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Implementing a New Group of TPW Cells as National Standard: Impact on Calibration Services

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Abstract The definition of the kelvin is based on the triple-point temperature of highly pure water having the isotopic composition of ocean water (more specifically, the isotopic composition is equivalent to that of VSMOW). Belgian national metrology realizes the triple point of water (TPW) as the mean of temperatures measured in three sealed cells. In order to take into account the isotopic composition effect on TPW temperature, the ensemble of cells was replaced in 2006. Three new cells, with isotopic analysis of the contained water, were bought from different manufacturers. The new group of cells was compared to the old TPW national realization in order to quantify the effect of moving towards a new reference. Two different standard thermometers were used in all the cells to take 10 daily measurements on two different ice mantles. The measured resistances were corrected for hydrostatic head, self-heating, and isotopic composition (when available) before calculating the difference. A difference of about 87 μK was found between the old and the new national references. This difference is transferred to customers' thermometers and cells through calibrations, and the change has to be documented in each new calibration certificate. An additional consequence of the new ensemble cell implementation is the significant reduction in the spread of deviations of individual cells from the mean temperature. The maximum difference between two cells of the ensemble is 96 μK for the old reference cells and 46 μK for the new reference cells corrected for isotopic composition effects.

Keywords Calibration · Fixed point · Isotopic composition · Triple point of water

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1 Introduction

The International System of Units (SI) defines the kelvin, unit of the thermodynamic temperature, as the fraction 1/273.16 of the temperature of the triple point of water (TPW). The practical realization of this definition is through sealed glass (or quartz) cells containing only water and water vapor. As direct thermodynamic temperature measurements are complex, a practical temperature scale is used worldwide for dissemination through calibration services. In the present version, the International Temperature Scale of 1990 (ITS-90) [1], the TPW plays an important role as temperatures in the range 13.8033 K to 1234.93 K are determined from the ratio of a standard platinum resistance thermometer (SPRT) resistance at any given temperature in this range to its resistance at the TPW. Any uncertainty in the TPW realization will propagate to the whole range.

International equivalence of thermometry calibrations is established through international comparisons. The most recent comparison of water triple-point cells, CCT-K7 [2], organized by the Bureau International des Poids et Mesures (BIPM), pointed out that important discrepancies exist between TPW temperatures realized in different countries. A difference of as much as 163 μK was observed among the 20 high-quality national standards. Further investigations led to the conclusion that an important part of this effect is attributed to the variation of isotopic composition of water used in the TPW cells.

Unfortunately, the initial definition of the kelvin, as adopted in 1954 by the 13th General Conference of Weights and Measures did not specify a reference isotopic composition of water. The information available for the practical realization of ITS-90 temperature [3] is more explicit and advises to use water with the isotopic composition of ocean water. However, the usual practice in TPW cell manufacture was to use continental water, whose isotopic composition varies with latitude and altitude. In addition, distillation and degassing procedures during the cell fabrication process can introduce additional variations in isotopic composition.

The International Committee for Weights and Measures (CIPM) decided in 2005 to clarify the definition of the kelvin. Recommendation 2 CIPM-CI 2005 [4] stated that this definition refers to water having the isotopic composition of VSMOW (Vienna Standard Mean Ocean Water), the reference used by the International Atomic Energy Agency.

The implementation of this recommendation is the task of national metrology institutes (NMIs). The influence of isotopic composition must be taken into account when realizing the national reference of the kelvin. Two possibilities exist: to use cells with water of VSMOW composition, or to use cells with water of known isotopic composition and correct the triple-point temperature as indicated in the Consultative Committee for Thermometry (CCT) report [5]. Like most NMIs, the Belgian National Metrology Institute (SMD) had an ensemble of TPW cells of high quality but had no information regarding the isotopic composition of the water inside the cells. The national reference was based on the mean of three TPW cells from different manufacturers (see details in Table 1).

A new cell of specified isotopic composition was acquired in 2006 and compared to the national reference. Measurements indicated that the temperature realized by the

Table 1 List of TPW cells and their characteristics (including isotopic composition when available)

Cell	Cell manufacturer	Cell type and serial number	Isotopic composition	
			$^{2}\delta$ (‰)	$^{18}\delta$ (‰)
Old ensemble of cells used as national TPW standard				
O1	NPL[a]	Type 32 Serial 951	unknown	
O2	NPL[a]	Type 32 Serial 1070	unknown	
O3	Hart Scientific	5901A-1117	unknown	
New ensemble of cells used as national TPW standard				
N1	NMi-VSL[b]	VSL-03T 026	−51.1	−6.93
N2	Hart Scientific	5901A-Q5017	−2	−0.7
N3	Isotech	AII /50/545	+33.5	+3.6

[a] Cell manufactured by the National Physical Laboratory, United Kingdom
[b] Cell manufactured by the Nederlands Meetinstituut – Van Swinden Laboratorium, Netherlands

ensemble of cells was 59 μK lower than that associated with the VSMOW-defined TPW. Therefore, SMD decided to acquire two more cells of known isotopic composition and from different manufacturers for the purpose of establishing a new national definition of the kelvin and a new TPW reference for dissemination of the ITS-90.

In order to quantify the difference between the old and new reference standards, 10 daily measurements were performed on two different ice mantles with two different standard platinum resistance thermometers (SPRT), first for the old ensemble of cells plus one of the new reference cells, and then for the three new cells. A detailed description of the experimental procedure and instrumentation is presented in Sect. 2. The results were compared to the measurements available for the ensemble of old cells. In Sect. 3, the measurements are analyzed in order to quantify the difference between the old and new TPW national reference standards.

As the NMI mission is not only to maintain but also to transfer the internationally agreed definitions of the units to the users, an estimation of the impact of changing the national reference on calibrations performed by our institute has been done.

The conclusions focus on the necessity and modality to inform thermometry users about the changes in the national standard as a result of the clarification of the definition of the kelvin.

2 Equipment and Experimental Techniques

2.1 TPW Cells

The TPW cells used for these measurements are classified into two categories: "old" cells (O1–O3) without any available information on isotopic composition, and "new" cells (N1–N3). Two of the new cells are from commercial providers; the other is part of the ensemble of cells designed by NMi-VSL (Netherlands National Metrology Laboratory), especially for research on TPW cells [6]. The cell used as a reference to compare the old and new ensembles of cells is cell N1. Details of cell manufacturer, type, dimensions, and isotopic composition of water contained are given in Table 1. Isotopic composition is reported as deviations δ from V-SMOW were $^{2}\delta$ refers to deviation from the ratio mol ^{2}H per mol ^{1}H and $^{18}\delta$ to the variation in mol ^{18}O per mol ^{16}O.

A water-hammer test and a McLeod-gauge test, when possible, were performed on all the cells prior to each ice-mantle realization. The ice mantle is realized following the usual laboratory procedure: crushed CO_2 is inserted into the cell inner well to form an initial ice layer around the inner tube. Then, the well is filled with alcohol and an immersion cooler filled with a mixture of crushed CO_2 and alcohol is inserted into the well. After 1 h, the ice mantle is thick enough to last for at least one month in the maintenance bath. The only exception for this procedure was with cell N1, whose inner well diameter was too small to allow the immersion cooler insertion. In that case, the ice mantle was realized by continuously filling the inner well with crushed CO_2. This procedure takes the same amount of time as the inner cooler method, so, from the point of view of stress induced into the ice mantle, they are equivalent.

The precooled thermometers are immersed in the cells at least 30 min before acquisition starts. Before inserting the thermometers, an inner melt layer is induced in the cells by first inserting a glass rod at ambient temperature into the inner well and then gently rotating the cell to free the mantle around the well. Neither a foam pad nor a bushing was used in the inner well.

2.2 Instrumentation

The temperature of the TPW cells was measured using two SPRTs (SPRT 1 is a Hart Scientific Model 5681 and SPRT 2 is a Leeds & Northrup Model 8167). The measurements are performed as ratios of SPRT resistance with respect to a 25 Ω temperature-controlled standard resistor (Tinsley 5685A). The resistance AC bridge used is an ASL F18, operating at 25 Hz, with a detector gain of 10^4, a bandwidth of 0.1 Hz, and automatically driven by a computer program. Each acquisition data file contains 150 measurements (every 10 s): 70 at 1 mA current followed by 50 readings at $\sqrt{2}$ mA current (to calculate the zero-power resistance ratio) and again 30 at 1 mA (to check for SPRT equilibrium and repeatability). If the repeated measurements do not agree within 20 μK, the acquisition continues and another set of 150 readings is performed. From the data set, the mean and standard deviations based on 20 values are calculated. Mean ratio values, converted to resistance, are then corrected for self-heating (using the two-current measurements) and hydrostatic head.

2.3 Measurement Procedure

Cell comparisons are always measured on simultaneous TPW realizations in the same maintenance bath. As the maintenance bath cannot hold more than five cells, the complete experimental design was split into two stages. In the first stage, the three cells of the old national reference ensemble (cells O1, O2, and O3) were compared with one cell from the new ensemble (test cell N1). The second stage compared the three cells of the new reference ensemble (N1, N2, and N3). The complete measurement set took about 4 months.

Data were acquired according to a full factorial experimental design with two factors, cells and SPRTs. Therefore, the daily data for each cell consists of two measurements, each one with a different thermometer. The order of SPRT insertion in the cells was randomized, and a check for ice mantle reattachment was performed every 3 h. The mantles were prepared at least one week before the beginning of the measurements and data were then collected daily for two consecutive weeks (5 days per week).

2.4 Uncertainties

The general rules and definitions of the ISO Guide to the Expression of Uncertainty in Measurements [7] were applied to establish the expanded uncertainty of cell comparison.

The type-A uncertainty components considered for the two cell comparisons were short-term repeatability (u_{A1}) and reproducibility (u_{A2}). Short-term repeatability was estimated from the standard deviation of bridge readings over a short time period when all factors remain constant. The calculated value is $u_{A1} = 4\,\mu K$. Reproducibility includes effects such as: mantle age, difference between mantles, stability of the standard resistor, manipulation of the SPRT, and differences between different SPRT designs. This component was calculated as the pooled standard deviation of the mean of three series of 60 measured differences between cells (the cells of the national reference ensemble compared two by two). Each series was composed of temperature differences between daily measurements on cells for ten days, two different mantles, and three SPRTs. The calculated value is $u_{A2} = 12\,\mu K$.

Two Type-B uncertainty components were identified: the uncertainty in the exact immersion depth of the SPRT ($u_{B1} = 2\,\mu K$) and the uncertainty introduced by spurious thermal exchanges ($u_{B2} = 3\,\mu K$). The combined expanded standard uncertainty of the measured temperature differences of two TPW cells is, with a coverage factor $k = 2$, $U = 26\,\mu K$.

3 Data Analysis

Measured resistances are converted to temperature after correcting for self-heating, hydrostatic head, and, when available, isotopic composition. The correction for isotopic composition is evaluated using a linear function [5]:

$$T_{\text{corrected}} = T_{\text{measured}} - A_{^2\text{H}}\,{}^2\delta - A_{^{17}\text{O}}\,{}^{17}\delta - A_{^{18}\text{O}}\,{}^{18}\delta$$

The depression constants are taken from Kiyosawa's data [8]: $A_{^2\text{H}} = 628\,\mu K$, $A_{^{18}\text{O}} = 641\,\mu K$, and $A_{^{17}\text{O}} = 57\,\mu K$. The deviation ${}^{17}\delta$ is not available from the analysis certificates delivered with the cells and is therefore estimated from the known correlation [9] between delta values in continental surface water: $1 + {}^{17}\delta = (1 + {}^{18}\delta)^{0.528}$.

The temperature deviation of one individual cell from the national reference is calculated as

$$T_{\text{cell}} - T_{\text{national reference}} = \left(\frac{R_{\text{cell}}}{R_{\text{national reference}}} - 1 \right) \left. \frac{dT_{90}}{dW_{\text{r}}} \right|_{\text{TPW}} (K)$$

where T_{90} is the ITS-90 temperature [1] in kelvin and W_{r} is the ITS-90 reference function.

The national reference is the arithmetic mean of values measured on the same day with the same SPRT in the three cells of the ensemble (O1, O2, and O3 for the old reference ensemble and N1, N2, and N3 for the new ensemble).

The goal of these experiments is to quantify the impact of changing the national reference ensemble of cells on calibrations realized by the national laboratory. Cell N1 was therefore compared first with the old national reference and then with the new reference. In the first stage, the TPW was realized simultaneously in four cells (O1, O2, O3, and N1) and measured with two SPRTs during two consecutive weeks. Temperature deviations of each individual cell from the mean of the old ensemble of cells (O1, O2, and O3) were calculated daily. Table 2 shows the mean of all daily measurements together with the standard deviation of the mean.

In the second part of the experimental procedure, the TPW was realized in the three new cells (N1, N2, and N3) and daily deviations of each cell from the mean of the new ensemble were calculated. The mean of all daily deviations for the new ensemble of cells are summarized in Table 2.

The mean measured deviation of test cell N1 from the old national reference is 59 μK. The same cell, when compared with the new TPW reference, shows a difference of −28.5 μK. Therefore, the old ensemble of water cells realizes a mean temperature 87.5 μK higher than the new ensemble of cells corrected for isotopic composition effects. Figure 1 shows graphically the deviation of the N1 test cell from the old and new reference standards and the resulting difference in TPW realizations.

This difference has an impact on cell calibration by direct comparison with the national reference. The same client cell, when calibrated against the new national

Table 2 Deviations of individual cell temperatures from the national reference

Cell	Mean temperature deviation of cell from the national reference (μK)	Standard deviation of the mean (μK)	Maximum difference between two cells of the ensemble (μK)
National TPW reference standard based on OLD ensemble of cells			
O1	−58.4	1.2	95.2
O2	36.8	2.1	
O3	−35.8	2.8	
N1	59.0	2.7	
National TPW reference standard based on NEW ensemble of cells			
N1	−28.5	2.3	45.7
N2	18.7	1.9	
N3	7.8	2.4	

Cell N1 from the new ensemble is also compared with the old ensemble of cells

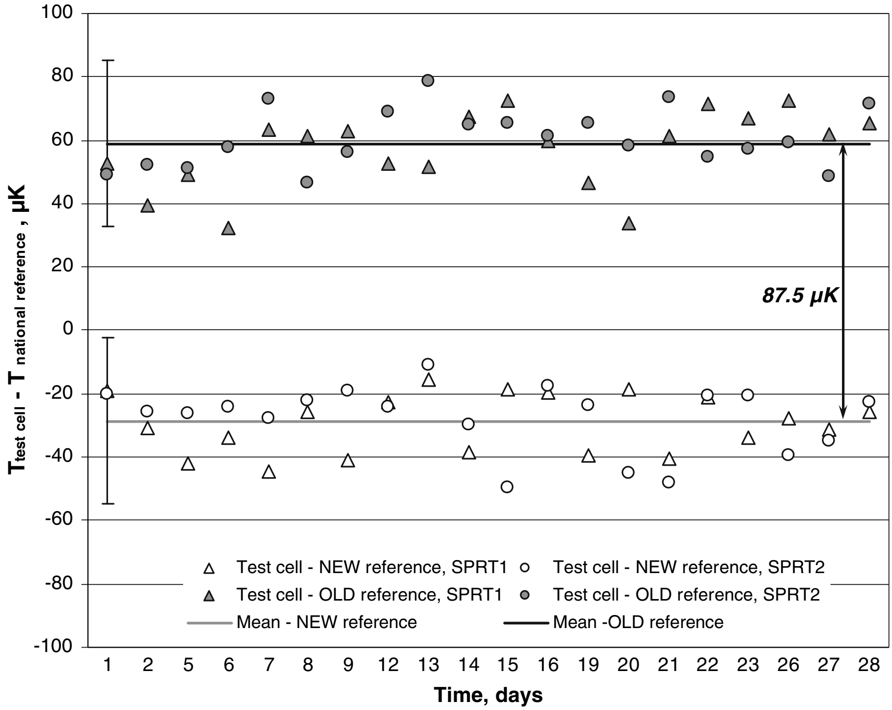

Fig. 1 Temperature differences between test cell N1 and the old and new national realizations of the TPW (mean of three cells) measured on two different mantles with two SPRTs. The new cells were corrected for isotopic composition effects. The uncertainty bar ($k = 2$) is the estimated cell comparison measurement uncertainty

reference, will show a difference of (87±26) μK (taking into account the cell comparison uncertainty with $k = 2$) with respect to previous calibrations with the old ensemble of reference cells. A comment about the transition to a new reference ensemble of cells in order to accurately account for isotopic composition effect on the realization of TPW has to be added to the cell calibration certificate to make the client aware that it is not their cell that has changed, but rather the definition of the national reference.

An additional effect of moving towards a new TPW reference is presented in Fig. 2: the spread of deviations of individual cell temperature from the mean is reduced by 50% for the new ensemble of cells. This is a direct effect of the implementation of the CIPM recommendation that the kelvin be based on the TPW having the isotopic composition of VSMOW. Cell manufacturers have modified their fabrication procedure in order to fill cells with water of almost VSMOW isotopic composition. The range of the measured deviations of each cell from the mean would have been even lower if only cells of commercial origin composed the ensemble. As shown in Table 2, this range is 46 μK for our ensemble of new cells. If only cells of commercial origin (N2 and N3) are considered, this range is only 11 μK. The Netherlands National Institute, the manufacturer of cell N1, deliberately chose not to alter the composition to that of VSMOW but rather to analyze the water and then apply a correction based on the isotopic composition.

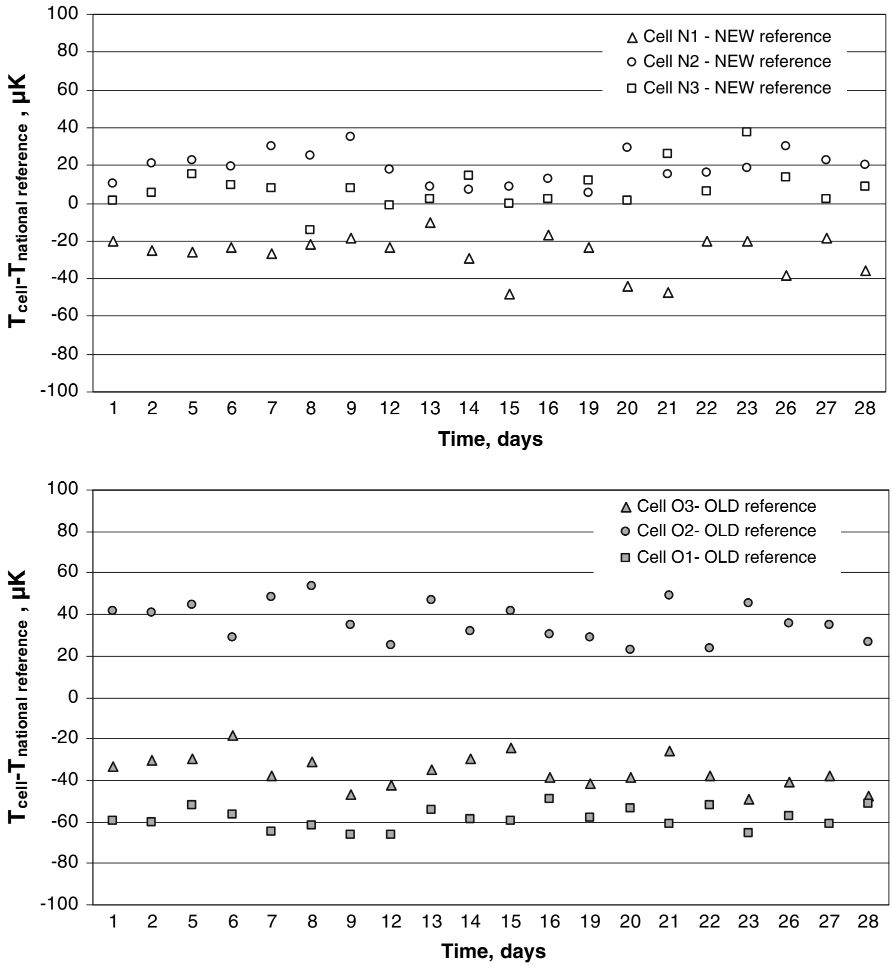

Fig. 2 Temperature deviations of individual cells from the mean realization temperature. The upper chart shows data for the new reference ensemble corrected for isotopic composition effects, and the lower chart shows data for the old reference ensemble

4 Conclusion

The International Committee of Weights and Measures recommended in 2005 that the definition of the kelvin refers to the TPW having the isotopic composition of VSMOW. To conform to this recommendation, SMD (Belgium National Metrology) decided to replace the ensemble of TPW cells used as the national reference as no information regarding the isotopic composition of the contained water is available for the old cells.

The mean temperature of three new cells, corrected for isotopic composition, was compared with the mean of the three old cells in order to quantify the effect of moving towards a new reference ensemble. A mean difference of about 87.5 μK was found between the new and old definitions of the TPW at SMD. This deviation will impact client cell calibrations and will therefore be documented in each new calibration certificate.

An additional benefit of taking into account the isotopic composition is the reduction by 50% in the spread of individual cell TPW realizations of the reference ensemble. The maximum difference between two cells was 95 μK for the old ensemble of cells and is now 46 μK for the new ensemble when isotopic corrections are applied.

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