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REPORT ON THE INTERNATIONAL COMPARISON OF WATER TRIPLE-POINT CELLS

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La Section Thermométrie

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Roger Pello

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ABSTRACT

The reference temperatures of a large number of triple point of water cells collected from manufacturing sources around the world have been compared at the BIPM and in twelve national laboratories. This allowed an assessment to be made of the reproducibility of the realizations of the triple point of water and the equivalence of the experimental procedures.

The results show that, in most cases, the temperature of the cells agree to within ±0,1 mK. In some cases, however, much larger differences and temperature changes were observed, for which no obvious explanation has so far been found.

The results also provide a comparison of a large number of national reference cells.

1. INTRODUCTION

This international comparison of triple point of water cells was organized by the BIPM following Recommendation T2 (1993) concerning the use of such cells, adopted by the Comité Consultatif de Thermométrie at its 1993 meeting [1].

On the basis of this Recommendation, the BIPM invited national laboratories to contribute cells for the comparison from different manufacturing sources around the world and then arranged for their circulation among the participating laboratories. Each laboratory was asked to use its usual method for preparation of the ice mantles, to monitor the cells regularly (at least twice a week), and to check the resistance of the thermometers used for the measurements regularly, using, for example, the melting point of gallium.

To expedite the comparisons and free individual laboratories from the need to measure a large number of cells, the six cells to be used and the six participating laboratories were each divided into two groups of three. It was agreed that the BIPM would participate in each group and make an initial comparison of all six cells, and so link data from the two groups of laboratories. Some time after the beginning of the comparison six other laboratories expressed an interest in participating so a third group was formed.

2. ORGANISATION OF THE COMPARISON

2.1 Composition of the cell sets

The cells collected by the BIPM came from: the IMGC (one cell), the KRISS (two cells), the VNIIM (two cells), the NPL (two cells). From its own stock the BIPM took a cell made by the ETL and one made by the former ASMW (now the PTB). Two other cells of the type usually used by the NIST were purchased from Jarrett (USA). The origin, manufacturing source and identification are listed in Table 1, 2 and 3, along with their dimensions.

It was decided that all the cells involved in the comparison would be compared with a reference cell kept at the BIPM, prior to their circulation and after their return to the BIPM.

For this purpose BIPM cell PT131 was chosen because it has shown good stability over nearly 20 years of use.

It was also decided that when two cells of the same type were available, one would be used as a travelling cell and the other one kept at the BIPM as additional reference. These cells were then compared with one another at the end of the circulation.

On this basis, the sets were formed as follows:

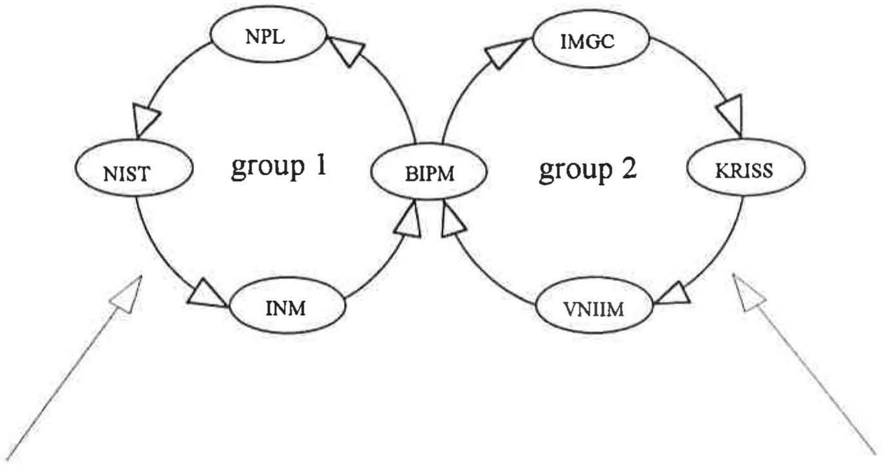
Reference: PT131

Set 1, circulating in Group 1: PT2R, PT34 and PTK1

Set 2, circulating in Group 2: PT1984, PT723, and PTJ2

Additional reference set kept at the BIPM: PT712, PTK2, PT2011 and PT4R.

2.2 Circulation scheme



Triple point of water cells from:	Triple point of water cells from:
VNIIM	USA (NIST-type)
IMGC	NPL
KRISS	ETL

Figure 1. The circulation scheme.

When the comparison was already well under way, six other laboratories expressed their interest in participating in the comparison, so a third group was constituted. As it was too late to include them in the circulation scheme, these laboratories were asked to send one or two cells to the BIPM, where they were compared with the BIPM reference cell and the travelling cells. Here again the BIPM acted as a link between the groups. As the laboratories of Group 3 made no measurements on the travelling cells, they participated in the comparison in a different way from those in Groups 1 and 2.

2.3 Participating laboratories

- Group 1: NPL (United Kingdom), NIST (USA), INM (France)
- Group 2: IMGC (Italy), KRISS (Rep. of Korea), VNIIM (Russia)
- Group 3: MSL (New Zealand), IPQ (Portugal), SISIR (Singapore), INMETRO (Brazil), NMi (The Netherlands), INM (Romania).

2.4 Time schedule for the comparison

The triple point of water cells used in the comparison were collected early in 1994. Measurements began in February 1994. The cells sets were dispatched to the laboratories in June and July 1994.

The laboratories in Groups 1 and 2 were given about three months to compare the cells and send them on to the next laboratory. The last laboratory of the group was asked to return them to the BIPM, at the latest, by August 1995. The last set was in fact returned in October 1995. The first cells sent by laboratories of Group 3 arrived at the BIPM in May 1995 and the last comparisons involving cells from this group were made in December 1995.

2.5 Description of the triple point of water cells

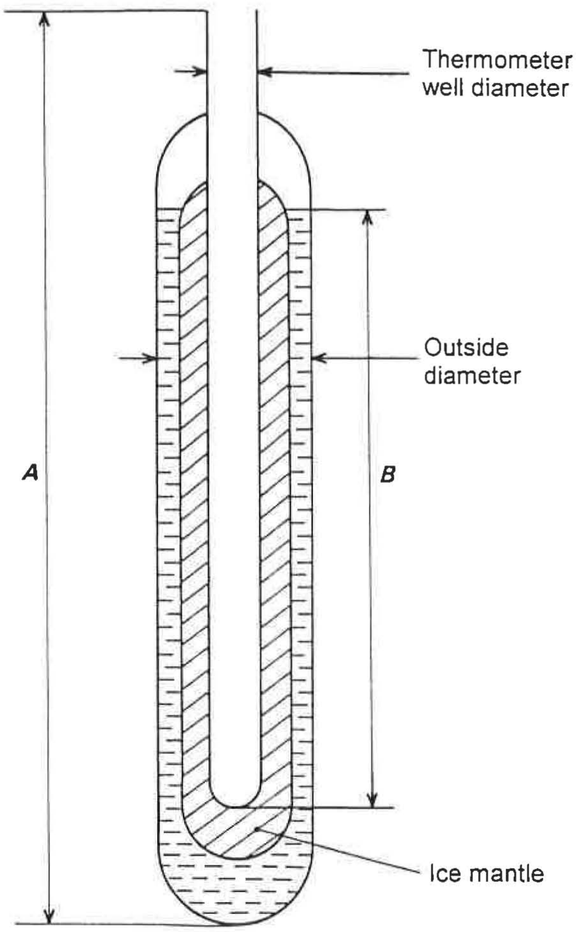


Figure 2. A triple point of water cell.

Country	Manufacturer	Identification	Cell reference in this report	Depth of bottom of therm. well below water surface /mm (*B*)	overall length /mm (*A*)	outside diameter /mm	therm. well diameter /mm
United Kingdom	NPL	712 †	PT712	220	373	40	12
	NPL	723 (a)	PT723	220	371	40	12
USA	Jarrett	1984 (a)	PT1984	270	440	63	11,5
	Jarrett	2011 †	PT2011	275	450	63	13,5
Italy	IMGC	34 (a)	PT34	255	430	55	9,5
Russia	VNIIM	2 (a)	PT2R	214	469	50,8	9,5
	VNIIM	4 †	PT4R	200	483	51	9,5
Korea	KRISS	1 (a)	PTK1	278	425	50	12
	KRISS	2 †	PTK2	270	426	50	12
Japan	ETL	II (a)	PTJ2	250	430	64,5	12

Table 1. Dimensions of the cells collected by the BIPM:

(a): travelling cells.
† : cells kept at the BIPM as part of the additional reference set.
(*A*), (*B*): see Figure 2.

Country	Laboratory	Identification	Depth of bottom of therm. well below water surface /mm (*B*)	overall length /mm (*A*)	outside diameter /mm	therm. well diameter /mm
United Kingdom	NPL	555	216	372	40	12
USA	NIST	4	290	347	52,1	13
Italy	IMGC	31	255	430	55	9,5
Russia	VNIIM	T2-95	(a)	(a)	(a)	(a)
France	INM	673	(a)	(a)	(a)	(a)
New Zealand	MSL	PEL 84 7(b)	270	385	60	10
	MSL	84/2 (b)	270	400	60	10
Portugal	IPQ	033 (b)	260	400	61	11
	IPQ	299 (b)	215	380	40	12
Singapore	SISIR	10281 (b)	278	445	64,5	11,5
Brazil	INMETRO	494 (b)	215	370	40	12
The Netherlands	NMi	VSL89T084 (b)	200	330	38	8,5
	NMi	VSL94T214 (b)	258	430	56,5	8,5
Romania	INM	no ref. (b)	160	335	50	11,5

Table 2. Dimensions of the cells used by the participating laboratories.
(a): not specified.
(b): cells sent by the laboratories of Group 3
(*A*), (*B*): see Figure 2

Origin	Manufacturer	Cell reference	Depth of bottom of therm. well below water surface /mm (*B*)	overall length /mm (*A*)	outside diameter /mm	therm. well diameter /mm
BIPM	ASMW(PTB)	PT131	273	437	49,8	13

Table 3. Dimensions of the BIPM reference cell.
(*A*), (*B*): see Figure 2.

2.6 Gallium melting point cells

Some laboratories used the gallium melting point as a check of the stability of their thermometers. The gallium cells of the KRISS, the NPL and the BIPM have bodies of PTFE. The NPL constructed and filled its cell. The BIPM and the KRISS cells are of commercial type (Engelhard and Isotech respectively).

3. ABSTRACTS OF THE NATIONAL LABORATORY REPORTS (Groups 1 and 2)

3.1 NPL

At the NPL the travelling cells were compared with the NPL reference cell N_o 555. The resistance of the thermometer was regularly checked at the melting point of gallium.
Storage apparatus: Between measurements, cells in individual acrylic or polyethylene tubes are suspended in an ice-flaking machine.

Preparation of the triple point of water cells: Each cell is cooled in ice for at least one hour. The thermometer well is rinsed with acetone and dried with compressed air. Crushed solid carbon dioxide is then poured into the well to a level close to that of the water. The process is stopped when the ice sheath appears to be about 6mm to 8mm thick. The well is then filled with ice-cold water.
Measurements begin twenty hours after completion of the formation of the ice sheath. A water-ice interface is formed and the thermometer is pre-cooled before insertion into the well. The cell and the thermometer are then placed in a wooden box to protect them from stray radiation. Measurements begin twenty minutes later. The thermometer is transferred from cell to cell, each cell being measured at least twice in each set.

Instrument types: ASL F18 bridge. Currents: 1 mA and √2 mA.
Standard resistor: Tinsley 25 Ω, type 5684S. (The temperature is monitored and correction is applied to allow for small departures from 20°C).
Thermometer: Chino (Japan) type : R800-2.

Comments: When the individual cell temperatures were compared, the results showed that the largest differences were between cells PTK1 and PT2R, the former cell averaging 0,20 mK above the latter, with a maximum difference of 0,28 mK. However, the maximum difference occurred 39 days after the initial preparation, by which time the ice mantle at the re-entrant well on PT2R had become very large.

The results are given by the NPL in the form of graphs and tables indicating the resistance thermometer readings (corrected for self heating and hydrostatic pressure) as a function of time for each of the cells: NPL reference No 555, PT34, PTK1, PT2R.
In order to have a common presentation for all the laboratories, the BIPM calculated the following quantities on the basis of these results: day to day differences between the NPL reference and the travelling cells (and between the travelling cells), average value of the series converted into temperature differences. The uncertainty stated by the NPL for the comparison of two cells is 0,044 mK at the level of two standard uncertainties, i.e. at the 2 σ level. The standard uncertainty given in the following tables is therefore 0,022 mK.

NPL (T_{cell} - T_{NPLref}) / mK			
	PT34	PTK1	PT2R
average	0,082	0,125	-0,078
standard uncertainty	0,022	0,022	0,022

Table 4. Difference in temperature measured at the NPL, between the NPL reference cell and the travelling cells.

NPL	Temperature difference / mK		
	PTK1-PT34	PT2R-PT34	PT2R-PTK1
average	0,043	-0,157	-0,200
standard uncertainty	0,022	0,022	0,022

Table 5. Difference in temperature measured at the NPL between the travelling cells.

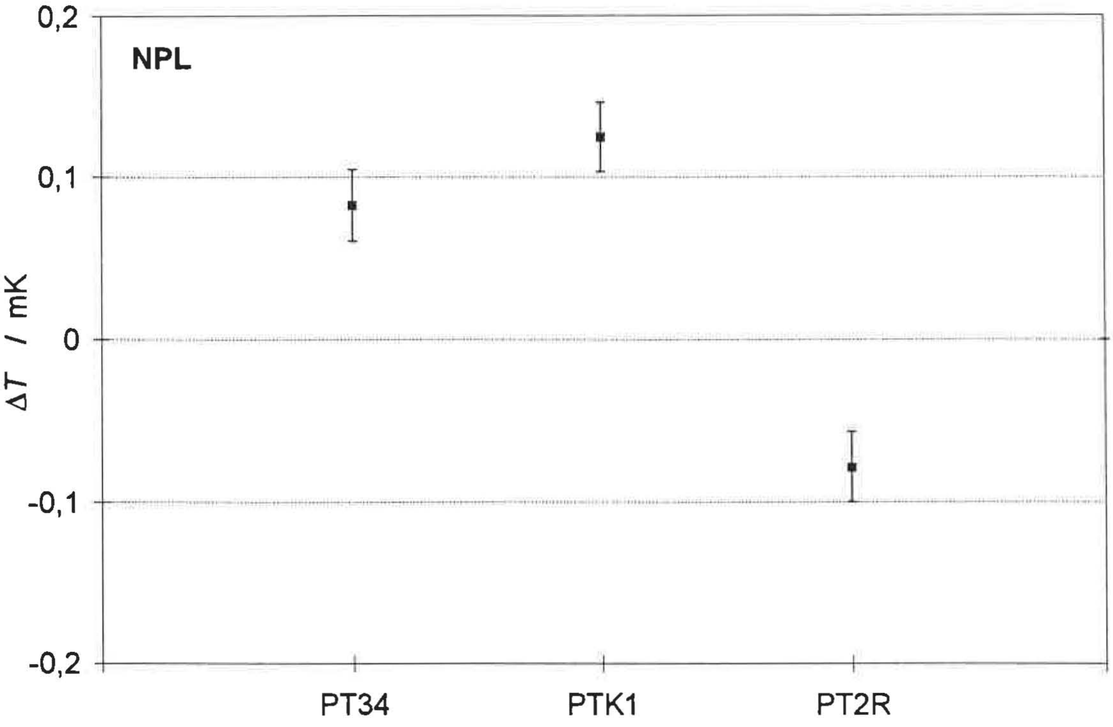


Figure 3. Difference in temperature $\Delta T = (T_{cell} - T_{NPLref})$ measured at the NPL, between the NPL reference cell and the travelling cells (1σ uncertainty bars).

Seven measurements at the gallium melting point were also made during the 44 days of the experiment. These show that part of the small changes observed in the resistance measurements during this period were probably due to variations in the thermometer or the measuring system. They also show the excellent repeatability of the temperature of this fixed point: no drift and maximum variation 0,048 mK.

The experimental standard deviation for each series was calculated at the BIPM with the aim of comparing the dispersion of the resistance measurements obtained with the gallium cell and with triple point cells. The standard deviation expressed as a temperature is 0,017 mK for the gallium and ranges from 0,011 mK (PTK1) to 0,049 mK (PT2R) for the triple point of water.

3.2 NIST

At the NIST the travelling cells and one NIST control cell were compared against the NIST reference triple point of water cell No 4.

Storage apparatus: Cells are stored in a commercial maintenance bath at +7 m°C, in which the mantles of the cells can be maintained for months.

Preparation of the triple point of water cells: Cells are prepared with dry ice and alcohol as immersion cooler. Starting temperature of cells, 0,1°C (no cracks appeared during mantle construction in the course of the present comparison). Measurements begin after at least seven days.

Instrument types: ASL F 18 bridge at 30 Hz. Currents: 1mA and √2 mA.

Standard resistor: Tinsley 100 Ω type 5685A at 25 °C within ± 0,01 °C.

Thermometer: L & N model 8167 (S/n 1881990).

Comments:

Aluminium bushings were used in each triple point of water cell to improve thermal contact.

In each of the three experiments performed, two travelling cells and the NIST control cell No 3 were compared against NIST cell No 4. The measurement order was (cell 4, X, Y, Z, cell 4), where X, Y, Z are the cells under test in random order.

The estimated standard uncertainty is 0,01 mK.

The graphs sent by NIST show that the repeatability of its successive measurements (within ±0,02 mK) is clearly better than that observed in the other laboratories, the BIPM included.

	$(T_{cell} - T_{NISTref})$ / mK		
Triple point cell	Experiment I	Experiment II	Experiment III
PT34	-0,03		-0,04
PTK1	0,00	0,00	
PT2R		-0,15	-0,16
NIST Control 3	0,00	0,00	-0,01

Table 6. Difference in temperature measured at the NIST between the NIST reference cell, the travelling cells and the NIST Control cell 3.

The BIPM then calculated the average value and the differences between the travelling cells.

	NIST $(T_{cell} - T_{NISTref})$ / mK			
	PT34	**PTK1**	**PT2R**	**NIST 3**
average	-0,035	0,000	-0,155	-0,003
standard uncertainty	0,01	0,01	0,01	0,01

Table 7. Difference in temperature measured at the NIST between the NIST reference cell, the travelling cells and the NIST Control 3 cell (average values).

NIST	Temperature difference / mK		
	PTK1-PT34	PT2R-PT34	PT2R-PTK1
average	0,035	-0,120	-0,155
standard uncertainty	0,01	0,01	0,01

Table 8. Difference in temperature measured at the NIST between the travelling cells.

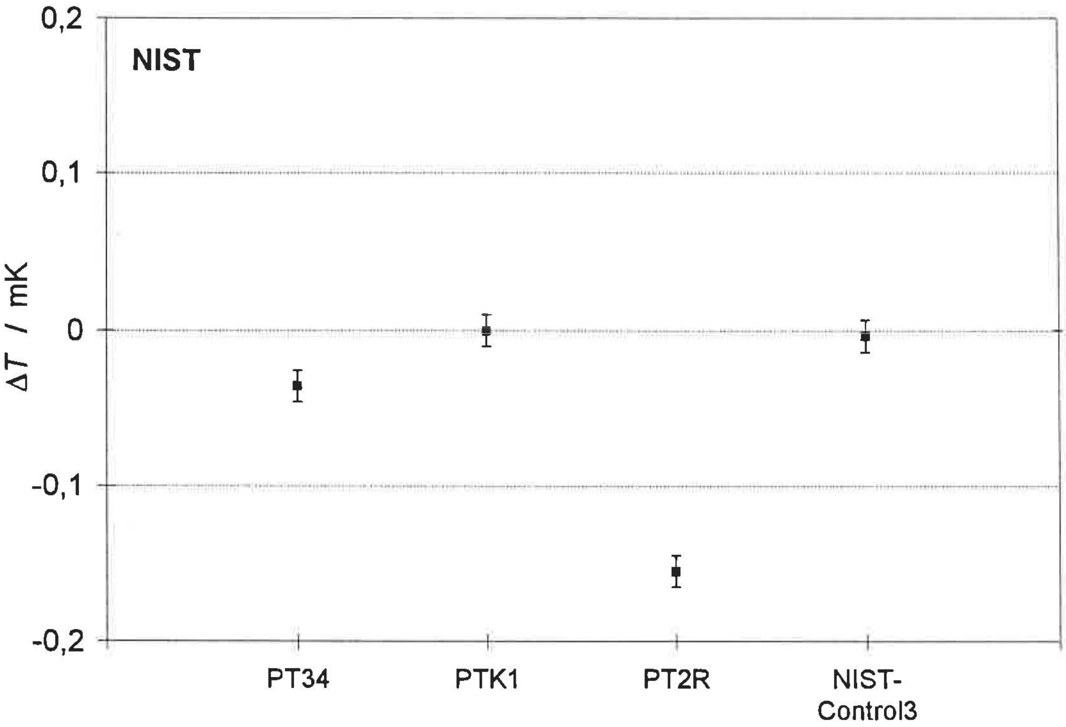


Figure 4. Difference in temperature $\Delta T = (T_{\mathrm{cell}} - T_{\mathrm{NISTref}})$ measured at the NIST, between the NIST reference cell, the travelling cells and the NIST Control cell 3 (1σ uncertainty bars).

3.3 INM (France)

At the INM the travelling cells were compared against the INM reference cell No 673. *Storage apparatus:* Cells were held before use in an ISOTECH distillated water stabilized bath, stable within ±2 mK.

Preparation of the triple point of water cells: The cells are pre-cooled in a water-ice mixture. Some alcohol is then introduced into the thermometer well and the ice mantle is formed by means of a brass rod cooled in liquid nitrogen. The process is stopped when the diameter of mantle reaches about half the internal diameter of the cell. The thermometer well is then rinsed with cold water at least twice.

Measurements do not begin until at least 24 hours after the preparation. A water-ice interface is formed and the pre-cooled thermometer inserted into the well. The measurements begin 20 minutes later. A measurement cycle involving four cells lasts 5 to 6 hours. After completion of 6 cycles, the measurement order of the cells was reversed for the last 6 cycles.

Instrument types: Guildline 9975 bridge. Currents: 1 mA and √2 mA.
Standard resistor: Tinsley or Guildline type, kept in an oil bath at 25°C within ± 0,1°C.
Thermometers: two L&N thermometers.
Comments:
Several experiments were carried out on all the cells to allow estimation of the uncertainties: modification of the environmental conditions (head and stem of the thermometer), influence of the immersion depth. The dimensions of travelling cell PT2R are such that it did not properly fit into the water bath of the INM. Some modifications of the usual experimental arrangement had to be made. The possible influence of these modifications on the measurements was studied and the results lead to an increase in the uncertainty associated with the measurements on PT2R.

All the temperature differences and uncertainties reported in these tables were calculated by the INM.

INM (France) $(T_{cell} - T_{INMref})$ / mK			
	PT34	**PTK1**	**PT2R**
average	-0,04	0,01	-0,23
standard uncertainty	0,05	0,05	0,1

Table 9. Difference in temperature measured at the INM (France) between the INM reference cell and the travelling cells.

INM (France)	Temperature difference / mK		
	PTK1-PT34	**PT2R-PT34**	**PT2R-PTK1**
average	0,05	-0,19	-0,25
std uncertainty	0,05	0,1	0,1

Table 10. Difference in temperature measured at the INM (France) between the travelling cells.

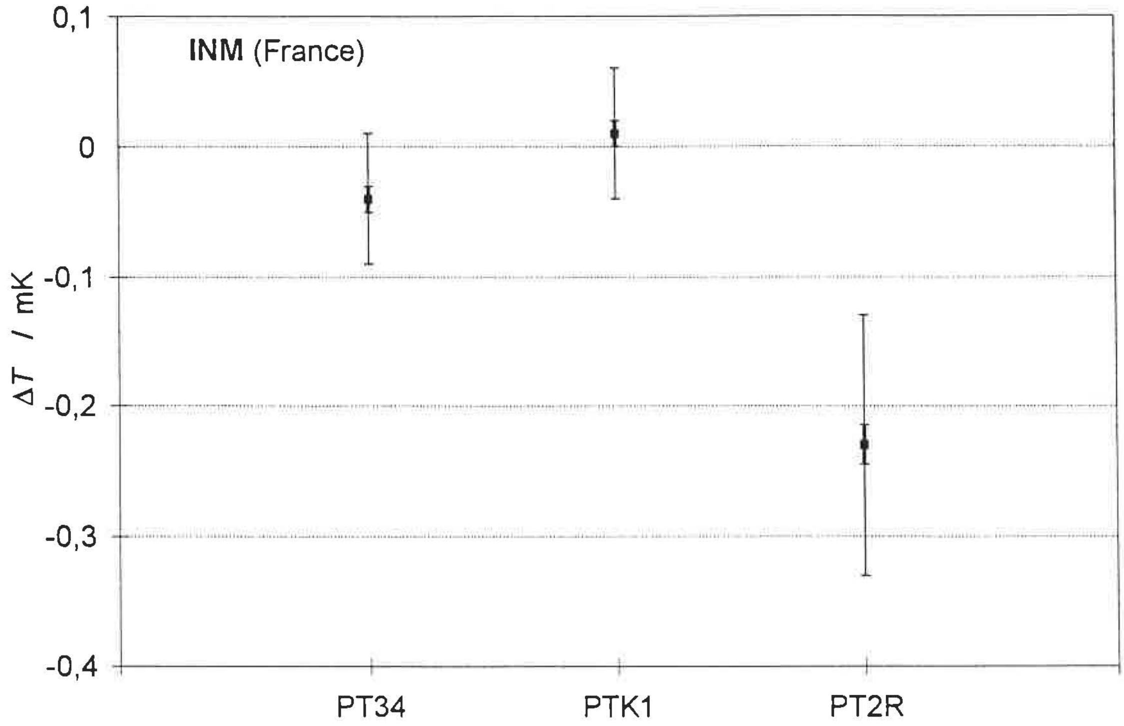


Figure 5. Difference in temperature $\Delta T = (T_{\text{cell}} - T_{\text{INMref}})$ measured at the INM (France), between the INM reference cell and the travelling cells. Uncertainty bars (1σ): thick lines correspond to type A uncertainties only, thin lines to combined uncertainties (A and B). This presentation of the uncertainty bars has been explicitely asked by the INM.

3.4 IMGC

At the IMGC the travelling cells were compared against the IMGC reference cell No 31.

Storage apparatus: An ice bath in the form of a stainless-steel container placed in a refrigerator controlled at about 5°C, is used to reduce the ice consumption.

Preparation of the triple point of water cell: The cell is pre-cooled in ice at least for one night. Some ethyl alcohol is then introduced into the thermometer well and the ice mantle is frozen with a 6 mm diameter brass rod repeatedly immersed in liquid nitrogen. The ice mantle thickness is 4 mm to 6 mm (no cracks appeared in the ice during mantle construction in the course of the present comparison). Ethyl alcohol is then removed and the well rinsed out 3 times with pre-cooled demineralized water to avoid exothermic reaction.

Measurements begin one day after the preparation. A water-ice interface is formed and the pre-cooled thermometer quickly transferred into the cell. A heavy black cloth is then placed over

the bath to protect the thermometer from thermal radiation. After 20 minutes for the first cell and 10 minutes for the others the thermometer is usually stable and the measurements begin. They are controlled by dedicated software.
The measuring sequence of the four cells is reversed each day.

Instrument type: ASL F18 bridge at 25 Hz. Currents: 2mA and 2,82mA.
Standard resistor: Tinsley 25 Ω, type 5685A placed in a temperature controlled enclosure Tinsley 5648.
Thermometers: L&N model 8167-25 (USA), S/n 42 and Chino Works R800-2 (Japan), S/n RS5YA-2.

Comments:
The IMGC sent a detailed report on several series of comparisons. Three IMGC cells (Nos 32, 33 and 34) were first compared with a common reference cell (IMGC No 31), using two different thermometers. Results are summarized in the following tables and show the reproducibility of the triple point of water and the influence of the thermometers. Mean values are given for 14 daily measurements.

Thermometer LN42			
	$(T_{cell32} - T_{cell31})$ / mK	$(T_{cell33} - T_{cell31})$ / mK	$(T_{cell34} - T_{cell31})$ / mK
mean	0,032	-0,018	-0,007
std. dev. of mean	0,009	0,012	0,014
Thermometer RS 5YA-2			
mean	0,027	-0,031	-0,003
std. dev. of mean	0,005	0,007	0,006

Table 11. Temperature dispersion among the IMGC reference cells measured at the IMGC.

Cell No 34 was then sent to the BIPM for use as a travelling cell under the label PT34 by the laboratories of Group 1.
When the travelling cells of Group 2 were received by the IMGC, they were compared with IMGC reference cell No 31 over four series of comparisons (two runs, each time with both thermometers). Problems due to humidity inside the sheaths of the thermometers were also studied.
The average differences for the two thermometers were calculated at the BIPM. The standard uncertainty on the comparison of cells is taken from the IMGC report.

IMGC	$(T_{cell} - T_{IMGCref})$ / mK		
	PT1984	**PTJ2**	**PT723**
average	0,022	-0,017	-0,045
std. uncertainty	0,077	0,077	0,077

Table 12. Difference in temperature measured at the IMGC, between the IMGC reference cell and the travelling cells.

IMGC	Temperature difference / mK		
	PTJ2-PT1984	**PT723-PT1984**	**PT723-PTJ2**
average	-0,039	-0,067	-0,029
std. uncertainty	0,077	0,077	0,077

Table 13. Difference in temperature measured at the IMGC, between the travelling cells.

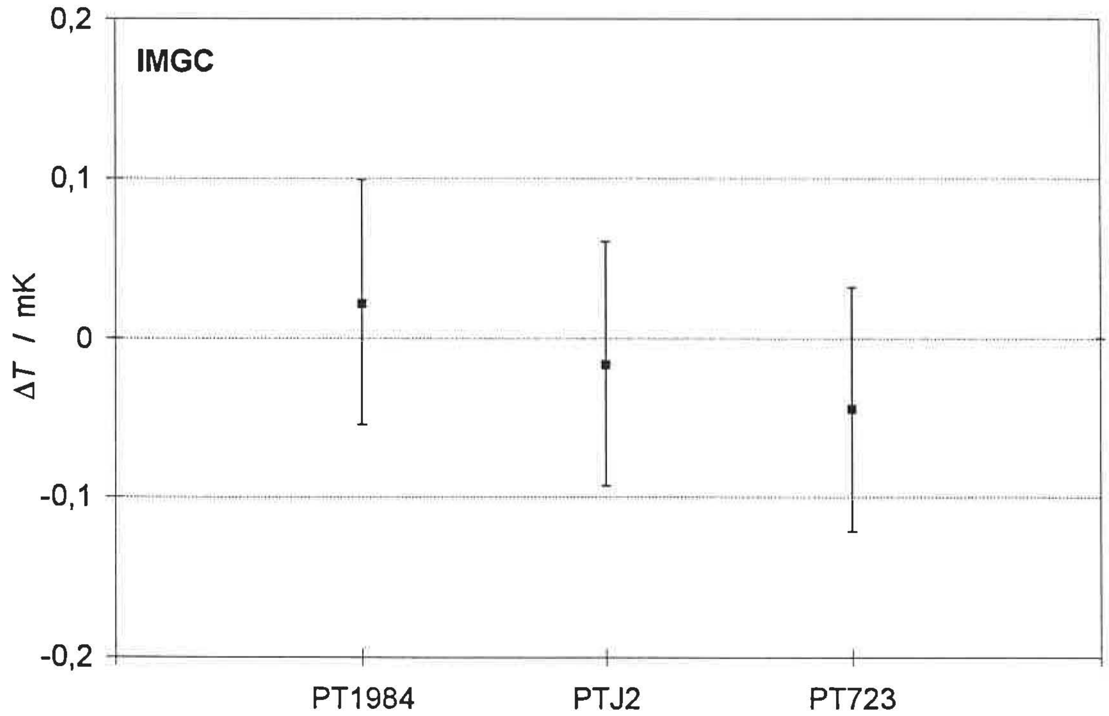


Figure 6. Difference in temperature $\Delta T = (T_{cell} - T_{IMGCref})$ measured at the IMGC, between the IMGC reference cell and the travelling cells (1σ uncertainty bars).

3.5 KRISS

At the KRISS the travelling cells were not compared against a reference triple point of water cell. The resistance measurements of the thermometer in the cells were made daily and the thermometer itself was regularly checked by means of a gallium melting point.
Storage apparatus: The storage conditions are not specified.
Preparation of the triple point of water cells: Cells are prepared with dry ice.

Measurements are made two times a day for the three triple point of water cells, and one or two times a day, at intervals of about two days, for the gallium melting point. The cells and the thermometer are covered with a piece of cloth. The same order of the measurements is repeated each day.

Instrument types: Guildline current comparator N9975, S/n 58285.
Standard resistor: Guildline 10 Ω, S/n 5515 kept in a bath at 25°C within ± 0,1°C.
Thermometer: L&N 8633-Q, S/n 1854020 annealed 4 hours at 450°C before the measurements.
Comments: The KRISS is the only laboratory which based the stability of its comparison on a gallium melting point rather than on a reference triple point of water cell. Numerical results are given in the form of series of $R_{(0,01°C)}$, $R_{(Ga)}$ and the corresponding calculated values of $W_{(Ga)}$ for the thermometer. The $W_{(Ga)}$ values show excellent stability (the standard error is about 2 parts in 10^8). The large number of measurements at the gallium point allows the comparison of the repeatability of the temperature measurements at this point and at the triple point of water to be made. The absence of significant drift and the small dispersion observed at the NPL with the gallium point is confirmed here. The standard deviations of 25 measurements at the gallium point and 65 measurements for the triple point of water were calculated at the BIPM. Results are given in Table 14.

	Gallium cell	PT1984	PT723	PTJ2
Standard deviation of the resistance measurements / Ω	0,0023	0,0037	0,0036	0,0025
Temperature equivalent of the standard deviation / mK	0,023	0,037	0,036	0,025

Table 14. Standard deviation of the resistance measurements at the KRISS.

The temperature difference between the triple point cells was calculated by the BIPM from the average values of the daily differences in the thermometer resistance (same calculation as with the NPL values).
It is important to note that the KRISS only sent raw data without any correction. In particular, no correction for hydrostatic pressure was made.This makes it difficult to carry out an accurate comparison of these results with those from other laboratories.
The standard uncertainty in the resistance measurements given by the KRISS is 7×10^{-6} Ω, corresponding approximately to 0,07 mK.

KRISS	Temperature difference / mK		
	PTJ2-PT1984	**PT723-PT1984**	**PT723-PTJ2**
average	0,022	0,000	-0,022
std uncertainty	0,07	0,07	0,07

Table 15. Difference in temperature measured at the KRISS between the travelling cells.

3.6 VNIIM

At the VNIIM the travelling cells were compared against the VNIIM reference cell T2-95.
Storage apparatus: The thermostat is filled with snow.

Preparation of the triple point of water cells: Two methods were used:
In the first, ice mantles were formed using a metal rod precooled in liquid nitrogen. The process takes 25 minutes. Small cracks were observed in the mantle.
In the second, mantles were formed using crushed solid carbon dioxide at the level of water, the process taking 40 minutes. Cracks at the top of the ice mantle were observed. The thickness of the ice mantle is 10 mm to 12 mm.

Measurements begin one day after the preparation. Before and after each measurement free rotation of the ice mantle is checked. A thick black cloth covers the thermometers. Two thermometers were used in each of the two experiments described here, and the influence of the thermometer immersion depth was studied.

Instrument types: Guildline current comparator N9975.

Standard resistor: made in Russia, type P-3030. Kept in a thermostat at 20°C within ± 0,05°C.

Thermometers: 25 Ω made by the VNIIM, S/n 395 and S/n 12.

Comments: The use of different thermometers did not cause a significant change in the measurement of temperature differences. In both experiments, the PT1984 cell showed the higher temperature.

When freezing the cells with solid CO_2 , the temperature of PTJ2 was 0,05 mK higher than when using liquid nitrogen. With the other cells no significant differences were found.

The temperature stability was twice as good when the ice mantle was formed with solid CO_2 than with liquid nitrogen.

VNIIM	$(T_{cell} - T_{VNIIMref})$ / mK	
	Ice mantle preparation method	
	Liquid nitrogen	dry ice
PTJ2	0,047	0,101
PT723	0,063	0,043
PT1984	0,119	0,116
std. uncertainty	0,024	0,024

Table 16. At the VNIIM: influence of the ice-mantle preparation method (values are averaged for the two thermometers).

Values averaged for both methods were calculated by the BIPM:

VNIIM	$(T_{cell} - T_{VNIIMref})$ / mK		
	PT1984	PTJ2	PT723
average	0,118	0,074	0,053
std uncertainty	0,024	0,024	0,024

Table 17. Difference in temperature measured at the VNIIM between the VNIIM reference cell and the travelling cells.

VNIIM	Temperature difference / mK		
	PTJ2-PT1984	PT723-PT1984	PT723-PTJ2
average	-0,044	-0,065	-0,021
std uncertainty	0,024	0,024	0,024

Table 18. Difference in temperature measured at the VNIIM between the travelling cells.

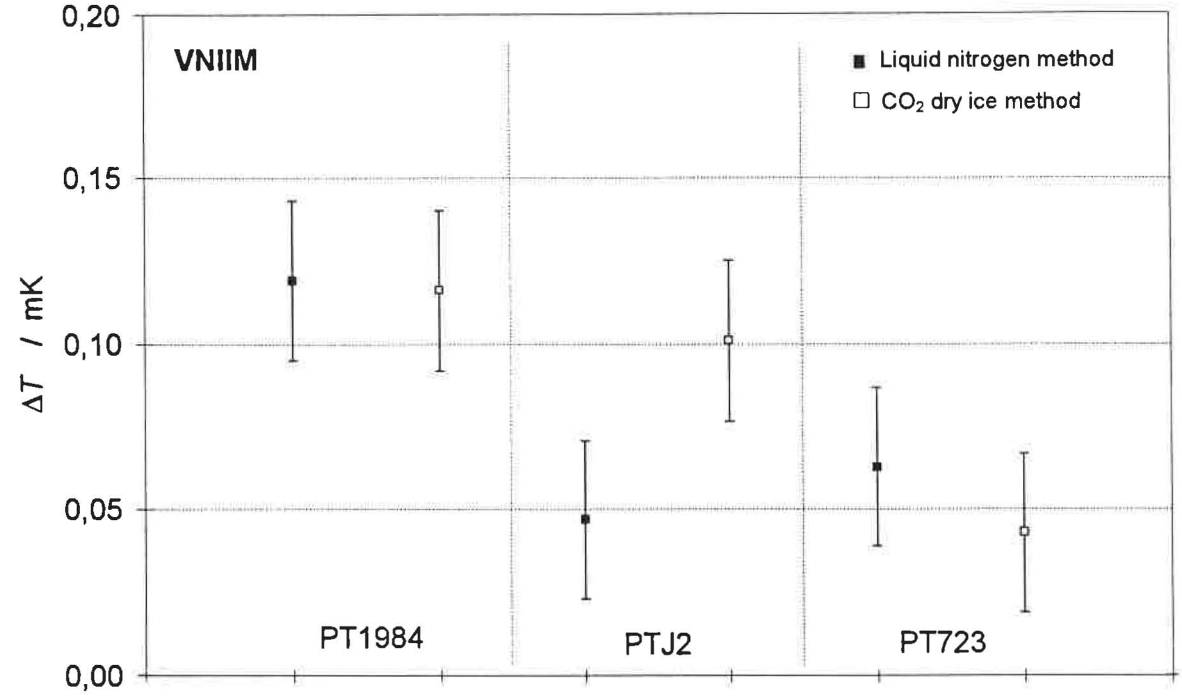


Figure 7. Difference in temperature $\Delta T = (T_{cell} - T_{VNIIMref})$ measured at the VNIIM between the VNIIM reference cell and the travelling cells, using two different methods for the preparation of the ice mantle (1 σ uncertainty bars).

4. MEASUREMENTS AT THE BIPM

4.1 Preparation of the cells

Storage apparatus: Between measurements, cells are stored in an ice bath described in the " Supplementary Information for the ITS-90 " [2].

Preparation of the triple point of water cells: Cells are precooled for at least 2 hours, typically over one night. Some alcohol is introduced into the thermometer well and then crushed dry ice. Using this process it takes from 25 to 40 minutes (depending on the cell size) to produce an ice sheath from 8 mm to 10 mm thick. The well is then rinsed and filled with ice cold water.

4.2 Measurement procedure and facilities

Measurements do not begin until at least two days after the preparation. An ice-water interface is formed by means of a rod at room temperature and the presence of a free surface of water is checked before and after the measurements. A black cloth protects the cells and the thermometer from thermal radiation from the outside. Measurements begin after at least 45 minutes after the thermometer is inserted into the cell. A determination of temperature takes about 50 minutes, the self heating correction being determined each time. The order in which the cells are measured is randomly chosen each day.

Instrument types: Guildline 9975 bridge. Currents 1mA and √2 mA.

Standard resistor: Tinsley 10Ω.

Thermometers: L&N and Tinsley.

Comments: Cells were kept up to three months in ice.

4.3 Determination of the difference in temperature of two cells

The difference in temperature between two cells is found the following way. Let x and y be the values of the resistance of the thermometer when it is in cells X and Y respectively. The measurements of x and y are repeated n times, x_i and y_i being the ith pair. The difference in resistance is converted into a difference in temperature by means of the coefficient dT/dR, characteristic of the thermometer. The difference in temperature is calculated as the average value of the successive differences, after correction for self heating and hydrostatic pressure:

$$T_X - T_Y = \frac{dT}{dR}\,\frac{1}{n}\sum_{i=1}^{n}(x_i - y_i).$$

4.4 Uncertainties

Type A uncertainties:

Type A uncertainties are calculated in the usual way from the dispersion of the experimental results. A typical value for the experimental standard deviation of the mean S of the series is 0,017 mK.

Type B uncertainties:

When calculating the temperature difference between two cells, some sources of uncertainty are strongly correlated. These make a much reduced contribution to the uncertainty of the difference. For example, the uncertainty in the absolute value of the standard resistor or a possible long term drift of the thermometer have negligible influence.

The sources of type B uncertainty that are not correlated for measurements of temperature difference, their estimated values and a typical value for the experimental standard deviation S, are given in Table 19.

Source of uncertainty	uncertainties / mK
Bridge linearity and precision	0,01
Self heating correction	0,01
Hydrostatic pressure correction	0,009
Stray thermal exchanges	0,029
Temperature correction of the standard resistance	0,013
Standard deviation of the mean (10 measurements) S	0,017
Combined standard uncertainty	0,04

Table 19. Uncertainties in the comparison of cell temperatures.

The combined standard uncertainty U_c in the measurement of T_X - T_Y is expressed as:

$$U_c^2 = S^2 + \sum_{i=1}^{5} U_i^2 \ ,$$

where U_i represents the value of the ith type B uncertainty.

5. CHARACTERIZATION OF THE BIPM COMPARISON SYSTEM

Each set of travelling cells was measured by the corresponding group of three national laboratories and by the BIPM. From the individual results an estimate can be made of the reproducibility of the triple point given by these cells. Comparison of the results obtained by laboratories of the same group provides a means to evaluate the equivalence of the measurement procedures. This is meaningful, however, only if the travelling cells are stable: that is they must be stable to within limits not greatly exceeding the uncertainties of the measurements. The assessment of stability was, therefore, one of the main concerns of the BIPM: the comparison depends on the stability of the references kept at the BIPM and on the stability of its measurement system.

5.1 Stability of the measurement system

A comparison cycle involving 5 cells lasts 6 to 7 hours. During this period, the standard resistance temperature is monitored so that corrections for temperature drift can be made. Variations of the thermometer characteristics due to manipulation when passing it from cell to cell are assumed to be negligible. The standard resistor was, nevertheless, recalibrated by the Electricity section of the BIPM during the course of the comparison. The resistance ratio $W_{(Ga)}$ of the thermometer was determined three times using the BIPM reference triple point of water cell and a gallium cell. The value of $W_{(Ga)}$ was stable to 5 parts in 10^7, representing 0,1 mK on the interval (T_{TP} - T_{Ga}). These variations have no significant influence on the temperature differences calculated from the resistance measurements over the 18 months of the comparison.

Other types of thermometer were also tested, but no significant change was found in the comparison of the cells, and the same thermometer was used over the whole comparison.

5.2 Stability of the reference cell

Five cells were compared in a random order, in each of the daily measurement cycles. The reference cell was always one of them, both as a common reference and as a means of checking the stability of the whole measurement system. Furthermore, a cell taken from the additional reference set was always used in conjunction with the reference cell. This allowed calculation of day-to-day temperature differences between the reference and the additional reference over a long period of time. The PTK2 cell was first used as such an additional reference, but unfortunately it was damaged after several months of measurements [3]. It was then replaced by PTK1. Figure 8 shows all the recorded temperature differences between these additional references and the main reference PT131. Values are plotted as a function of the number of the measurement, starting from the first comparisons in March 1994 and ending with the last comparisons in December 1995. On the plot, different points correspond to different days but they are not necessarily equally spaced in time.

This data was used to estimate the stability of the reference pairs. Several statistical tests were applied to the two series to confirm that they can be considered as randomly distributed populations and, more specifically, to check for drift or abnormal oscillations.

The two series have approximately the same number of elements (49 and 53) and their experimental standard deviations are almost equal: 0,054 mK and 0,056 mK respectively. The mean values are slightly different, but this is of no consequence as the stability is the only point of interest.

When comparing two cells, their temperature difference is usually calculated as the average value of 10 successive measured differences determined over 10 different days. As a first step, therefore, the standard deviations of subsets of 10 elements were compared with the standard deviation of the whole population. They were found to be very similar, showing that the dispersion of the measurements did not change significantly with time.

More accurate tests were:

- non-parametric test of the series[4].

This test is based on the number of continuous series of elements situated on each side of the median. It shows that at the 95% confidence level the two populations can be considered as randomly distributed. No slopes, or fast oscillations were detected.

- comparison of the long-term and short-term variances [4].

This also showed that at the 95% confidence level, the system can be considered under statistical control, with no significant drift nor abnormal oscillations.

- Calculation of the Allan variance shows no drift or abnormal oscillations.

In addition, the stability of both the reference cell and the travelling cells can be checked against the additional reference set.

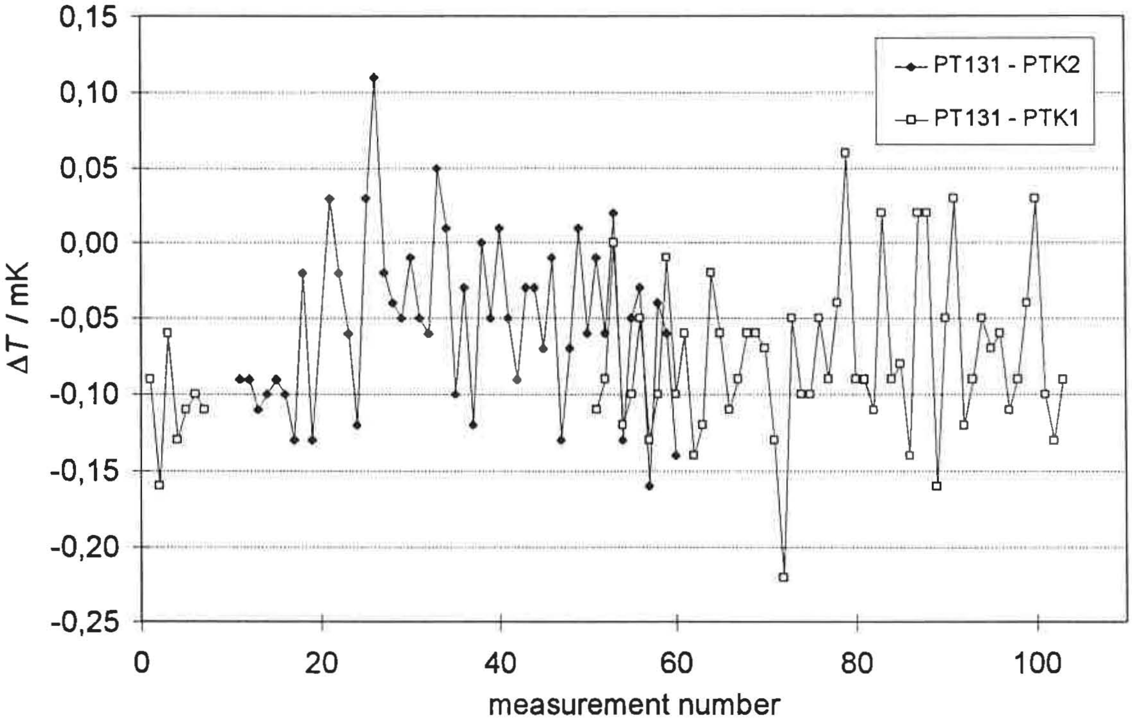


Figure 8. Temperature difference ΔT between the reference cell PT131 and two additional reference cells, first PTK2 and later PTK1, over the whole period of the international comparison. Diamonds (-◆-): $\Delta T = T_{PT131} - T_{PTK2}$. Squares (-□-): $\Delta T = T_{PT131} - T_{PTK1}$.

5.3 Stability of the additional reference set

The right side of Figure 9 shows the change in the temperature difference between the reference and each of the cells of the additional reference set: the difference found before the travelling cells were sent $(T_{cell} - T_{ref})_{before}$ is subtracted from the value $(T_{cell} - T_{ref})_{after}$ obtained 18 months later.

The type B uncertainties of the two measurements are strongly correlated, so that the uncertainty in the differences

$$(T_{cell} - T_{ref})_{after} - (T_{cell} - T_{ref})_{before}$$

plotted in this graph is essentially the quadratic sum of the experimental standard deviations of the mean. The uncertainty bars shown are 3σ values.

The changes are about 0,02 mK, clearly smaller than the uncertainty on the calculated differences. Moreover, the average value of the changes in the reference set is even smaller: 0,009 mK.

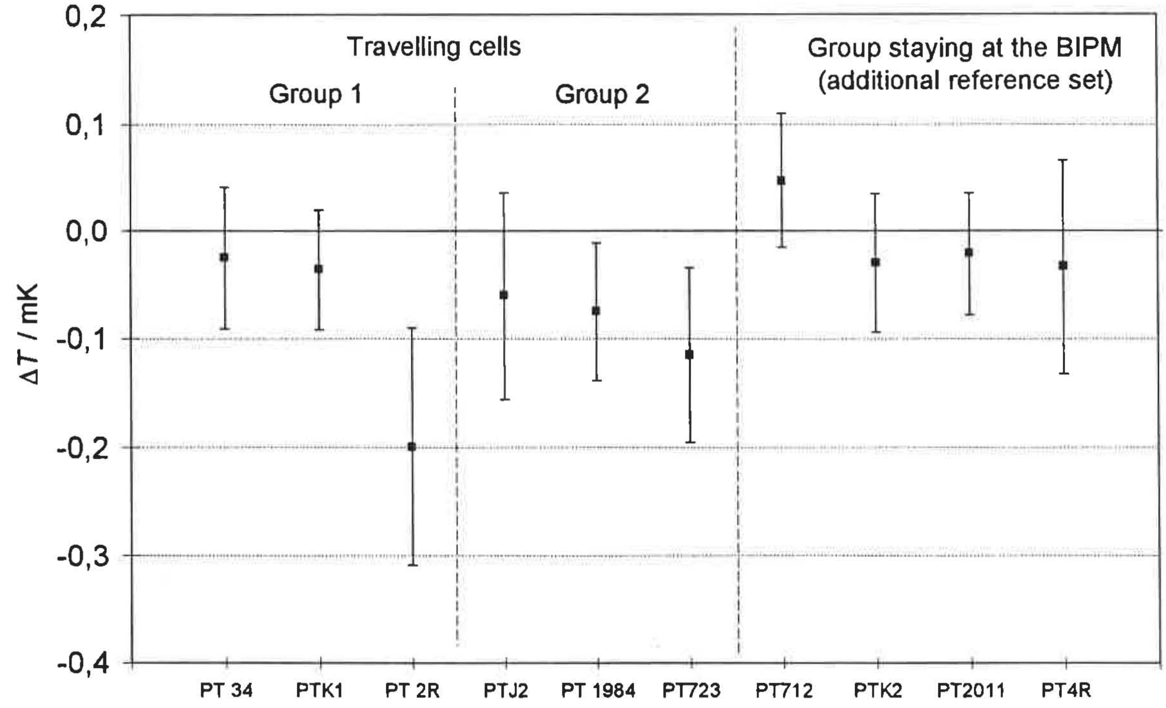


Figure 9. Stability of the travelling cells and of the additional reference set staying at the BIPM: change of the difference $(T_{cell} - T_{ref})$ before and after circulation. (3σ uncertainty bars). $\Delta T = (T_{cell} - T_{ref})_{after} - (T_{cell} - T_{ref})_{before}$.

5.4 Conclusion

From all these verifications we conclude that if changes in the comparison system occurred, their amplitude is hidden by the dispersion of the measurements. This dispersion can reasonably be described by a random population of constant mean value and of standard deviation of 0,055 mK.

As a consequence, no correction for drift or variation of the reference was made when using the BIPM system to compare cells over the whole period of the international comparison.

5.5 Other investigations on the dispersion

Figure 8 shows that the day to day variations of the measurements can be as large as 0,15 mK. To check if this dispersion was related to changes in the experimental conditions from one day to another, the temperature in the reference cell was measured four times per day during two consecutive days. Each measurement was made following exactly the procedure used for the comparison of several cells, except that after removing the thermometer from the cell, it was returned to the same position, instead of being transferred to another cell. The standard deviations of the measurements made each day were 0,04 mK and 0,05 mK. These values are very close to those observed for measurements made on successive days, either with this cell or with other types of cell.

Our conclusion is that the data dispersion cannot be reduced by comparing a smaller number of cells several times per day. Moreover, comparing five cells per day over two or three weeks has the benefit that they are observed over a longer period without loosing precision in the comparison.

5.6 Stability of the travelling cells

Figure 9 shows that some cells exhibit a change in temperature significantly larger than the uncertainties of the measurements. This is especially true for PT2R with a change of -0,2 mK, whereas PT4R, of the same type and origin (VNIIM), was stable. Cells PT723 (travelling cell) and PT712 (kept at the BIPM) were both constructed by the NPL but show changes of opposite signs. Apart from PT2R, changes are about 0,05 mK. This is not negligible, being comparable with the uncertainties given by the participating laboratories. Moreover, the relative changes within the sets of travelling cells are smaller, leading to closer results for laboratories of the same group.

triple point cell	[$(T_{cell} - T_{ref})_{after}$ - $(T_{cell} - T_{ref})_{before}$] / mK	standard uncertainty / mK
PT 34	-0,02	0,022
PTK1	-0,04	0,019
PT 2R	-0,20	0,036
PTJ2	-0,06	0,032
PT 1984	-0,07	0,021
PT723	-0,11	0,027
PT712	0,05	0,021
PTK2	-0,03	0,022
PT2011	-0,02	0,019
PT4R	-0,03	0,033

Table 20. Stability of the travelling cells and of the additional reference set (set staying at the BIPM).

6. OVERALL RESULTS

6.1 Group 1

As three cells were available, two temperature differences can be calculated:

$(T_{PTK1} - T_{PT34})$ and $(T_{PT2R} - T_{PT34})$.

These values were derived by the BIPM from the results given by the NIST and the NPL, the associated standard uncertainty being that given by the laboratory for the comparison of two cells.

For the INM, the data are available directly in the laboratory report with the corresponding uncertainty. They are shown in Figure 10, together with the results obtained by the BIPM before the cells were sent (BIPM Start) and after their return (BIPM End). The approximate date of the measurements is also given on the graph. Numerical values and uncertainties are summarised in Table 21.

The temperature differences $(T_{PTK1} - T_{PT34})$ are close and clearly lie within the uncertainties of the measurements. The mean difference is 0,04 mK with a standard uncertainty of 0,006 mK. The mean is well within the limits generally accepted for the reproducibility of the triple point of water [7].

Laboratories also agree on the much larger difference $(T_{PT2R} - T_{PT34})$, about 0,2 mK, due to the cell PT2R which seems to be different from the other two. The standard deviation of the results (BIPM Start, NPL, NIST, INM) is 0,035 mK. Clearly the agreement is not so good.

6.2 Group 2

With the cells in set No 2, the two temperature differences calculated are: (T_{PTJ2} - T_{PT1984}) and (T_{PT723} - T_{PT1984}).

They were derived from the national reports the same way as with Group 1. Numerical values and standard uncertainties are summarised in Table 22.

Here again the BIPM, the IMGC, the KRISS and the VNIIM clearly agree within the uncertainties of the measurements, as shown on Figure 11. The standard deviations of the successive results are 0,026 mK and 0,031 mK for (T_{PTJ2} - T_{PT1984}) and (T_{PT723} - T_{PT1984}) respectively.

Difference in temperature / mK										
Cells	**BIPM** Start	uncert.	**NPL**	uncert.	**NIST**	uncert.	**INM Fr**	uncert.	**BIPM** End	uncert.
PTK1-PT34	0,041	0,04	0,043	0,022	0,035	0,010	0,050	0,050	0,038	0,04
PT2R-PT34	-0,196	0,04	-0,157	0,022	-0,120	0,010	-0,190	0,100	-0,370	0,04

Table 21. Group 1. Overall results: difference in temperature between the travelling cells as measured by the participating laboratories.

Difference in temperature / mK										
Cells	**BIPM** Start	uncert.	**IMGC**	uncert.	**KRISS**	uncert.	**VNIIM**	uncert.	**BIPM** End	uncert
PTJ2-PT1984	-0,042	0,04	-0,039	0,077	0,022	0,069	-0,044	0,024	-0,027	0,04
PT723-PT1984	-0,047	0,04	-0,067	0,077	0,000	0,069	-0,065	0,024	-0,087	0,04

Table 22. Group 2. Overall results: difference in temperature between the travelling cells as measured by the participating laboratories.

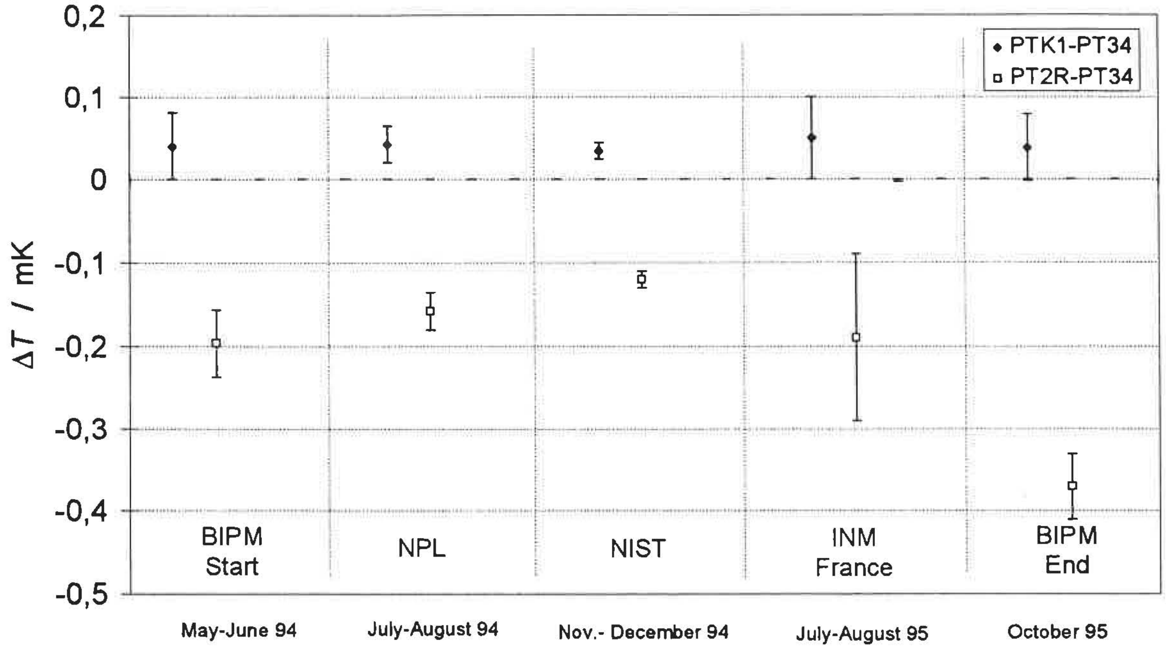


Figure 10. Group1. Difference in temperature ΔT between the travelling cells measured by the participating laboratories: ΔT (◆) = (T_{PTK1} - T_{PT34}) and ΔT (□) = (T_{PT2R} - T_{PT34}). Uncertainty bars represent the 1 σ uncertainty.

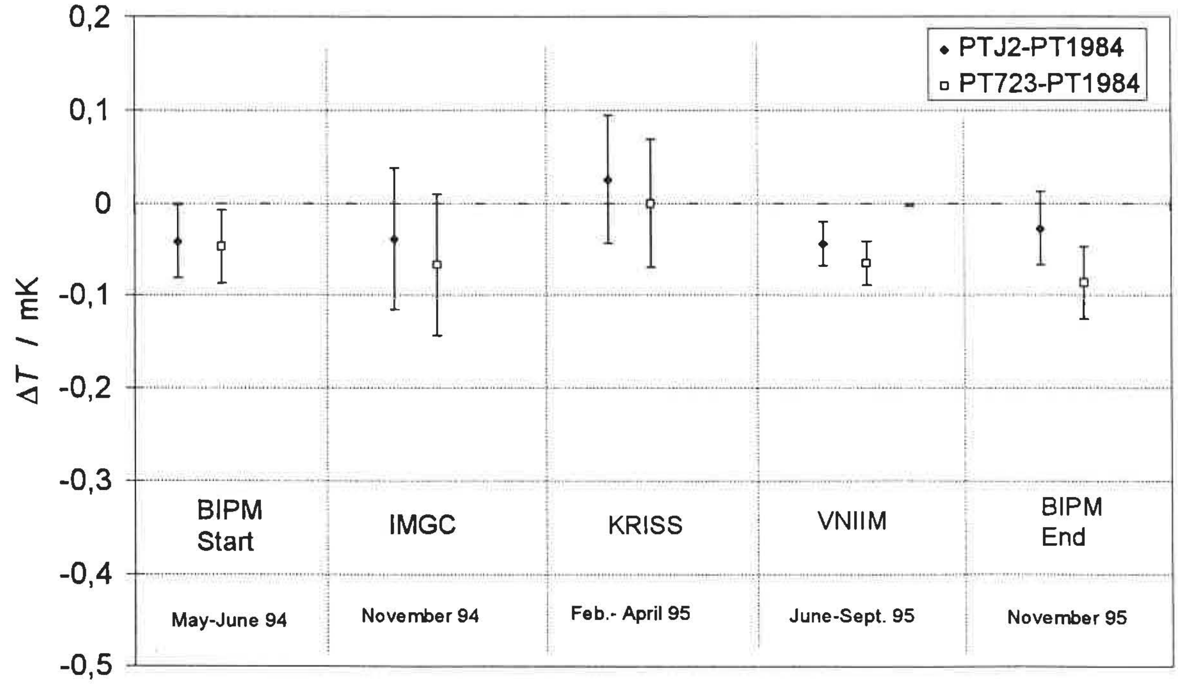


Figure 11. Group2. Difference in temperature ΔT between the travelling cells measured by the participating laboratories: ΔT(◆) = (T_{PTJ2} - T_{PT1984}) and ΔT(□) = (T_{PT723} - T_{PT1984}). Uncertainty bars represent the 1 σ uncertainty.

6.3 Comparison of the national reference cells

As the travelling cells were compared with national reference cells (the KRISS excepted), they can also be considered as transfer standards through which the national cells are indirectly compared with one another via the common reference.

Let $D_{\mathrm{Lab}} = (T_{\mathrm{travl}} - T_{\mathrm{Lab}})$ represent the temperature difference measured by a national laboratory between its reference cell and a travelling cell, and $D_{\mathrm{BIPM}} = (T_{\mathrm{travl}} - T_{\mathrm{ref}})$ the temperature difference measured by the BIPM between the common reference cell PT131 and the same travelling cell. The differences

$$D_{\mathrm{BIPM}} - D_{\mathrm{Lab}} = T_{\mathrm{Lab}} - T_{\mathrm{ref}}$$

were calculated for the NPL, the NIST, the INM France, the IMGC and the VNIIM reference cells. The value attributed to D_{Lab} and the corresponding uncertainty U_{Lab} is taken from the laboratory report.

Two values are available for D_{BIPM}: one before the travelling cell was sent and another one after its return to the BIPM. But there is no physical model to describe the behaviour of the travelling cells as a function of time between the two values: random steps may have occurred as well as linear drift. In the absence of other elements, it was decided to calculate D_{BIPM} as the mean of the two values D_{BIPM}(before) and D_{BIPM}(after). The uncertainty U_{A} on the mean value is calculated from the uncertainties of the two measurements. Then, assuming a rectangular probability distribution between two bounds D_{BIPM}(before) and D_{BIPM}(after), the uncertainty U_{Circ} associated with the behaviour of the cell during its circulation is calculated as follows:

$$\Delta T = \tfrac{1}{2}\,(D_{\mathrm{BIPM}}(\text{before}) - D_{\mathrm{BIPM}}(\text{after})),$$

and $$U_{\mathrm{Circ}} = \Delta T / \sqrt{3}\,.$$

The combined standard uncertainty U_{c} of the difference $(T_{\mathrm{Lab}} - T_{\mathrm{ref}})$ is then:

$$U_{\mathrm{c}}^2 = U_{\mathrm{Lab}}^2 + U_{\mathrm{A}}^2 + U_{\mathrm{Circ}}^2\,.$$

The results obtained from the three travelling cells were averaged for the Group 2. Two cells only were used for Group 1 as PT2R was found to be too unstable.

Numerical results are given in Table 23, and plotted in the Figure 12. They show excellent agreement between the national reference cells: the maximum difference is smaller than 0,14 mK and the standard deviation of the five values is 0,06 mK.

laboratory	[$T_{\text{Lab ref}}$ - $T_{\text{BIPM ref}}$] / mK	standard uncertainty / mK
NPL	-0,030	0,045
NIST	0,091	0,040
INM Fr.	0,088	0,063
IMGC	0,049	0,089
VNIIM	-0,046	0,051

Table 23. Temperature difference between the reference cells belonging to the national laboratories and the BIPM reference cell (indirect comparison).

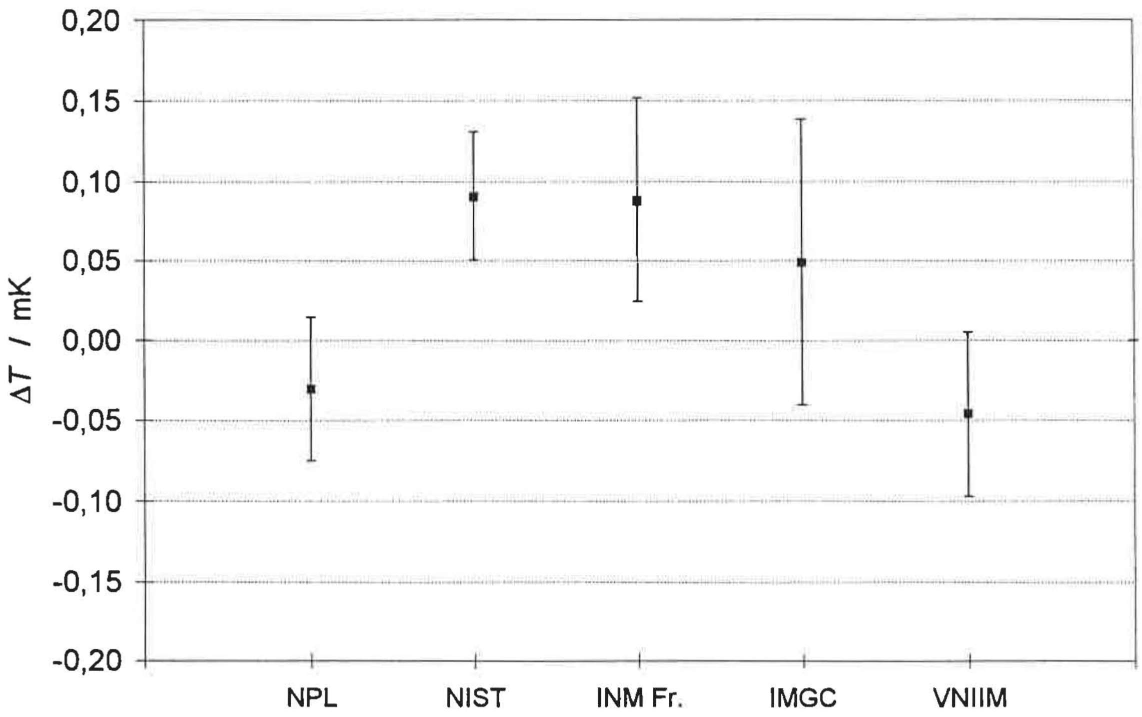


Figure 12. Difference in temperature $\Delta T = (T_{\text{lab ref}} - T_{\text{BIPM ref}})$, between the national reference cells and a BIPM reference cell (indirect comparison). Uncertainty bars represent the 1σ uncertainty.

6.4 Conclusions

The results plotted in Figure 10 and Figure 11 show that seven laboratories, using similar or different procedures and facilities, agree within their standard uncertainties (1σ) when measuring temperature differences between cells of different origin. The only exception is the last temperature measurement with PT2R in October 1995 at the BIPM, but is clearly due to a significant change of the cell. The consistency between the results reported by the laboratories is so close that it is evident that the uncertainties reported by most of the individual laboratories are too large. The laboratories report individual studies of the influence parameters. From the analysis of these reports it is not possible to draw conclusions about the influence parameters which have the strongest effects. A closer investigation is required.

The temperatures at which the triple point of water is realized are generally within ± 0,1mK of one another, but larger differences are sometimes observed. This means that if significant discrepancies were to be observed among the national temperature scales, the source of the disagreement could well lie in the realization of the triple point of water cells. These results also show that uncertainties arising from the reproducibility of the triple point of water are significant when attempting to establish a temperature scale at the highest level of accuracy. It could so be wise for a national laboratory to maintain a set of cells of different origin to avoid systematic differences with other scales, as well as to detect any possible abnormal behaviour of the triple point cells. The systematic use of a gallium cell [5, 6] is an alternative way to check stability, as the repeatability of the gallium point has shown to be at least as good as that of the most stable triple point of water cells.

APPENDIX 1. GROUP 3

The six other laboratories not included in the circulation scheme sent one or two cells to the BIPM where they were compared with the common reference cell and to the travelling cells. They were also invited to answer the questionnaire sent to the participants in groups 1 and 2. Some of these laboratories also included results of measurements related to the comparison. Abstracts from these reports are given at the end of the Appendix 1.

A1.1 Comparisons of cells from Group 3 at the BIPM

Group 3 cells were compared with BIPM reference cell PT131, following the procedures developed for Groups 1 and 2. For this reason, the results of the comparisons (T_{cell} - T_{ref}) for the three groups are plotted on the same graph in Figure 13. The values given for Groups 1 and 2 are those measured before circulation.

The uncertainty bars correspond to the BIPM standard uncertainty of 0,04 mK. Shown on the right side, the values measured for the cells from Group 3 agree among themselves with the travelling cells and with the additional reference set to within ±0,1 mK [7]. A clear exception is the cell sent by the INMETRO, which lies about 0,5 mK lower than the others. According to INMETRO this cell does not differ significantly from its other references. This means either that the cell was damaged during transport or that all the INMETRO cells are low in temperature.

The results also show that cells from the same laboratory do not necessarily agree closely. A difference of 0,12 mK was measured between the two cells sent by the NMi, and one of 0,17 mK between the cells sent by the IPQ.

Cell	$(T_{cell} - T_{ref})$ / mK
NPL 723	0,060
NPL 712	-0,037
(ETL) J2	0,065
1984(NIST-type)	0,107
2011(NIST-type)	0,111
IMGC 34	0,068
VNIIM 2R	-0,128
VNIIM 4R	-0,188
KRISS 1	0,109
KRISS 2	0,096
MSL 82/2	0,033
MSL 84 7	0,038
IPQ 033	0,033
IPQ 299	-0,137
SISIR	0,064
INMETRO	-0,526
NMi 94T214	0,043
NMi 89T084	-0,075
INM Rom.	-0,071

Table 24. Groups 1, 2 and 3: temperature differences between the cells and the BIPM reference cell.

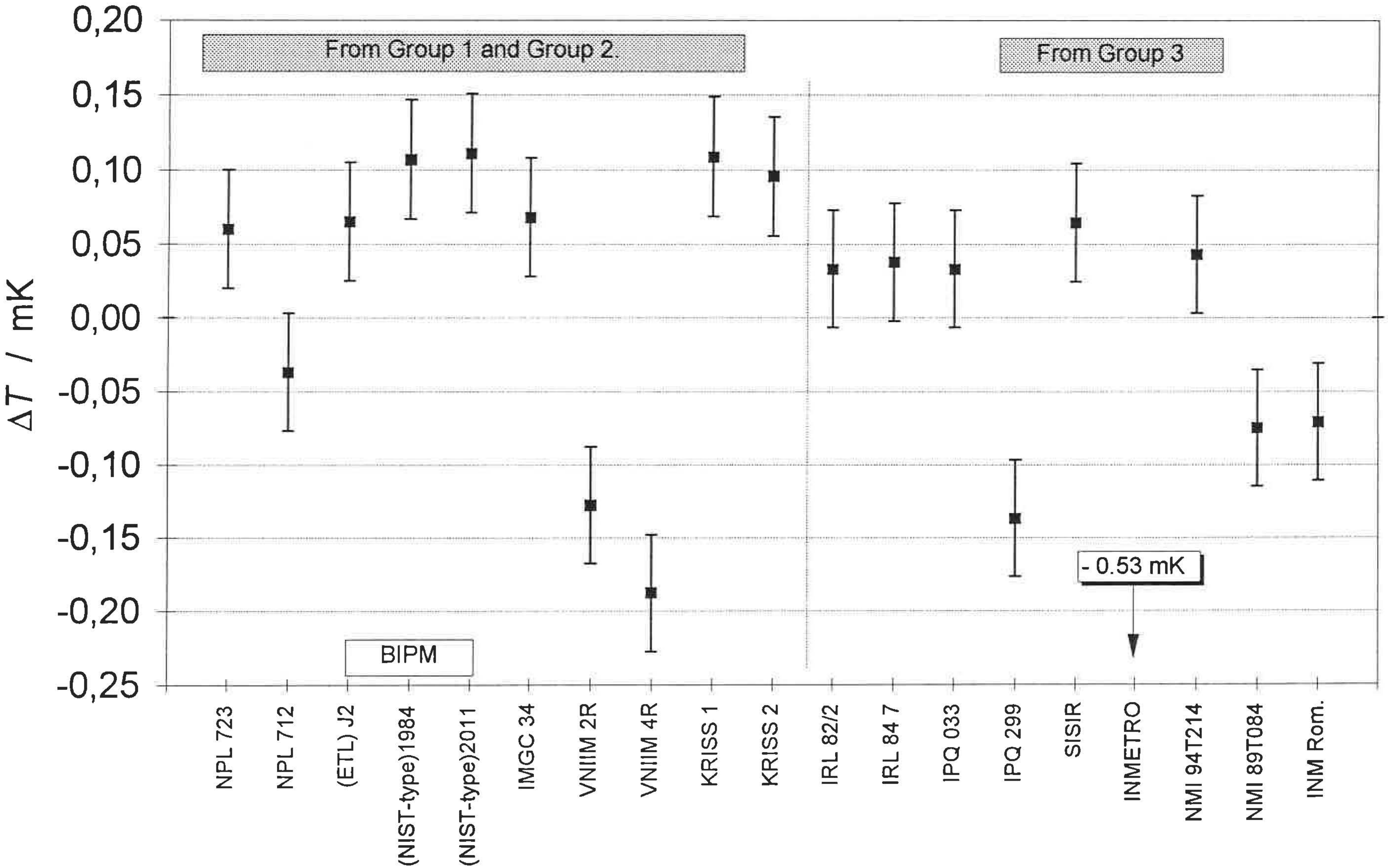


Figure 13. Groups 1, 2 and 3: temperature differences measured at the BIPM between the cells and the BIPM reference cell. $\Delta T = (T_{\text{cell}} - T_{\text{BIPM ref}})$. Uncertainty bars represent the 1σ uncertainty.

A1.2 Group3: abstracts from the laboratory reports

A1.2.1 MSL

The MSL sent two triple point of water cells first to the NMi, which compared them to two of its own reference cells. Four cells (two from the MSL and two from the NMi) were then sent to the BIPM. The cell MSL84/2 was not manufactured at MSL and known to have some preparation dependence. It was submitted as an example of a suspect cell of unacceptable quality to MSL.

Storage apparatus: cells are maintained under ice in a large self-draining vacuum flask. The assembly has a lid which shields the thermometer from any radiation and a piece of black felt covers its head.

Measurements begin ten days after formation of the ice mantle to allow all the ice crystals around the mantle to fully anneal.

Instrument types: ASL F18 bridge at 0,02 Hz. Currents : 1mA and $\sqrt{2}$ mA.

Standard resistor: Wilkins type maintained in a temperature controlled bath with a long term stability better than 0,02 K

Thermometer: The thermometer was not specified.

Comments: The MSL is the only laboratory giving an extensive uncertainty budget on the realization of the triple point, including information on the purity and on the isotopic composition of the water it used to fill its cells. This water has a slightly lower concentration of heavy isotopes [8] than mean ocean water, which depresses the point by 40 μK (with a standard uncertainty of 20 μK).

A1.2.2 IPQ

The IPQ sent two cells to the BIPM.

Date of fabrication of the IPQ cells: 1968 for the cell No 299

1995 for the cell No 033.

Storage apparatus: Yellow Spring bath, type 18233, controlled at ± 0,007°C.

Preparation of the triple point of water cells: cells are cooled with crushed solid CO_2.

Measurements begin 30 minutes after insertion of the thermometer into the well. A black cloth is used to protect the thermometer from radiation. Measurements are recorded with a chart recorder.

Instrument types: ASL F18 bridge. Currents : 1mA and $\sqrt{2}$ mA or 2 mA and $2\sqrt{2}$ mA.

Standard resistor: Tinsley 25Ω or 100Ω controlled at 20°C.

Thermometer: Tinsley or Yellow Spring.

Comments: IPQ cell No 299 was compared with BCR cell No 643 in May 1994 and with EUROMET cell No 679 in May 1995. The EUROMET results will be published in 1996 by the INM (France), the pilot laboratory.

A1.2.3 SISIR

The SISIR sent one cell to the BIPM.

Storage apparatus: cells are stored in a temperature controlled bath.

Preparation of the triple point of water cells: The lower parts of cells are cooled with crushed solid CO_2 in alcohol, the upper parts by freon gas cooled by liquid nitrogen.

Measurements begin 2 days after preparation. An ice-water interface is formed before measurements. Sufficient time is allowed for the thermometer to reach equilibrium in the cell. Protection of the triple point of water cell from light and thermal radiation is provided during measurements. At least two sets of readings are taken with twenty readings for each cell.

Instrument types: model 6010A DC bridge from Measurement International. Currents: 1 mA and $\sqrt{2}$ mA.

Standard resistor: Tinsley 25Ω maintained in a oil bath at 23,0 °C within ± 0,05 °C.

Thermometer: The thermometer was made by NIM.

Comments: The bridge is calibrated before measurements.

A1.2.4 INMETRO

The INMETRO sent one cell to the BIPM.

Storage apparatus: Cells are stored in a temperature controlled bath from ISOTECH model ITL-M-18233.

Preparation of triple point of water cells: cells are prepared using dry ice or liquid nitrogen. The process takes 4 hours. Once the mantle is ready and the well of the cell cleaned, a small amount of alcohol is poured into the well to improve the thermal contact.

Measurements: data are taken by hand.

Instrument types: Guildline bridge model 9975. Currents: 1 mA and $\sqrt{2}$ mA.

Standard resistor: Guildline model 9330 kept in a controlled bath Guildline model 9732 VT at 20°C.

Thermometers: Rosemount model 162 CE and Tinsley model 5187SA.

Comments: No significant difference was noticed at the INMETRO between the two cells kept in its laboratory.

A1.2.5 NMi

The NMi sent two cells to the BIPM.

Date of fabrication of the NMi cells: 1994 for the cell No VSL 94T214
1989 for the cell No VSL 89T084.

Storage apparatus: cells are stored in a temperature controlled bath made by NMi. A wooden lid with three further layers of polystyrene foam attached to its under side covers the bath.

Preparation of the triple point of water cells:

Each cell is precooled for at least 4 hours, typically for over one day. To form the ice mantle, the cell is cooled with a special system of two concentric tubes which allow liquid nitrogen to flow through the thermometer well. Alcohol is used in the thermometer well to ensure thermal contact. The freezing process takes approximately 15 to 25 min. The ice mantle diameter is approximately 35 mm.

Measurements begin one day after the preparation. A mixture of water-glycol is poured into the thermometer well to the same level as the water in the cell. An ice water interface is formed before inserting the thermometer into the cell. A black cloth prevents the cells from exposure to light during measurements.

Instrument types: ASL F18 bridge. Currents 1mA and √2 mA.

Standard resistor: Tinsley Wilkings 25Ω.

Thermometers: made by L&N, Rosemount and Tinsley.

Comments:

The NMi sent a detailed report on experiments concerning its thermometers, its experimental procedures and on the comparisons made between its cells and the cells from the MSL before they were sent to the BIPM.

cell	(T_{cell} - $T_{NMI\ reference}$) / mK	Uncertainty (2 σ level) / mK
VSL 94T214	0,05	0,06
VSL 89T085	-0,07	0,07
MSL PEL847	-0,01	0,08
MSL 84/2	-0,22	0,04

Table 25. Temperature difference measured at the NMi between MSL and NMi cells, and a NMi reference cell.

The NMi's report concludes that the difference between the NMi's local cells and the New-Zealand PEL847 cell is not significant, but that cell MSL 84/2 has a significantly lower realization temperature.

The BIPM received three of these cells: VSL 94T214, MSL PEL847, MSL 84/2, plus VSL 89T084. Comparison of the temperature differences measured by the NMi and the BIPM show:

-that neither laboratories found significant difference between the cells VSL94T214 and MSL PEL847.

-that repeated experiments at the BIPM showed no significant difference between MSL PEL847 and MSL84/2, whereas the NMi measured a discrepancy of more than 0,2 mK.

It should be noted that the NMi found a value of 0,12 mK for ($T_{VSL94T214}$ - $T_{VSL89T085}$), (see Table 25) and the BIPM found the same value for cell VSL 89T084. Since cells VSL89T085 and VSL89T084 are of identical design and construction it is reasonable to suppose that the cell MSL84/2 may really have changed its reference temperature. This behaviour is consistent with the behaviour observed by the MSL.

A1.2.6 INM (Romania)

The INM sent one cell to the BIPM

Date of fabrication of the INM cell: 1970.

Storage apparatus: Cells are stored in slush ice (without plastic container).

Preparation of triple point of water cells: Cells are cooled with CO_2 in alcohol. The process takes 10 to 20 minutes.

Measurements: Data acquisition is manual with more than 10 measurements.

Instrument types: Guildline bridge type 9975. Currents : 1mA and $\sqrt{2}$ mA.

Standard resistor: 10Ω Russian made with temperature correction.

Thermometer: Tinsley.

Comments: No significant difference was noticed at the INM between the cells kept in its laboratory (maximum difference of 10^{-4} K).

APPENDIX 2. STRANGE BEHAVIOUR OF SOME CELLS

During the course of the comparison, three cells exhibited behaviour [9, 10] for which no explanation has been found.

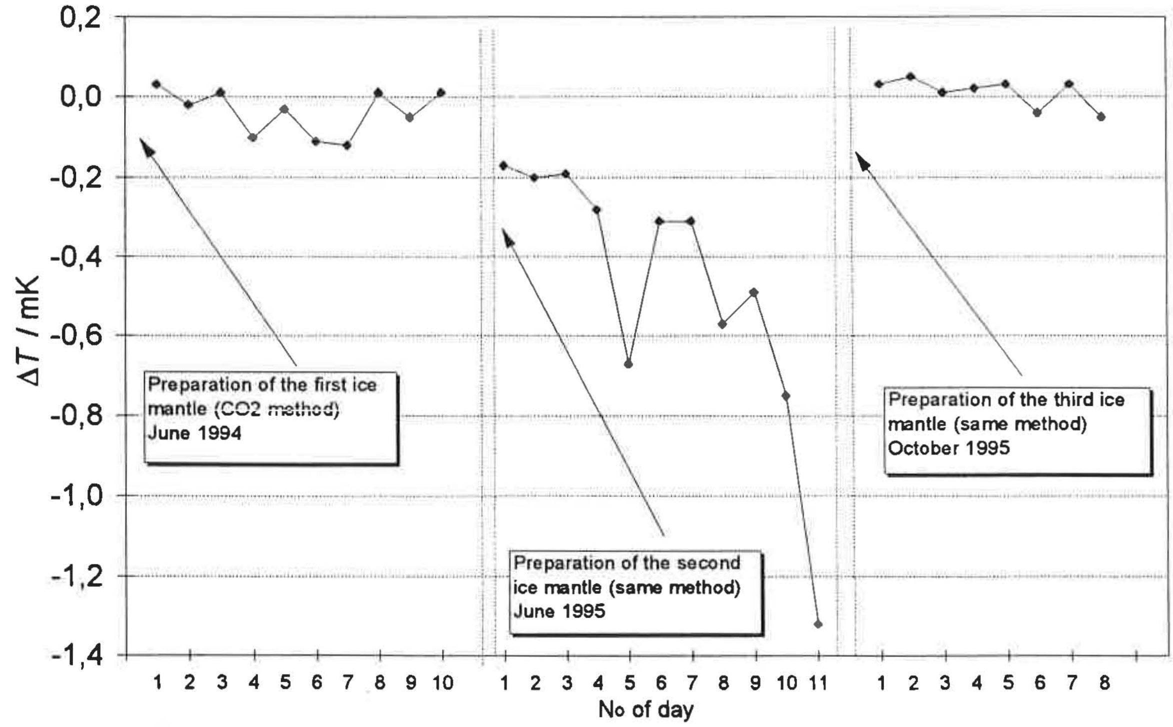


Figure 14. Strange behaviour of PT712. Temperature difference $\Delta T = (T_{PT712} - T_{BIPMref})$ measured at the BIPM. Standard uncertainty: 0,04 mK.

Figure 14 shows that the temperature of the cell PT712 was stable in June 1994. In 1995, it was again compared with reference cell PT131. During this second period, it drifted rapidly, its temperature decreasing by more than 1 mK in 10 days. The other three cells taking part in this comparison remained perfectly stable. The first explanation proposed was that the cell was leaking, but no visible damage was found. The ice mantle had been made the same way as for the other cells and showed no visible defect.

When the cell was checked again in October 1995 it had, surprisingly, retrieved its previous value. The values found in June 1995 were discarded, but no satisfactory explanation has been discovered.

Other cells showed significant instabilities: see Figure 15 and Figure 16. Here again, other cells measured at the same time were stable. The case of PT494 (the INMETRO cell) is different from the others, as it is both unstable and very low in temperature.

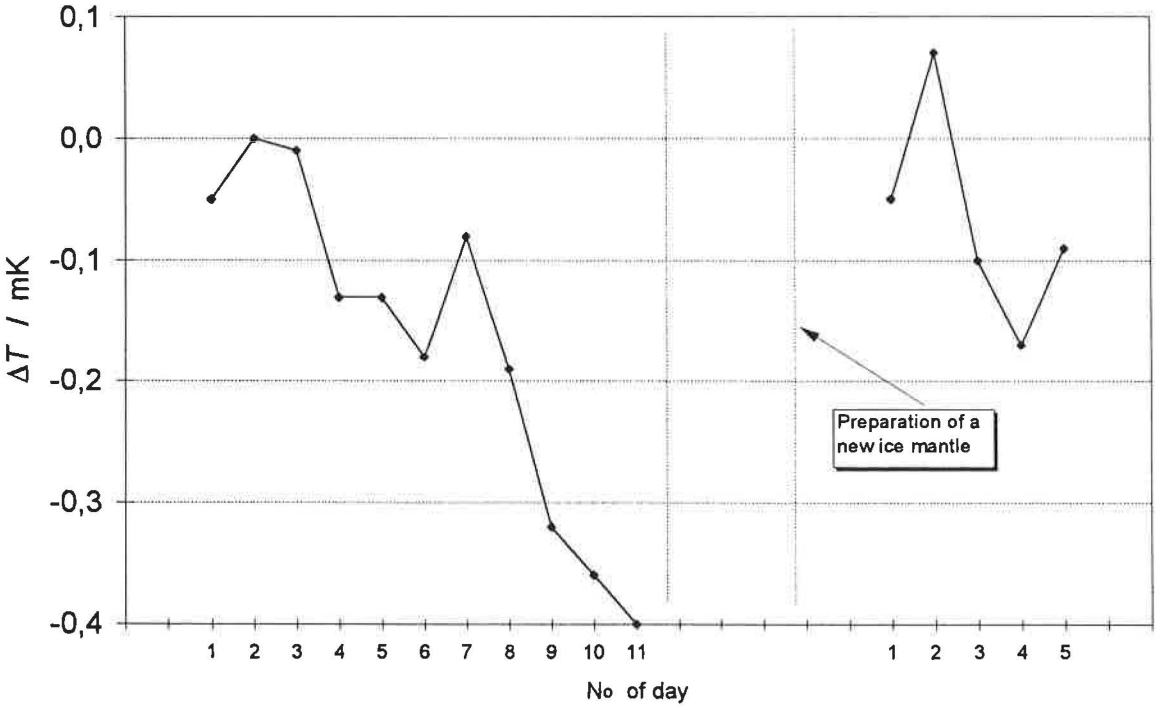


Figure 15. Strange behaviour of the PT299 cell.Temperature difference $\Delta T = (T_{PT299} - T_{BIPMref})$ measured at the BIPM. Standard uncertainty: 0,04 mK.

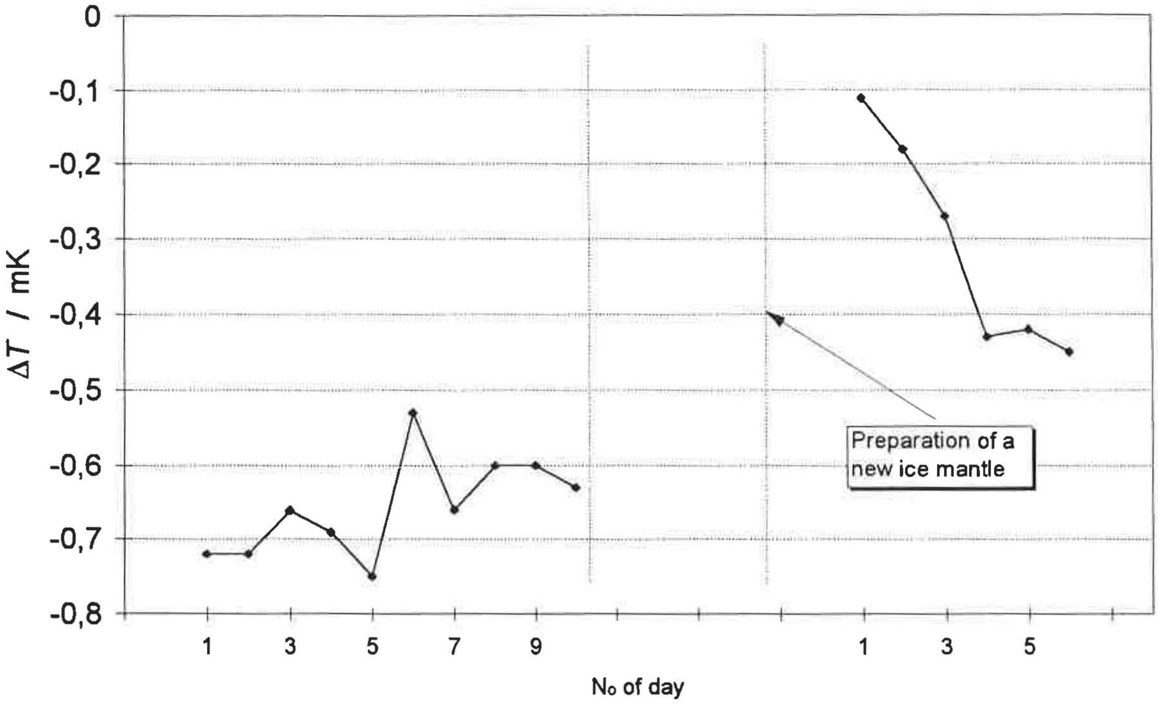


Figure 16. Strange behaviour of the PT494 cell.Temperature difference $\Delta T = (T_{PT494} - T_{BIPMref})$ measured at the BIPM. Standard uncertainty: 0,04 mK.

Cell MSL 84/2 behaved similarly (see paragraph A1.2.5): its temperature probably increased by about 0,2 mK when transported from the NMi to the BIPM.

List of acronyms used in this report

BIPM	Bureau International des Poids et Mesures, Sèvres (France)
ETL	Electrotechnical Laboratory, Tsukuba (Japan)
IMGC	Istituto di Metrologia G. Colonnetti, Turino (Italy)
INM	Institut National de Métrologie, Paris (France)
INM	Institutul National de Metrologie, Bucuresti (Romania)
INMETRO	National Institute of Metrology, Standardization and Industrial Quality (Brazil)
IPQ	Portuguese Institute for Quality, Monte Da Caparica (Portugal)
MSL	Measurements Standards Laboratory, Lower Hutt (New Zealand)
KRISS	Korea Research Institute of standards and Science, Taejon (Rep. of Korea)
NIM	National Institute of Metrology, Beijing (People's Rep. of China)
NIST	National Institute of Standards and Technology, Gaithersburg (USA)
NMi / VSL	Nederlands Meetinstitut, Delft (The Netherlands)
NPL	National Physical Laboratory, Teddington (UK)
PTB	Physikalisch-Technische Bundesanstalt (Germany)
SISIR	Singapore Institute of Standards and Industrial Research (Singapore)
VNIIM	D.I. Mendeleyev Institute for Metrology, Saint - Pétersbourg (Russia)

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INMETRO	P.R. da Fonseca Santos
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