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# Analysis of the Comparison of TPW Realizations in Europe in Light of CCT Recommendation 2 (CI-2005)

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**Abstract** Three comparisons of different triple-point-of-water (TPW) realizations in Europe have been organized under the auspices of EUROMET (EUROMET Projects 278, 549, and 714). Thirty European national metrology institutes were involved in these three comparisons that took place from 1994 to 2005. The aim of these successive projects was to assess the uncertainties associated with the practical realization of the triple point of water in Europe. Fifty-four TPW local cells were compared to a traveling standard cell (ref 679) circulated with an isothermal enclosure. The same equipment was used for the three projects, and LNE-INM regularly checked the stability of the TPW standard cell. Recently, LNE-INM has devoted efforts to bring the French standard at the triple point of water into close agreement with CIPM Recommendation 2 (CI-2005). The isotopic fractionation between water and ice when the cell is in use was experimentally studied. Several new TPW cells delivered by the manufacturer with water samples were added to our batch of reference cells. A French laboratory analyzed the isotopic compositions of these samples. These actions allow the French national definition of temperature at the triple point of water to be changed. A new temperature was associated with TPW cell 679 in agreement with the CIPM recommendation. In this presentation, the latest TPW cell measurements carried out by LNE-INM are presented. The results from EUROMET Projects 278, 549, and 714 are investigated in light of these changes.

**Keywords** Comparison · CIPM recommendation · EUROMET · Isotopic fractionation · Triple point of water

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## 1 Introduction

Three comparisons of different triple-point-of-water (TPW) realizations in Europe have been organized under the auspices of EUROMET (EUROMET Projects 278, 549, and 714). Thirty European national metrology institutes were involved in these three comparisons carried out from 1994 to 2005.

- EUROMET Comparison 278 in which 12 countries took part between January 1994 and June 1997.
- EUROMET Comparison 549 in which fifteen countries took part between February 2000 and October 2003.
- EUROMET Comparison 714 in which four countries took part between June 2004 and September 2005.

The goal of these comparisons was not extensive research on the triple-point-of-water behavior, but to assess the uncertainties associated with the practical realization of the triple point of water in the various European laboratories by circulating one cell with an isothermal enclosure.

LNE-INM/CNAM supplied the circulating TPW cell and the isothermal enclosure, established the schedule, and followed the progress of the comparisons. The same circulating equipment and protocol were used for the three comparisons. The stability of the circulating TPW cell during the time of the comparison was studied by LNE-INM/CNAM.

Recently, LNE-INM has devoted efforts to bring the French standard at the triple point of water into close agreement with CIPM Recommendation 2 (CI-2005) [1]; so, the results of EUROMET Projects 278, 549, and 714 can now be analyzed in light of these recent developments.

## 2 Results of EUROMET Comparison 714

The results of EUROMET Comparisons 278 and 549 were published previously [2,3]. Consequently, they are not presented in this paper. The results of EUROMET Comparison 714 were never published and are presented below. Table 1 lists the participants.

### 2.1 Procedures

The circulating triple-point-of-water cell is an NPL-made cell No. 679. The isothermal enclosure was designed and constructed at LNE-INM/CNAM. This equipment was also used for EUROMET Projects 278 and 549. The local preparation using the local cell and the local enclosure followed the local procedure, whereas the realization with the circulating instrument was strictly defined by a precise procedure common to all participating laboratories.

The comparison was performed by measuring the difference in temperature between the circulating and the local TPW cells. The difference in the observed standard platinum resistance thermometer (SPRT) resistances (corrected for the hydrostatic head effect and self-heating, and possibly the calibration of the measurement instrument)

**Table 1** Participating laboratories in EUROMET project 714

| Laboratory | Country | Participants |
|---|---|---|
| ▶ Laboratoire National d'Essais-Institut National de Métrologie/Conservatoire National des Arts et Métiers (LNE-INM/CNAM), pilot laboratory | France | E. Renaot (coordinator), M. Hoang |
| ▶ AS METROSERT Ltd (METROSERT) | Estonia | R. Vendt |
| ▶ Malta Standard Authority, National Metrology Services (MSA) | Malta | N. Testa, J. Bartolo |
| ▶ Latvian National Metrology Centre Ltd (LNMC) | Latvia | A. Klints |
| ▶ National Scientific Centre « Institute of Metrology (NSC) | Ukraine | L. Nazarenko, G. Gorne, E. Ivanova |

for the two cells was converted to a temperature difference using the $dT/dR$ for the SPRT.

Only five laboratories are involved in this comparison, an insufficient number to define a reliable EUROMET Comparison Reference Value (ECRV714); so, it was suggested that the reference value defined at the time of EUROMET Comparison 549 be used. The uncertainty contribution $u_{(\text{stability549,714})}$ from the stability of cell 679 between EUROMET Comparisons 549 and 714 was taken into account. For each cell, the value $(T_{\text{local}} - T_{\text{ECRV714}})$ and the associated uncertainty were calculated.

$$u^2_{(T_{\text{local}}-T_{\text{ECRV714}})} = u^2_{(T_{\text{local}}-T_{\text{circulating}})} + u^2_{(T_{\text{ECRV714}}-T_{\text{circulating}})}$$

$u_{(T_{\text{local}}-T_{\text{circulating}})}$ is established by the participating laboratory.

$$u^2_{(T_{\text{ECRV714}}-T_{\text{circulating}})} = u^2_{(T_{\text{ECRV539}}-T_{\text{circulating}})} + u^2_{(\text{stability549,714})}$$

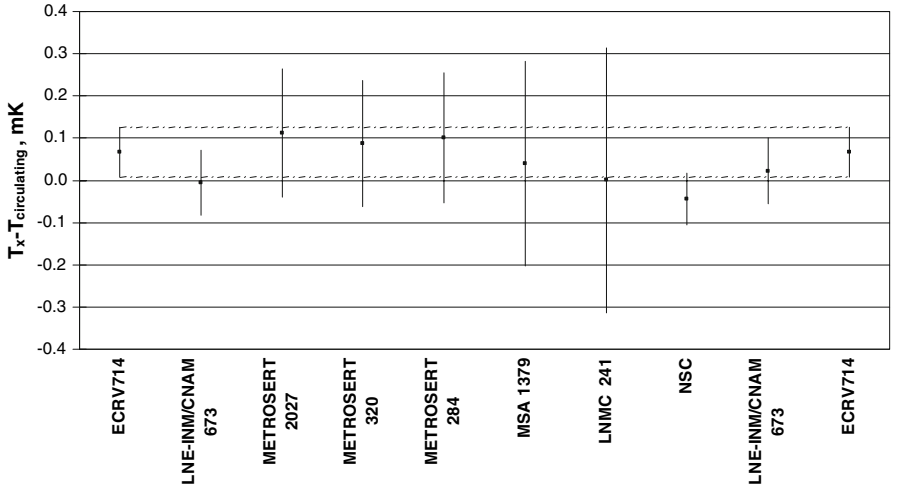


**Fig. 1** Results of EUROMET Comparison 714

### 2.2 Results

The results of the comparison are given in Fig. 1. The dotted line corresponds to the expanded uncertainty ($k = 2$) for ECRV714, $U_{(T_{\mathrm{ECRV714}} - T_{\mathrm{circulating}})}$, and the vertical bars to $U_{(T_{\mathrm{local}} - T_{\mathrm{circulating}})}$.

## 3 French Reference at the Triple Point of Water

### 3.1 French Reference before January 2007

Before January 2007, the national reference was defined as the average value of the temperatures realized by a batch of nine cells. For these cells, information about their isotopic composition and impurity content is unavailable. The ITS-90 temperature of the defining fixed point $T_{90\ \mathrm{TPW}}$ was associated with the mean temperature of the batch:

$$T_{\mathrm{INMmean}} = \frac{\sum_{i=1}^{N} T_{\mathrm{INMcell}\ i}}{N} = T_{90\mathrm{TPW}}$$

The uncertainty of the realization of this defining fixed point of the ITS-90 was established from the dispersion of the temperatures realized by the different cells included in the standard bath using the following evaluation:

$$u_{T_{\mathrm{INMmean}}} = \frac{T_{\max} - T_{\min}}{2\sqrt{3}} = 60\,\mu\mathrm{K}$$

We assume that $T_{\mathrm{INMmean}} - T_{90\mathrm{TPW}} = (0 \pm 120)\ \mu\mathrm{K}$
For each individual cell the following correction was calculated:

$$C_{\mathrm{INMcellX}} = T_{\mathrm{INMmean}} - T_{\mathrm{INMcellX}}$$

if we consider the cell UME6 (French transfer cell in CCT-K7) [4],

$$(T_{\mathrm{UME6}} - T_{\mathrm{INMMean}})_{\mathrm{beforejanuary2007}} = (-21 \pm 45)\,\mu K$$

### 3.2 French Reference from January 2007

To clarify the definition of kelvin, the International Committee of Weights and Measures (CIPM Recommendation 2 (CI-2005)) agreed that this definition refers to water of a specified isotopic composition,

0.000 155 76 mol $^{2}$H per mol $^{1}$H,
0.000 379 9 mol $^{17}$O per mol $^{16}$O, and
0.002 005 2 mol $^{18}$O per mol $^{16}$O,

this being the isotopic composition of Vienna-Standard Mean Ocean Water (V-SMOW), a standard reference material distributed by the International Atomic Energy Agency.

### 3.2.1 Isotopic Fractionation Between Water and Ice

In 2005 and 2006, LNE-INM/CNAM bought three new triple-point-of-water cells with fused silica housings. One cell (Hart Scientific 1426) was used to study the isotopic fractionation between water and ice when the cell is in use.

To prepare the ice mantle, a metal rod pre-cooled in liquid nitrogen was inserted into the thermometer well. This operation was repeated several times to obtain an adequate mantle thickness (4 to 8 mm) that was uniform over its whole length. A few days after, the cell was voluntarily broken. A sample of liquid water and a sample of molten ice were sent to a Chemical Analysis Laboratory of the Commissariat à l'Energie Atomique (CEA). The isotopic composition of the two samples are given in Table 2, where

$$\delta^2\mathrm{H}(^0/_{00}) = [(^2\mathrm{H}/^1\mathrm{H}) - (^2\mathrm{H}/^1\mathrm{H})_{\mathrm{V-SMOW}}]/(^2\mathrm{H}/^1\mathrm{H})_{\mathrm{V-SMOW}}$$

$$\delta^{18}\mathrm{O}(^0/_{00}) = [(^{18}\mathrm{O}/^{16}\mathrm{O}) - (^{18}\mathrm{O}/^{16}\mathrm{O})_{\mathrm{V-SMOW}}]/(^{18}\mathrm{O}/^{16}\mathrm{O})_{\mathrm{V-SMOW}}$$

The influence of the isotopic composition can be described by [5,6]

$$\Delta T_{\mathrm{isotopic}} = -A_{\mathrm{D}}\delta\,^2\mathrm{H} - A_{17\mathrm{O}}\delta\,^{17}\mathrm{O} - A_{18\mathrm{O}}\delta\,^{18}\mathrm{O}$$

with $A_{\mathrm{D}} = 628\,\mu\mathrm{K}$, $A_{18\mathrm{O}} = 641\,\mu\mathrm{K}$, and $A_{17\mathrm{O}} = 57\,\mu\mathrm{K}$

We conclude that the isotopic fractionation effect is not more than $(1.2 \pm 1.6)\,\mu\mathrm{K}$.

### 3.2.2 Change in the French Reference

At present, LNE-INM/CNAM has two cells of known isotopic composition based on isotopic analyses carried out by CEA. Nevertheless, the impurity content is unavailable. After January 2007, the national reference was defined as equal to the average value of the temperatures realized by only two cells (Hart Scientific 1422 and 1020). The isotopic composition of the water in cell 1020 is very close to the V-SMOW definition.

**Table 2** Isotopic fractionation between water and ice

| | $\delta^2\mathrm{H}(^0/_{00})$ | $U_{\delta^2\mathrm{H}(^0/_{00})}$ | $\delta^{18}\mathrm{O}(^0/_{00})$ | $U_{\delta^{18}\mathrm{O}(^0/_{00})}$ | $\Delta\mathrm{T}_{\mathrm{isotopic}}$ (μK) | $\mathrm{U}_{\Delta T_{\mathrm{isotopic}}}$ (μK) |
|---|---|---|---|---|---|---|
| Liquid water | −115.7 | 0.5 | −15.65 | 0.05 | 84.2 | 1 |
| Molten ice | −114.2 | 0.5 | −15.31 | 0.05 | 83.0 | 1 |

$$\Delta T_{\text{isotopic1422}} = 83\,\mu\text{K}$$
$$\Delta T_{\text{isotopic1020}} = -0.4\,\mu\text{K}$$

The TPW cells 1020 and 1422 were compared with the cells UME 6 (transfer cell in CCT-K7) and NPL 673 (this cell was integrated into our batch of reference cells 13 years ago). The differences $T_x - T_{\text{UME6}}$ are given Table 3. The correction for isotopic composition is applied to cells HS 1020 and HS 1422. The expanded uncertainty of the comparison of the two TPW cells by LNE-INM/CNAM is estimated to be 60 µK. Since January 2007, the ITS-90 temperature of the defining fixed point is the mean of the temperatures realized by cells HS 1422 and HS 1020, with

$$T_{\text{HS1020}} = T_{\text{INMMean}} + 10\,\mu\text{K}$$

$$T_{\text{HS1422}} = T_{\text{INMMean}} - 10\,\mu\text{K}$$

The change in the French reference at the TPW due to the application of CIPM Recommendation 2 (CI-2005) can be determined through cell UME6:

$$(T_{\text{UME6}} - T_{\text{INMMean}})_{\text{sincejanuary2007}} = (-126 \pm 45)\,\mu\text{K}$$

Consequently, the change of the reference is equivalent to 105 µK.

It is now possible to attach a smaller uncertainty component to the realization of $T_{90\text{TPW}}$. The uncertainty budget for the LNE-INM/CNAM realization of the triple point of water is presented in Table 4. This estimation will be modified according to the future results of the EUROMET Comparison EUROMET.T-K7.

$$T_{\text{INMmean}} - T_{90\text{TPW}} = (0 \pm 80)\,\mu\text{K}$$

**Table 3** Differences $(T_x - T_{\text{UME6}})$

| Cell X | $(T_x - T_{\text{UME6}})$ (µK) | $U_{(Tx-T_{\text{UME6}})}$ (µK) |
|---|---|---|
| NPL 673 | −36 | 60 |
| HS 1020 | 136 | 60 |
| HS 1422 | 117 | 60 |

**Table 4** Uncertainty budget for the LNE-INM/CNAM realization of the triple point of water

| Source of uncertainty | Standard uncertainty (µK) |
|---|---|
| Impurities | 30 |
| Isotopic composition | 10 |
| Reproducibility | 25 |
| Combined standard uncertainty | 40 |
| Expanded uncertainty ($k = 2$) | 80 |

## 4 Analysis of the Comparison of TPW Realizations in Europe

LNE-INM/CNAM checked the stability of cell No. 679 from August 1993 to September 2005. Cell No. 679 was compared several times with cell No. 673; the results are presented in Fig. 2. Variations in $(T_{673} - T_{679})$ were analyzed assuming that the cells do not change in the same way. The statistical analysis of the results allows us to obtain

$$(T_{673} - T_{679})_{\text{mean}} = (28 \pm 20)\,\mu\text{K}.$$

As

$$(T_{673} - T_{\text{INMMean}})_{\text{afterjanuary2007}} = (-156 \pm 45)\,\mu\text{K},$$

we can calculate

$$(\text{T}_{679} - T_{\text{INMMean}})_{\text{afterjanuary2007}} = (-184 \pm 50)\,\mu\text{K}$$

It is assumed that $T_{\text{INMmean}} - T_{90\text{TPW}} = (0 \pm 80)\,\mu\text{K}$. So,

$$(T_{679} - T_{90\text{TPW}}) = (-184 \pm 95)\,\mu\text{K}.$$

The laboratories participating in the EUROMET Comparisons 278, 549, and 714 that do not have TPW cells with known isotopic compositions can use the results of the EUROMET comparisons in order to position their reference with respect to $T_{90\text{TPW}}$:

$$(T_{\text{LabX}} - T_{90\text{TPW}}) = (T_{\text{LabX}} - T_{679}) + (T_{679} - T_{90\text{TPW}})$$

with

$$u^2_{(T_{\text{LabX}} - T_{90\text{TPW}})} = u^2_{(T_{\text{LabX}} - T_{679})} + u^2_{(T_{679} - T_{90\text{TPW}})}$$

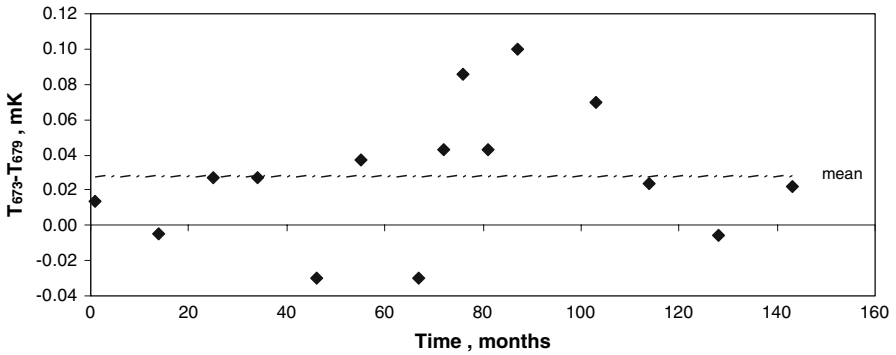


**Fig. 2** $T_{673} - T_{679}$ from August 1993 to September 2005. The expanded uncertainty associated with one determination of $\text{T}_{673} - \text{T}_{679}$ is equal to 60 µK

## 5 Conclusion

Three comparisons of triple-point-of-water (TPW) realizations in Europe were organized under the auspices of EUROMET (EUROMET Projects 278, 549, and 714) from August 1993 to September 2005. The same circulating cell (cell 679) was used for these comparisons.

To achieve accordance with CIPM Recommendation 2 (CIPM 2005), the French national definition of temperature at the triple point of water was modified. The isotopic fractionation between water and ice when the cell is in use was studied. It appears that the effects are not significant (no more than $(1.2 \pm 1.6)\,\mu\mathrm{K}$). The national reference is now defined as equal to the average value of the temperatures realized by a batch of cells of known isotopic composition.

The value of $T_{679} - T_{90\mathrm{TPW}}$ was determined together with its associated uncertainty. The laboratories participating in EUROMET Comparisons 278, 549, and 714 that do not have TPW cells of known isotopic composition can position their reference to achieve agreement with CIPM Recommendation 2 (CI-2005) by using the results of these comparisons and the analysis presented in this paper.

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