

INTERNATIONAL COMPARISON OF WATER TRIPLE POINT CELLS LEADING TO A MORE PRECISE DEFINITION OF THE KELVIN

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Abstract: The water triple point serves to define the kelvin, the unit of thermodynamic temperature, in the International System of Units (SI) and it is the most important temperature fixed point in the International Temperature Scale of 1990 (ITS-90). The International Bureau of Weights and Measures (BIPM) has carried out an international comparison of water triple point cells from twenty National Metrology Institutes. This work allows one to determine the variation within a large number of water triple point cells of different origin as well as the variation between the national references of the participating laboratories.

A large portion of the observed variation could be attributed to differences in the isotopic composition of the cell water. The Consultative Committee for Thermometry (CCT) of the Metre Convention has therefore recommended that the isotopic composition of the water should be specified as that of Vienna Standard Mean Ocean Water (V-SMOW). This clarification of the kelvin definition has been included in the recent new version of the SI brochure.

1. INTRODUCTION

The kelvin, unit of thermodynamic temperature, in the International System of Units (SI), is defined by assigning the temperature 273.16 K to the triple point of water [1]. In addition, the water triple point is the most important temperature fixed point of the International Temperature Scale of 1990, the ITS-90 [2], because it serves as a reference temperature for measurements with standard platinum resistance thermometers between 13.8033 K and 1234.93 K. Any uncertainty in the realization of the water triple point is propagated over this whole temperature range. The water triple point is realized by using commercial or self-made water triple point cells.

The Consultative Committee for Thermometry (CCT) of the Metre Convention decided in its 21st meeting in 2001 to carry out a comparison of water triple point (WTP) cells and charged the BIPM with its organization. In addition to its importance for thermometry, the results of this comparison are particularly important for the international review of declared Calibration and Measurement Capabilities (CMCs) of National Metrology Institutes in the framework of the Mutual Recognition Arrangement (MRA) [3]. The latter gives users reliable quantitative information on the comparability of national metrology services and provides the technical basis for wider agreements negotiated for international trade, commerce and regulatory affairs. The results of this comparison allow to verify the related CMCs of the participants, but this aspect will here not be developed further.

This paper describes the experimental aspects of the comparison as well as the results. The full comparison report is available elsewhere [4]. An analysis of the results allows the identification of the main reason for temperature differences between cells as a lack of precision in the definition of the kelvin. This has been remedied in the new, 8th edition of the SI brochure, where the kelvin definition is now accompanied by a clarification, which specifies the isotopic composition of the cell water.

2. THE COMPARISON OF THE WTP CELLS

2.1 Objectives of the comparison

The comparison had two objectives: (1) to compare a large number of high quality WTP cells of different origin and (2) to compare the national realizations of the water triple point of the participating institutes.

2.2 Organization of the comparison

The following twenty member laboratories of the CCT participated in this comparison: CEM (Spain), CENAM (Mexico), CSIR-NML (South Africa), INRIM (Italy), IPQ (Portugal), KRISS (Rep. of Korea), LNE (France), MSL (New Zealand), NIM (China), NIST (USA), NMIA (Australia), NMIJ (Japan), NMi-VSL (Netherlands), NPL (UK), NRC (Canada), PTB (Germany), SMU (Slovakia), SPRING (Singapore), UME (Turkey) and VNIIM (Russia).

Each laboratory sent a cell to the BIPM, where all cells were compared with two reference cells. The

participants were asked to select the cells carefully so that the dispersion of the results would be a measure of the reproducibility of the WTP using high-quality cells. In particular, no floating material should be visible, the cell should produce a sharp “click” if gently inverted and it should not show any known abnormal behavior. To achieve the second objective, each laboratory stated a value for the temperature difference of the transfer cell, relative to the corresponding national standard, representing 273.16 K. This difference had to be accompanied by a detailed uncertainty budget.

After the comparison at the BIPM, the transfer cells were sent back to the laboratories where they were checked for stability.

The participants were asked to perform measurements on two separately produced ice mantles. For each ice mantle, measurements were taken over two weeks, starting at least one week after the preparation of the ice mantle.

2.3 The experimental setup at the BIPM

The setup for measurements of the water triple point cells was modernized for this comparison to allow for more accurate measurements and more efficient operation [4,5]. The main improvements of the new system are the use of an automatically balancing bridge and the better temperature stability of the reference resistor.

The water triple point cells are kept in two WTP maintenance baths which can store up to five cells each. All measurements were made with the same 25.5 Ω standard platinum resistance thermometer (SPRT). An automatic ac bridge (resolution 2.5 μ K, specified accuracy 25 μ K) was used to measure the resistance of the SPRT against a 25 Ω reference resistor in a temperature regulated oil bath.

In total, 21 transfer cells plus the two BIPM reference cells, BIPM-1 and BIPM-131, were measured. During one day we could measure up to nine cells. Therefore, the cells were measured in separate groups of 7-9 cells, always including both reference cells. Seven groups were necessary to measure each cell at least twice. Each group required about four weeks, one for ageing and stabilization of the ice mantles, two for the comparison measurements and the last for the determination of immersion profiles. The NPL sent a second cell which was measured in two additional rounds.

Measurements on each group of cells were taken over two weeks, and normally each cell was measured every day. The first cell of a day was always BIPM-131, the last BIPM-1. The participants' cells were measured in between, in varying order. The mean of the bridge ratios obtained for the reference cells served as reference for all measurements made that day. This means that the results for all cells are expressed as temperature differences from the mean of the reference cells, obtained the same day. This scheme makes the comparison insensitive to long-term drift of equipment like the standard resistor or of the temperature of the oil bath. The only requirement is that the two reference cells are sufficiently stable during the period of the comparison. Effects of changes of the SPRT during one day due to its manipulation cannot be completely removed and contribute to the observed dispersion of the results.

Before the measurement of a cell, an inner melt was produced by inserting an aluminum rod at room temperature. Measurements were made at currents of 1 mA and $\sqrt{2}$ mA to determine the self-heating correction. The bridge ratio readings were made automatically under computer control. The full measurement sequence for a cell took about one hour.

2.4 The comparison uncertainty

Since the comparison system was largely modified for the purpose of this comparison, its performance was carefully tested before the comparison. This also allowed to derive an uncertainty budget (Table 1).

The bridge was tested with a calibrator and did not show a significant non-linearity, we however observed a small differential non-linearity, probably related to the analog-to-digital converters. The temperature stability of the standard resistor, stored in an oil bath, is better than 1 mK, and does not contribute to the uncertainty. A long-term drift of the resistor has no effect, because the results of each day are expressed as temperature differences from the two reference cells, measured the same day.

Detailed investigations were made to estimate the other contributions, as described in [4]. The total uncertainty for the temperature difference of a transfer cell from the BIPM reference is 13 μ K.

It is obvious that all contributions are of similar importance, being close to 5 μK . It is therefore difficult to improve the total uncertainty significantly. It is, however, considerably smaller than the temperature differences between the cells, and therefore adequate for this comparison.

Source of uncertainty	Contribution / μK
repeatability (incl. noise, SPRT changes, TPW changes, etc.)	3-7 (depends on TPW cell)
reproducibility (effect of ice mantle)	generally negligible (otherwise included)
bridge accuracy	negligible
differential bridge non-linearity	5
self-heating correction	6
hydrostatic pressure correction	5
stray thermal exchanges	5
temperature stability of std. resistor	negligible
long term stability of the temp. reference	4
Sum in quadrature ($k=1$)	12-13

Table 1: Uncertainty budget for the temperature difference between a transfer cell and the BIPM reference.

3. RESULTS

3.1. Comparison of transfer cells

The WTP cells were compared in nine groups, which all included the two BIPM reference cells. This allows us to combine the results of all groups, based on the assumption that the reference cells did not change during the comparison. The results for one of the groups are shown in Figure 1.

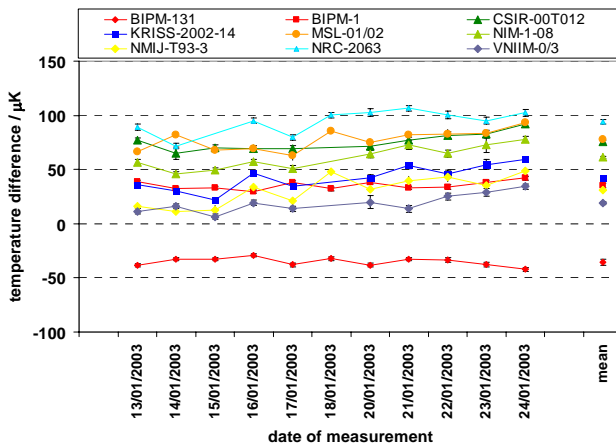


Figure 1: Temperature differences of a group of transfer cells from the mean of the two reference cells, BIPM-1 and BIPM-131, measured over two weeks.

Some of the details of this figure show a correlated behavior of most of the transfer cells, for example the temperature increase during the last two days. Similar behavior was observed for some of the other groups. This indicates that the reference cells were not perfectly stable. This is no surprise because they are of similar quality to the participants' cells.

We therefore used a least-squares technique as a means to use all cells together as a reference set. The basic idea is to apply temperature corrections ΔT_j to all cells measured on day j , where the index j runs over all measurement days. The corrections are defined by the condition that an adequately formed sum of variances χ^2 is minimized. The corrections ΔT_j obtained in this way represent small changes of the reference cells, initially supposed to be perfectly stable. This procedure led to a considerable reduction of the sum of variances of about 30 % and removed the correlated features.

As each transfer cell was measured at least twice, the individual results were averaged. The results for all transfer cells are shown in Figure 2.

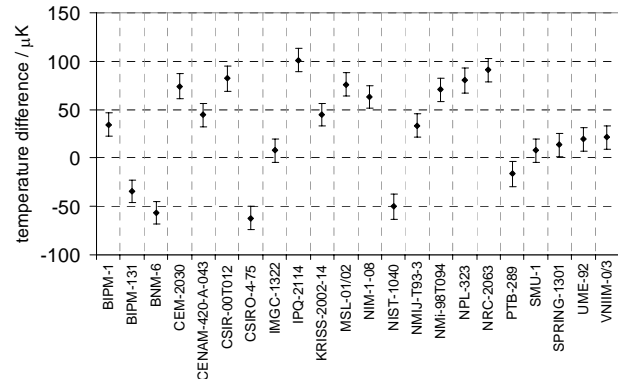


Figure 2: Temperature differences between the transfer cells. The zero line has been arbitrarily chosen as the average of the BIPM cells.

Most cells are within a band of 150 μK , the standard deviation is 50 μK . The two largest groups of cells of the same type are Jarrett/Isotech cells (CEM, IPQ, NPL, NRC) and Hart Scientific cells (IMGC, NIST, SPRING). The results are similar within each group.

3.2. Comparison of national references

The deviations of the national references from the BIPM reference are obtained from the results of the comparison of transfer cells and from the calibration results provided by the laboratories:

$$\Delta T_{ref,i} \equiv T_{ref,i} - T_{ref,BIPM} \\ = (T_{transfer,i} - T_{ref,BIPM}) - (T_{transfer,i} - T_{ref,i})$$

where $T_{ref,i}$ and $T_{transfer,i}$ are the temperatures of the reference cell(s) and the transfer cell of laboratory i and $T_{ref,BIPM}$ is the temperature attributed to the BIPM reference group.

The references of the laboratories are in many cases groups of cells of different type. Only a small number of laboratories applied a temperature correction for chemical impurities and the isotopic composition of the cell water. It is important in this respect to note that the *Supplementary Information for the ITS-90* [6] explicitly states that the isotopic composition of the cell water shall be that of ocean water.

The temperature differences between the national references of the water triple point are shown in Figure 3.

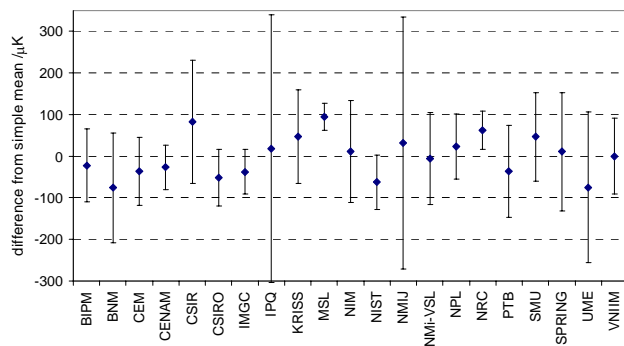


Fig. 3: Differences between the national references of the WTP. The uncertainties correspond to $k=2$. The zero line is the simple mean of the results. MSL and NRC are the only participants which applied a correction for the isotopic composition of the cell water.

The standard deviation of the results is 50 μK , identical to the standard deviation of the transfer cells (Fig. 2).

4. ANALYSIS OF THE RESULTS

There are two results with small uncertainty which differ significantly from the others, those for MSL and NRC. These two laboratories are the only ones who applied corrections for the deviation of the isotopic composition of the cell water from that of ocean water, represented by the reference material Vienna Standard Mean Ocean Water (V-SMOW). All

known and significant effects which influence a water triple point cell reduce its temperature. Examples are the depletion of water of ^2H during distillation, dissolved impurities and residual gas. It can therefore be expected that correction for these effects leads to higher temperatures.

There were several other participants who knew the isotopic composition of their cells but did not correct for deviations from ocean water. If the corresponding corrections are applied to the official results of the comparison (Fig. 3), all those laboratories are closely grouped together (Fig. 4).

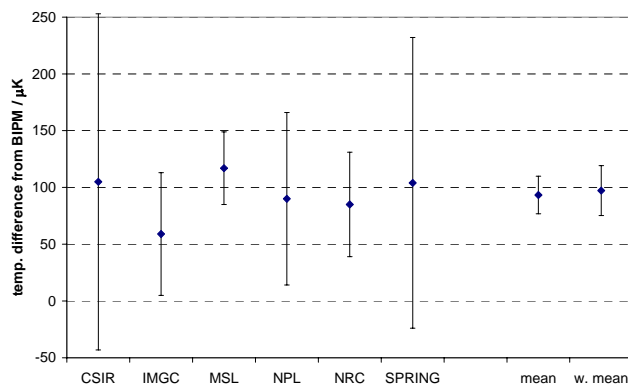


Fig. 4: Results for six laboratories, based on the ocean water definition. The uncertainties are at the 2σ -level.

The temperature difference between the mean of the results based on the ocean water definition and the results of the other cells is 86 μK .

Although the statistical basis is not very large, it can be expected, that a more wide-spread use of isotope analysis and application of the resulting corrections would reduce the spread of the realizations by a factor of about 2 from 50 μK to 25 μK . At least a part of the remaining spread might be due to chemical impurities.

5. THE CCT RECOMMENDATION ON THE ISOTOPIC COMPOSITION OF THE CELL WATER

This work has demonstrated a lack of specification of the physical system serving to define the kelvin: Most of the laboratories used the triple point cells as they were, and formed groups to randomize some of the systematic differences. Other laboratories applied the recommendation of the *Supplementary*

Information for the ITS-90 to correct for deviations of the isotopic composition from that of ocean water. To improve this situation, the Consultative Committee for Thermometry formed a task group to study this problem and to prepare a recommendation. The conclusions of this work are cited in the following.

By comparison with other waters, ocean waters are relatively uniform in isotopic composition. By using deep waters, avoiding surface evaporation effects, the uniformity is such that the related variation of the triple point temperature is below 1.5 μK [7]. The composition of continental surface waters varies widely with altitude, latitude and season. The characteristic difference from ocean water is a depletion of the heavy isotopes ^2H and ^{18}O [8].

The uniformity of ocean water makes it an ideal reference for the definition of the isotopic composition of the cell water. In addition, a reference material for studies of the isotopic composition of waters is available as V-SMOW (Vienna Standard Mean Ocean Water). This is available from the International Atomic Energy Agency (IAEA) and the National Institute of Standards and Technology of the United States (NIST).

Absolute measurements of the isotope ratios for V-SMOW give the following amount-of-substance ratios (in mole per mole) [9]:

$$\begin{aligned} (^2\text{H}/^1\text{H})_{\text{V-SMOW}} &= 0.000\,155\,76\,(5) \\ (^{18}\text{O}/^{16}\text{O})_{\text{V-SMOW}} &= 0.002\,005\,20\,(45) \\ (^{17}\text{O}/^{16}\text{O})_{\text{V-SMOW}} &= 0.000\,379\,9\,(8) \end{aligned}$$

The task group recommended that the definition of the kelvin refers to a specified isotopic composition, identical to the results for V-SMOW stated above. This composition is now stated in a note following the definition of the kelvin in the 8th edition of the SI brochure, published in May 2006 [1].

Since V-SMOW is not available in sufficiently large quantities, the isotopic composition of the cell water will always differ more or less from V-SMOW. It is therefore recommended to sample the composition of the water during cell manufacturing and to apply a correction for the deviation of its composition from that of V-SMOW, using published sensitivity coefficients [9,10]. This procedure will be explained in detail in a new *mise en pratique* for the definition of the kelvin which is currently prepared.

6. CONCLUSIONS

The comparison of realizations of the water triple point temperature highlighted the lack of definition of the term “water” in the kelvin definition in the SI brochure and in the official text for the ITS-90. A significant portion of the observed standard deviation of 50 μK between different realizations can be attributed to different isotopic composition of the cell water.

As a consequence, the CCT recommendation to refer to water of a specified isotopic composition has been included in the recent, 8th edition of the SI brochure. Cells containing water of a slightly different composition can be corrected using known sensitivity coefficients.

It is expected that this procedure leads to a much reduced spread between realizations in the future.

ACKNOWLEDGEMENTS

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The contents of section 5 is based on the work of the CCT water triple point task group, of which one of the authors was a member.

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