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BIPM Project

Intercomparison of water triple-point cells

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ABSTRACT

The paper presents the results of an intercomparison between 3 triple point of water cells circulated by the Bureau International des Poids et Mesures (BIPM), and a cell which is one of those used as a reference cell at the National Physical Laboratory. All 4 cells were prepared, stored and measured in the manner normally adopted at NPL.

The results of the intercomparison show that over the course of about 6 weeks the temperatures of the 3 circulated cells generally agreed within 0.20 mK, with a maximum difference of 0.27 mK. Over the same period, the total variations of temperature measured in the 3 individual cells were 0.04 mK, 0.08 mK and 0.18 mK, respectively; the NPL cell varied by 0.10 mK. Gallium point measurements made over a similar period confirmed that these differences were partly due to small drifts in the thermometer resistance or in the measuring system.

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1. INTRODUCTION

The project was organised by the BIPM following a recommendation [T2 (1993)] concerning the use of triple point of water cells which was adopted at the 1993 meeting of the Consultative Committee for Thermometry.

On the basis of this recommendation, the BIPM collected together a number of cells from different manufacturing sources around the world, and arranged for their circulation to the participating laboratories. Each laboratory was instructed to use its usual method of 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 as a reference.

To expedite the comparisons and to avoid the necessity for each laboratory to measure a large number of cells, the 6 cells to be used were divided into 2 groups of 3 cells, and the 6 participating laboratories were separated into 2 groups each comprising 3 laboratories plus the BIPM, which would initially intercompare all 6 cells and act as a link between the two groups of laboratories.

At NPL, it was decided to include in the intercomparison an NPL cell which is normally used as a reference cell; in addition, occasional measurements with a gallium melting point cell would be included.

2. DESCRIPTION OF APPARATUS

Triple point cells circulated by BIPM

These comprised 3 cells, identified and described as follows:

Cell no. 34, supplied by IMGC, Italy.

It has a nominal outside diameter of 56 mm, an overall length of 406 mm, a thermometer well of nominal internal diameter 10 mm and the bottom of the well is approximately 255 mm below the water surface when the cell is in a vertical position.

Cell no. 1, supplied by KRISS, Korea.

It has a nominal outside diameter of 50 mm, an overall length of 395 mm, a thermometer well of nominal internal diameter 12.5 mm and the bottom of the well is approximately 277 mm below the water surface.

Cell no. 2R, supplied by VNIIM, Russia.

This cell has an outside diameter of 51 mm, an overall length of 460 mm (including a protecting cover for the glass seal at the bottom), a well of internal diameter 9.5 mm and a water depth such that the bottom of the well is 212 mm below the water surface.

Triple point cell used by NPL

This is a cell numbered 555, made at NPL; it has an outside diameter of 40 mm, with an

overall length of 372 mm. It contains a thermometer well with an internal diameter of 12 mm, and the water level is 216 mm above the bottom of the thermometer well.

2.1.3 Gallium melting point cell used by NPL

A cell (no. 6) with a PTFE body, constructed and filled at NPL, was used occasionally as an additional check on the stability of the thermometer. Before each measurement, the gallium was solidified; the cell was then placed in an oil bath at 30 °C and a small heater was employed to create a liquid/solid interface adjacent to the thermometer well before insertion of the SPRT.

2.2 Storage apparatus

Between measurements, the water cells were stored in individual acrylic or polyethylene tubes suspended in ice contained in the storage compartment of an ice-flaking machine.

For measurement, each water cell was transferred to a stainless steel Dewar (vacuum) vessel, where it was packed directly in ice. The length of the Dewar was such that the body of the cell was totally immersed in ice, only the top of the thermometer well protruding. The Dewar was placed in a wooden box (internal dimensions 220 x 220 x 1050 mm high), the thermometer was inserted and a wooden lid was fitted to protect the cell and the thermometer from external radiation.

2.3 Measurement apparatus.

The equipment consisted of a Chino standard platinum resistance thermometer (Type R 800-2), measured by comparison with a Tinsley 25 ohm standard resistor (Type 5684 S), using an Automatic Systems Laboratories resistance bridge (Type F18).

3. PREPARATION OF WATER TRIPLE POINT CELLS

Each cell was cooled in ice for at least 1 hour; its thermometer well was then carefully dried with compressed air, after rinsing with acetone. Next, crushed solid carbon dioxide was poured into the well to a level similar to that of the water; it was continually topped up until the ice sheath appeared to be about 6 to 8 mm thick. From this stage onwards, no further CO₂ was added, that in the cell being allowed to sublime until the ice cap was reasonably uniform in thickness. Any remaining CO₂ was then tipped out, and the well was filled with ice-cold water. The cell was then repacked in ice and left for around 20 hours before being prepared for use by melting an interface between the ice sheath and the thermometer well by the insertion of a metal rod into the well for a few seconds. The freedom of the sheath was checked by ensuring that it would rotate freely around the well, before any measurements were commenced.

4. MEASUREMENTS

The first measurements were commenced just over 18 hours after completion of the formation of the ice sheaths on the cells.

After freeing the ice sheath of a cell by creating a water-ice interface around the thermometer well and then setting it up in the Dewar so that the body of the cell was covered by ice, the Dewar was placed in the wooden box to protect the thermometer and cell from stray radiation, and the pre-cooled thermometer was carefully inserted. After at least 20 minutes, measurements were commenced, using an F18 resistance bridge. The bridge was used in the "manual" mode, with a chart recorder connected across the analogue output socket; the trace was used to subdivide the last digit of the bridge reading to 1 part in 10^8 of ratio, (equivalent to $2.5 \times 10^{-7} \Omega$, ie to 0.002₅ mK). The temperature of the standard resistor was monitored, and corrections were applied to allow for small departures from 20°C. Measurements were made with currents of 1 mA and $\sqrt{2}$ mA, and self-heating was corrected for by subtracting the difference between the two values from that measured with 1 mA.

On completion of the measurements in the first cell, the thermometer was transferred directly to the second cell, which was contained in a Dewar of ice standing in a box identical to that used previously; measurements were commenced about 20 minutes later. Thereafter, the SPRT was transferred from cell to cell, each cell being measured, with the 2 currents, at least twice in each set. When the day's comparisons were finished, the cells were transferred back to their normal overnight storage container.

On examination of the circulated cells prior to their measurement next day, it was observed that the ice sheaths were very thin at the bases of their thermometer wells; it seemed unlikely that they would remain useable for more than a few days, so following the completion of the day's set of measurements, the ice sheaths on these 3 cells were melted and the preparation process described in (3) above was repeated.

The following day, the measurement sequence above was repeated, after which the thermometer was measured at the melting point of gallium. Measurements of all cells were made at intervals over the next week or so; on some days the gallium point was included.

On the 9th day following its initial preparation, NPL cell 555 was found to have a broken ice sheath, so it was melted and then re-made. Five days later it was again necessary to prepare a fresh ice mantle on 555, and 18 days later it was necessary to prepare it again because it was considered that its ice sheath was of inadequate thickness and length.

The comparisons were concluded 44 days after the preparation of the circulated cells on the second day of the comparisons; at this stage it was observed that there was considerably more ice around the bottom cap of each ice sheath than when the cell was first prepared.

5. RESULTS

The results have been listed in Table I, which give the resistance of the standard platinum resistance thermometer, corrected for self-heating, at the various stages of the measurements in the water cells. It also lists the corrected resistances of the thermometer when measured in the NPL gallium melting point cell.

The measured resistance of the thermometer when in the circulated water cells has been adjusted to allow for the small temperature differences which occur at the level of the centre of the thermometer sensing resistor due to the effects of the different depths of water in the cells. For convenience, the readings taken in the 3 circulated cells have been adjusted by the following amounts to bring them to the level of the NPL cell (corresponding to -0.73 mK per metre of water).

Cell No	Depth of bottom of thermometer well below water surface	Difference from NPL Cell 555	Correction
	216 mm		
2R	212	4 mm	-0.000 003 °C
	255	39	+0.000 028
	277	61	+0.000 044

Table II lists the mean resistance thermometer reading measured in all 4 cells on each day, together with the departure of each cell from the mean. The individual resistances measured in each water cell have been plotted in Figure 1; the mean of the resistances measured in the 4 water cells have been plotted, together with the resistance in the gallium cell, in Figure 2.

6. UNCERTAINTIES

(a) Water Triple Point Cell Comparisons

Considering only the **differences between the measured temperatures in the various water cells on each occasion of comparison**, the same thermometer being transferred from cell to cell over a period of a few hours on each day, many of the uncertainties normally associated with measurements of SPRTs in water triple point cells were reduced. For example, there are unlikely to have been any differences in temperature in the cells due to spurious heat flux differences in the surroundings to the cells and the SPRT because all measurements were made in identical cell enclosures. Similarly, in view of the short period over which each set of comparisons was made, changes due to drifts in the standard resistor or the bridge are unlikely to have had much effect on the results. The uncertainty components which were considered relevant have been estimated from the results, under the following headings, and expressed as 2 sigma values (ie at 95% confidence level):

Type A: determined from the differences between repeated measurements of the same cell, on the same day, using the same SPRT. 0.03 mK

Type B: (i) resistance measurement - due to short-term variations in the standard resistor caused by small changes in temperature; electrical interference from adjacent equipment. 0.025

(ii) hydrostatic correction due to different water levels in the cells 0.001

(iii) determination of thermometer self-heating corrections, including uncertainty in $\sqrt{2}$ current ratio 0.02

Combined uncertainty (2 sigma) = 0.044 mK

(b) Gallium Melting Point Measurements

Considering the changes in the temperature in the gallium cell, as indicated by the resistance of the thermometer, over the total period of the comparisons, the associated uncertainties are virtually the same as for the water cell comparisons.

7. ANALYSIS OF RESULTS

(a) The results in Table I and Figure 1 show that over the total period of the measurements the thermometer indicated the following maximum changes (expressed in temperature units) in each cell.

Cell 1: maximum change over the 44 days following its preparation = 0.043 mK
(between 15 and 22 July).

Cell N34: maximum change over the 44 days following its preparation = 0.083 mK
(between 23 June and 15 July).

Cell 2R: maximum change over the 44 days following its preparation = 0.181 mK
(between 24 June and 5 August).

Cell 555: maximum change over the 44 days following its initial preparation,
(including 3 new preparations) = 0.100 mK

(b) The mean water triple point values, measured each day (Table II and Figure 2), show a maximum range equivalent to 0.071 mK (24 June to 5 August).

(c) The total range of the measured resistances at the gallium melting point was equivalent to 0.048 mK (11 July to 18 July).

- (d) The curves in Figure 2 show fairly good correlation between the mean water triple point and the gallium melting point at the various stages of the measurements, indicating that the measured changes at both fixed points were partly due to changes in the residual resistance of the thermometer, or in the resistance measurement system.
- (e) The maximum differences between the temperatures in the 4 cells occurred between No1 and 2R, an initial difference (No1 - 2R) of 0.18 mK on 23 June gradually increasing to 0.28 mK towards the end of the measurements.
- (f) The average differences between the temperatures in the individual cells and the mean values of all 4 cells are set out at the foot of Table I. They range from +0.09 mK (Cell 1) to -0.11 mK (Cell 2R).

8. CONCLUSIONS

Comparing the temperatures recorded in the individual cells with the mean of the temperatures in all 4 cells on each day, the average difference was within 0.05 mK for Cells N34 and 555, 0.09 mK for Cell 1 and 0.11 mK for Cell 2R. Cell 1 was always at the highest temperature, while 2R was at the lowest.

When the individual cell temperatures were compared, the results showed that the largest differences were between Cells 1 and 2R, 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 their initial preparation, by which time the ice mantle on 2R had become very large at the base of the re-entrant well, and the inner water/ice interface temperature may have been influenced by thermal conduction to the ice mixture outside the cell.

The total variations in the temperatures measured in the individual cells over the 44 days of the experiment ranged from 0.043 mK (Cell 1) to 0.181 mK (Cell 2R). For comparison, the measurements made in the gallium cell showed a total range of 0.048 mK, while the mean temperatures in the 4 water cells exhibited a range of 0.071 mK; in general, the gradual changes in the mean water triple point temperatures were reflected in the gallium measurements, indicating that they were probably largely due to variations in the thermometer or in the resistance measuring system.

Summarising - the results showed a maximum difference in temperature of 0.28 mK, between 2 of the 3 circulated water triple point cells which were intercompared. Over the period of the measurements (approximately 44 days) the overall changes in temperature measured in the individual cells ranged between 0.04 mK (Cell 1), 0.08 mK (Cell N34) and 0.18 mK (Cell 2R); during this period the NPL Cell (555) changed by 0.10 mK. However, gallium point measurements made from time to time indicated that part of those changes was probably due to variations in the thermometer or the measuring system.

TABLE I

**RESISTANCE THERMOMETER READINGS (CORRECTED FOR SELF-HEATING;
READINGS IN WATER CELLS ALSO ADJUSTED FOR HYDROSTATIC PRESSURE
DIFFERENCES FROM NPL CELL 555)**

Date	NPL cell 555	Cell N34	Cell 1	Cell 2R	Gallium cell
21/6/94	PREPARED	PREPARED	PREPARED	PREPARED	
22/6/94	25.6265707 Ω	25.6265785 Ω PREPARED	25.6265798 Ω PREPARED	25.6265659 Ω PREPARED	
23/6/94	25.6265721	25.6265813	25.6265819	25.6265642	28.6531685 Ω
24/6/94	25.6265722	25.6265794	25.6265820	25.6265708	
27/6/94	25.6265671	25.6265796	25.6265809	25.6265683	28.6531669
30/6/94	— PREPARED	25.6265776	25.6265824	25.6265667	
05/7/94	25.6265671 PREPARED	25.6265766	25.6265802	25.6265597	
08/7/94	25.6265684	25.6265752	25.6265797	25.6265605	
11/7/94	25.6265709	25.6265753	25.6265791	25.6265594	28.6531639
15/7/94	25.6265672	25.6265730	25.6265786	25.6265579	
18/7/94	25.6265652 PREPARED	25.6265732	25.6265810	25.6265595	28.6531687
19/7/94	25.6265732	25.6265751	25.6265802	25.6265630	
20/7/94	25.6265732	25.6265766	25.6265810	25.6265613	28.6531678
22/7/94	25.6265697	25.6265745	25.6265829	25.6265592	
25/7/94	25.6265645	25.6265753	25.6265819	25.6265582	
28/7/94	25.6265661	25.6265758	25.6265824	25.6265582	
1/8/94	25.6265632	25.6265771	25.6265819	25.6265542	28.6531676
3/8/94	25.6265659	25.6265766	25.6265804	25.6265558	
5/8/94	25.6265650	25.6265783	25.6265799	25.6265527	28.6531666

TABLE II

**MEAN RESISTANCE THERMOMETER READINGS AND DEPARTURES FROM MEAN
(CORRECTED FOR SELF-HEATING AND ADJUSTED FOR HYDROSTATIC PRESSURE
DIFFERENCES FROM NPL
CELL 555)**

Date	MEAN of all 4 cells	NPL Cell 555 - MEAN	Cell N34 - MEAN	Cell 1 - MEAN	Cell 2R - MEAN
21/6/94	PREPARED	PREPARED	PREPARED	PREPARED	PREPARED
22/6/94	25.6265737 Ω	-0.0000030 Ω	0.0000048 Ω PREPARED	0.0000061 Ω PREPARED	-0.0000078 Ω PREPARED
23/6/94	25.6265749	-0.0000028	0.0000064	0.0000070	-0.0000107
24/6/94	25.6265761	-0.0000039	0.0000033	0.0000059	-0.0000053
27/6/94	25.6265740	-0.0000069	0.0000056	0.0000069	-0.0000057
30/6/94	(25.6265756)	— PREPARED	(0.0000020)	(0.0000068)	(-0.0000089)
05/7/94	25.6265709	-0.0000038 PREPARED	0.0000057	0.0000093	-0.0000112
08/7/94	25.6265710	-0.0000026	0.0000042	0.0000087	-0.0000105
11/7/94	25.6265712	-0.0000003	0.0000041	0.0000079	-0.0000118
15/7/94	25.6265692	-0.0000020	0.0000038	0.0000094	-0.0000113
18/7/94	25.6265697	-0.0000045 PREPARED	0.0000035	0.0000113	-0.0000102
19/7/94	25.6265729	0.0000003	0.0000022	0.0000073	-0.0000099
20/7/94	25.6265730	0.0000002	0.0000036	0.0000080	-0.0000117
22/7/94	25.6265716	-0.0000019	0.0000029	0.0000113	-0.0000124
25/7/94	25.6265700	-0.0000055	0.0000053	0.0000119	-0.0000118
28/7/94	25.6265706	-0.0000045	0.0000052	0.0000118	-0.0000124
1/8/94	25.6265691	-0.0000059	0.0000080	0.0000128	-0.0000149
3/8/94	25.6265697	-0.0000038	0.0000069	0.0000107	-0.0000139
5/8/94	25.6265690	-0.0000040	0.0000093	0.0000109	-0.0000163

AVERAGE DEPARTURE FROM MEAN	-0.0000032 Ω	0.0000048 Ω	0.0000091 Ω	-0.0000109 Ω
STANDARD DEVIATION	0.0000020	0.0000020	0.0000022	0.0000028

FIGURE 1 Resistance thermometer readings in individual cells

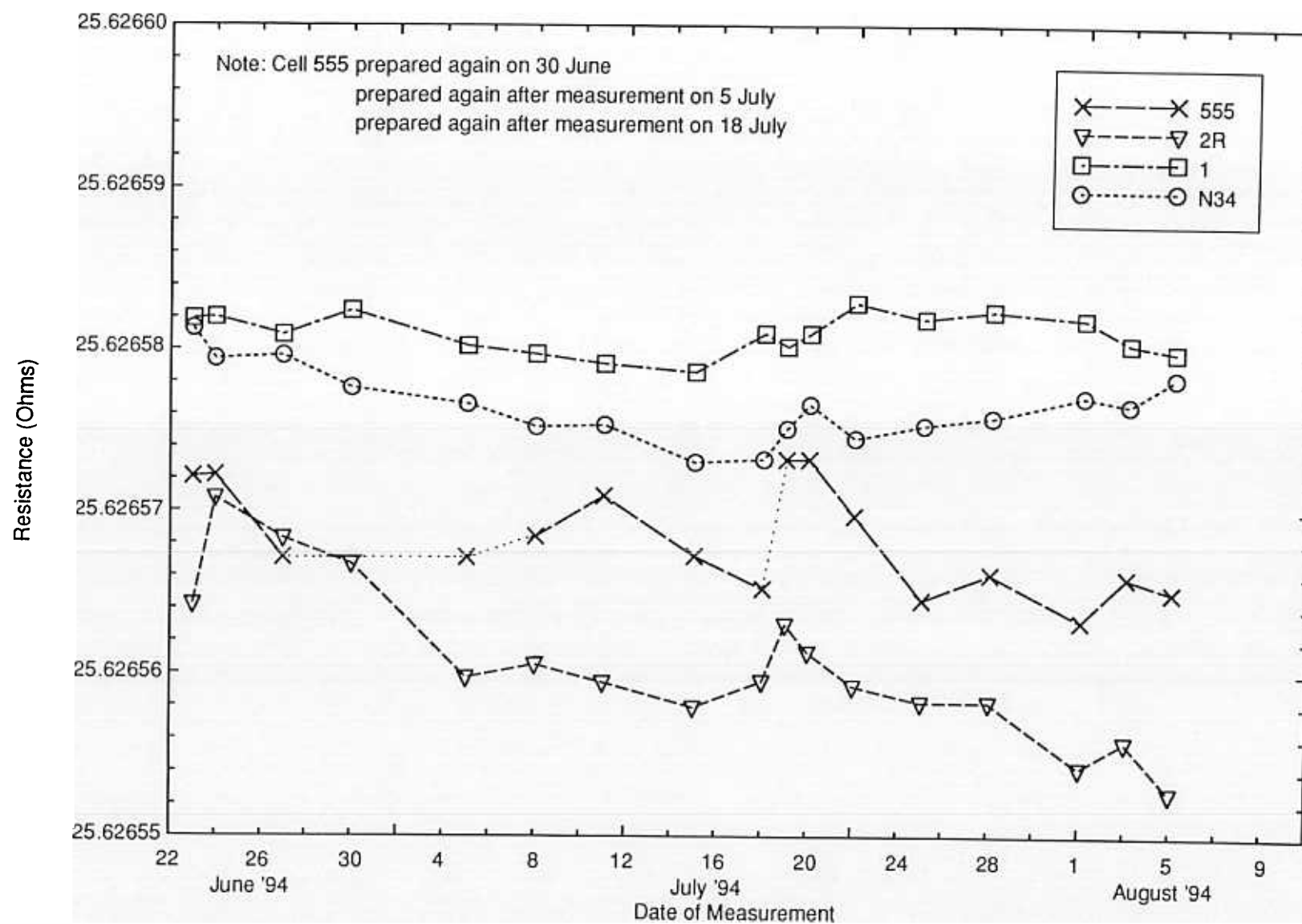


FIGURE 2 Comparison of resistance thermometer readings in water triple point cells and gallium melting point cell

