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Establishment of a New National Reference Ensemble of Water Triple Point Cells

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Abstract The results of the Bilateral Comparison EURAMET.T-K3.5 (w/VSL, The Netherlands) with the goal to link Switzerland's ITS-90 realization (Ar to Al) to the latest key comparisons gave strong indications for a discrepancy in the realization of the triple point of water. Due to the age of the cells of about twenty years, it was decided to replace the complete reference ensemble with new "state-of-the-art" cells. Three new water triple point cells from three different suppliers were purchased, as well as a new maintenance bath for an additional improvement of the realization. In several loops measurements were taken, each cell of both ensembles intercompared, and the deviations and characteristics determined. The measurements show a significant lower average value of the old ensemble of 0.59 ± 0.25 mK ($k = 2$) in comparison with the new one. Likewise, the behavior of the old cells is very unstable with a drift downward during the realization of the triple point. Based on these results the impact of the new ensemble on the ITS-90 realization from Ar to Al was calculated and set in the context to performed calibrations and their related uncertainties in the past. This paper presents the instrumentation, cells, measurement procedure, results, uncertainties and impact of the new national reference ensemble of water triple point cells on the current ITS-90 realization in Switzerland.

Keywords Calibration · ITS-90 · National reference · water triple point cells

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1 Introduction

Since the year 2011 ROTH+CO. AG is officially designated as the National Laboratory for Temperature and holder of the National Temperature Standard in Switzerland. That includes the maintenance and improvement of the ITS-90 realization [1] and ensuring the traceability of the Swiss temperature measurements. For this reason, a bilateral comparison with the Dutch Metrology Institute (VSL) was held during the years 2013/2014 to establish a new link to the latest International Key Comparisons CCT-K3/EUROMET.T-K3 from the argon fixed point (−189 °C) up to aluminum fixed point (660 °C) and support the CMC submissions at the BIPM in 2014. Before the year 2011, the ITS-90 in Switzerland was realized and linked by the Federal Institute of Metrology METAS.

The results of this Bilateral Comparison EURAMET.T-K3.5 [2] show the following E_n-values, which represent the normalized deviations in relation to the measurement uncertainties: Ar (0.71), Hg (0.40), Ga (0.84), In (0.74), Sn (0.34), Zn (1.05), Al (0.98). At the fixed point of Zn and Al appeared with values around unity a possible discrepancy in the realization and the claimed related uncertainties. The E_n-values above and the used cells in the bilateral comparison gave some indications of a possible error in the triple point of water (TPW) realization due to the propagation of the uncertainty and errors by the factor of the corresponding W-value, which is the ratio between the measured resistances at the fixed point and the TPW.

In the last two decades the long-term behavior of water triple point cells has been extensively studied. In 2001, Hill [3] supposed a long-term drift in water triple point cells made of borosilicate glass. In 2007, Strouse and Zhao [4,5] investigated the influence of borosilicate vs. fused-quartz on the cell aging and found a significant higher drift downward in cells made of borosilicate. At approximately the same time the EUROMET.T-K7, a regional key comparison of water triple point cells [6], showed additional indications for a drift related to the use of borosilicate. In particular, the significant deviations of the same type of cell in this comparison, which is also part of the Swiss ensemble, underpinned the reconsideration of the TPW national reference ensemble as a whole. Additionally, the International Committee for Weights and Measures (CIPM) decided in 2005 to define the TPW with the isotopic composition of VSMOW (Vienna Standard Mean Ocean Water) [7]. This new definition influenced every national TPW realization and must be taken into account [8].

Due to long-term strategies and the conclusions as mentioned above, the decision was made to replace all cells of the current ensemble. For that reason, three new water triple point cells from three different suppliers were purchased, as well as a new maintenance bath for an additional improvement of the realization.

This work is dedicated to the establishment of a new national reference by intercomparing the cells of the new and old ensembles.

2 Cells and Instrumentation

The old ensemble contains two type of cells, labelled as Model A and Model C: 1x VSL Type 3 (O1) and 2x NPL Type 32 (O2, O3). The new ensemble contains two

Table 1 Cells of the new and old ensembles

Cell	Manufacturer (year)	Model	Inner diameter of the well (mm)	Immersion depth of the well (mm)	Isotopic Comp./Corr. (μK)
N1[a,b]	VSL (2009)	A	9	280	Yes/+27.2
N2	Hart Scientific (2014)	B	13.6	260	Yes/−2.8
N3	Isotech (2014)	C	12	218	No
O1	VSL (1995)	A	9	263	No
O2	NPL (1994)	C	12	223	No
O3	NPL (1987)	C	12	226	No

[a] With traceability to the national reference of VSL

[b] Transfer cell to link the cells

cells of the same Model A and Model C (N1, N3), whereby the Model C has a new manufacturer in the meantime: Isotech Type B12-40-210. The third new cell (N2) labelled as Model B has the following manufacturer/type: Hart Scientific 5901C-G.

The cells have different designs in size, material, immersion depth and diameter of the inner well. The water of two new cells (N1, N2) was analyzed by partner laboratories of the manufacturers, and the isotopic composition and correction determined [9] . For the entire old ensemble is no information about the isotopic composition available. In addition, one new cell (N1) was calibrated with an uncertainty of 0.1 mK ($k = 2$) by the manufacturer VSL, traceable to the national reference of the Netherlands. This cell acts as transfer cell in the related measurements to link the cells of both ensembles. An overview about the ensembles including the approximate date of manufacture of the cells is given in Table 1.

For the realization of the ice mantles the following procedure was applied: Crushed dry ice and some drops of alcohol were inserted into the inner well to form an initial ice layer around the end of the inner tube. Then, a mixture of crushed dry ice and alcohol was filled into a “immersion freezer” and inserted into the well, which was filled with alcohol on the same level as the water in the cell. After approximately one hour, the ice mantle was thick enough for using the cell for a period of two months in combination with the new maintenance bath.

The measurements were taken with two SPRTs of different types. The ratio of SPRT resistance with respect to a 25 Ω standard resistor measured with an AC bridge (25 Hz, Gain 10^4, 0.5 Hz bandwidth, 0.1 ppm resolution) was used to compare the temperatures of the cells.

Table 2 shows the new purchased maintenance bath and the other used instruments in this intercomparison.

3 Measurement Procedure

The measurements were taken with separate realizations of each ensemble in two stages. In the first stage, the new ensemble (N1, N2, N3) was realized and the cells

Table 2 Instrumentation

Instrument	Manufacturer	Type
SPRT 1	YSI	8163Q
SPRT 2	Tinsley	5187
Bridge	ASL	CTR9000 (F18)
Reference resistor	Tinsley	5685A[a]
Maintenance bath	Isotech	ITL-M-18233

[a] With enclosure 5648

intercompared. In the second stage, the old ensemble (O1, O2, O3) and the transfer cell (N1) were realized and intercompared. This procedure was repeated twice.

The ice mantles were prepared one week before the measurements. The data were daily collected with two different SPRTs in two consecutive weeks (10 days). Neither a bushing nor a foam pad was used in the inner well. After inducing an inner melt layer with a glass rod at room temperature, the precooled SPRTs were placed in two cells. The first measurement starts with one SPRT/cell by the following software-driven sequence: Stabilization time of 15 min → Measurements of 5 min with 1 mA → Switchover to $\sqrt{2}$ mA and wait for 2 min → Measurements of 5 min with $\sqrt{2}$ mA → Switchover to 1 mA and wait for 2 min → Measurements of 5 min with 1 mA → Extrapolate to 0 mA, and then the SPRT is moved manually to another cell. During the first measurement, the second SPRT is in the stabilization phase for 34 min. Then, the second measurement is taken by the same procedure above with a replaced stabilization time of 2 min. During the second measurement, the first SPRT is in the stabilization phase for 21 min and the measurement is again taken with only 2 min stabilization time. This procedure is repeated so long until each cell is measured with both SPRTs. The approach above leads to different stabilization times of the first two measurements (15 min and 34 min) in comparison with the subsequent measurements (21 min). This is a weak point in the experimental design and should be avoided. A later investigation of the required stabilization time showed a minimum of 20 min to obtain proper data. A stabilization time of only 15 min biases the value of this measurement with about $+35\ \mu\text{K}$. The bias in the final calculated mean is attenuated by the randomized order of SPRTs and cells in each stage, because only the first measurement of a day is affected. Considering the probability for that case and the number of measurements the overall effect seems not greater than $+5\ \mu\text{K}$.

4 Definition of the National Reference

The national reference of the TPW at ROTH+CO. AG is represented by the mean of an ensemble of three cells. To calculate, observe and maintain this mean, the method in [10] is applied. This method is given by the following derivation:

The national reference T_{National} is set by the definition

$$T_{\text{National}} = (T_1 + T_2 + T_3)/3, \tag{1}$$

where T_1, T_2, T_3 are the temperatures of the corresponding cells.

The temperature deviation ΔT_i of the individual cell i ($i = 1, 2, 3$) from the national reference is then given by:

$$\Delta T_i = T_i - T_{\text{National}}. \tag{2}$$

From relations (1) and (2) follows that the sum of these differences equals zero:

$$\Delta T_1 + \Delta T_2 + \Delta T_3 = 0. \tag{3}$$

The temperature deviations ΔT_i of the individual cells from the national reference can be deduced from the paired comparison of the corresponding cells, e.g., for cell 1:

$$\Delta T_1 = (\Delta T_{12} - \Delta T_{31})/3. \tag{4}$$

5 Uncertainties

By using the same equipment and procedures for the two resistance measurements many of the errors cancel out and lower uncertainties can be achieved [9]. Therefore, the uncertainty budget includes only two type A contributions related to the daily observed scattering (u_{A1}), differences between mantle realizations (u_{A2}) and four type B contributions related to additional heat flux (u_{B1}), the hydrostatic corrections (u_{B2}), the isotopic correction (u_{B3}) and the mantle aging (u_{B4}). u_{A1} is the pooled standard error of the daily scatterings, and u_{A2} is the observed difference between the mantle realizations. Treating the mantle aging as a type A contribution is only valid if the measurements are independent and uncorrelated. At least for the old cells, this is not the case. As shown in Fig. 2, they are strongly correlated in time and a type A approach leads to an underestimation of the uncertainty. Therefore, the type B mantle aging contributions were estimated by a rectangular distribution with the maximum difference of the daily results as width. All other type B values are the combined uncertainty of the estimated values of the two corresponding cells.

In principle, there is no need to include the common uncertainty components such as impurity, residual gas pressure and isotopic composition in a uncertainty budget for a determination of the differences between cells because any effect related to these components alters the measured differences, but not directly the uncertainties of their determination.

For two cells (N1, N2) was an analysis of the isotopic composition available and the resulting correction to VSMOW was applied. That means the budget needs to include a related uncertainty of this component. Considering the very low uncertainties in both analyses (0.8 μK, 3.1 uK), a more conservative estimate of 5 μK was made according to the lowest recommended value in [9]. Due to the lack of information in the isotopic composition of cell N3 and the old ensemble as a whole, no corrections were applied and the greatest recommended value of 35 μK in [9] for that case was used.

The main contribution in the uncertainty budget takes place in the heat flux and was estimated by the deviation of the immersion profiles to the expected ITS-90 hydrostatic pressure line over a depth of 6 cm (Fig. 1). The resulting values are much larger than typical values [9]. The immersion profiles are obtained by changing the immersion depth of the SPRT (10 cm from the bottom in 2 cm steps) manually → 10 min of

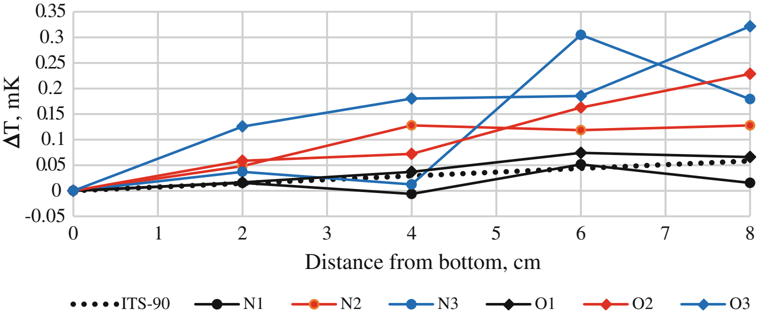

Fig. 1 Immersion profiles of each cell with SPRT1

Table 3 Uncertainty budget of the actual temperature differences from transfer cell N1 in mK

	Component	New ensemble		Old ensemble		
		ΔT_{N2N1}	ΔT_{N3N1}	ΔT_{O1N1}	ΔT_{O2N1}	ΔT_{O3N1}
u_{A1}	Daily scattering	0.018	0.022	0.038	0.035	0.017
u_{A2}	Different realizations	0.004	0.011	0.065	0.049	0.012
u_{B1}	Heat flux	0.072	0.068	0.024	0.072	0.108
u_{B2}	Hydrostatic correction	0.008	0.008	0.008	0.008	0.008
u_{B3}	Isotopic correction	0.007	0.035	0.035	0.035	0.035
u_{B4}	Mantle aging	0.019	0.024	0.158	0.068	0.058
$U_i k(k=2)$	Expanded uncertainty	0.16	0.17	0.36	0.24	0.26

stabilization at every position → 10 min of measure → extrapolate to 0 mA. Thus, possible causes for the larger values could be in the procedure: A too short stabilization time and/or the position of the SPRT in the well was not optimal through changing the position manually, especially for the cells with larger diameters. Stray thermal effects in the setup/laboratory could be also a possible source for the larger values [9]. Since the causes are not yet identified, the larger values have to remain in this budget (Table 3).

6 New National Reference Versus Old National Reference

The new cells differ nonsignificantly within their ensemble, and therefore the new national reference equals each new cell (Table 4). The daily measurements show a very stable behavior of the cells with almost zero slopes per day of −0.003 mK (N2, N3), with respect to cell N1, as shown in Fig. 2.

The cells of the old ensemble show significantly lower values with respect to cell N1 (Table 4), which equals the new national reference. In addition, in the daily measurements of the old cells is recognizable a clear pattern of a drift downward with slopes per day of −0.055 mK (O1), −0.013 mK (O2) and −0.019 mK (O3), as shown in Fig. 2.

Table 4 Results of the actual temperature difference from transfer cell N1 in mK

Cell	New ensemble		Old ensemble	
	$\Delta T_{i\text{N1}}$	$U_{i\text{N1}(k=2)}$	$\Delta T_{i\text{N1}}$	$U_{i\text{N1}(k=2)}$
1	–	–	−0.65	0.36
2	0.02	0.16	−0.69	0.24
3	0.02	0.17	−0.38	0.26

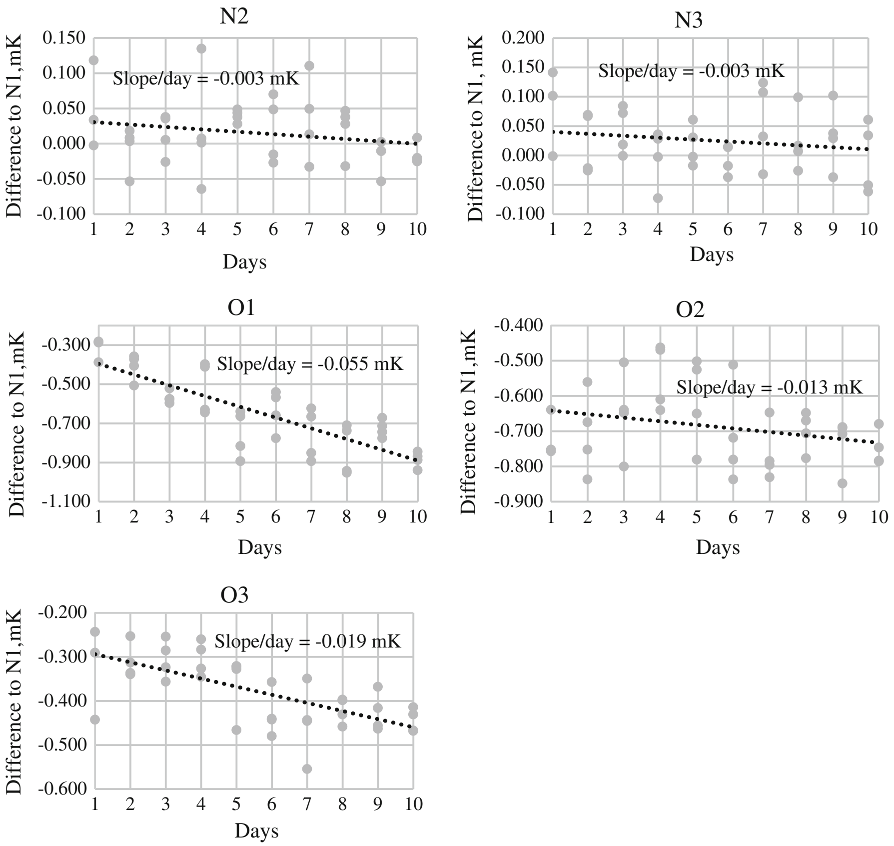

Fig. 2 Slopes of the cells with respect to cell N1

The final difference between new and old national reference results in 0.59 mK with an uncertainty of ± 0.25 mk ($k = 2$).

Figure 3 shows the daily obtained measurements (colored data points) in respect to the mean of the three new cells, the new national reference (zero line). The black data points represent the mean of the corresponding cell, based on the daily data. The old ensemble and thereby the old national reference are linked to the new ensemble and national reference by the transfer cell N1.

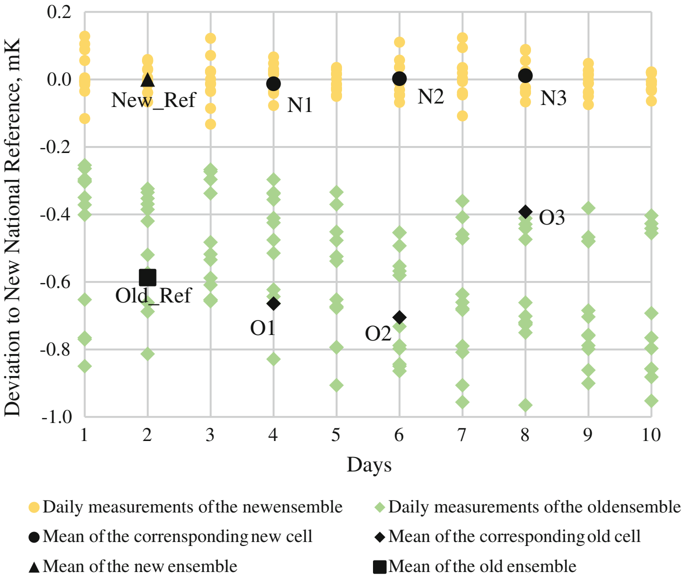

Fig. 3 Temperature deviations of the individual cells and the old national reference to the new national reference

Table 5 Impact on the W-values with a correction of the TPW values

Fixed point	ΔW	ΔT (mK)	Fixed point	ΔW	ΔT (mK)
Al	−1.353E−05	−4.22	Ga	−4.486E−06	−1.14
Zn	−1.030E−05	−2.95	Hg	−2.388E−06	−0.59
Sn	−7.590E−06	−2.04	Ar	−6.092E−07	−0.14
In	−6.449E−06	−1.70			

7 Impact on the National ITS-90 Realization

Considering the influence of the TPW on the W-value of every other fixed point and the significantly difference between new and old national references at the TPW, the impact of this shift should be investigated. Therefore, a correction in the TPW resistance values in the data of the Bilateral Comparison EURAMET.T-K3.5 was applied (final difference between new and old national references) and a new possible degree of equivalence calculated. A generally too low TPW leads to a general increase in the W-values. Thus, a positive correction leads to a general decrease in the W-values as shown in Table 5. Due to the propagation of the TPW, the magnitude of the shift downward is correlated with the fixed point temperature.

The result confirms the expectation of an improvement in the DoE at the most fixed point realizations. The given discrepancies in Al and Zn obtained with EURAMET.T-K3.5 shift both toward a very satisfactory position. The E_n-values improve to the following values: Ar (0.57), Hg (−0.22), Ga (0.12), In (0.24), Sn (−0.28), Zn (0.31),

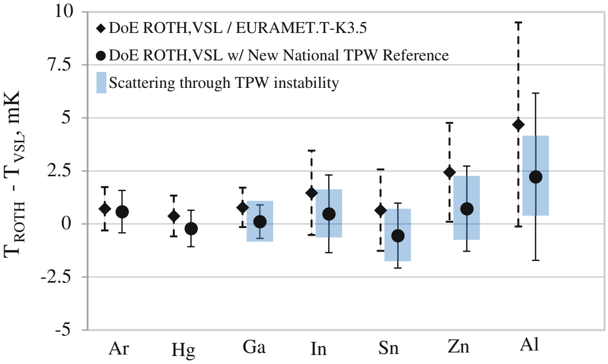

Fig. 4 Degree of equivalence (DoE) between ROTH+CO. AG and VSL with an applied correction to the TPW data of the Bilateral Comparison EURAMET.T-K3.5

Al (0.46). Figure 4 shows the DoE given by the bilateral comparison and the new DoE calculated with the correction. The blue line indicates the possible scattering of the correction due to the observed instability (drift downward during a realization) of the old cells and the use of daily measurements to calculate the W-values of the SPRT fixed point calibration.

In the past, the claimed uncertainties at the fixed points were generally increased by a factor of 1.5 for SPRT calibrations. Due to this conservative approach, no discrepancies exist in the dissemination of the kelvin.

The experimental determination of the impact will take place with the next EURAMET Key Comparison of the ITS-90 realization.

8 Conclusion

A new and traceable national reference ensemble of water triple point cell was successfully established and the difference from the old ensemble determined by an intercomparison study.

The new cells show a very good agreement within the ensemble and a very stable behavior. By contrast, the old ensemble has much lower values and a continuous drift downward during the realization. The results of the measurements verify the hypothesis of a discrepancy in the TPW realization. Considering the significantly difference between both ensembles, the uncertainty at the TPW during EURAMET.T-K3.5 was clearly underestimated. The impact of the new national reference at the TPW on the entire ITS-90 realization was calculated and will be confirmed with a new comparison.

The comparison of the new cells can also be considered as an independent study and equivalence test of three different types of cells available in the current market.

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