratories usually report their isotope δ-values for water in this normalized way.

Since 2005 the CCT has recommended the application of the following algorithm to correct the TPW temperature realized by a water sample of known isotopic composition [4]:

$$\Delta T_{iso} = - A_D \cdot \delta D - A_{18O} \cdot \delta^{18}O - A_{17O} \cdot \delta^{17}O , \tag{2}$$

where ΔT_{iso} is the temperature correction to be applied to the water sample (with respect to 273.16 K),
$A_D = (628 \pm 20)\mu K$
$A_{18O} = (641 \pm 50)\mu K$
$A_{17O} = (57 \pm 5)\mu K$.

The values of the isotopic correction constants at that time were based on the results of freezing point measurements performed by Kiyosawa on mixtures of ^{18}O and D enriched waters [5], and the results of TPW measurements performed by White et $al.$ [6] on five TPW cells.

The experimental basis was flawed by some intrinsic weaknesses that reflected in large uncertainties in the derived correction constants:

- The waters used by Kiyosawa were 10-100 fold higher in $^2H/^1H$ ratio and 4-40 fold higher in $^{18}O/^{16}O$ ratio than VSMOW, so the CCT Ad-Hoc Task Group represented by the authors of [4] had to perform an extreme extrapolation back to the natural range.
- Kiyosawa relied only on the manufacturer's specifications for the enrichment levels of the enriched isotopes and simply assumed the non-enriched isotopes were of 'natural' composition.
- Kiyosawa did not present any uncertainty analysis.
- Four of the five waters measured by White et $al.$ [6] were natural, while the fifth was a highly D-depleted water. The derivation of the isotopic correction constants was then affected by the high correlation of the D, ^{18}O and ^{17}O concentrations of the five samples (the D-depleted water was also strongly depleted in ^{18}O and ^{17}O), which makes the individual isotope effects indistinguishable.

In 2010 White and Tew [7] performed a critical review of the existing literature available at that time, and derived new values and standard uncertainties for the isotopic correction constants, based on data from solid-liquid isotopic fractionation measurement, enthalpies of fusion and freezing points of the relevant isotopologues and TPW temperature measurements on TPW cells containing waters of different isotopic composition.

The values derived by White and Tew were:
$A_D = (671 \pm 10)\mu K$
$A_{18O} = (603 \pm 3)\mu K$
$A_{17O} = (60 \pm 1)\mu K$
which are the values currently recommended for use with the ITS-90 in the Technical Annex for the ITS-90 [8] and in the Guide to the Realization of the ITS-90 [9].

It should be noticed that, while the measurement of δD and $\delta^{18}O$ of water samples can be routinely performed by many laboratories around the world with standard uncertainties usually better than 1 ‰ and 0.1 ‰, respectively, the measurement of $\delta^{17}O$ is difficult and certainly not available as a standard measurement service.

Moreover, the original reference V-SMOW and SLAP waters are exhausted. Their successors for realizing the V-SMOW-SLAP scale, V-SMOW2 and SLAP2, have been prepared with utmost care to resemble the originals to within the uncertainties. Only for SLAP2 the δD value is -427.5 ‰ instead of 428 ‰.

Recent work

The work we performed is described in detail in two Metrologia papers [10-11]. Briefly, first we prepared gravimetrically ten water mixtures by mixing thoroughly isotopically assessed parent waters, then we manufactured ten TPW cells using the ten water mixtures and finally we measured the TPW temperatures realized by the manufactured cells.

Five of the ten manufactured cells contained waters with a range of ^{2}H isotopic abundances encompassing widely the natural abundance range, while their ^{18}O and ^{17}O abundances were kept approximately constant and realizing the Meijer-Li relationship for natural waters [12]. This led to the determination of the isotopic correction constant $A_D = 673$ µK with a standard uncertainty of 4 µK.

The other five manufactured cells contained waters with ^{18}O and ^{17}O abundances exceeding widely the natural abundance range while maintaining the Meijer-Li relationship. The ^{2}H isotopic abundance was kept close to that of VSMOW. This led to the determination of a newly defined isotopic correction constant $A_O = 630$ µK with a standard uncertainty of 10 µK that, when multiplied by δ^{18}O, returns the isotopic correction due to the combined effects of ^{18}O and ^{17}O isotopes.

Proposal

We propose to replace the current correction algorithm (2) and correction coefficients [7] in the Technical Annex for the ITS-90 [8] and in the Guide to the Realization of the ITS-90 [9] with:

$$\Delta T_{iso} = - A_D \cdot \delta D - A_O \cdot \delta^{18}O \tag{3}$$

$A_D = (673 \pm 4)$µK
$A_O = (630 \pm 10)$µK

The advantages of this new algorithm are:
- It requires only the knowledge of δ^2H and δ^{18}O, implicitly taking into account the effect of δ^{17}O.
- It is more accurate because it is based on the recent direct and most accurate determinations [10-11].

The limitation of this algorithm is that it can be applied only to natural waters and this excludes those TPW cells for which enriched water was added to the initial source water to compensate for the isotope depletion during the purification process. Although some TPW manufacturers are known to have adopted such practice, this is not recommended: after adding enriched water, full isotope analysis is required (including the difficult measurement of δ^{17}O) and the application of equation (2) produces a less accurate and less reliable result.

In order to obtain, after the purification process, water very close to VSMOW, it is advisable to let the initial water evaporate to the atmosphere under elevated temperature (say 40 ºC). If, for instance, one allows 50% of the water to evaporate, typical enrichments of 40 ‰ and 7 ‰ for δD and δ^{18}O, respectively, will be achieved. This process is easy and cheap and the Meijer-Li relationship remains valid as for all natural processes.

For the existing TPW cells that have been manufactured with addition of enriched water, we recommend to use the following algorithm:

$$\Delta T_{iso} = - A_D \cdot \delta D - A_O \cdot \delta^{18}O - A_{17O} \cdot \{ \delta^{17}O - [(1 + \delta^{18}O)^{0.528} - 1] \} \tag{4}$$

$A_{2H} = (673 \pm 4)$µK
$A_O = (630 \pm 10)$µK
$A_{17O} = (60 \pm 1)$µK

which requires full isotopic analysis and the application of the A_{17O} coefficient from White and Tew [7].

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Last update 16 April 2017