EUROMET • European Collaboration in Measurement Standards

Thermometry

EUROMET Project No 549

Comparison of realization of the triple-point of water

Final Report

BNM/INM –CNAM

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1. Introduction

A comparison of the different triple point of water (TPW) realizations in Europe has been organised under the auspices of EUROMET (project N°549). This project is a re-activation of the EUROMET Project 278 in which twelve countries took part between January 1994 and June 1997 [1].

The re-activation answers to a request of twelve more countries. The goal of this project is not to deal with an extensive research on triple-point of water behaviour. The aim of this project based on the circulation of one cell and an adapted isothermal enclosure, was to assess the uncertainties associated to the practical realization of the triple point of water in the various European laboratories.

The Bureau National de Métrologie-Institut National de Métrologie (BNM-INM, France) as the pilot Laboratory, supplied the circulating TPW cell and the isothermal enclosure. It established the schedule and followed the progress of the comparison. The comparison was organised in five stages. Table 1 lists the participating laboratories and Table 2 the order in which the measurements were conducted.

After measurements by a group of participants, the cell and the isothermal enclosure were returned to the BNM-INM for a stability test before shipping to the next group. The results of the stability test are given Section 5.

The national metrological institutes of fifteen countries: the BNM-INM, NML, SMD, OMH, MIRS, GUM, MIKES, SP, JV, UME, CMI, BEV, SMU, EIM, and the SMS/SPI (see Table 1 for acronyms), were involved in this work which lasted from February 2000 to October 2003.

The number of participating laboratories in each stage was fixed by their availability to carry out the measurements and the constraints of the ATA carnet.

Table 1. Participating laboratories

Laboratory	Country	Participants
Bureau national de Métrologie-Institut National de Métrologie (BNM-INM/CNAM), pilot laboratory	France	E. Renaot (coordinator), M. Hoang, G. Bonnier
National Metrology laboratory (NML)	Ireland	M.White
Service de la Métrologie (SMD)	Belgium	A.Van Der Linden, G. Bairy
National Office of Measure (OMH)	Hungary	T. Kovacs, S. Németh
University of Ljubljana, faculty of Electrical Engineering (MIRS/FE-LMK)	Slovenia	J. Bojkovski
Centrale Office of Measures (GUM)	Poland	R. Kuna
Centre for Metrology and Accreditation (MIKES)	Finland	T. Weckström
Sveriges Provnings- och Forskningsinstitut (SP)	Sweden	J. Ivarsson
Justervesenet (JV)	Norway	C. Rauta, F. Helgesen
TUBITAK, Ulusal Metroloji Enstitüsü (UME)	Turkey	A. Uytun, S. Ugur
Cesky Metrologicky Institut (CMI)	Czech Republic	J.Kryl
Bundesamt fü Eich- und Vermessungswesn (BEV)	Austria	F. Adunka
Slovak Institut of Metrology (SMU)	Slovakia	J. Ranostaj, S. Duris
Hellenic Institute of metrology (EIM)	Greece	M. Anagnostou, E. Kokkini
State Metrology Service (SMS/SPI)	Lithuania	A. Pauza, V. Augevicius

Table 2: Comparison programme

First stage	BNM-INM NML SMD
Second stage	BNM-INM OMH MIRS/FE-LMK GUM
Third stage	BNM-INM MIKES SP JV UME CMI
Fourth stage	BNM-INM BEV SMU EIM
Fifth stage	BNM-INM SMS/SPI BNM-INM

2. TPW and isothermal enclosure

The circulating triple point of water cell is an NPL-made cell N°679. This cell was also the circulating cell for the EUROMET Project 278. During the last ten years this cell has been compared several times to one cell (N°673) belonging to the batch of water triple point cells that constitutes the BNM-INM reference for this fixed point. BNM-INM keeps a chronological accounts of these comparison.

The isothermal enclosure was designed and constructed at BNM-INM (Figure 1). During the measurement, with a normal platinum resistance thermometer (length of the glass sheath: 48 cm) part of the head is inside the enclosure's cover. This arrangement prevents visible and infrared radiation from penetrating the ice and reaching the thermometer sensor. The bottom of the SPRT is not in direct contact with the bottom of the thermometer well. The distance is approximately 5 mm. For thermometers longer than 48 cm, the laboratory had to adjust the position of the thermometer in order to position its bottom approximately 5 mm above the bottom of the well. Several holes in the cell's cover and in the lower part of the support allow the water resulting from melted ice to be drained away. This water is then pumped out from the bottom of the enclosure.

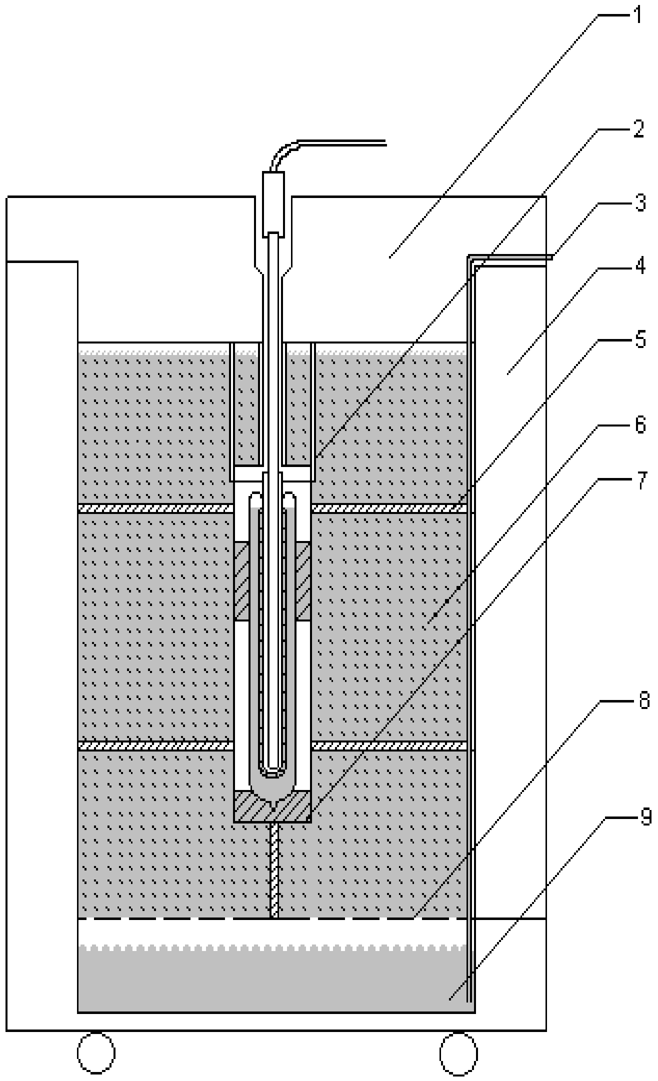

Figure 1: Isothermal enclosure

1: cover of the enclosure; 2: plastic cover of the cell full of crushed ice; 3: water extraction; 4: isothermal container; 5: cell holder; 6: crushed ice; 7: plastic container with foam rubber; 8: base containing drain holes; 9: water container

The BNM-INM studied the immersion-temperature effects of cell N° 679 in the enclosure by using a Leeds & Northrup thermometer (N°1807664). The experimental measurements agree with the theoretical values calculated using dT/dh given by the ITS-90, see figure 2. All the thermometers used in this comparison were glass-sheathed SPRT. The behaviour relative to the depth of immersion was expected to be the same for all SPRTs.

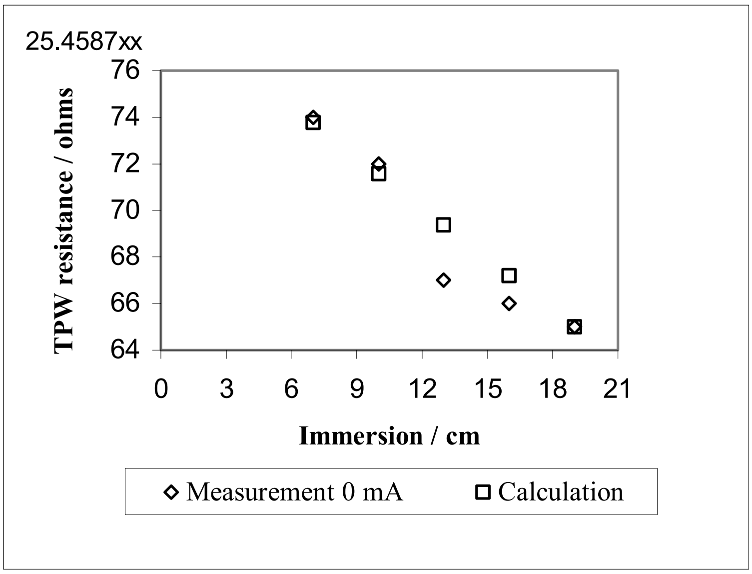

Figure 2: Immersion temperature effects

3. Procedures

The aim of this project was to allow each participating laboratory to compare the temperature water triple-point realized by the local facilities (cell+enclosure+procedure) to the temperature materialised by the circulating instrument. The local preparation using the local cell and the local enclosure was performed according to the local procedure, whereas the realization with the circulating instrument was strictly defined by a precise procedure common to all the participating laboratories. This protocol is very close to the one used for the EUROMET Project 278.

The stability of the circulating instrument was tested by measuring T_{673}-T_{679} at BNM-INM earlier and during the programme (See part 5).

All the participants were required to use the same procedure for preparing the circulating cell. First, the isothermal enclosure is filled with crushed ice. When the isothermal enclosure is cooled, the circulating cell is introduced into the plastic container (7 in Figure 1). After, at least 3 hours alcohol is introduced into the thermometer well. In order to prepare the ice mantle a metal rod precooled in liquid nitrogen is inserted into the thermometer well. This operation is repeated several times in order to obtain an adequate mantle thickness (4 to 8 mm) which is uniform over its whole length. The alcohol is then removed and the well is washed out with pure water or alcohol precooled to a temperature of 0°C. Finally, precooled pure water or alcohol is once again poured into the well. The level of this liquid is adjusted to that of the free surface water in the cell when the thermometer is present. To avoid exothermic heat during measurements, special care must be taken to prevent mixing water and alcohol in the thermometer well. A second ice/water interface, immediately adjacent to the well surface, is formed by producing a layer of water (melted ice) by inserting a rod at room temperature into the well for about 30 seconds. The effectiveness of this layer should be verified prior to any measurement by checking the free rotation of the mantle.

The cell must left at rest for at least 20 hours in order to release any mechanical stress in the ice mantle. Three cycles of measurement using different freezes was prescribed by the comparison procedure. During one cycle the measurements must be performed at least the second, third, and fifth day after the realization of the mantle

The comparison was performed by measuring the difference in temperature between the circulating and local TPW cells. The difference in the observed resistances (corrected for the hydrostatic head effect and self-heating, and possible calibration of the measurement instrument) for the two cells was converted to a temperature difference using the dT/dR for the SPRT.

$$T_{local} - T_{circulating} = [R_{local} - R_{circulating}] \cdot [dT/dR]_{TPW}$$

4. Description of the local facilities

Table 3 presents the cell features and the different local procedures used for this comparison. The electrical measurements are performed using a Guildline 9975 (two Laboratories), a Measurement International (three Laboratories) or an ASL F18 (ten Laboratories) bridge. The resistance platinum thermometers used for difference temperature determination come from different manufacturers: Leeds &t Northrup, Tinsley, ISOTECH, Hart Scientific, VNIIM.

5. Control of the transfer cell during the comparison

The BNM-INM checked the stability of the cell N° 679 during the comparison. It was compared with cell N°673 at the beginning and at the end of the comparison and also between stages (Table 4). Variations in T_{673}-T_{679} were analysed assuming that the cells do not change in the same way. Taking into account the combined standard uncertainty on T_{673}-T_{679} (0.035 mK) the temperature realized in cell N°679 may be considered as stable during the entire comparison. Nevertheless a component of uncertainty associated to the stability of the circulation realization has been established using the BNM-INM results.

$$u_{stability} = \frac{(T_{673} - T_{679})_{\max} - (T_{673} - T_{679})_{\min}}{2 \cdot \sqrt{3}}$$

$u_{stability.}$= 0.029 mK

Table 4: Stability test on cell No 679 during the comparison

Dates	T_{673} - T_{679}
February 2000	0.086 mK
First stage	
July 2000	0.043 mK
Second stage	
January 2001	0.100 mK
Third stage	
May 2002	0.070 mK
Fourth stage	
April 2003	0.024 mK
Fifth stage	
September 2003	0.003 mK

In order to be able to compare the results obtained during the EUROMET Projects 278 and 549 the Table 5 gives:

- The means of the differences T_{673} - T_{679} measured by the BNM-INM during the EUROMET Projects 278 and 549
- The differences $T_{673} - T_{\text{mean BNM-INM batch}}$ and $T_{679} - T_{\text{mean BNM-INMbatch}}$ determined on 1997 (EUROMET Project 278) and on 2002 (EUROMET Project 549). $T_{\text{mean batch}}$ is the mean of the temperatures given by the cells that constitute the standard batch of BNM-INM at the TPW.

Table 5: Stability tests on cells No 673 and 679 during the last five years

	T_{673} - T_{679}
EUROMET comparison 278	0.007 mK
EUROMET comparison 549	0.054 mK

	$T_{673} - T_{\text{mean BNM-INM batch}}$	$T_{679} - T_{\text{mean BNM-INM batch}}$
1997	0.010 mK	-0.017 mK
2002	0.005 mK	-0.066 mK

We can notice that:

- The cell No 673 has a very good stability for six years.
- The temperature realized by the cell No 679 decreases of around 0.050 mK during the same time. At present time, the source of this variation is not established.

6. Uncertainties

In this comparison, we apply the general rules for expressing uncertainty in physical measurement as they are established in the ISO *Guide* [2].

The comparison consisted of measuring the difference in temperature between the circulating instrument and the local one, therefore the laboratories had to evaluate the uncertainty components related exclusively to this difference. So, the uncertainty budget doesn't include the sources of uncertainty affecting the local and the circulating realizations of the triple point of water as: chemicals impurities, gas pressure, spurious heat flux,….

In this interlaboratory comparison we consider the contribution of some uncertainties to be negligible because these uncertainties are expected to be strongly positively correlated, for example:

- The electrical measurement on the circulating and the local cells are made with the same bridge and practically the same ratio.
- The same standard resistor stabilized in temperature is used.
- The thermal resistances have approximately the same magnitude in the circulating and the local cells. The corresponding self-heating corrections are very close.

So, the following sources of uncertainty:

- Bridge accuracy
- Resistor calibration.
- Self heating-correction

are neglected.

Consequently, the standard uncertainty in the difference is smaller than the standard uncertainty in the value of the SPRT resistance.

A] Uncertainty on $(T_{local} - T_{circulating})$ reported by the laboratory

Commentary on the uncertainty components

Type A evaluation

Component u_{A1}

This corresponds to the repeatability of measurement results under the following conditions:

- Same measurement procedure
- Same observer
- **Same Thermometer left in place**
- Same bridge
- **Same isothermal enclosure**
- repetition over a **short period of time** (i.e. without changing the ice mantle)

This component takes in account the noise affecting the measurements.

Component u_{A2}

Through the different measurements performed in a given Laboratory on TPW cells the standard deviation of the measurements can be obtained. The standard deviation can be considered to be an estimate of the reproducibility of the measurements due to changes in the influencing quantities.

The observed temperature differences between the circulating and the local cells dependent on various factors including the following:

- crystal size
- age of the mantles
- difference between mantles
- method of handling the cells before preparation of the mantle. If the cell is stored for a considerable time in the same position before preparation of the mantle, the impurities may not be uniformly distributed in the water and handling can then modify the local impurities concentration
- undesirable thermal reaction in thermal contact fluids (mixing alcohol + water)
- stability of SPRT (repeated measurements with reinsertion of SPRT)
- different types of SPRTs (thermometer's geometrical characteristics can influence the observed difference in temperature between the circulating and local TPW cells).
- influence of spurious heat flux linked with the temperature of the surrounding

Type B evaluation

Component u_{B1}
The source of this standard uncertainty is electrical measurement. This component takes in account:

- the stability of bridge
- the stability of reference resistor (temperature effect)

during the time of a pair of the measurements (one on local cell, one on circulating cell)

Component u_{B2}
This is the uncertainty of the correction related to the hydrostatic pressure. This component takes in account the uncertainties associated at once to the local and the circulating cells.

In this interlaboratory comparison we consider the contribution of some uncertainties to be negligible either because their values are very small, or because these uncertainties are strongly positively correlated. This applies, in particular to the uncertainty on the self-heating correction. . All the measurements are corrected for self-heating effect. As the thermal resistances have approximately the same magnitude in circulating and local cells the difference between the self-heating correction is very small. In addition the uncertainties on self-heating corrections in circulating and local cells are strongly correlated.

For each Laboratory the combined standard uncertainty, $u_{(Tlocal\ -\ Tcirculating)Lab}$ is calculated from the different components presented Table 6.

B] Final uncertainty on *(T_{local} - $T_{circulating}$)*

The uncertainty contribution from the stability of the circulating cell, u_{stab} , is added to the value of $u_{(Tlocal\ -\ Tcirculating)Lab}$ at the end of the circulation. So, finally

$$u^2\left(T_{local} - T_{circulating}\right) = u^2\left(T_{local\ cell} - T_{circulating}\right)Lab \ + u^2_{stability}$$

The corresponding expanded uncertainty (coverage factor=2) is given Table 3

7. Results

The aim of the comparison is to compare each local realization with that realized in the circulating one. The results of the temperature differences derived from the resistance measurement are given in Table 3. The differences correspond to averages.

The mean of the twenty-six values of (T_{local}- $T_{circulating}$) is calculated. Using this mean the difference (T_{mean} -$T_{circulating}$) can be established, T_{mean} corresponds to the mean of the temperatures materialized by the twenty-six cells involved in this comparison.

$$\frac{(T_{local1}-T_{circulating})+(T_{local2}-T_{circulating})+.........+(T_{local26}-T_{circulating})}{26}=\frac{T_{local1}+T_{local2}+.....+T_{local26}}{26}-T_{circulating}=T_{mean}-T_{circulating}$$

(T_{mean} -$T_{circulating}$) is equal to 0.067 mK associated to a standard uncertainty of 0.015 mK.

The results (T_{local}- $T_{circulating}$) with their related expanded uncertainties are presented Figure 3. The straight line corresponds to *(T_{mean} -$T_{circulating}$)*. The dotted lines are connected with the expanded uncertainties on *(T_{mean} -$T_{circulating}$)*.

For each cell the value (T_{local} - T_{mean}) was calculated.

(T_{local} - T_{mean}) = (T_{local} - $T_{circulating}$) - (T_{mean} - $T_{circulating}$)

The values of *(T_{local}-T_{mean})* are given Table 7.

The uncertainty on *(T_{local}-T_{mean})* is obtained from:

$$u^2_{(T_{local}-T_{mean})}=u^2_{(T_{local\ cell}-T_{circulating})Lab}+u^2_{stability}+u^2_{(T_{mean}-T_{circulating})}$$

The corresponding expanded uncertainty (coverage factor=2) is given Table 7

Figure 4, the results are presented in the shape of a histogram. This simplified presentation shows there are none results that differ significantly from the general behaviour and that approximately half of the results range between -0,05 mK and 0,05 mK. Twenty results (74 %) are within ± 0,1 mK of the mean.

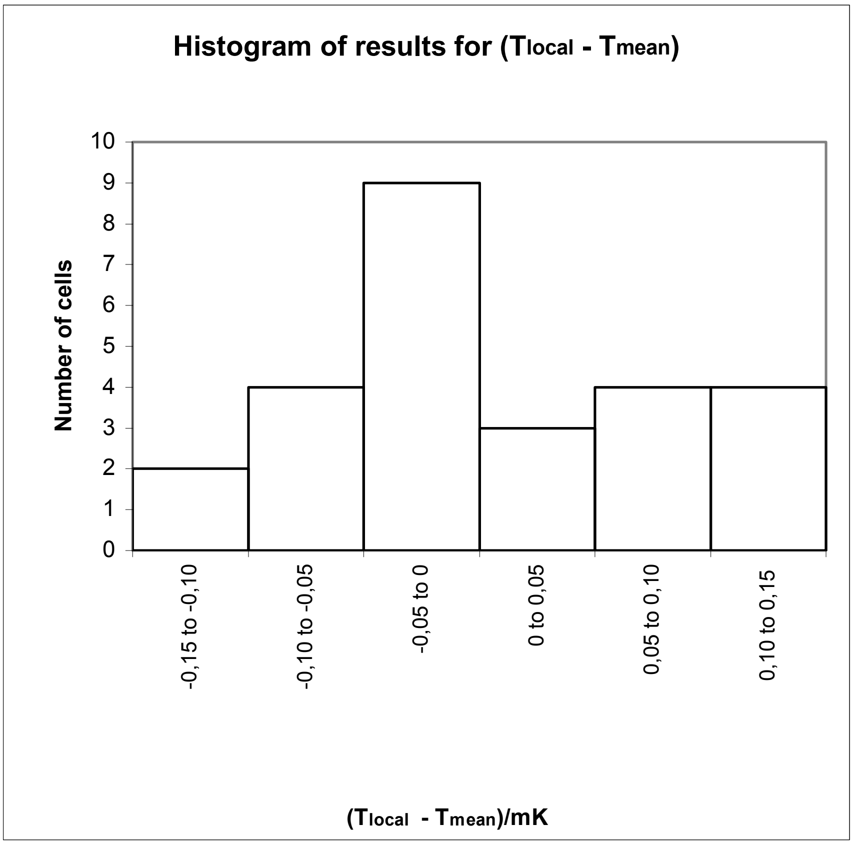

Figure 4: Histogram of results for *(T_{local}- T_{mean})*

8. Conclusions

EUROMET project No 549 was based on the circulation of one TPW cell and an isothermal enclosure. Fifteen European Laboratories were involved in the comparison of twentysix TPW cells. During the comparison, the stability of the circulating TPW was periodically checked by comparisons with another BNM-INM cell.

Twelve results are stated to lie between -0,05 mK and +0,05 mK of the mean value. Twenty results (74 %) are within ± 0,1 mK of the mean value.

References

[1] E. Renaot, M. Elgourdou and G. Bonnier, Interlaboratory comparison of realization of the triple point of water, *Metrologia* 2000*, **37***, 693-699.

[2] Guide to the expression of uncertainty in measurement, *ISO/TAG 4/WG 3*; June 1992

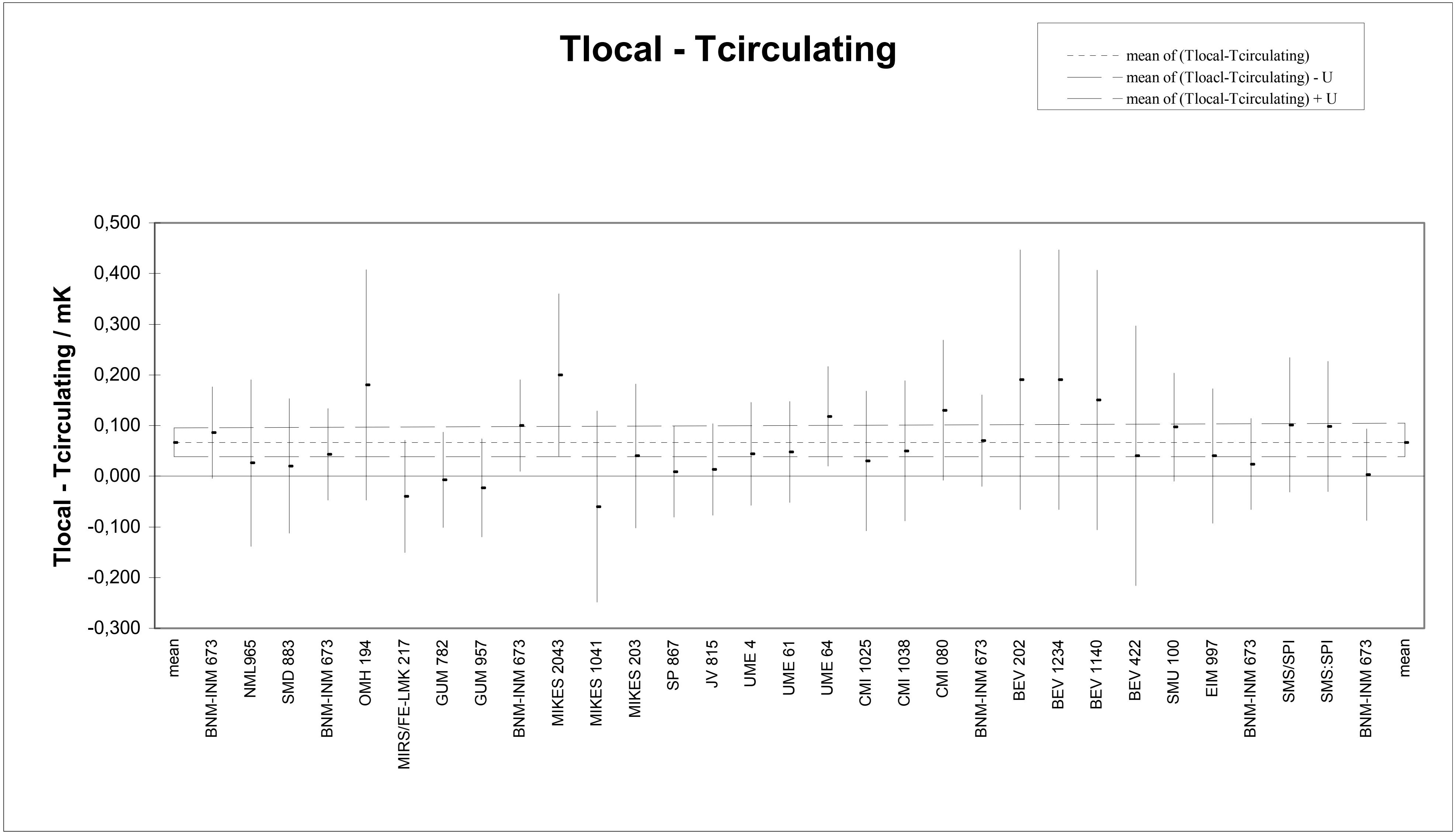

Figure 3: Temperature differences derived from the resistance measurement

Table 3 :cell features, local procedures, results and associated uncertainties

Labo.	Cell			Preparation	Isothermal enclosure and bath	$T_{local}-T_{circulating}$ in mK	$U(T_{local}-T_{circulating})_{Lab}$ coverage factor:2 in mK	$U(T_{local}-T_{circulating})$ U_{Stab} added coverage factor:2 in mK
	Type	N°	Delivery date					
BNM-INM	NPL	673	1993	Metal rod precooled in liquid nitrogen	ISOTECH bath	0.054	0.070	0.090
NML	NPL	965	1997	Carbon dioxide	Insulated container full of ice	0.026	0.154	0.1640
SMD	NPL	883	1996	Heat pipe made by POND Engineering Laboratories	ISOTECH bath	0.020	0.120	0.133
OMH	OMH	194	old	Powered dry ice	Hart Scientific bath	0.180	0.220	0.227
MIRS/FE-LMK	NMi	94 T 217	1994	Metal rod precooled in liquid nitrogen	ISOTECH bath	-0.040	0.095	0.111
GUM	NPL NPL	782 957	1995 1998	Carbon dioxide ‘’	Insulated container full of ice	-0.007 -0.023	0.075 0.078	0.095 0.097
MIKES	Jarrett NPL Forschung	A112043 1041 203	1998 2000 1990	Carbon dioxide ‘’ ‘’	ISOTECH bath	0.200 -0.060 0.040	0.150 0.180 0.130	0.160 0.189 0.142
SP	NPL	867	1996	Cold (-45 °C) ethanol	ISOTECH bath	0.009	0.070	0.090
JV	NPL	815	1995	Carbon dioxide	Bath	0.013	0.070	0.090
UME	UME UME UME	4 61 64	1995 2000 2000	Metal rod precooled in liquid nitrogen Powered dry ice	Hart Scientific bath	0.044 0.048 0.118	0.084 0.082 0.080	0.102 0.100 0.098
CMI	NPL NPL ISOTECH	1025 1038 E11-080	1999 1999 1999	Ice mantle maker ISOTECH ‘’ ‘’	ISOTECH bath	0.030 0.050 0.130	0.126 0.126 0.126	0.138 0.138 0.138
BEV	BEV Hart Hart BEV	202 1234 1140 422		Metal rod precooled in liquid nitrogen ‘’ ‘’	Bath	0.190 0.190 0.150 0.040	0.250 0.250 0.250 0.250	0.256 0.256 0.256 0.256
SMU	ISOTECH	C12-100	2002	Metal rod precooled in liquid nitrogen	ISOTECH bath	0.097	0.090	0.107
EIM	NPL	997	1999	Metal rod precooled in liquid nitrogen	Hart Scientific bath	0.040	0.120	0.133
SMS/SPI	Hart Hart	1195 1196	2000 2000	Metal rod precooled in liquid nitrogen	Hart Scientific bath	0.101 0.098	0.120 0.115	0.133 0.128

Table 6: Uncertainty budgets

Laboratories	BNM-INM	NML	SMD	OMH	MIRS/FE-LMK	GUM	MIKES	SP
Components								
A1	0,015	0.040	0.015	0.020	0.020	0.015	0.047	0.007
A2	0,025	0.029	0.050	0.030	0.020	0.016	0.074	0.028
B1	0,020	0.058	0.030	0.100	0.035	0.030	0.015	0.015
B2	0,005	0.007	0.006	0.015	0.015	0.004	0.001	0.014
Combined standard uncertainty $u(T_{local} - T_{circulating})_{Lab}$ -	0,035	0.077	0.060	0.108	0.047	0.037	0.090	0.035

Laboratories	JV	UME	CMI	BEV	SMU	EIM	SMS/SPI
Components							
A1	0.006	0.020	0.050	0.037	0.035	0.020	0.046
A2	0.011	0.010	0.006	0.002	0.028	0.050	0.009
B1	0.002	0.034	0.037	0.118	0.003	0.016	0.030
B2	0.032	0.002	0.003	0.012	0.003	0.017	0.015
Combined standard uncertainty $u(T_{local} - T_{circulating})_{Lab}$ -	0.035	0.041	0.063	0.124	0.045	0.059	0.058

Table 7 : Summary of results and associated uncertainties

Laboratory	Cell	T_{local}-$T_{circulating}$ in mK	$U(T_{local}$-$T_{circulating})$ U_{Stab} added coverage factor:2 in mK	T_{local}-T_{mean} in mK	$U(T_{local}$-$T_{mean})$ U_{Stab} and U_{Tmean} added coverage factor:2 in mK
BNM-INM	673	0,054	0,070	-0.013	0,095
NML	965	0,026	0,154	-0,041	0,167
SMD	883	0,020	0,120	-0,047	0,136
OMH	194	0,180	0,220	0,113	0,229
MIRS/FE-LMK	217	-0,040	0,095	-0,107	0,114
GUM	782	-0,007	0,075	-0,074	0,099
GUM	957	-0,023	0,078	-0,090	0,102
MIKES	2043	0,200	0,150	0,133	0,163
MIKES	1041	-0,060	0,180	-0,127	0,191
MIKES	203	0,040	0,130	-0,027	0,145
SP	867	0,009	0,070	-0,058	0,095
JV	815	0,013	0,070	-0,054	0,095
UME	4	0,044	0,084	-0,023	0,106
UME	61	0,048	0,082	-0,019	0,104
UME	64	0,118	0,080	0,051	0,102
CMI	1025	0,030	0,126	-0,037	0,141
CMI	1038	0,050	0,126	-0,017	0,141
CMI	080	0,130	0,126	0,063	0,141
BEV	202	0,190	0,250	0,123	0,258
BEV	1234	0,190	0,250	0,123	0,258
BEV	1140	0,150	0,250	0,083	0,258
BEV	422	0,040	0,250	-0,027	0,258
SMU	100	0,097	0,090	0,030	0,110
EIM	997	0,040	0,120	-0,027	0,136
SMS/SPI	1195	0,101	0,120	0,034	0,136
SMS:SPI	1196	0,098	0,115	0,031	0,132