The Establishment of ITS-90 Water Triple Point References to ±2µK, and the Assessment of 100 Water Triple Point Cells Made Between 2001 and 2006

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ABSTRACT

The difficulty with all triple point measurement is to establish a reference whose temperature is known exactly in relationship to the ITS-90 value [1], and so during 2000 two water triple point cells were constructed (KT cells) whose isotopic composition was known ±2µK, and which could be redistilled internally to remove the last vestiges of impurities leached from the cells. Measurements using their built in Mcloed gauges showed no residual air (Fig. 1) [2]. Using these as reference cells (KT001 was 7µK lower, KT002 1µK higher than V-SMOW), a selection of water triple point cells were analysed for their isotopic composition, and also compared to the reference cells. This process has continued during the past 5 years with 100 cells now analysed. Some of the Isotech cells were included in CCT-K7, others have been analysed by PTB and another has been intercompared to NIST's reference cells.

This presentation details these results and concludes that no evidence has yet suggested the KT cells are incorrect.

1. INTRODUCTION

Since the 1960's Jim Cross of the Jarrett Instrument Company has claimed his cells are +0, -40µK of the applicable temperature scale [3, 4]. This claim was based on work by Furukawa and Bigge published in 1982 which analysed the performance of NIST's stock of water triple point cells all of which were model A11 made by Jarrett. During 1996 the manufacturing technology of the Jarrett cells was passed to Isothermal Technology Ltd who have carefully maintained the Jarrett method of manufacture. Since 2001 selected cells have been sampled and the samples analysed to ascertain their isotopic composition compared to V-SMOW. This is useful since the uncertainties associated with isotopic analysis are only ± 2µK [5].
There are 3 main sources of error in a water triple point cell [6, 7] (excluding errors associated with measurement):

- The isotopic composition of the cell's water may not be that of SMOW.
- There may be air trapped inside the cell.
- There will be impurities in the water.

Isotopic composition can be measured to great accuracy from a small sample of the cell's contents. Air and impurities can be estimated by comparing the cell to one or more reference cells. The difference between the temperature predicted from the isotopic analysis and that measured gives some measure of dispersion due to impurities.

2. REFERENCE CELLS CLOSELY ASSOCIATED TO ITS-90

This article presents data from a group of cells made in a still designed to produce pure, air-free water of isotopic composition close to V-SMOW. For this, a reference cell is required. A cell was designed and made based on Stimpson's construction, but with the addition of a McLeod gauge (Fig. 1). Two cells (KT001 and KT002) were filled with water from the still and samples of water from the cells were sent for isotopic analysis to a facility with the ability to analyse its deviation from V-SMOW to an equivalent uncertainty of ±2μK.

3. METHOD OF INTERCOMPARISON

Reference and referred cells were made up at the same time using ice mantle makers, heat pipes small enough to go down the triple point re-entrant tubes and having a container of 400cc of liquid nitrogen at the emergent end [11]. Three fillings of this container and 20 to 30 minutes of cooling gave a good ice mantle in each cell. The cells were left 7 to 10 days in a water triple point maintenance bath model ITL-M-18233 and intercompared over the subsequent 3 to 4 days.

Furniture in the form of 2 foam buttons at the base of the re-entrant tube, copper centralizing bushings and Teflon guide tubes at the emergent end of the re-entrant tube were used to guide and support the selected SPRT found to give most consistent results.

A software program was developed for a MI 6010 Bridge using 3 currents to ascertain the exact resistance of the thermometer as follows. The first current is selected and 60 measurements each of 20 seconds duration are made reversing the current after each measurement.

The first 24 measurements are discarded being the self-heating time of the thermometer and the mean and standard deviation of the last 36 measurements are made, the current is changed and the 20 minute process repeated. After the third current, the original current is reselected to check that the freed mantle had not reconnected itself to the re-entrant tube, and the repeatability of the system (typical currents were $\frac{1}{\sqrt{2}}$, 1, $\sqrt{2mA}$).

The zero current resistance can be calculated in 3 ways and from the three resistances the mean is calculated. Correction is made for the exact hydrostatic head and the final resistance is obtained.

The thermometer is transferred to the second cell and after a 30 minute wait the process is repeated. 4 cells can be measured in 1 day, 1 reference and the 3 unknown using the above technique.

The cells are then repositioned in the maintenance bath and the measurements repeated again on a second and third day. The reason the cells are moved is that we do not repeat the measurements in the same sequence.

All measurements are eventually referred back to a specially selected Tinsley 25Ω resistor with tempco of less than 0.1ppm/°C and maintained at 20°C ±0.007°C in a stirred oil maintenance bath model 455 whose temperature is continuously monitored and recorded.

The distillation apparatus is used to produce a variety of water triple point cells with different immersion depths and diameters. A selection of cell sizes have been included in the graphs.

4. DESCRIPTION OF GRAPHS

Graph 1 shows results of a variety of cells. During 2001/2 the spread of intercomparisons was from -60µK to -15µK Vs ITS-90 with a mean value -30µK. The spread of isotopic composition was from -18µK to + 15µK with a mean value of -2µK to V-SMOW. A mean value of 28µK could be attributed to impurities and air. By 2003 however the spread of results has reduced and the mean values from the intercomparison results and isotopic composition has become smaller at 14µk, suggesting the impurities are less. The results for 2004 are very similar to 2003 with again 14µK difference between the comparison value and the isotopic analysis. The results for 2004 and to June 2005 are separated into two time periods because the results of CCT-K7 were available from January 2005. During the first part of 2005 it was decided to move the target temperature up 20µK, so that instead of +0-40µk the cell target was changed to ± 20µK to ITS-90.

Graph 2 shows cells produced to the revised target temperature of ±20µk to ITS-90. The target isotopic composition was set at 15µK above SMOW and the target intercomparison value at 0µK to ITS-90. The mean values achieved were +14 ±2µK and +2 ±15µK respectively, giving just 12µk for impurities and air. To put these results into context they are superimposed into a figure 26 from CCT-K7. There were 4 cells made by Jarrett/Isotech as part of CCT-K7, in particular NRC's cell 2063 appears in Graph 1 of this article. Graph 1 suggests it was 15 ±13µK below ITS-90. Figure 26 of K7 has it at +90 ±13µK or -5 ±13µK to K7's estimated ITS-90 temperature. Thus there is agreement within 10µK between K7 and the Jarrett/Isotech cells. Well within measurement uncertainties. All Jarrett/Isotech cells in CCT-K7 were within +0 -40µk of BIPM's estimate of the ITS-90 temperature.

5. OTHER INTERNATIONAL INTERCOMPARISONS

Cell A11/213 was sent to NIST who found it 20 to 30µK below their reference cell.

In graph 1 of this article it measured -25 ±15µK to ITS-90 again agreement within the uncertainties of ±15µK.

Cells B11/551, 552 and 553 (Graph 1) were analysed by PTB [8] who found by inductively coupled plasma mass spectrometry that there was less than 10µK of impurities in the samples they analysed. They also analysed the isotopic composition, which agreed closely (within 10µK of ours).

6. CELL STABILITY

In 2001 using KT001 and KT002, other reference cells were chosen as day-to-day reference cells. Cell A11/2011 is a cell made by Jarrett in America, NMI 119 is a cell made in Holland and E11/213 is a cell made in England. All cells are made from Borosilicate glass. These 5 cells were intercompared again in detail during autumn 2006 and maintained the same values as in 2001, see Table I [9].

7. CONCLUSION

Analysing the cell contents for isotopic composition is a useful and valid addition to the usual techniques of intercomparing cells and gives an accurate indication of the cell's ideal triple point value. All cells except those with a flask are lower in temperature than predicted by the isotopic content, probably due to a very small amount of contamination caused by leaching from the glass [10].

In the case of the cells with a flask the water can be repurified after sealing leaving any dissolved glass and other impurities in the flask. Such cells, complete with isotopic analysis provide the closest association to the ITS-90 value of the water triple point and hence the KTTS Scale. It is now possible to produce cells, based on Stimpson's original design which can be associated to V-SMOW within ±2µk and this is a smaller uncertainty than can be provided by traditional measurements. Conventional shaped cells can be produced on a commercial basis which are within ±20µk V-SMOW, and can be provided with a certificate of isotopic analysis.

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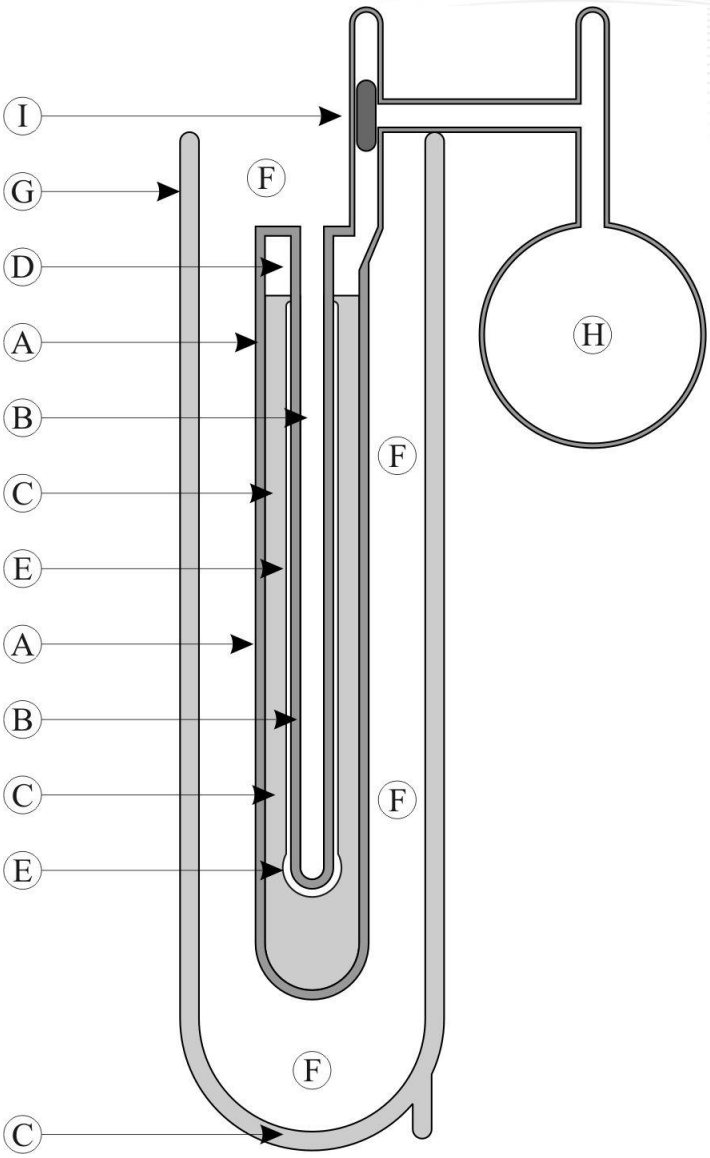
Table I. Reference Cells of Isotech compared to KT001 in 2001 and 2006

Reference Cell	2001	2006
KT001[a, b] Vs V-SMOW	-7 ±1µK	-7 ±1µK
A11-2011[b] Vs KT001	+7 ±15µK	+10 ±15µK
E11-213[b] Vs KT001	-18 ±15µK	-15 ±15µK
VSL-119[b] Vs KT001	-10 ±20µK	-4 ±20µK

[a] The value of KT001 is based entirely on its isotopic analysis and assumes the newly redistilled water is completely free of dirt and air. On regular production cells dirt and air contribute typically 15µk depression. By redistilling the water in KT001 this will be reduced considerably, however the complete set of results maybe offset downwards by a few µK.
[b] The four cells above were all made of borosilicate glass. The results above suggest that the cells A11-2011, E11-213 and VSL-119 have not drifted during their five years of continuous and intensive use and that the temperatures we assigned to them can be relied on.

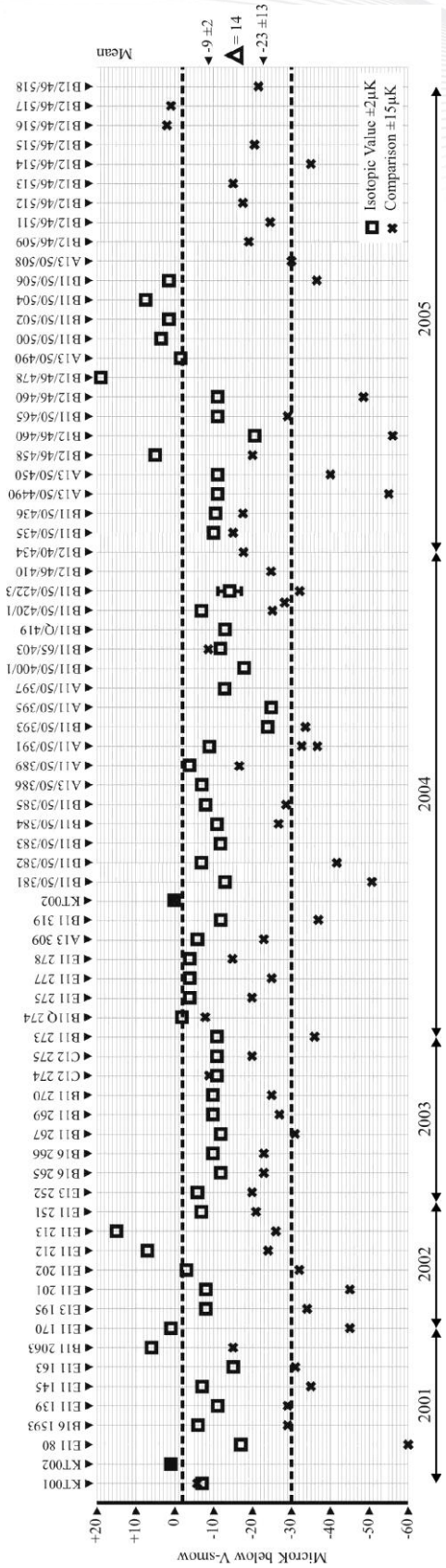
FIGURE CAPTIONS

Fig. 1. A Triple Point Apparatus with Mcleod Gauge.



A, Triple Point Cell; **B**, Thermometer Well; **C**, Liquid Water; **D**, Water Vapour; **E**, Ice Mantle; **F**, Ice Bath; **G**, Vacuum Vessel; **H**, Flask for Redistillation; **I**, Mcleod Gauge.

Graph. 1. Comparing Isotopic Composition of Measured Value for Cells in 2001, 2002 & 2003 / Analysis of Water Triple Point Cells during 2004 and the first six months of 2005.



Graph. 2. Isotech's Water Triple Point Cell Temperatures Compared to SMOW and ITS-90 since June 2005.