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EUROMET Intercomparison of Mercury Triple Point Cells at NPL

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ABSTRACT

Under a EUROMET Agreement "Intercomparison of Mercury Point Cells" (A280) the INM mercury cell was measured at NPL and the melting plateaus compared with those of an NPL mercury cell. The results indicated an agreement in the value of the two cells to better than 0.1 mK. The estimated uncertainty of the comparison was 0.2 mK at 95% confidence.

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1. INTRODUCTION

The International Temperature Scale of 1990 (ITS-90) specifies the fixed points at which a standard platinum resistance thermometer may be calibrated. One of these fixed points is the triple point of mercury defined as being 234.3156 K (-38.8344°C). This point has been realised in several laboratories in Europe, and it was suggested that these realisations should be compared. Consequently, as part of the Euromet framework, an agreement No. A280 "Intercomparison of Mercury Point Cells" was made to circulate a mercury triple point cell around several European Standards Laboratories. The French laboratory Institut Nationale de Métrologie (INM) co-ordinated the intercomparison and provided the cell.

The INM intercomparison mercury cell was conveyed to the National Physical Laboratory (NPL) in the UK for measurement and comparison with the mercury cell used by the NPL Temperature Calibration Unit. The results described below indicate an agreement between NPL and INM to better than 0.1 mK. The uncertainty of the comparison is estimated as 0.2 mK at a 95% confidence level.

2. MEASUREMENTS

To set up the triple point condition, the cells were wrapped in soft paper and placed inside pyrex glass tubes which were then suspended in cooled liquid baths. The NPL cell was measured in its dedicated Dewar vessel filled with methanol. This was stirred by a magnetic stirrer and the temperature was controlled by a thermostated dip-cooler. Some of the development work for this type of system is described in the NPL report "Cells for the realisation of the triple point of mercury" by Chattle and Butler (QU79 - Jan88). The body of the cell, manufactured in stainless steel, had a height of 195 mm and a diameter of 38 mm. The mercury was 99.9999% pure. The re-entrant well (of internal diameter 8 mm) terminated approximately 20 mm from the base of the cell. Methanol was used as the contact fluid in the re-entrant well. The cell is shown in Figure 1.

The INM cell was measured in a Heto bath containing acetone which used mechanical (propeller) stirring with the temperature thermostatically controlled by fixed cooling and variable heating. The re-entrant well of the cell contained acetone as the contact fluid.

The measurements were made in two rounds. The first round was made using Tinsley long-stem platinum resistance thermometer (PRT) No. 221403. A further round of measurements were made using Tinsley PRT No. 261194. Measurements were made using an Automatic Systems Laboratories (ASL) F18 ac resistance bridge except that an ASL F17 bridge was used for the measurements of the first four melts and freezes of the INM cell.

The following series of measurements were made:

5 melts and 1 freeze of the NPL cell in a Dewar of methanol using PRT 221403.

3 melts and 2 freezes of the INM cell in a Heto acetone bath using PRT 221403.

1 melt and 1 freeze in the NPL system using PRT 261194.

5 melts and 1 freeze in the INM system using PRT 261194.

4 melts in the NPL system using PRT 261194.

The results were recorded both on continuous chart recordings and as several individual direct measurement points which were noted in a log book. Self-heating effects were measured by temporarily increasing the usual 1 mA current to $\sqrt{2}$ mA. Immersion effects were noted after the PRT was raised by 2 cm and 4 cm.

2.1 MEASUREMENTS WITH THE NPL SYSTEM

Most of the measurements on the NPL system were made during melts with the equipment set with the normal parameters used in the Calibration Unit.

The melts lasted around 20 ± 3 hours. The two freezes performed were of shorter duration. The length of the plateau did not show a correlation with the small changes in the setting of the bath temperature. A few short tests of the plateau sensitivity to the bath temperature were made by increasing the bath setting by ~0.5 K and once by 1 K. Little effect was noticed on the thermometer reading. The plateau range (10-90% of the melt) was ≤ 0.2 mK. (There was one exception of a 0.4 mK plateau range, where the immersion test actually produced a step change in the plateau value). The small change in temperature during the melt usually occurred linearly.

2.2 MEASUREMENTS WITH THE INM SYSTEM

The first three measurements on the INM cell were made with it placed in a "short" glass tube as the INM cell only has a short upwards extension to the re-entrant well at the top of the cell. Later a longer glass tube was used to improve the immersion of the cell within the Heto bath. With some practice it was still possible to safely insert the thermometer in the opening of the re-entrant tube, though it was below the top surface of the bath housing.

Although three freezes were made with the INM cell, the triple point was predominantly realised during melting plateaus (similar to the procedure for the NPL cell). The melts lasted on average around 10 hours (shorter than the duration in the NPL apparatus) although one lasted for 19 hours. The plateau ranges were 0.1-0.2 mK excepting the first two realisations, when the new apparatus was still being explored. During the later melts the sensitivity to the bath temperature was found to be around 0.2 mK/K. This was established with the bath temperature about 1 K or more above the normal setting which would be nominally ≤ 0.5 K above the triple point temperature.

One or two experiments were conducted where the level of the acetone bath was adjusted by a few centimetres, thereby reducing the cell immersion, though the top of the cell was still well below the acetone level. No effect on the result was obtained.

3. RESULTS

The results of the experiments have been tabulated in Table 1. There are two rounds of results using two thermometers. The measurements on the second round are probably slightly superior as more experience had been gained and the same ASL F18 bridge was used throughout. The resistance given for each plateau is a directly measured value. The majority of direct measurements were taken in the first half of the plateaus, though some were also taken at the end of a plateau or during bath sensitivity measurements. All measurements were made at 1 mA (or $\sqrt{2}$ mA for the self heating checks).

The tabulated values can be taken as being representative of the 25% melted point. The setting of the bath, the range of the plateau and its duration are also tabulated. Additional comments on each run, indicating the measurement apparatus and any special points to note, complete the table.

The use of a 25% value (as against 50%) is a more realistic representation of the value of the mercury point used in a customers' calibration. At NPL several customers' thermometers might be measured during a working day (up to a maximum of about 9). A monitor PRT would first be used to determine that the plateau was stable and that the value was in accord with previous measurements determined by that monitor PRT. This might take 15-20 minutes. Each customer's PRT would be measured for about 20 minutes including self heating and immersion tests. The insertion of "warm" PRTs might speed the progress of the plateau; however as indicated from the intercomparison experiments, the melt would be far from finished after a working day. With the very small range of the mercury melt, the difference between 25% and 50% melted is < 0.1 mK.

The self heating effect of 1 mA on PRT 221403 showed a variation between 3.0 and 3.3 mK, while PRT 261194 showed 3.4 to 3.6 mK. Only a few immersion tests were made in the first round with 221403. Those measured were $< |0.1|$ mK. On the second round an immersion test was performed in every realisation. The effect at +2 cm was -0.1 to -0.2 mK, while at +4 cm it was -0.2 to -0.4 mK. With the one exception noted above (and in the table) the thermometer returned to its initial plateau value when returned to its original position.

The two mercury cells have a similar height of mercury above the PRT sensor so the correction of 1.0 mK for the hydrostatic effect is the same for both cells. As the hydrostatic effect for mercury is relatively large, at 0.07 mK/cm, it appears to account for the reduction in temperature consistently observed during the immersion tests. Further the effect was of the same sign and value when measured during the two freezes.

From the second round of results, in which PRT 261194 was used, the measured values in the NPL cell suggest that there was little or no thermometer instability during the measurements. Hence to compare the two cells, the resistance values of a thermometer in the NPL cell and the INM cell may be compared directly. The average NPL value in the second round, with PRT 261194, was 21.80891_6 Ω with a range of 5 μΩ. This was less than 0.1 mK higher than the average value in the INM cell of 21.80891_0 Ω with a range of 14 μΩ.

Three freezes were carried out in the first round. The first was not measured as it was only traced with a coarse resolution. The second was some 2 mK below the melting value, for reasons which are not clear but the measurement is almost certainly invalid. The third value was about 0.2 mK below the melting value for the INM cell. In the second round the two triple points that were realised during freezes measured about 0.1 mK cooler than those realised during melts.

No advantage is gained in comparing W values ie the resistance ratio $R_{Hg}/R_{0.01°C}$. Some measurements were made in a water triple point cell (0.01°C) and these are shown in the results. In the first round PRT 221403 was only measured once in a water cell with a result 1.7 mK lower than that given on its calibration certificate of the previous year. In the second round, using PRT 261194, four measurements were made, usually when a cell change-over occurred. The first measurement was some 0.5 mK below the three later values which all agreed within 0.1 mK.

4. UNCERTAINTY BUDGET

The components of Type A (random) and Type B (systematic or non random) uncertainty in the comparison of the two mercury triple point cells are assessed, following the INM guidelines, as follows.

Type A		2σ/mK
Repeatability of plateau determination at 25-50% melted (Five plateaus each on the second round).		0.10
Type B		2σ/mK
i)	Electrical effects, eg Variation in standard resistors or difference in the pick-up in the two rooms.	0.04
ii)	Differences in self heating in different cells.	0.03
iii)	Thermometer repeatability	-*
iv)	Thermal conditions of the two baths.	0.05
v)	Hydrostatic pressure correction.	0.03
vi)	Differences in the metal purity	0.10
Type A + Type B (summed in quadrature)	TOTAL	0.16

* Thermometer repeatability is subsumed in the Type A uncertainty.

The above analysis is the uncertainty in the comparison: it does not include the following, which would have to be assessed if an absolute determination was being made:

purity of mercury
bridge accuracy
frequency effects
effect of $R_{tp}(H_2O)$ uncertainty on W(Hg)

5. CONCLUSION

The two cells give the same temperature fixed point, when realised in different baths, well within the 0.16 mK uncertainty of the comparison.

TABLE 1 SUMMARY OF RESULTS OF THE NPL/INM MERCURY CELL INTERCOMPARISON

Cell	Chart Code	PRT	R/Ω melt	R/Ω freeze	Range/mK	Bath setting °C	Duration/hrs	Comments
-	Certificate	221403	25.46707					Water triple point 2 Oct 92
NPL	1	221403	21.49809_5	-	0.25	-38.2	5.0	W=0.84415817 8 July 93 F18 Bridge 100Ω Std Res 240741
NPL	2	221403	21.49809_6	-	0.1	-38.2	6.5	F18 Bridge 9 July 93 100Ω Std Res 240741 only part of plateau charted
NPL	3	221403	21.49808_0	-	0.15	-38.2	~25.0	F18 Bridge 13 July 93 100Ω Std Res 240741
NPL	4	221403	21.49808_9	-	0.3	-38.2 (37.4)	22.0	F18 Bridge 16 July 93 100Ω Std Res 240741 Terminated early
NPL	5	221403	-	-			8.0	F18 Bridge 20 July 93 100Ω Std Res 240741 Freeze: coarse measurement only
NPL	6	221403	21.49809_6	-	0.1	-38.4	>23.0	F18 Bridge 21 July 93 100Ω Std Res 240741 Deduce bath setting for plateau; as ~-38.6°C (this is not quite hot enough to melt)
	R_{tp}(water)	221403	25.46690_4					Water triple point 22 Jul 93
INM	C	221403	21.49809_1	-	1.0	-80 + 40.8	9.0	F17 Bridge 9 Aug 93 25Ω Std Res EL264 Steady increase near end, not sharp end. Short glass tube

Cell	Chart Code	PRT	R/Ω melt	R/Ω freeze	Range/mK	Bath setting	Duration/hrs	Comments
INM	D	221403	-	21.49791_9	-	-80 +36.4	-	F17 Bridge 10 Aug 93 25Ω Std Res EL264 Part freeze, short glass tube
INM	E	221403	21.49809_2	-	0.2	-80 +41.2	13.0	F17 Bridge 10 Aug 93 25Ω Std Res EL264 Short glass tube
INM	F	221403	-	21.49806_7	0.3	-80 +40	~9.0	F17 Bridge 11 Aug 93 25Ω Std Res EL264 change to long glass tube
INM	G	221403	21.49807_4	-	0.2	-80 +42.5 (-80 + 44.5)	~5.0	F18 Bridge 13 Aug 93 25Ω Std Res EL264
-	Certificate	261194	25.83482	-	-	-	-	Water triple point 26 Jul 93
NPL	1	261194	21.80891_4	-	0.2	-38.2 (-37.7)	12.0	F18 Bridge 26 Aug 93 25Ω Std Res 240710
NPL	2	261194	-	21.80890_4	<0.1	-39.2 (-40.2)	5.0	F18 Bridge 27 Aug 93 25Ω Std Res 240710 Terminated early
	R_{tp}(water)	261194	25.83479_5					Water triple point 27 Aug 93
INM	3	261194	21.80891_1	-	0.1	-80 +41.2 (-80 +41.8)	8.0	F18 Bridge 1 Sep 93 25Ω Std Res 240710
INM	4	261194	21.80891_5	-	0.15	-80 +41.0	19.0	F18 Bridge 3 Sep 93 25Ω Std Res 240710
INM	5	261194	21.80890_8	-	0.1	-80 +41.5	6.5	F18 Bridge 6 Sep 93 25Ω Std Res 240710

Cell	Chart Code	PRT	R/Ω melt	R/Ω freeze	Range/mK	Bath setting	Duration/hrs	Comments
INM	6	261194	-	21.80889_0	0.2	-80 +39.6	22.0	F18 Bridge 7 Sep 93 25Ω Std Res 240710 part frozen/part melted sensitivity in bath 0.2 mK/K
INM	7	261194	21.80890_1	-	0.2	-80 +41.0	7.0	F18 Bridge 8 Sep 93 25Ω Std Res 240710 warm bath to shorten plateau
INM	8	261194	21.80891_5	-	0.2	-80 +41.2	6.5	F18 Bridge 10 Sep 93 25Ω Std Res 240710 hot bath, alter liquid level
	R_{tp}(water)	261194	25.83485_4	-	-	-	-	Water triple point 14 Sep 93
NPL	9	261194	21.80891_4 21.80889_5	-	0.4	-38.2	23.0	F18 Bridge 27 Sep 93 25Ω Std Res 240710 2 jumps after immersion tests, each 0.1 mK. Forced melt at end
NPL	10	261194	21.80891_9	-	0.2	-38.2	18.0	F18 Bridge 30 Sep 93 25Ω Std Res 240710 slow rise at end
	R_{tp}(water)	261194	22.83486_0	-	-	-	-	Water triple point 30 Sep 93
NPL	11	261194	21.80891_9	-	0.1	-38.0	27.0	F18 Bridge 5 Oct 93 25Ω Std Res 240710 slow rise after 20 hours for 7 hours then forced melt
NPL	12	261194	21.80891_6	-	0.15	-38.2	21.0	F18 Bridge 7 Oct 93 25Ω Std Res 240710 odd "glitch" = 0.3 mK for 30 min. Forced to melt at end
	R_{tp}(water)	261194	25.83484_9					Water triple point 8 Oct 93

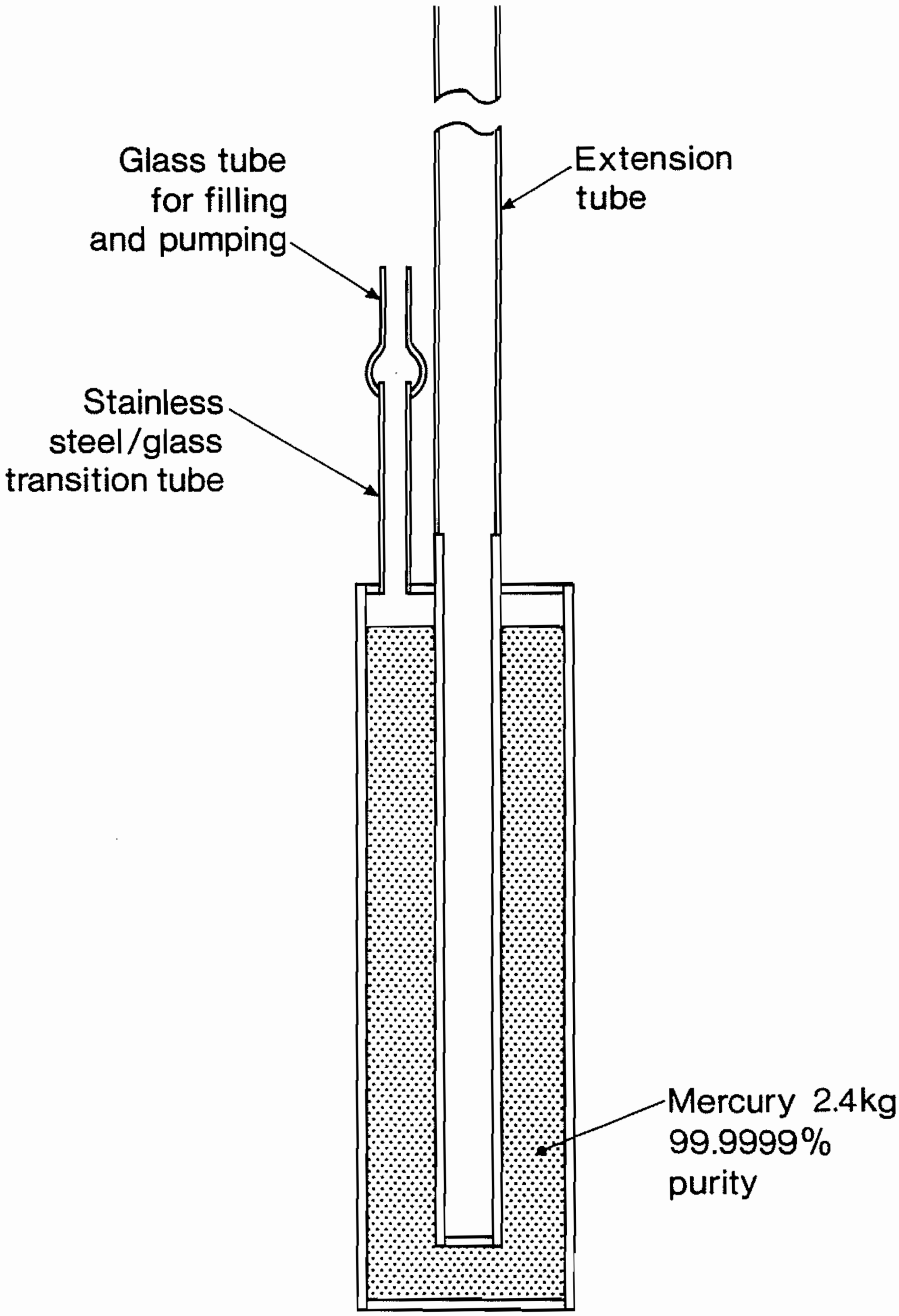

Figure 1 - Mercury triple-point cell