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# Isotope and Impurity Content in Water Triple-Point Cells Manufactured at NMi VSL

**Andrea Peruzzi · O. Kerkhof · M. J. de Groot**

**Abstract** The isotopic and impurity content of 15 water triple-point cells, manufactured at NMi VSL in the past three years, were investigated. The isotopic analyses were performed on water specimens sampled at three different stages of the manufacturing process. This allowed us to separate and quantify the influence of the source water and of the manufacturing process (distillation, degassing) on the final isotopic composition of the water in the cells. Inductively coupled plasma mass spectrometry (ICPMS) was conducted on selected water samples to investigate the potential contamination of the source water during the manufacturing process, and to evaluate the impact of impurities on the water triple-point temperature. The temperature differences among the manufactured cells were measured, and correlations between the observed differences and the results of isotope and chemical analysis were studied.

**Keywords** Impurities · Isotopic composition of water · Water triple-point cells

## 1 Introduction

The triple point of water (TPW) is the unique physical state of water in which all three phases (solid, liquid, and vapor) coexist at thermodynamic equilibrium. As it provides a way to reproduce exactly the same temperature (within a few tens of microkelvins), it is the cornerstone of modern thermometry:

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- the kelvin (the unit of both the thermodynamic temperature scale and the current international temperature scale, ITS-90 [1]) is defined by assigning a numerical value (273.16 K) to the temperature of the water triple point.
- any ITS-90 temperature $T_{90}$ in the range 13.8033–1234.93 K is determined in terms of the ratio between the resistance $R(T_{90})$ of a standard platinum resistance thermometer (SPRT) at the temperature $T_{90}$ and the resistance $R(273.16\,\mathrm{K})$ at the triple point of water.

In key comparison CCT-K7 [2], significant discrepancies were observed among 20 different national realizations of the water triple-point temperatures. The differences were attributed to various effects, the principle two being the different isotopic compositions and the different impurity contents of the water samples enclosed within the measured cells.

As regards the isotopic composition of the water to be used in the realization of the WTP, at the time CCT-K7 was carried out, the definition was not entirely clear or formally binding (water was required to be "*of substantially the isotopic composition of ocean water*," see [3]). In fact, most laboratories, even those having sufficient information, did not correct for the isotopic composition of the water.

The CCT and its Working Groups addressed the difficulties related to isotopic and impurity effects in the realization of the water triple-point temperature by taking the following actions:

1. The definition of the kelvin was clarified in a 2005 Recommendation to the CIPM [4], by requiring the isotopic composition of the water used to realize the triple-point temperature to be that of VSMOW (Vienna Standard Mean Ocean Water, International Atomic Energy Agency reference material as specified in [5]).
2. An algorithm to correct the realized temperature for cell water deviating from VSMOW isotopic composition was identified [6].
3. The methodologies to be used for the estimation of the uncertainties and the correction of fixed-point temperatures attributable to the influence of chemical impurities were standardized in [7].

From the results of CCT-K7 and the above-mentioned documents, the accuracy of the water triple-point realization appears to be dominated by how well the isotopic and impurity content of the cell water is known. As a consequence, it can be expected that a more widespread use of isotopic and chemical analysis and application of the corresponding correction algorithms would reduce the spread of the realizations observed in CCT-K7.

In the past 3 years, 15 TPWCs were manufactured at NMi VSL. The isotopic and impurity content were investigated for the active water enclosed within the manufactured cells, and for specimens sampled at the production stages. This allows us to understand the extent of the isotopic fractionation and contamination/purification effects from each one of the production stages. The results of these investigations are reported here.

The temperature differences among the manufactured cells were measured with the aim of correlating the values with the results arising from isotopic and chemical analyses.

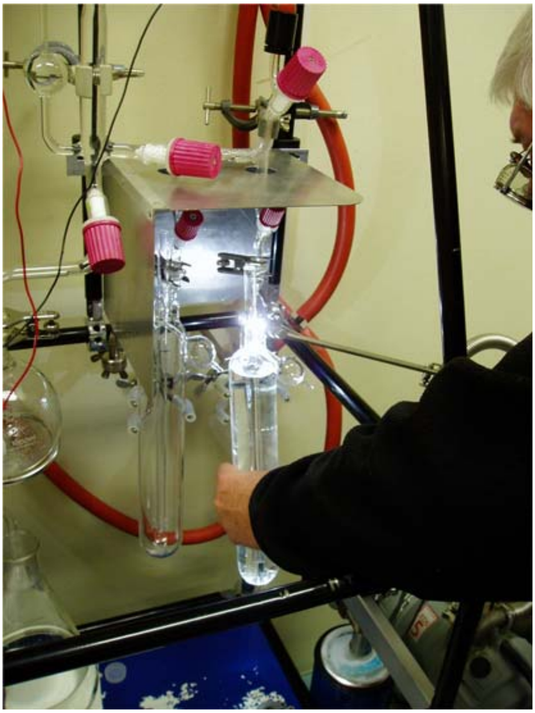

**Fig. 1** Manufacture of a water triple-point cell at NMi VSL. The glass blower is sealing off a new water triple-point cell from the distillation system

## 2 Water Triple-Point Cell Manufacturing

In 1989, NMi VSL inherited from the Kamerlingh–Onnes Laboratorium (KOL, Leiden) the know-how for the manufacture of the TPWCs and since then several production units were further developed by its thermometry section. The system described in [8] is still in use.

In 2003, prompted by the investigations on isotopic and impurity effects on the water triple-point temperature performed by White et al. [9] and Hill [10], the design of the NMi VSL cell was modified by adding to the cell a glass bulb (see Fig. 1) that, after filling, sealing and measuring the cell for some time, can be filled with water and removed with a flame without breaking the seal of the cell [11]. This allowed chemical and isotopic analyses of the active water enclosed in the cells.

In 2006, two relevant modifications were applied to the fabrication of the cells:

1. The use of quartz instead of borosilicate glass as shell material.
2. Preconditioning of the shell inner surface with $HNO_3$ instead of HF.

The use of quartz is intended to reduce the dissolution of impurities in the water by eliminating the leaching of metallic ions and reducing the catalytic $OH^-$ attack on the silica [12]. The pre-leaching of the shell with $HNO_3$ promotes the formation of a uniform layer of silica gel that protects the shell inner surface from further dissolution [13]. A total of 15 cells were produced from 2003 to 2006 (see Table 1).

**Table 1** Overview of the production of water triple-point cells at NMi VSL in the past 3 years

| Water triple-point cell | Shell material | Shell preconditioning | Date of sealing | Current use |
|---|---|---|---|---|
| Cell 1 | Borosilicate | HF | 23/09/2003 | Sold |
| Cell 2 | Borosilicate | HF | 11/09/2003 | Sold |
| Cell 3 | Borosilicate | HF | 03/12/2004 | EUROMET.T-K7 |
| Cell 4 | Borosilicate | HF | 26/11/2004 | EUROMET.T-K7 |
| Cell 5 | Borosilicate | $HNO_3$ | 16/02/2006 | EUROMET.T-K7 |
| Cell 6 | Borosilicate | HF | 08/05/2004 | Research |
| Cell 7 | Borosilicate | HF | 03/11/2003 | Broken |
| Cell 8 | Borosilicate | HF | 13/06/2003 | Research |
| Cell 9 | Quartz | $HNO_3$ | 23/02/2006 | Broken |
| Cell 10 | Quartz | $HNO_3$ | 30/03/2006 | EUROMET.T-K7 |
| Cell 11 | Quartz | $HNO_3$ | 23/03/2006 | Sold |
| Cell 12 | Quartz | $HNO_3$ | 17/07/2006 | EUROMET.T-K7 |
| Cell 13 | Quartz | $HNO_3$ | 14/07/2006 | EUROMET.T-K7 |
| Cell 14 | Quartz | $HNO_3$ | 28/04/2006 | Sold |
| Cell 15 | Quartz | $HNO_3$ | 28/04/2006 | Sold |

**Table 2** Overview of the isotopic analysis performed on the water specimens sampled from the production stages. The uncertainties ($k = 1$) on the measured $\delta^{18}$O and $\delta^{2}$H were, respectively, 0.08‰ and 0.8‰

| Water triple-point cell | Source water | | Receiver water | | Bulb water | |
|---|---|---|---|---|---|---|
| | $\delta^{18}$O (‰) | $\delta^{2}$H (‰) | $\delta^{18}$O (‰) | $\delta^{2}$H (‰) | $\delta^{18}$O (‰) | $\delta^{2}$H (‰) |
| Cell 1 | – | – | – | – | −6.93 | −51.1 |
| Cell 2 | – | – | – | – | −6.30 | −45.5 |
| Cell 3 | −6.15 | −43.0 | −8.93 | −68.8 | −8.60 | −66.9 |
| Cell 4 | −6.15 | −43.0 | −8.84 | −67.4 | −8.51 | −65.8 |
| Cell 5 | −5.95 | −39.4 | −2.93 | −19.9 | – | – |
| Cell 6 | – | – | – | – | −3.93 | −29.1 |
| Cell 7 | −6.09 | −42.0 | – | – | −4.66 | −32.7 |
| Cell 8 | – | – | – | – | −6.22 | −47.1 |
| Cell 9 | – | – | −2.38 | −11.3 | −9.54 | −74.7 |
| Cell 10 | −6.36 | −45.2 | −3.19 | −31.4 | −8.51 | −64.8 |
| Cell 11 | −6.20 | −44.9 | −9.19 | −72.6 | −9.21 | −70.5 |
| Cell 12 | −4.27 | −15.4 | −4.71 | −22.5 | −4.86 | −20.5 |
| Cell 13 | −4.27 | −15.4 | −6.05 | −35.0 | −6.35 | −36.7 |
| Cell 14 | −6.55 | −42.9 | – | – | −8.47 | −63.1 |
| Cell 15 | −6.55 | −42.9 | – | – | −8.33 | −63.1 |

## 3 Water Sampling

Three sets of samples were prepared by sampling the water at three stages of the production:

1. Water used to fill the first boiler of the double-distillation system (source water in Table 2).
2. Water sampled from the receiver at the end of the double-distillation process (receiver water in Table 2).
3. Water taken from the removed bulb (bulb water in Table 2).

In 2006 we purchased two commercial TPWCs (one from Hart Scientific and one from Isotech). Both cells were delivered with an additional ampoule containing the same water enclosed in the corresponding cell. The water contained in the two ampoules was partitioned into identical samples for analysis.

Another set of samples was prepared in an attempt to identify the optimal source water for use with our double-distillation production process; it included various water samples from Curaçao, Dutch Antilles (ocean water before desalination, desalinated ocean water, and tap water) and from the Atlantic Ocean (sampled at different latitudes, courtesy of Dutch Navy).

## 4 Isotopic Analysis

The isotopic analysis of all samples was performed by the Centre for Isotope Research (CIO), University of Groningen.

The concentrations of $^{18}$O and $^{2}$H, expressed as permil deviations from VSMOW, were measured with uncertainties (k = 1) of, respectively, $0.08‰$ and $0.8‰$. Table 2 summarizes the results of the analysis performed on the three sets of samples taken from the production stages of NMi VSL cells.

Figure 2 is a graphical overview of all the isotopic analyses. Clearly, whatever the origin of the sample, there is a strong correlation between the content of $^{18}$O and $^{2}$H. Often this correlation is described with the equation $\delta^2\mathrm{H} = 8\delta^{18}\mathrm{O} + 10$ known as the Global Meteoric Water Line (GMWL, solid line in Fig. 2). In fact, the GMWL is valid only for meteoric waters and not for ocean and triple-point cell waters, for which the balance between equilibrium and nonequilibrium processes is different. This is clearly shown in Fig. 2, where the large majority of the samples lie below the GMWL. Also, VSMOW (full circle in Fig. 2) does not lie on the GMWL. Note that the $\delta^2\mathrm{H} - \delta^{18}\mathrm{O}$ correlation for the measured samples can still be described by a straight line with approximately the same slope as the GMWL, but with a different intercept. The deviation of the $\delta^2\mathrm{H} - \delta^{18}\mathrm{O}$ correlation line from the GMWL depends to a large extent on the source of the water and to a lesser extent on the details of the distillation and degassing during the manufacturing process.

The samples taken from the production stages of the NMi VSL cells are more depleted than the samples from Hart Scientific and Isotech cells. This can be due either to differing isotopic composition of the source water (NMi VSL uses continental fresh water, commercial suppliers could be using ocean water or continental water spiked with enriched water) or to differences in distillation and degassing processes during the manufacture of the cell. The Atlantic Ocean and Curacao samples are very close to VSMOW composition, as expected.

## 5 Applying Isotopic Corrections

For nearly VSMOW water samples, the effect of the different isotopes on the triple-point temperature realized by the sample can be expressed by a linear function of the

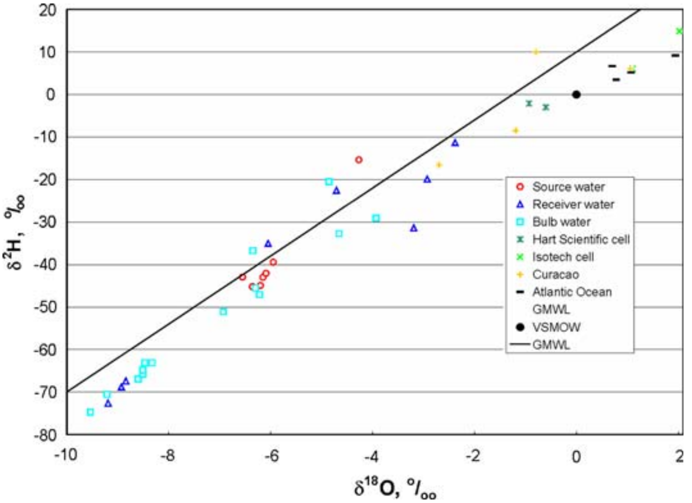

**Fig. 2** Graphical representation of the results of all the isotopic analysis. The solid line is the Global Meteoric Water Line (GMWL). The full circle is Vienna Standard Mean Ocean Water (VSMOW). The two experimental points for Hart Scientific and Isotech are the results of two different laboratories for the same water samples

permil deviations of each isotope from VSMOW [6]:

$$T_{\text{measured}} = T_{\text{VSMOW}} + A_{^2\text{H}}\delta^2\text{H} + A_{^{18}\text{O}}\delta^{18}\text{O} + A_{^{17}\text{O}}\delta^{17}\text{O}$$

with $A_{^2\text{H}} = (628 \pm 20)\,\mu\text{K}$, $A_{^{18}\text{O}} = (641 \pm 50)\,\mu\text{K}$, and $A_{^{17}\text{O}} = (57 \pm 5)\,\mu\text{K}$ ($k = 1$ for all uncertainties).

As $^{17}$O and $^{18}$O content are strongly correlated for any water sample through the relation [14] $1+\delta^{17}\text{O} = \left(1 + \delta^{18}\text{O}\right)^{0.528}$, knowledge of the $^{18}$O and $^2$H content allows the isotopic correction $T_{\text{VSMOW}} - T_{\text{measured}}$ to be applied to the realized temperature with an uncertainty of a few microkelvin.

Table 3 provides an overview of these calculations. Figure 3 is a graphic representation of the same results. Double distillation depletes the source water by about 20 µK; degassing enriches the water by 1–2 µK. Ultra-high purity water is less depleted than purified tap water and thus more suitable as starting water. Figure 3 shows that:

1. The effect of the manufacturing process is predictable and reproducible within about 10 µK.
2. A wise selection of the source water can easily lead to cell water very close to VSMOW.

## 6 Chemical Analysis

The Chemistry Department of PTB (Germany) measured a set of five water samples in 2005 and another set of six samples in 2006 with ICPMS (inductively coupled plasma

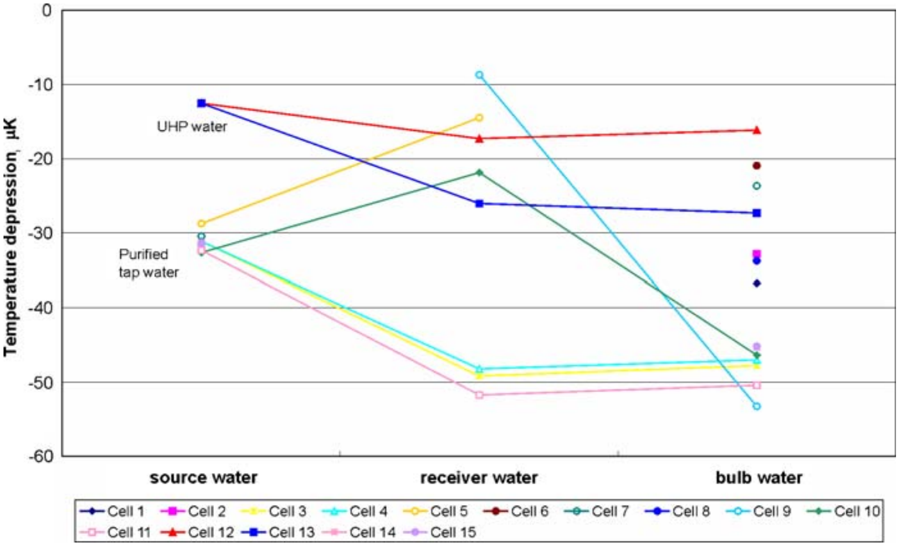

**Fig. 3** Calculated temperature deviations from VSMOW due to isotopic composition of the production stages samples

**Table 3** Overview of the isotopic corrections to be applied to the temperatures realized by the NMi VSL cells

| Water triple-point cell | $\delta^2$H bulb water (‰) | $\delta^{18}$O bulb water (‰) | $\delta^{17}$O bulb water (‰) | Correction due to $\delta^2$H (µK) | Correction due to $\delta^{18}$O (µK) | Correction due to $\delta^{17}$O (µK) | Total correction (µK) |
|---|---|---|---|---|---|---|---|
| Cell 1 | −51.1 | −6.93 | −3.7 | 32.1 | 4.4 | 0.2 | 37 |
| Cell 2 | −45.5 | −6.30 | −3.3 | 28.6 | 4.0 | 0.2 | 33 |
| Cell 3 | −66.9 | −8.60 | −4.5 | 42.0 | 5.5 | 0.3 | 48 |
| Cell 4 | −65.8 | −8.51 | −4.5 | 41.3 | 5.4 | 0.3 | 47 |
| Cell 5 | – | – | – | – | – | – | – |
| Cell 6 | −29.1 | −3.93 | −2.1 | 18.3 | 2.5 | 0.1 | 21 |
| Cell 7 | −32.7 | −4.66 | −2.5 | 20.5 | 3.0 | 0.1 | 24 |
| Cell 8 | −47.1 | −6.22 | −3.3 | 29.6 | 4.0 | 0.2 | 34 |
| Cell 9 | −74.7 | −9.54 | −5.1 | 46.9 | 6.1 | 0.3 | 53 |
| Cell 10 | −64.8 | −8.51 | −4.5 | 40.7 | 5.4 | 0.3 | 46 |
| Cell 11 | −70.5 | −9.21 | −4.9 | 44.3 | 5.9 | 0.3 | 50 |
| Cell 12 | −20.5 | −4.86 | −2.6 | 12.9 | 3.1 | 0.2 | 16 |
| Cell 13 | −36.7 | −6.35 | −3.4 | 23.1 | 4.1 | 0.2 | 27 |
| Cell 14 | −63.1 | −8.47 | −4.5 | 39.6 | 5.4 | 0.3 | 45 |
| Cell 15 | −63.1 | −8.33 | −4.4 | 39.6 | 5.3 | 0.3 | 45 |

mass spectrometry). The samples were all taken from NMi VSL production stages, except for one PTB reference sample for each set as described in Table 4.

The results of ICPMS analysis are regarded as semi-quantitative by the performers themselves due to intrinsic features of the technique and of the sample manipulation. The analysis was "limited" to the following 60 elemental impurities: $^{7}$Li; $^{9}$Be; $^{11}$B;

**Table 4** Description of the 11 water samples measured with ICPMS

| Sample identification | Cell | Production stage |
|---|---|---|
| 1 | PTB reference 2005 | Purified tap water |
| 2 | Cell 7 | Source water (purified tap water) |
| 3 | Cell 3 and Cell 4 | Source water (purified tap water) |
| 4 | Cell 4 | Receiver water |
| 5 | Cell 3 | Bulb water |
| 6 | PTB reference 2006 | Purified tap water |
| 7 | Cell 11 | Bulb water |
| 8 | Cell 10 | Bulb water |
| 9 | Cell 14 and Cell 15 | Receiver water |
| 10 | Cell 12 and Cell 13 | Source water (ultra-high purity) |
| 11 | Cell 12 | Bulb water |

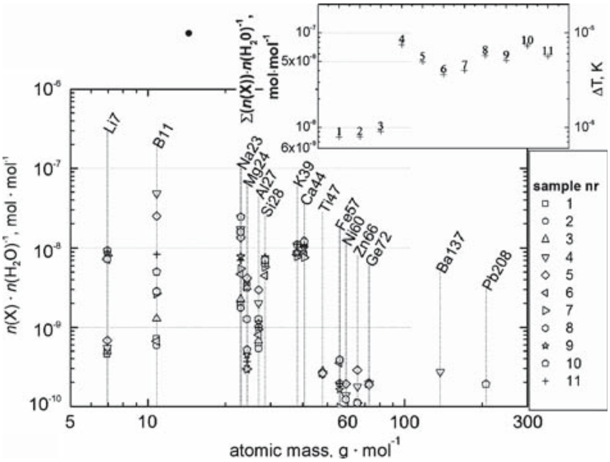

**Fig. 4** Impurity analyses of the water samples expressed as the amount concentration of individual impurities for different samples. Inset shows the total amount concentration summed over all impurities and the resulting temperature effect for all numbered samples

$^{23}$Na; $^{24}$Mg; $^{27}$Al; $^{28}$Si; $^{39}$K; $^{44}$Ca; $^{45}$Sc; $^{47}$Ti; $^{51}$V; $^{52}$Cr; $^{55}$Mn; $^{57}$Fe; $^{59}$Co; $^{60}$Ni; $^{65}$Cu; $^{66}$Zn; $^{69}$Ga; $^{72}$Ge; $^{75}$As; $^{77}$Se; $^{85}$Rb; $^{88}$Sr; $^{89}$Y; $^{90}$Zr; $^{93}$Nb; $^{95}$Mo; $^{101}$Ru; $^{103}$Rh; $^{105}$Pd; $^{107}$Ag; $^{111}$Cd; $^{115}$In; $^{118}$Sn; $^{121}$Sb; $^{125}$Te; $^{127}$I; $^{133}$Cs; $^{137}$Ba; $^{139}$La; $^{140}$Ce; $^{141}$Pr; $^{146}$Nd; $^{149}$Sm; $^{153}$Eu; $^{157}$Gd; $^{159}$Tb; $^{163}$Dy; $^{165}$Ho; $^{166}$Er; $^{169}$Tm; $^{172}$Yb; $^{175}$Lu; $^{178}$Hf; $^{181}$Ta; $^{182}$W; $^{185}$Re; $^{189}$Os; $^{193}$Ir; $^{195}$Pt; $^{197}$Au; $^{202}$Hg; $^{205}$Tl; $^{208}$Pb; $^{209}$Bi; $^{232}$Th; and $^{238}$U. The result of this analysis is given in Fig. 4, where only the dominant impurities, i.e., with an amount concentration higher than 0.1 nmol mol$^{-1}$, are displayed. The amount concentration is expressed as the amount of the impurity X relative to the amount of water $n(\mathrm{X}) \cdot n(\mathrm{H_2O})^{-1}$.

Results of ICPMS analysis are not used to apply corrections to the triple-point temperatures realized by the cells, but are only used to estimate the uncertainty contribution from the presence of impurities. The estimated uncertainty contribution results from the total impurity concentration (summed over all impurities) divided by the cryoscopic constant of $0.0739 K^{-1}$ mol mol$^{-1}$. The largest total amount concentration is 73 nmol mol$^{-1}$. This amounts to an uncertainty ($k = 2$) of 9 μK or less for the analyzed samples. There is no obvious difference between the samples taken from borosilicate glass or quartz containers. This suggests that if quartz is more resistant than borosilicate, the impurities are from the distillation process and distillation unit that is made of borosilicate glass. This uncertainty does not include a component for possible long-term drift due to dissolution of shell material as suggested by Hill [10].

## 7 Water Triple-Point Temperature Measurements

The differences between the triple-point temperatures realized by the manufactured cells were measured in different runs with groups of four to five cells in each run. Each run corresponded to a different ice mantle for the measured group of cells. Each cell was measured repeatedly for at least three separate ice mantles. The reference temperature for each run was the national reference water triple-point temperature as defined in CCT-K7. To compare results obtained in different runs, we assumed the national reference to be perfectly stable. A separate paper will describe in detail the new definition of the national reference from the outcome of the measurements on the cells produced from 2003 to 2006.

Figure 5 reports the temperature differences among the produced cells with the Dutch national reference (as defined during CCT-K7) as the baseline. The uncertainty in the measured differences was 34 μK ($k = 2$).

Cell 6 was about 100 μK lower than all of the other cells. As it was suspected to be contaminated, it was considered a faulty cell and it was not used further.

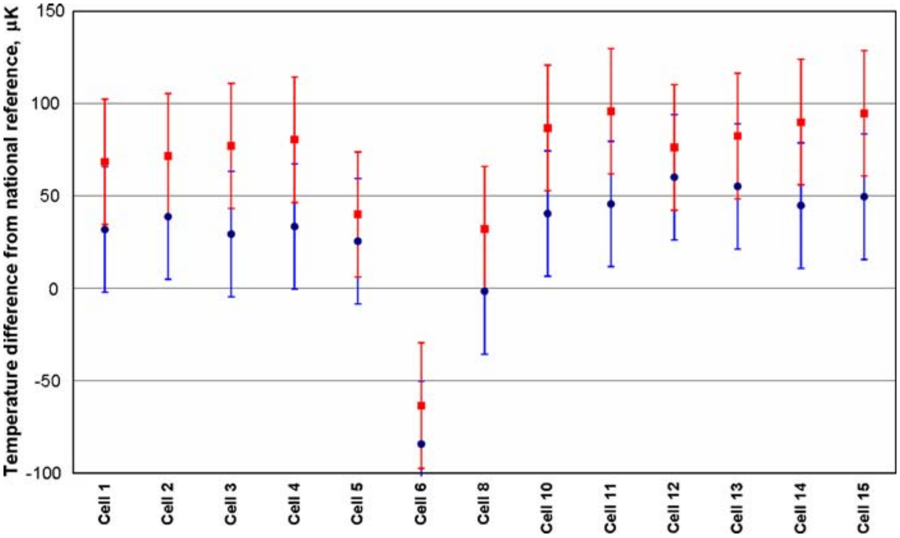

**Fig. 5** Differences between the temperatures realized by the NMi VSL cells and the present Dutch national reference before (circles) and after (squares) applying the isotopic corrections

## 8 Conclusions

The results of the isotopic analyses showed that the correlation between $\delta^2 H$ and $\delta^{18}$Oof the water specimens sampled from different stages of the TPWC manufacturing process can still be described by a straight line having approximately the same slope of the GMWL but a different intercept.

The temperatures realized by all the cells produced from 2003 to 2006 were higher than the Dutch national reference as defined in CCT-K7. Before applying the isotopic correction, the average difference between the new cells and the old cells (which defines the present national reference) was +37 μK with a standard deviation of 17 μK. After applying the isotopic correction, the average difference between the new cells and the old cells was +73 μK with a standard deviation of 20 μK. The spread between the cell temperatures is not reduced, as expected, after applying the isotopic correction, but an eventual reduction of the spread could be overshadowed by the uncertainty.

The knowledge of the impurity content is semi-quantitative and incomplete and does not support correcting for the impurities. The ICPMS analysis can still be used to estimate the uncertainty contribution arising from the presence of impurities. If the maximum overall estimate method is applied (see details in [7]), an uncertainty contribution of 1–9 μK is estimated for the impurity contribution to the realization uncertainty.

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