PRIMARY LABORATORY COMPARISONS

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INTRODUCTION

The most accurate measurements made in a Primary Temperature Laboratory are during intercomparisons of ITS-90 fixed point cells, and in particular intercomparing water triple point cells.

To assess the stability of the water triple point, a laboratory ideally needs to be able to measure differences of just one or two micro degrees.

One method used is to make a large number of measurements and statiscally manipulate the results, however if a high degree of accuracy can be achieved initially the number of measurements can be reduced.

Traditionally, to measure the resistance of an SPRT in a water triple point cell two currents are applied and from the two resistances obtained at the two powers, the zero power resistance can be calculated.

At the Northern Temperature Primary Laboratory (NTPL) we found the spread of results too large to give a satisfactory result.

Consulting the literature, and in particular Tischler & Prado [3] we eventually developed a 3 current technique from which we were able to calculate the zero current resistance to within 1 or 2 micro degrees.

This paper describes in detail our method.

WATER TRIPLE POINT TEMPERATURE MEASUREMENT AT N.T.P.L.

APPARATUS

THE FIXED RESISTOR

The resistors used at NTPL are the Wilkins design produced by H. Tinsley & Co. Ltd. They all have a history of calibration with uncertainties of ±0.05ppm. They have all been evaluated for use with AC and DC. All have their temperature coefficient defined from 18°C to 22°C. We have a special 25 ohm resistor with Tempco of less than 0.1ppm/°C which we use for critical measurements.

At NTPL all resistors are kept in a Resistor Maintenance Bath controlled at 20 ±0.005°C and are constantly monitored. This gives rise to uncertainties of ±1μK or less for Cell inter-comparison measurements.

THE THERMOMETERS

At the levels of measurement we need to work (measuring to within 1μK) we found that the Barber type of design exhibited a small amount of stem conduction (typically 0.075mK) or thermal effect when the handle was held. This effect took up to 1 hour to die away. The Meyers design thermometers performance (such as the ISOTECH 670 or the YSI 8163) were superior and so were adopted for this type of work.

THE MEASURING SYSTEM

A TTI 3 produced for Isotech by Measurements International was used for the best measurements in conjunction with a combined software program that will be described later.

INTER-CONNECTIONS

All cabling runs and connection points have been fully evaluated to ensure that there are no poor connections or dry joints. The laboratory itself has a faraday screen and supplies are double filtered.

THE TRIPLE POINT CELLS

Water Triple Point Cells from various sources are evaluated at the NTPL on behalf of clients. These vary considerably in volume, length, diameter and of course depth of immersion. At the small levels of uncertainty that we require, each Cell must be considered individually, however, there are some general rules we use.

Firstly, let me acknowledge a debt to Dr. George Furukawa [2] whose published work on Water Triple Point Cells over 20 years has been an example to other researchers. Many of his findings have been confirmed and adopted at NTPL. His work however has been almost exclusively with Water Triple Point Cells produced by the Jarrett Instrument Company (now Jarrett-Isotech). We have found that some of the methods he describes do not work well for the smaller Cells produced by for example NPL and NMI. The Jarrett designs originate from NBS (type A) and NRC (type B) and both designs are large enough to give around 30cm of immersion and are about 50mm in diameter. NPL/NMI Cells give 20cm of immersion and are about 35mm in diameter. Thus the NPL/NMI design only contains about 30% of the water that a Jarrett-Isotech Cell contains. Even smaller cells with immersions of only 110mm also exist.

PRODUCING THE ICE MANTLES

Over the years we have read and tried many methods of ice mantle production. The final method chosen by a Laboratory will, I suspect depend on the availability of cold sources and the inclination of the poor devil who has to sit with his or her hands in cold water for an hour or more.

In our laboratory, carbon dioxide is not readily available but Liquid Nitrogen is convenient and cheaply so. We have two 25 litre dewars so that Liquid Nitrogen is available any time for cooling rods or for cold traps. We have tried a number of methods to build the mantle using Liquid Nitrogen but without inducing strain, our solution is a heat (or coolth) pipe attached to a container in which we pour Liquid Nitrogen. This automatically produces a mantle of exceptional uniformity and without strain, since coolth is transferred at or close to the triple point temperature.

To know how much water we have turned to ice is important. We wish to turn 60% to ice. We therefore calibrate the side of the Cell (because ice is 8% less dense than water the level of water increases as the ice mantle thickens). This is also useful when calculating the hydrostatic head. Once the mantles are complete the Methanol is removed and the re-entrant tube is dried and filled with water at 0.007°C. The Cells are left in a maintenance bath of our own design at +0.007°C for a week with occasional inspections to melt any ice bridges that may form.

FREEING THE MANTLES

With care taken not to invert the Cells, one or more 6mm Aluminium rods are introduced into the re-entrant tubes of the Cells to free the mantle. The mantle should rotate by slightly tipping the Cell **not** by twisting the Cell, we confirm Dr. Furukawa's conclusion that Cells whose mantles rotate with a twist of the Cell are not free enough to sustain a water/re-entrant tube interface for the duration of a test measurement.

We have further found that in the NPL/NMI type of Cell the mantle re-attaches itself to the re-entrant tube much more quickly than with the large Jarrett-Isotech types. This may give rise to anomalous results reported in some International inter-comparisons. As the ice mantle re-attaches itself to the Cell re-entrant tube the temperature drops and the self heating effect increases, so that it is very easily detected.

For 'small' Cells we find it necessary to use our aluminium rod for 60 seconds each time we begin a measurement group. For the larger Cells, after an initial 60 seconds, subsequent measurements only require 20 seconds to free the mantle. The smaller Cells mantles melt more quickly than those of the larger Cells, crack more easily during creation and `re-stick' more quickly, to the re-entrant tube. However, because of their smaller diameter re-entrant tube it is not necessary to put in Copper bushings in order to centralise the thermometer. A small foam `pill' is placed in the bottom of each Cell during measurements since it is known that the bottom of the Cell will be at a different temperature than elsewhere, because the ice is in contact with the bottom of the re-entrant tube.

HYDROSTATIC HEAD CORRECTION

1 metre below the surface of a Water Triple Point Cell the temperature is 0.73mK colder. If I wish to know the temperature within 1 or 2 microkelvins I must correct for the depth to an accuracy of 1 to 2mm. The method we adopt at NTPL is to etch a band around the Cell 2cm wide. Beginning at the water/water vapour interface and graduated in 0.2mm steps. We make ice mantle until the water level is at the top of our 12mm band. This is about 60% of ice.

We measure the depth from the water/water vapour interface to the centre point of the thermometer

and make a correction as the mantle melts and the level drops. This is particularly important where Cells of mixed origins and variable sizes are being inter-compared.

CENTRALIZING THE THERMOMETERS

Most Jarrett-Isotech Cells have a larger re-entrant tube than the thermometers that will perform the measurements and so Copper centralizing bushings have been made and are placed on the foam cushions in the bottom of the re-entrant tubes. At the top Teflon guides keep the thermometer central all the way out of the Cell.

LIGHT PIPING

To eliminate light piping and strain on the thermometer cable a box like structure is placed over the thermometer followed by two thicknesses of dense black material. During March 1998, 4 Water Triple Point Cells of the Jarrett/Isotech Type B were NAMAS certified.

We used $^{1}/_{2}$, 1 and /2mA and lastly we repeated $^{1}/_{2}$mA as the currents. As usual we made 3 sets of measurements spread over 3 or 4 days, beginning a week after making up the Cells - what we found, very much in agreement with Dr. Tischler's work is a much improved grouping of results.

METHOD

The TTI 3 bridge made for Isotech by Measurements International was programmed with exact currents; $^{1}/_{2}$mA, 1mA and /2mA.

The bridge has been programmed and automatically runs through a sequence of measurements as follows:

It takes 60 readings each averaged over 20 seconds at $^{1}/_{2}$mA, ignoring the first 24 the programme records the last 36 readings, averages them and gives the standard deviation to 2 sigma confidence level. The current is changed in sequence to 1mA, /2mA and lastly $^{1}/_{2}$mA, at each current the programme repeats its 60 measurements and averages the last 36.

The two $^{1}/_{2}$mA readings must be within 20µK of one another to show that the measurements are stable and are then averaged to give a mean value.

The zero power resistance can be calculated in 3 ways, extrapolating from /2 and 1mA, 1mA and $^{1}/_{2}$mA and /2 and $^{1}/_{2}$ mA. The 3 values thus obtained are averaged. The averaged zero power resistance is then adjusted for hydrostatic head errors.

1 measurement sequence takes about 90 minutes permitting 4 or 5 Cells to be inter-compared over a normal working day. The whole measurement sequence is repeated twice again over about 72 hours and the three sets of results are again averaged.

Table 1 shows the daily readings and the averaged values.

TABLE 1

REF. CELL NMI 254	TEST CELLS				
	JB.2059	**JB.2054**	**JB.2056**	**JB.2057**	
25.565 2167	25.565 2182	25.565 2182	25.565 2189	25.565 2180	Day 1 - mean zero power values H.H. corrected
25.565 2140	25.565 2163	25.565 2185	25.565 2176	25.565 2184	Day 2
25.565 2105	25.565 2155	25.565 2160	25.565 2133	25.565 2165	Day 4
25.565 2137	25.565 2167	25.565 2176	25.565 2166	25.565 2176	Mean values

As can be seen from Table 1 the total spread of results is reduced to around ±25 micro degrees over a 4 day period and the average values of the 4 Jarrett-Isotech Cells agree within ±5 micro degrees. All Jarrett-Isotech Cells being 30 to 40 micro degrees above the NMI reference Cell. To fully appreciate these results Appendix 1 shows the spread of results obtained at IMGC during an inter-comparison, with the NTPL results superimposed. But how does the method work long term?

We recompare our Cells annually and so we are building up a history of our Cells. At the level of 1 or 2 micro kelvins it is difficult to know exactly what we are measuring when we reintercompare Cells.

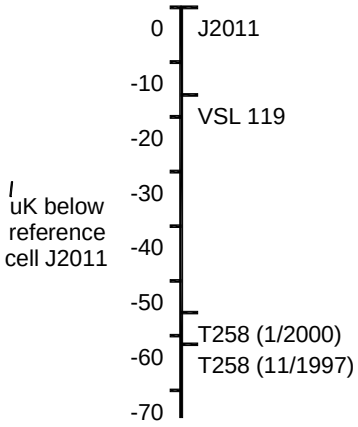
We are somewhat fortunate in that we certify 30 to 50 Cells per year from 3 sources comparing each to our 2 Reference Cells. If our Reference Cells (one an A11 Isotech-Jarrett design (JA2011), the other of NMI design (NMI 119)), were drifting, this would be noticed over the year.

In January 2000 we rechecked one of our secondary Water Triple Point Cells (T258) against our Reference Cells. We then compared these results to our original measurements in November 1997. The Cell T258 was within 5μK of it's 1997 value.

Testament to the stability of the Cells, and to the measurement technique.

TABLE 2

REPRODUCIBILITY OF T259 WATER TRIPLE POINT CELL OVER A 2 YEAR PERIOD



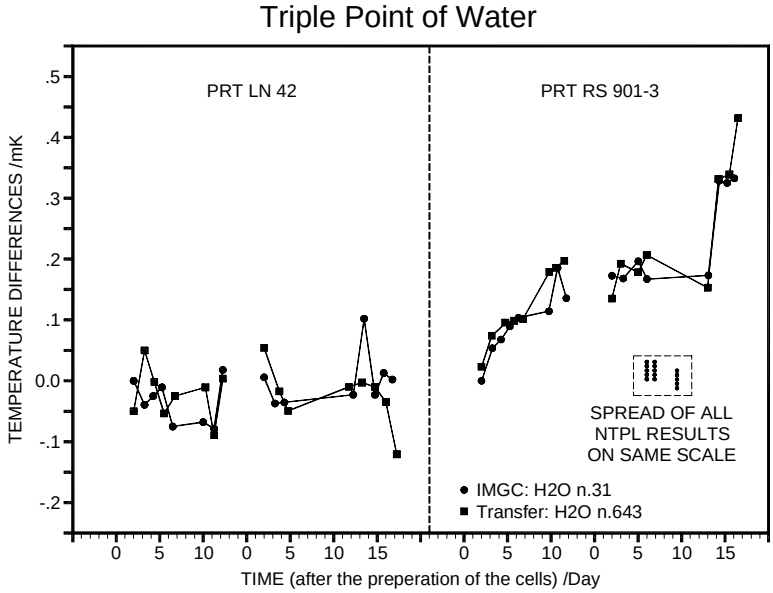
Most International intercomparisons are between Cells with similar depths of immersion. However in reality Cells exist with quite varying depths of immersion. In correcting for hydrostatic head a

correction of 0.73µK/metre is applied as per the supplementary information to ITS-90. Mendez-Lango [1] have suggested that, depending how the ice mantle is made this correction factor can increase, as high at 0.93µK/metre. This uncertainty or variation would give rise to considerable errors, however space does not permit me to elaborate on the magnitude of the errors.

CONCLUSION

Three current measurement techniques combined with a statistical software programme are enabling easy and reproducible measurements of temperature differences as small as 1 or 2 micro degrees to be made on a routine basis. Further work on hydrostatic head correction is urgently required to establish an accurate figure in the meantime 0.73µK/metre has to be assumed if intercomparisons of different length Cells are to be reproducible in different countries. If however, the correction is not 0.73µK/metre then the ITS-90 value of the Cell's water surface maybe higher or lower than measurements suggest significantly.

APPENDIX 1



Temperature differences between the IMGC and transfer cell.

REFERENCES:

(1) Effect of Crystal Size, Form and Stability on the Triple Point of Water
Mendez-Lango E., Centro National de Metrologia (CENAM), Queretaro, Mexico.

(2) Effects of Different Methods of Preparation of Ice Mantles of Triple Point of Water Cells on the Temporal Behaviour of the Triple-Point Temperatures
Furukawa T. G., Mangum W. B., and Strouse F. G., Metrologia 1997, 34, 215-233

(3) Totally Frozen Water Triple Point Cells: A Comparison Between the INTI (Argentina) and the ICAITI (Guatemala)
Tischler M., and Prado F. N., Metrologia 1997, 34, 371-374