

# Research Activities on Water Triple Point Cells in the Netherlands

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## 1 Background

NMi VSL has been producing water triple point cells (WTPCs) since many years. The know-how for the manufacture of the WTPCs was inherited from Kammerlingh-Onnes Laboratorium (KOL, Leiden) in 1989 and several production units have been developed by the Thermometry Section of NMi VSL as described in De Groot et al. in [1]. In 2002, prompted by the investigations performed elsewhere on isotopic and impurity effects on the WTP temperature [2,3], the design of the cell was adapted to allow attention to isotopic and impurity effects. Currently NMi VSL is one of the few NMIs in the world which is maintaining an active production of WTPCs. After the next publication of the recent CCT Key Comparison on WTPCs (CCT K7) and whatever the recommendations on the isotopic and impurity issues to the CCT in June 2005 will be, it is expected that the thermometry community will move in the direction of more controlled isotopic and impurity composition of the water used in WTPCs. The goal of this document is to inform the CCT about the research lines of NMi VSL on WTPCs and about the isotopic and chemical analysis capability in the Netherlands.

## 2 Isotopic and impurity effects influencing the WTP temperature

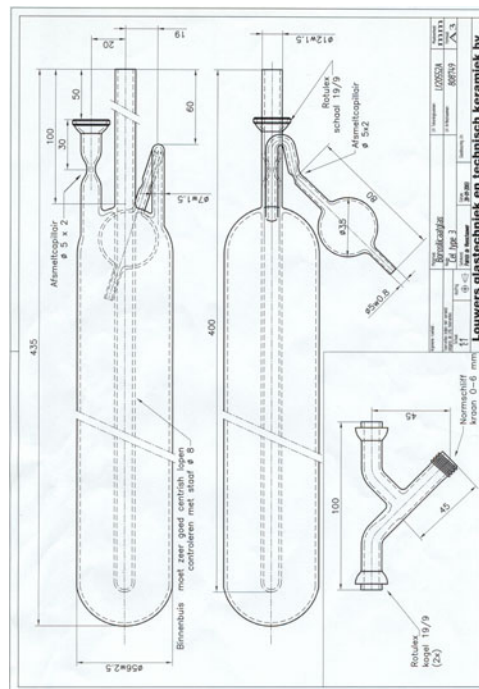
From the analysis of the uncertainty budgets of the WTP measurements, reported by all the countries participating to CCT K7, the two dominant sources of uncertainty in the realization of the WTP are the isotopic composition and the impurity content of the water in the WTPC.

A correct approach to the minimization of these two uncertainty components requires that:

1. The production parameters must be controlled, in order to minimize the amount of impurities present in the water sealed into the WTPC and the deviation of the isotopic composition from V-SMOW. The parameters affecting the isotopic composition during the fabrication process are: the source of the water (continental fresh water and relative latitude, season, ocean water etc...) and the distillation and degassing procedures. The parameters affecting the impurity content are: the pre-conditioning of the cell enclosure (cleaning, etching, leaching, heat treatments), the source of the water, the ion filtering, the distillation and degassing procedures and the dissolution of the cell enclosure in the water.
2. The isotopic composition and the chemical impurities of the water sealed into the WTPC must be measured, in order to allow for application of the required corrections. The isotopic and chemical analysis must be performed directly in the "active" water (i.e. the water that has been sealed within the cell enclosure).

### 3 The WTPC design and the water analysis

The design and production of the cell as has been described by de Groot et al. in [1], was modified in 2002 by adding to the cell a glass bulb (see Figure 1). After filling, sealing and measuring the cell for sometime, the bulb can be filled with active water and removed with a flame without breaking the seal of the cell. The water removed with the bulb can be analyzed again for isotopic composition and impurity content.



**Figure 1:** New design of NMI VSL WTPC.

The water is sampled from each one of the following production steps:

- Starting water
- Water after double distillation
- Water after degassing
- Water from glass bulb

Each sample is analyzed for isotopic and impurity content.

#### 3.1 Isotopic analysis of water

The isotopic analysis is performed by the Center for Isotope Research (CIO), University of Groningen. The standard uncertainty is  $\pm 0.8$  per mil for D and  $\pm 0.08$  per mil for  $^{18}\text{O}$  ( $^{17}\text{O}$  is not measured at present). A set of typical measured isotopic concentration values for NMI water production system is reported in table 1.

$\delta\text{D}$ starting water	$\delta^{18}\text{O}$ starting water	$\delta\text{D}$ after distillation	$\delta^{18}\text{O}$ after distillation	$\delta\text{D}$ after degassing	$\delta^{18}\text{O}$ after degassing	$\delta\text{D}$ bulb water	$\delta^{18}\text{O}$ bulb water
- 42.5	- 6.12	- 68.3	- 8.89	- 48.0	- 6.48	-	-

**Table 1:** Isotopic analysis of water at different steps of the production process. Both  $\delta\text{D}$  and  $\delta^{18}\text{O}$  are expressed in per mil with respect to the VSMOW-SLAP scale.

### 3.2 Impurity analysis of water

ICPMS (Inductively-Coupled Plasma Mass Spectrometry) was performed by the Chemistry Section of NMI VSL on samples of water from different stages of the production process. To verify the validity of ICPMS measurements at NMI, two identical sets of water samples from stages A, B, C and D were prepared. One set was sent to PTB for ICPMS analysis and the other set will be measured with ICPMS at NMI. So far the traceability of the ICPMS measurements proved to be problematic for the suspected dominant impurities (Si and B, from glass dissolution in the water). Preliminary ICPMS results suggest that impurity contribution to the uncertainty of the WTP temperature is dominant with respect to the component arising from the isotopic composition.

### 4 Research opportunities on WTPC in the Netherlands

By combining the efforts and know-how of NMI VSL, CIO and Kelvin-lab, in the Netherlands we have the potentialities to perform research in a number of areas related to the improvement of the WTPCs. In view of the 2005 CCT meeting, we would like to draw the attention of the CCT to the following research opportunities in the Netherlands and get feedback from the CCT on the relevance of these research lines for the international thermometry community.

#### 4.1 Re-determination of the depression constants for D, $^{18}\text{O}$ and determination of the depression constant for $^{17}\text{O}$ .

For nearly V-SMOW isotopic composition, the effect of the different isotopes can be approximated by a linear function of the delta values:

$$T_{meas} = T_{VSMOW} + A_D \cdot \delta D + A_{18O} \cdot \delta^{18}O + A_{17O} \cdot \delta^{17}O$$

Kiyosawa [4] made measurements of melting point elevation with various samples of water enriched with D and  $^{18}\text{O}$ . White et al. [2,5] estimated the isotopic depression constants  $A_D$  and  $A_{18O}$  from 3 different sources: 1) Values interpolated from reported freezing point or triple point temperatures of the nearly pure isotopomers  $^1\text{H}_2^{16}\text{O}$ ,  $\text{D}_2^{16}\text{O}$  and  $^1\text{H}_2^{18}\text{O}$ , 2) Values obtained from a set of measurements of 5 WTPCs with varying levels of isotope depletion, 3) Results of a reanalysis of Kiyosawa's measurements [4]. The same White et al. recommended the values of constants determined from the reanalysis of Kiyosawa's data ( $A_D = (628 \pm 6)\mu\text{K}$  and  $A_{18O} = (641 \pm 23)\mu\text{K}$ ) but clearly pointed out the remaining several potentially significant sources of uncertainty not included in the above-reported expanded uncertainty (based only on the Type A components):

- Kiyosawa measured the freezing point temperatures within a capillary instead of triple point temperatures in full sized cells.
- Kiyosawa assumed his solvent water to be pure  $^1\text{H}_2^{16}\text{O}$ , when in reality this was probably distilled tap water from fresh continental surface water in Japan.
- Uncertainties in the measurements of isotopic composition of the enriched waters were unknown.

In a recent paper [6], Kiyosawa reported an unexpectedly large linear dependence of the freezing points of isotopic mixtures of ordinary water and  $^{17}\text{O}$ , on the concentration of  $\text{H}_2^{17}\text{O}$ . Tew et al. [7] showed that, if the last Kiyosawa data are used to compute  $A_{17O}$ , the result would be  $A_{17O} = 596 \mu\text{K}$ , which is 10 times the value suggested by White et al. in [2] ( $57 \mu\text{K}$ ) and inconsistent with the same results in [2].

Moreover, when dealing with WTPCs, the concentration of  $^{17}\text{O}$  is never determined experimentally because it is difficult to measure and usually well correlated (for meteoric water) to  $^{18}\text{O}$  through Meijer et al. equation [8].

Therefore the trust of the international scientific community on the determined coefficients is not complete. It is expected that a substantial improvement in the accuracy of the coefficients can be obtained with state-of-the-art instrumentation such as is available at CIO (for the isotopic analysis) and at NMi (for the triple point elevation measurements).

NMi and CIO propose to prepare 5-6 water samples with different composition in the isotopes D,  $^{18}\text{O}$  and  $^{17}\text{O}$  ( $\delta\text{D}$  ranging from  $-400\text{‰}$  to  $+2000\text{‰}$ ,  $\delta^{18}\text{O}$  ranging from  $-50\text{‰}$  to  $+1000\text{‰}$ ,  $\delta^{17}\text{O}$  ranging from  $-25\text{‰}$  to  $+2000\text{‰}$ ). The lowermost values correspond to the most depleted natural water on earth (Antarctic precipitation), the higher-end members will be prepared by gravimetric mixing of artificially enriched water and natural water with known isotopic composition. CIO has the know-how and the contacts to provide the necessary amount of D (1  $\text{€}/\text{g}$ ),  $^{18}\text{O}$  (10 grams needed, 100  $\text{€}/\text{g}$ ) and  $^{17}\text{O}$  (2 grams needed, 300  $\text{€}/\text{g}$ ).

The prepared samples will be isotopically analyzed and triple point cells will be manufactured from the same samples. By measurement of their corresponding triple point temperatures, the isotopic depression constant can be re-determined with an estimated standard uncertainty of 1 - 2 % for all three isotopes.

#### **4.2 Realize VSMOW-like water cells using desalinated ocean water**

On the basis of our past experience in making WTPCs, the final depletion in heavy isotopes of water sealed in the WTPC is mostly due to the starting isotopic composition of the source water used. In fact the effect of distillation and degassing is globally neutral from the isotopic composition point of view (distillation and degassing counterbalance each other, see Table 1). For this reason, using desalinated ocean water as starting water should lead to a final water which is very close to VSMOW composition.

Taking advantage of an NMi project in Curaçao, tap water from Curaçao will be isotopically analyzed by CIO. If the results will be as expected (and if the desalination plant does not affect significantly the isotopic composition of the ocean water), this water shall be used to make WTPCs.

#### **4.3 Effects of production parameters on isotopic and impurity content of WTPCs**

As anticipated in section 2, there are many aspects of the fabrication process that affect the final impurity and isotopic composition of the WTPC. The isotopic investigations of section 4.1 and 4.2 should be performed in parallel with impurity investigations.

NMi is planning to investigate the following factors that are likely to affect the impurity content of a WTPC:

- Enclosure material for the WTPC: is the dissolution of the cell enclosure in the water reduced if quartz instead of borosilicate is used as enclosure material?
- Preconditioning of the WTPC: are acid pre-leaching, steam cleaning and heat treatments effective in limiting the dissolution rate of cell enclosure in the water?
- Is the water contaminated during the distillation process with glass dissolved from the distillation system?

#### 4 References

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