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Evaluations of Water Triple Point Cells:

A Summary Report of Recent International Intercomparisons

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The triple point of water, at which water of defined isotopic content exists in its three possible phases (solid and liquid under its own vapor) is the most fundamental of the thermometric fixed points. The temperature value assigned to the ideal property of water in this equilibrium state is 0.01°C (ITS-90). But, when a property is expressed in an artifact, a physical standard, nothing is ever ideal. How far do actual cell realizations deviate from the assigned value? More than we thought. A number of studies suggest that the deviations of cells of various manufacture are not trivial.

The Importance of the Water Triple Point in Thermometry

- The water triple point is the only defining point of the Kelvin Thermodynamic Temperature Scale (KTTS), and the one defining point that ITS-90 has in common with the KTTS.
- The water triple point is one of the most accurately realizable of thermometric fixed points.
- The water triple point is the denominator of the resistance ratios ($Wt = Rt / Ro_{0.01}$) in which the calibrations of standard platinum resistance thermometers (SPRTS) are reported. The ratios are much more repeatable than the resistance values.
- The water triple point resistance is a valuable quality assurance check on a SPRT. A check of the water triple point resistance when a thermometer is returned from calibration will show whether it has shifted, e.g., from transportation. Also, if a water triple point measurement is made each time an SPRT is used, and that measurement conveyed to a control chart, valuable performance history is obtained. Further, if the SPRT has not shifted, costly recalibration can be avoided. Equipment to realize the water triple point costs less than a single NIST recalibration.

Studies of the Quality of Water Triple Point Cells

It was once dogma that a water triple point cell represented an almost mystical, unchallengeable, unmeasurable absolute. When thermometry having an accuracy and precision of several millikelvins was considered cutting edge, that attitude may have been appropriate. However, as a denominator of a ratio, the Degree to which the water triple point departs from the ideal proliferates error to the realization of the entire scale. Thus increasing attention is focused on the question: the ideal property of water is, by definition, without uncertainty, but what uncertainty can be expected from a real cell?

The Furukawa-Bigge Report (1983)

In 1982, a major study was undertaken at the NBS (National Bureau of Standards - United States), using 22 cells manufactured by the Jarrett Instrument Co. [1] The operating procedure used in this study permitted temperature determinations of about 0.000 001 °C (1 uK). This paper is worth study for its conclusions and also for the discussion of operating technique. The 22 Jarrett cells were separated into 10 measurement groups, of such group size that the measurements on a group could be made within a week to obviate problems from drift of the reference resistor. Four cells, designated K, M, P and R were selected as reference cells, and one or more of them was included in the measurements on each group.

The deviations of the temperatures of each reference cell from the average of the group are shown in Table 1. Jarrett cells (now Jarrett-Isotech) are claimed to be within 0.04 mK of the ideal value, and this study substantiates that claim.

TABLE I (FURUKAWA-BIGGE STUDY)

Measurement Group	Reference Cells K m°C	M m°C	P m°C	R m°C
a	-0.004	+0.010	-0.007	
b	+0.004	-0.007	+0.003	
c	-0.002	+0.008	-0.007	
d	-0.001	-0.012	-0.011	
e			-0.003	+0.003
f			+0.009	-0.009
i			-0.005	+0.005
j	-0.014			+0.014
k	-0.005			+0.005
n	-0.005			+0.009

Table 1. Performance of triple point of water cells in the Furukawa-Bigge study.

The BIPM Report

The Furukawa-Bigge study included only Type A and Type B Jarrett cells. In more recent years (1996), an intercomparison was undertaken by the International Bureau of Weights and Measures (BIPM, Paris) of cells made by a number of manufacturers, including Jarrett cells furnished by NIST and cells made by national laboratories (NPL, NMi, IMGC, VNIIM, KRISS). The participating national laboratories are listed in Table 2.

All the cells were compared to a reference cell kept at the BIPM prior to their circulation and after their return to BIPM. Cells were circulated in three groups, so that each cell in a group was measured by more than one national laboratory and no cell was measured by all participating laboratories. The BIPM report, identified as Rapport BIPM-96 18 and also as Document CCT196-1 121 is long, since it includes the reports of each participating laboratory, and it is possible here only to summarize it.

The cells showing the highest values are those which most closely realize the ideal temperature; these are the two Jarrett cells supplied by NIST and the two cells supplied by KRISS. (Obviously, a water triple point cell cannot be above the ideal temperature; the At of the four high cells reflects the temperature realized by the reference cell).

The report makes special comment on the "strange" behaviour of three of the cells - cells furnished by NPL (U.K.), Portugal and Brazil. New ice mantles were formed several times and exhibited aberrant behaviour each time. The mantles of these cells is shown in Figures 2 (a) (b) and (c).

The EUROMET Intercomparison Project

Yet a third international intercomparison of cells has been conducted as Euromet Project Ref. No. 278, CCT 96 122 (1996), co-ordinated by E. Renaot of the National Institute of Metrology, France [2]. The participating Laboratories are listed in Table 3. Again, cells participating were of the same manufacturers, although not necessarily the same cells as in the BIPM experiment, with the addition of cells made by PTB, FGW [3] and Spembly (now produced by NPL). Mantles were prepared by each laboratory's preferred method. This report, like BIPM'S, includes the individual reports of each laboratory, and, therefore, is also lengthy. The results are summarized in Table 4. This report also mentions the "strange" behaviour of some cells, as shown in Figure 2.

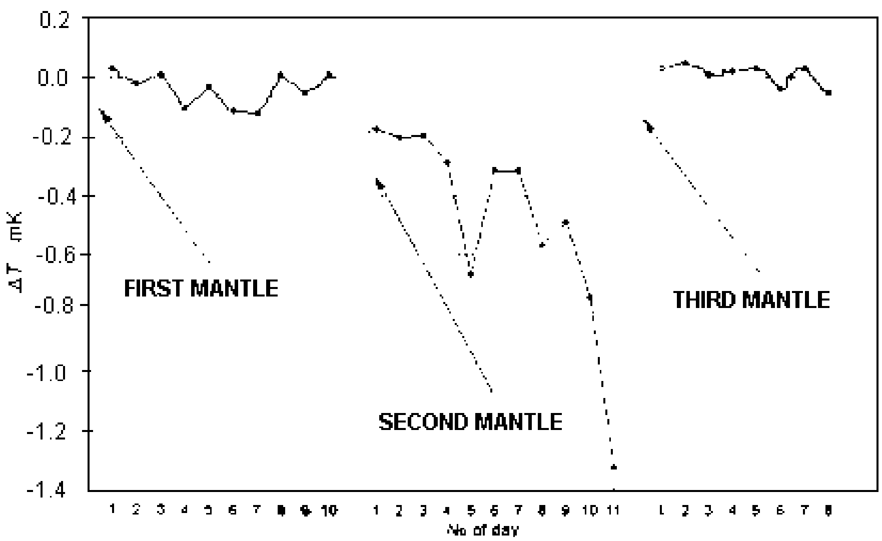

FIG 2 (a) "Strange" behaviour of cell PT 712 (NPL Production)
(1) June 94 (2) June 95 (3) October 1995

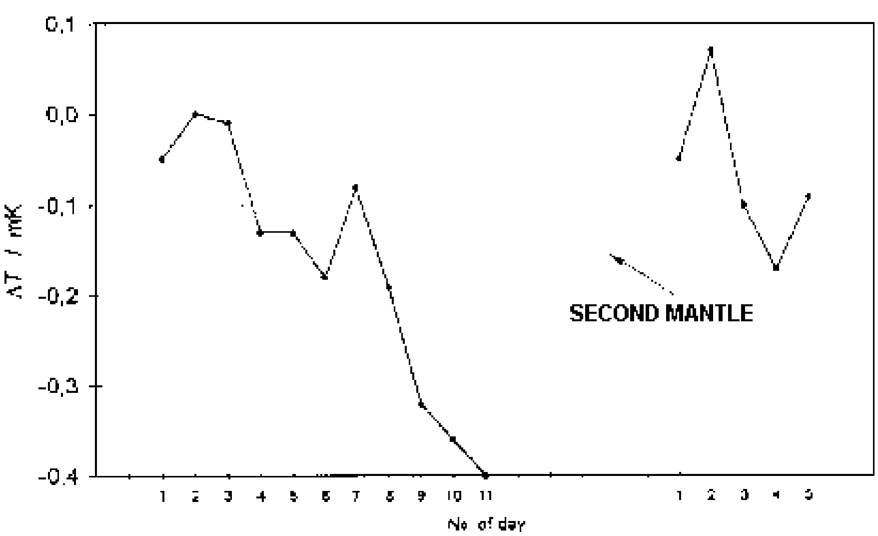

FIG 2 (b) "Strange" behavior of Cell PT-299
(NPL production)

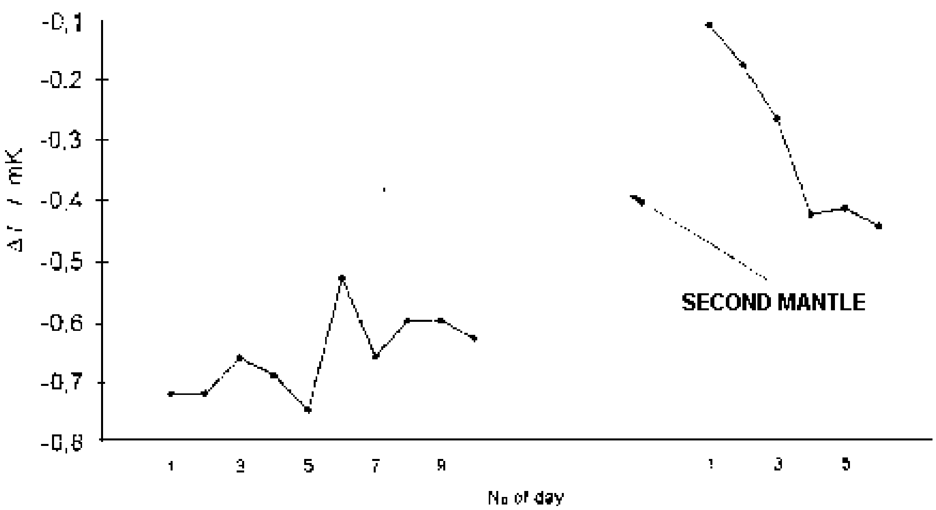

Fig 2 (c) "Strange" behaviour of Cell PT-494
(INMETRO production)

Conclusions

The Furukawa-Bigge report confirms that properly made water triple point cells can produce repeatable and reproducible results. The two European reports were a shock to the temperature community. No one would have predicted that disparity between cells of different production, or within the product of a single producers could be so large. It is a good general conclusion that a proper water triple point cell can and may be within 0.000 040 K (40 uK) of the ideal value. It has been shown that many, including some national standards, are not. What does this mean to thermometer calibrations, which are reported as ratios of the resistance at temperature divided by the resistance measured at the water triple point? A water triple point error (as in Figure I or Table 3) or an erratic behaviour (as in Figures a, b, c) proliferates through the entire calibration. An error of 50 uK at the water triple point causes an error of about 250 uK at the silver point (961°C); of 0.5 mK an error of about 3mK; of 1.4mK (as in figure 2b) an error of about 8mK. Where such an error is aberrant ("strange"), the result is an uncertainty. The studies cited indicate that even calibrations at some national laboratories may be subject to errors resulting from the error at the water triple point.

PARTICIPATING LABORATORIES - BIPM STUDY

BIPM	Int'l Bureau of Weights & Meas	France
NPL	National Physical Laboratory	UK
NIST	National lnst. Sci. and Tech.'	US
IMGC	Instituto "G. Colonnetti"	Italy
VNIIM	Mendeyev Institute	Russia
KRISS	Korean Res. lnst.	Korea
ETL	Japan	
INM	National Institute for Metrology	France
MSL	Measurement Science Laboratory	New Zealand
IPQ	Portugese lnst. for Quality	Portugal
SISIR	Singapore lnst. for Sci-Ind Res	Singapore
INMETRO	Brazil	
NMI	Nederlands Meetinstituut	Netherlands

INM	National lnst. for Metrology	Romania

Table 2. Participating laboratories BIPM study.

PARTICIPATING LABORATORIES - EUROMET STUDY

INM	National Institute for Metrology	France
NPL	National Physical Laboratory	UK
NMi	Nederlands Meetinstituut	Netherlands
PTB	Physikalisch-Technische Bund.	Germany
IMGC	Istututo "G. Colonnetti-	Italy
CEM	Spanish Center for Metrology	Spain
DTI	Danish Tech. Inst.	Denmark
IPQ	Portugese Inst. for Quality	Portugal
CMA	Center for Metr. and Acc'redit.	Finland
SP	Sweden	
JUST.	National Metrology Service	Norway
OFMET	Office of Metrology	Switzerland

Table 3. Participating Laboratories - Euromet study.

LABORATORY	CELL MADE BY	delta(T)
INM	NPL	+0.000
INM	NPL	+0.014
INM	NPL	-0.033
NPL	NPL	-0.050
NPL	NPL	-0.057
NMI	NMi	-0.148
NMI	NMi	-0.111
PTB	NPL	+0.020
PTB	NPL	-0.020
PTB	PTB	-0.008
PTB	FGW	+0.014
DTI	JARRETT	-0.037
CEM	JARRETT	-0.014
IMGC	IMGC	-0.021
IPQ	NPL	-0.05
CMA	NPL	-0.08
SP	SPEMBLY	-0.035
JUSTERV.	NPL	-0.33
JUSTERV.	NPL	-0.035
OFMET	NPL	-0.087
OFMET	NMI	+0.015
OFMET	IMGC	-0.114

Table 4. Performance of cells - Euromet study.

References

1. G.T. Furukawa, W.R. Bigge, Reproducibility of Some Water Triple Point Cells, Temperature, its measurement and control in science and industry, Vol 5 (ed. Schooley), American Institute of Physics.
2. Copies of these reports are available at charge from Bureau International des poids et Mesures, Pavilion de Breteuil, F-92313 Sevres, France
3. PTB= Physikalisch-Tecnische Bundesanstalt, Germany. FGW = Forschungsgemeinschaft fur technisches Glas, Germany.

Henry Sostmann is a registered Professional Engineer and consultant in temperature metrology, laboratory management and international standards for measurement quality, most recently for Isothermal Technology Ltd. He holds a B.A. degree from Rutgers University, with graduate studies at Drew University New York, New York University and the Polytechnic Institute of Brooklyn. He was vice-president of Basic Metrology at Yellow Springs Instrument Company. In 1994 he received the Wildhack Award of the National Conference of Standards Laboratories. He is editor of the Isotech Journal of Thermometry.