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INTERCOMPARISON OF WATER TRIPLE POINT CELLS FROM INTIBS AND INRIM

The triple point of water defines the unit of thermodynamic temperature, *kelvin*, and is the most important fixed point of the International Temperature Scale of 1990. Several international comparisons of cells for the realization of the water triple point were carried out to estimate the temperature values obtained in real conditions at national metrology institutes. A separate bilateral comparison was set up for INTiBS, Poland with INRiM, Italy, as CCT-K7 participant, in order to create a direct reference to CCT-K7 for the Polish institute. Results of the bilateral comparison carried out as EUROMET project no 895 are presented in this paper.

1. INTRODUCTION

The triple point of water (TPW) is an unique phase transition in thermometry. It defines the unit of thermodynamic temperature in the International System of Units (SI) – the *kelvin*. The *kelvin* by definition is equal 1/273,16 the thermodynamic temperature of the triple point of water or the thermodynamic temperature of the triple point of water by definition is equal 273,16 K. Furthermore, it is the most important fixed point of the International Temperature Scale of 1990 (ITS-90) [1], since it is fundamental for measurements with standard platinum resistance thermometers (SPRTs) between 13,8033 K and 1234,93 K. In this range, measurements are performed in terms of the resistance ratio $W(T_{90}) = R(T_{90}) / R(T_{TPW})$, where T_{90} is a temperature on ITS-90. Therefore, any uncertainty in the realization of the TPW is directly propagated over the whole SPRT temperature range.

This is the reason why international comparisons of cells for the realization of the TPW are periodically carried out to estimate the temperature values obtained in real conditions at National Metrology Institutes (NMIs). A previous international comparison of TPW cells was carried out by the BIPM between 1994 and 1996 [2]. Twelve

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NMIs, all members and observers of the Consultative Committee for Thermometry (CCT), and only these, were invited to participate in the comparison. For a large group of cells the TPW temperature agreed to within ± 100 μK. In some cases much larger differences, up to 530 μK, were observed. The standard uncertainty of the temperature differences was estimated as 40 μK. The differences of the comparison had appeared to be too large, so the CCT decided in 2001 to carry out a new comparison and charged BIPM with its organization. The world-wide comparison was a so-called key comparison and was designated as CCT-K7. The key comparisons were organized to review the calibration and measurement capabilities (CMCs) declared by NMIs in the framework of the Mutual Recognition Arrangement (MRA) [3, 4]. In CCT-K7 participated 21 institutes. TPW temperatures for the most of cells were found inside a range of about 160 μK and the standard deviation of all results was 50 μK. It was noticed that a few cells with known isotopic composition, close to the ocean water, distinguished themselves by a higher temperature of the TPW.

Parallel to CCT-K7, in Europe a comparison of realization of the TPW was carried out as EUROMET project no 549. In this project those European NMIs which are not members of CCT could participate as well. BNM-INM (France) was the pilot of the comparison; 20 institutes with 27 cells were involved in the project. The aim of this project, based on the circulation of one cell and an adapted isothermal enclosure, was to assess the uncertainties associated with the practical realization of the TPW in the various European laboratories.

The report of CCT-K7 [5] showed clearly the importance of isotopic composition for the temperature realised by a certain TPW cell, and thus that isotopic analysis on the water content is necessary for each TPW cell. An ad-hoc CCT Task Group prepared in 2005 a document “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” [6]. In parallel the regional extension of the CCT-K7 was started. The comparison was designated as EUROMET.T-K7. In this comparison as many as possible new water cells with an estimated isotopic composition, close to the composition of Vienna Standard Mean Ocean Water (V-SMOW) were used. This composition is the following [7]:

0,000 155 76 mole of ^{2}H per mole ^{1}H,

0,000 379 9 mole of ^{17}O per mole ^{16}O,

0,002 005 2 mole of ^{18}O per mole ^{16}O.

NMi VSL[2] (Delft, The Netherlands) organized the comparison and 23 European NMIs participated. NMi VSL prepared a set of 6 cells of known isotopic composition which were used as transfer cells by co-pilots of the project. Objectives of this comparison were:

– a direct comparison of water triple point cells to quantify the differences between the cells, providing a link to CCT-K7 to the EUROMET members that did not take part to CCT-K7,

[2] NMi-VSL – Nederlands Meetinstituut – Van Swinden Laboratorium, Netherlands

– a comparison of the national realizations of the WTP temperature. As all the participants will adopt the methodologies described in the above-mentioned documents (mostly concerning isotopic and impurity effects), it will be interesting to compare the new distribution of the national references to the one generated by CCT-K7.

The Polish Central Office of Measures (GUM[3]) in Warsaw was involved in this project. In Poland the national temperature scale is maintained by two organizations – GUM for long-stem standard platinum resistance thermometers (SPRTs) at temperatures from the triple point of argon (83,8058 K) to the freezing point of silver (1234,93 K), and by INTiBS (in Wrocław) for capsule type platinum thermometers (CSPRTs) from the triple point of equilibrium-hydrogen (13,8033 K) up to the water triple point (273,16 K). Since both laboratories use the water triple point, but only GUM could participate in EUROMET.T-K7, a separate bilateral comparison was set up for INTiBS[4] with INRiM[5], as CCT-K7 participant, in order to create a direct reference to CCT-K7 for the Polish institute. Results of the bilateral comparison carried out as EUROMET project no 895 are presented in the paper.

2. PROCEDURES OF THE COMPARISON

The above-mentioned TPW-cell comparisons were carried out according to the "Protocol for the CIPM key comparison of water triple point cells", which was added as Appendix 1 to the CCT-K7 final report [5]. The protocol, describing the objectives of the comparison, its organisation and the procedures to be followed by the participants are in short presented below.

These comparisons served two distinct objectives:

– a direct comparison of TPW cells to quantify differences between cells,

– a comparison of calibrations of these cells provided by the participants.

Each participating laboratory selects one of its cells for use as a transfer cell and directly compares it against its national standard. Next the selected transfer cell is sent together with the measurements results to the pilot of the comparison where all transfer cells are compared against a group of common reference cells. After the measurements all transfer cells are sent back to the laboratories to be re-compared with the same national standard as before to check the transfer cell stability.

Measurements should be made on the transfer cell with two separately prepared ice mantles, and for each ice mantle the direct comparison with the standard should be performed during two weeks with typically one measurement per day, starting at least 4, here 7 days after the preparation of the ice mantle. A minimum of 10 measurements per mantle should be reported. For each transfer cell, an immersion profile should be provided, to ensure that the measurement really senses correctly the temperature of the

[3] GUM – Główny Urząd Miar, Poland

[4] INTiBS – Instytut Niskich Temperatur i Badań Strukturalnych, Poland

[5] INRiM – Instituto Nazionale di Ricerca Metrologica, Italy

ice/water interface. Also the self-heating correction for the SPRT should be determined and applied. The self-heating correction is usually determined from measurements with currents 1 mA and $\sqrt{2}$ mA using the formula:

$$R(0mA) = 2R(1mA) - -R(\sqrt{2}mA). \tag{1}$$

Currents 2 mA and $2\sqrt{2}$ mA, or some other value, can be used as well.

A detailed uncertainty budget of the temperature realized by the transfer cell has to be provided, following the general guidance of the "Guide to the expression of uncertainty in measurement" [8]. This budget must include both the uncertainty of the national standard and of the direct comparison of the transfer cell to the standard.

In addition, the equipment used for the calibration should be described: the national standard, the technique used to prepare the ice mantle, the type of storage container, the type of thermometer, the type of resistance bridge, the reference resistor and whether or not it is temperature controlled, the measurement currents, the age of the mantles of the standard and reference cell and the results of isotopic and impurity analysis, if available.

Results of measurements are to be sent to the pilot institute. During the comparison they are to be kept confidential by the pilot until all the participants have completed their measurements and all the results have been received.

The procedure used for EUROMET 549 was somewhat different from that described above. The aim of EUROMET no 549 was to allow each participating laboratory to compare the temperature of TPW cell realized by the local facilities; such as cell, enclosure and procedure, to the temperature realized by the circulating instrument. The comparison was performed by measuring the difference in temperature between the circulating cell and localTPW cells. During the comparison, the stability of the circulating cell was periodically checked by comparison with another BNM-INM cell.

3. RESULTS OF THE COMPARISON

The results of CCT-K7 are presented as differences between the national standard and the pilot reference, and as differences between the national standard and the key comparison reference value (KCRV). The KCRV is based on the mean value of the results from all of the participants. The uncertainty of the KCRV was taken to be the standard deviation of the mean of the data set.

The results of the CCT-K7 comparison, published in the "Final report on CCT-K7" [5], are presented in Fig. 1.

The differences between the transfer cells are characterized by a standard deviation of 50 μK, the difference between the two extremes is 163 μK. CSIR, MSL and NRC realize systematically higher temperatures, because their realization is based on the recommendation of the "Supplementary Information" [9] to use water with the isotopic composition of ocean water. The NRC cell was produced by ISOTECH.

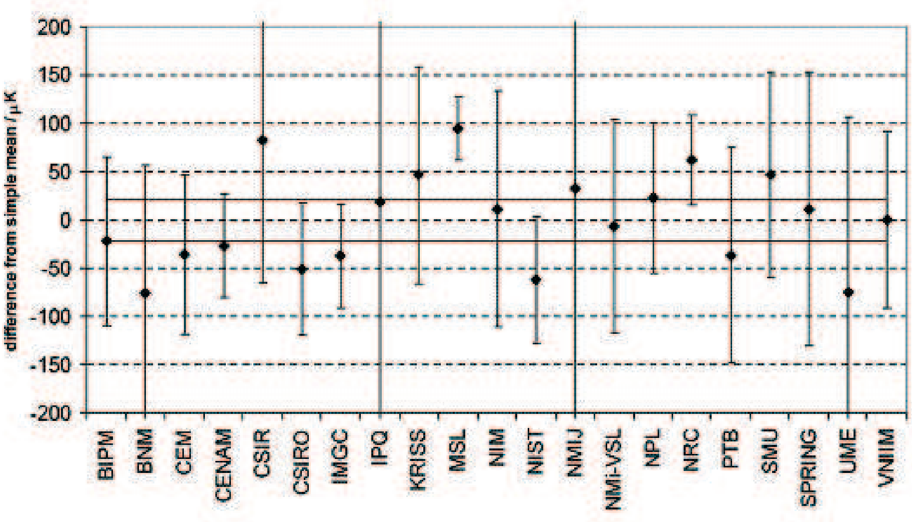

Fig. 1. Differences between the national references and the KCRV calculated as the simple mean. All uncertainty bars are calculated for k = 2. The two solid lines at ± 22 μK represent the uncertainty of the reference value[6]. (from "Final report on CCT-K7" – Fig. 30 [5]).

[6] The participants presented in the figure are:
BIPM – Bureau International des Poids st Mesures
BNM-INM – Bureau National de Metrologie – Institute National de Metrologie; France
CEM – Centro Espanol de Metrologia, Spain
CENAM – Centro Nacional de Metrologia, Mexico
CSIR-NML – National Metrology Laboratory, South Africa
CSIRO-NML – National Measurement Laboratory, Australia
IMGC – Instituto di Metrologia "G.Colonnetti", presently – INRiM, Italy
IPQ – Instituto Portugues da Qualidade, Portugal
KRISS – Korea Research Institute of Standards and Science, Rep. of Korea
MSL – Measurement Standards Laboratory, New Zealand
NIM – National Institute of Metrology, China
NIST – National Institute of Standards and Technology , USA
NMIJ/AIST – National Metrology Institute of Japan, Japan
NMi-VSL – Nederlands Meetinstituut – Van Swinden Laboratorium, Netherlands
NPL – National Physical Laboratory, United Kingdom
NRC – National Research Council of Canada, Canada
PTB – Physikalisch-Technische Bundesanstalt, Germany
SMU – Slovak Institute of Metrology, Slovakia
SPRING – National Metrology Centre, Singapore
UME – Ulusal Metroloji Enstitusu, Turkey
VNIIM – D.I. Mendeleev Institue for Metrology, Russia.

The results of EUROMET 549 of comparison have shown that for twelve water cells the triple point temperature values derived from the resistance of standard platinum resistance thermometers lied between – 50 μK and + 50 μK of the mean value. Twenty results (74 %) are within ± 100 μK of the mean value [10].

The results of EUROMET.T-K7 are not published yet.

4. EUROMET 895 RESULTS

In order to maintain as close a link as possible, the "Protocols of CCT-K7" and EUROMET. T-K7 were followed. Thus, at INTiBS the transfer cell was compared with the local National Standard before sending it to INRiM, where it was compared with the Italian National Standard. After return to INTiBS, the transfer cell was once more compared with the local National Standard, July and October 2007. With each comparison separate ice mantles were created, with up to 10 measurements on each mantle.

The equipment used for the comparison is summarized in Table 1.

Table 1. Equipment used at INTiBS for the comparison.

Description of national reference (1 or several cells, purchase or manufacture date, isotopic analysis):	
	Water Triple Point Cell, ISOTECH Type B11/50 Serial No:B11/50/465
	Isotopic Composition: delta ^{18}O = – 0,426 m Mole/Mole; delta ^{2}H = – 18,69 m Mole/Mole resulting in a correction of 12 μK (U = 1.3 μK)
Type of resistance bridge, AC or DC:	
	Measurements International Model 6015T, Serial No:1100328 – DC
Measurement current:	
	1 mA, 1,41 mA
Number and sampling frequency of repeated measurements:	
	100, 4 s
Type of reference resistor:	
	25 Ω, Tinsley Type 5685A serial No 274748 with thermostat Type 5648
Is reference resistor temperature-controlled? (If yes, state stability):	
	Yes, control ratio of 30
Type of thermometer, length of sensor:	
	In the first ice mantle: CSPRT L&N 1866336, 5 cm; In the second and third mantles: SPRT FLUKE – Hart No: 4113, 3,6 cm
Storage container for WTP cells:	
	Isotech Model ITL M 18233, No: 2515014-4

All reported values are already corrected for thermometer self-heating and for hydrostatic head. The ice mantles at both INTiBS and at INRiM were prepared with the same method, i.e. using a liquid-nitrogen-cooled copper rod. The transfer cell supplied by INTiBS is a relatively small, narrow cell produced by UME (Turkey), cell UME-51, exhibiting an immersion depth of 225 mm, while customary cells have an immersion depth of about 260 mm.

One of the initial requirements of the “Protocol” to be fulfilled is the measurement of the immersion profile on the transfer cell and the local reference, as a proxy of measurement capability. The profiles measured are shown in Fig. 2. The immersion profiles measured at INTiBS and INRiM follow the ITS-90 profile quite well, unlike some of the profiles obtained during CCT-K7, thus confirming the measurement capabilities of the two laboratories.

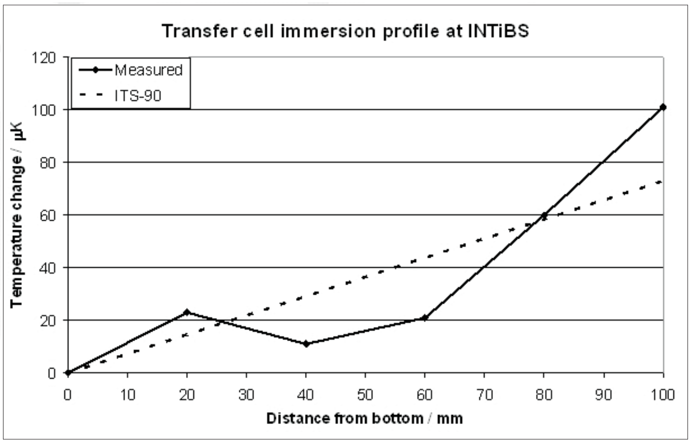

Fig. 2. Immersion profile of the transfer cell as measured at INTiBS.

Before transporting the transfer cell (UME 51) to INRiM, it was compared with the Polish National Standard at INTiBS (ISOTECH 465). After return to Poland, the transfer cell was once more compared with the local National Standard. Fig. 3 shows the results obtained during the both comparisons carried out at INTiBS. The dt values are equal to the differences of the temperature of the triple point of water in the transfer cell and the National Standard determined by the standard platinum resistance thermometer type Fluke-Hart no 4113.

All data obtained in Poland, are pooled to obtain a single value for the difference between the transfer cell and the Polish National Standard at INTiBS.

The mean value for the difference between the transfer cell and the National Standard at INTiBS is -304.7 μK, with a standard deviation of 82.7 μK and a standard deviation of the mean (27 values) of 16.2 μK.

At INRiM, the same cell has been compared with local cells IMGC-31 and IMGC-34 which have maintained the link with CCT-K7 to within a few μK. The

INRiM results are presented in Fig. 4. The given values for the National Standard are corrected for isotopic composition, hydrostatic head and for thermometer self-heating.

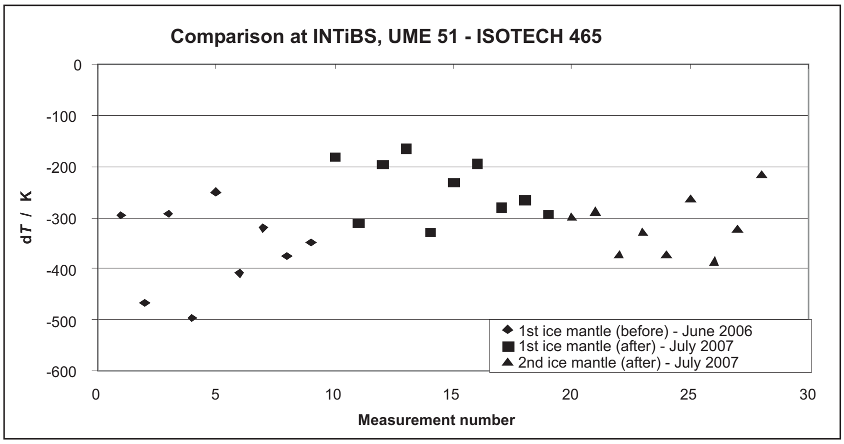

Fig. 3. Comparison results between the transfer cell and the Polish National Standard at INTiBS.

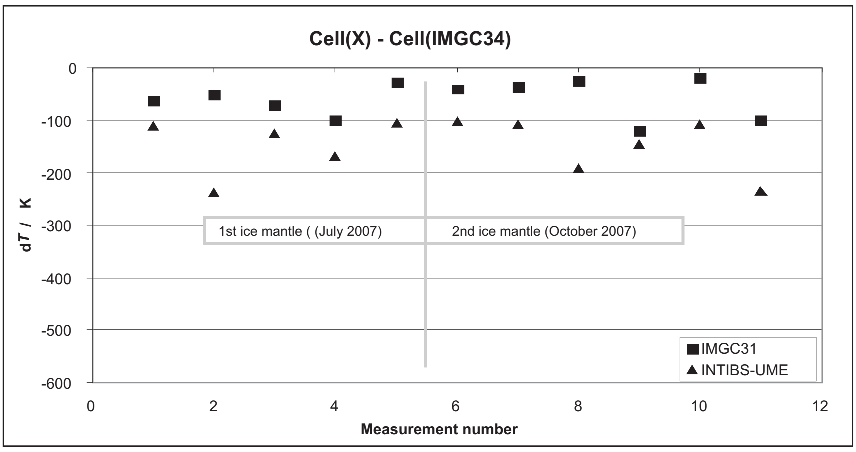

Fig. 4. Comparison results at INRiM between the transfer cell and the Italian National Standard cells IMGC-31 and IMGC-34.

Also here the temperature difference between the cells is expressed as a single value. The mean value for the difference between the transfer cell and the Italian National Standard represented by cells IMGC-31 and IMGC-34 is -119.0 μK, with a standard deviation of 49.5 μK and a standard deviation of the mean (11 values) of 15.7 μK.

The uncertainty budgets for the comparison at INTiBS and at INRiM are reported in Table 2.

Table 2. Uncertainty budgets, in μK, for the measurements at INRiM and INTiBS, at $k = 1$.

Origin	**INRiM Contribution (*k*=1)**	**INTiBS Contribution (*k*=1)**
National reference		
Chemical impurities (from nr of distillation cycles)	6	50
Isotopic variation (from analysis certificate)	1	2
Residual gas pressure in cell	10	2
Reproducibility	14	29
Comparison of transfer cell to national reference		
Repeatability for a single ice mantel (incl. bridge noise)	11	16
Reproducibility for different ice mantles	1	11
Reproducibility for different types of SPRTs	–	11
Hydrostatic head of standard cell	3	2
Hydrostatic head of reference cell	3	2
Self-heating of standard cell and reference cell	6	2
Perturbing heat exchanges	1	1
others		
Moisture	1	–
Total uncertainty	**23**	**62**

On the basis of the comparison of the transfer cell with the Polish National Standard and the Italian National Standard, the difference between the Polish and Italian National Standards, the degree of equivalence $D_{ij} = T_i - T_j$, is computed as

$$\boldsymbol{D}_{\mathbf{Pl-It}} = +\ \mathbf{186\ \mu K}, \tag{2}$$

with a standard uncertainty of

$$\boldsymbol{u}_{\mathbf{Pl-It}} = \mathbf{69{,}9\ \mu K}, \tag{3}$$

obtained by summation in quadrature of the individual standard deviations of the mean for the difference between the transfer cell and the local National Standard as measured at INRiM and at INTiBS and the declared uncertainty from the respective budgets. The extended standard uncertainty is thus

$$\boldsymbol{U_{\text{Pl–It}} = 140\ \mu\text{K}.} \tag{4}$$

The value for the quantified demonstrated equivalence at the 95% level, $QDE_{0.95}$, is computed as

$$\mathbf{QDE_{0.95} = 301,0\ \mu K}, \tag{5}$$

using the expression:

$$QDE_{0.95}(i,j) = \left|D_{ij}\right| + \left\{1,645 + 0,3295 * \exp\left[-4.05\left|D_{ij}\right|/u_{ij}\right]\right\} u_{ij}, \tag{6}$$

with D_{ij} and u_{ij} as defined above, where i = Pl and j = It.

The results for the Polish National Standard TPW (Isotech no 465), over 100 μK high obtained through measurements with the transfer cell, were quite disconcerting. Such a high value is rather improbable, especially since the INRiM Standard resulted 37 μK above the KCRV of CCT-K7. It was therefore decided to check these results with a direct comparison of the Polish Standard with two cells of the INRiM Standard, on only one ice mantle [10]. The preparation of the ice mantle in various cells was performed exactly like the previous comparison, and like CCT-K7. Also the same platinum thermometer, Leeds& Northrup no 42, was used as in all preceding comparisons. For the cell a check on the heat exchange between the inside of the thermometric well and the surrounding was made. No difference was found to within the uncertainty of measurement. The results of the direct comparison are shown in Fig. 5. Some of the measurements have been performed at a lower base current, which at most led to

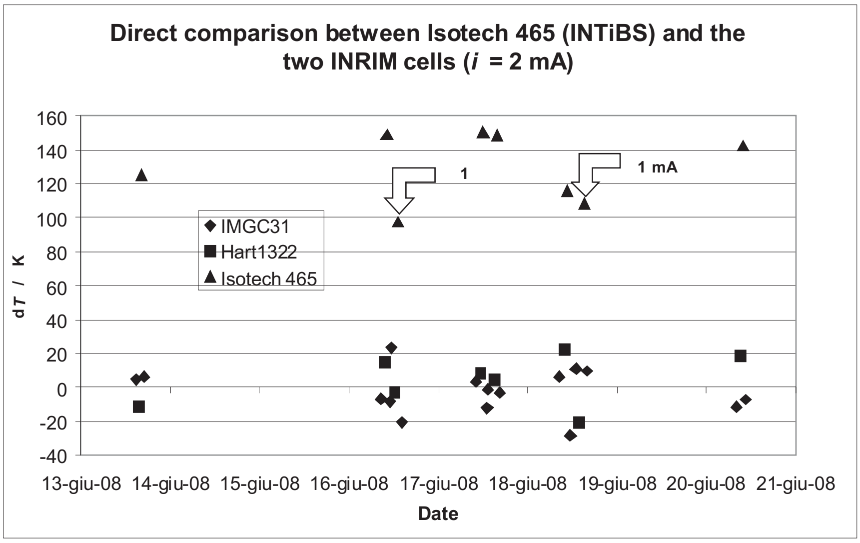

Fig. 5. The results of the direct comparison.

a modest influence of up to 20 μK, well within the scatter of the data. As can be seen, the conclusion of the previous comparison using the transfer cell is confirmed.

5. CONCLUSION

An analysis of the results coming from a set of international comparisons of cells for realization of the water triple point shows that a spread of TPW temperatures in the tested, high quality cells is within about 170 μK with an standard deviation of 50 μK. The cells which were manufactured with water of isotopic composition close to the composition of VSMOW ocean water showed a higher temperature, about 70 μK above the Key Comparison Reference Value – KCRV.

The bilateral comparison of the TPW cells between INTiBS and INRIM shows that the measurement procedure used by INTiBS is correct but the obtained difference of the temperature value between both National Standards is too high. It would thus be advisable to check this cell with cells from other laboratories in order to exclude any possible doubt.

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