

THE WATER TRIPLE POINT CELL – AN OPTIMAL REALIZATION

John P. Tavener
Managing Director

Isothermal Technology Limited, England
Tel: +44 (0)1704 543830 E-mail: info@isotech.co.uk

The Northern Temperature Primary Laboratory (N.T.P.L.) has, as the fulcrum of its realization of ITS-90 two reference water triple point cells; one of European design, certified by a respected National Laboratory to be within $\pm 0.1\text{mK}$ of its reference cells with a 95% confidence level, the other reference cell is a Jarrett/Isotech cell model A11 which includes a Mcloed gauge to enable us to measure any entrapped air. Both are within 10 micro Kelvins of each other and are higher in temperature than the water triple point cells tested against them.

The above is normal practice. It is also unsatisfactory in as much as there is no direct relation proven to ITS-90.

Cells of the highest temperature are selected because all known impurities lower the triple point temperature and any air remaining in the cell also lowers the temperature, thus the highest temperature cell should be closest to ITS-90. Unfortunately there is another variable, the Isotopic composition of the cell's water, and this can raise, as well as lower the water triple point temperature.

It follows that NTPL's selected reference cells could be higher than ITS-90, which would be as unsatisfactory as them being below ITS-90.

What would be the ideal requirements of a water triple point cell directly related to ITS-90? Firstly it should contain no dissolved impurities, secondly no air, but only water vapour above the cell. Thirdly it should have the Isotopic content specified by ITS-90.

Isothermal Technology Limited runs a still for the production of water triple point cells. During

the past twelve months the production of pure water from the still has been modified so that by a single control, water of Isotopic composition below at, or above that specified in ITS-90 can be produced. (See graph 2)

Unlike surface water, which can vary extremely by 0.25mK , ocean water more than 150km from shore varies only 0.003mK . From the results of thousands of water samples a Standard Mean Ocean Water (SMOW) has been defined in terms of Isotopic content. Since this is the only definition that exists,

and is accepted worldwide it is assumed that ITS-90 means this water.

In some designs of cells, such as the All a Mcloed gauge is incorporated permitting any air above the water in a triple point cell to be measured and quantified as a depression from ITS-90.

Two of the requirements for an optimal water triple point cell can be fulfilled.

The third requirement, that the water is free of impurities finds a solution described over 55 years ago.

E. H. Stimpson, in a paper dated 1945 describes a triple point cell having a flask attached by a thin hollow glass connecting tube. By transferring the cells water to the flask and gently distilling it back into the cell any impurities are left behind as a residue in the flask.

Once a cell was imagined it was relatively easy to produce practical embodiments of the design, and include a few parts per billion of colour to the water so that an observer could see what was happening in the cell.

Coloured photographs were taken to show the workings of two of the cells designated KT001 (blue) and KT002 (pink).

For their protection the design has been registered.

Picture 1

Shows KT002 on its support stand, necessary because of the fragile nature of the connected cell and flask. In the illustration about $\frac{2}{3}$ of the water is in the cell, $\frac{1}{3}$ in the flask. The Mcloed gauge is above the cell and facing the camera.

Picture 2

In this picture an Ice Mantle has been created using cold rods pre-cooled in liquid nitrogen, one can be seen in the cell's reentrant tube.

The Ice Mantle can be seen because as it forms, the ice rejects the impurities in the water including the dye, which concentrates at the Ice/Water interface.

About 30 minutes after the mantle is complete the impurities equalize and the defined edge to the Ice Mantle fades.

Picture 3

Shows the blue cell KT001. In this picture the water has been transferred from the cell into the flask leaving the clear Ice Mantle to melt.

Picture 4

Is a close up of the clear Ice Mantle melting.

Picture 5

All the ice has melted and has been transferred into the flask. The Mcloed gauge is clearly visible upper left in this picture.

Picture 6

To quietly distill the water back to the cell, the cell is placed in crushed ice in a dewar flask (right) whilst the flask remains at room temperature. The temperature difference is sufficient to distill the liquid slowly from the flask to the cell.

Picture 7

The distillation process half way through.

Picture 8

The distillation process complete. The flask is now empty and the cell full of clear, clean water.

What happened to the blue colorant?

Results

A full evaluation of the new cell will take a very long time but it is relevant and necessary to get some first impressions of the cells performance.

Entrapped Air

Inverting KT001 or KT002 so that vapour is trapped and then compressed into the Mcloed gauge produced no measurable air bubble, and since an air bubble the size of a small pea only reduces the triple point value by $0.3\mu\text{K}$ the depression due to air entrapment can be ignored because it is negligible.

Isotopic Analysis of KT001 & KT002

KT001 is $7 \pm 1\mu\text{K}$ below the SMOW definition.
KT002 is $0.8\mu\text{K}$ above SMOW.

Intercomparison with other Reference Standards

KT001 was made up together with NMI 119 and our A11 cells, left 4 days and intercompared twice over 3 days using our standard UKAS 3 current technique (described elsewhere).

Graph 3 shows KT001 to have the highest value of the three, but all 3 cells are within $10\mu\text{K}$.
KT002 was tested similarly, but some 2 months later and had a temperature $3\mu\text{K}$ above KT001.

Graphs

Graph 1

Shows the spread of results of KT001 measured over a 3 day period in terms of the absolute resistance of a Standard Platinum Resistance Thermometer YSI III using the 3 current techniques described elsewhere.

Graph 2

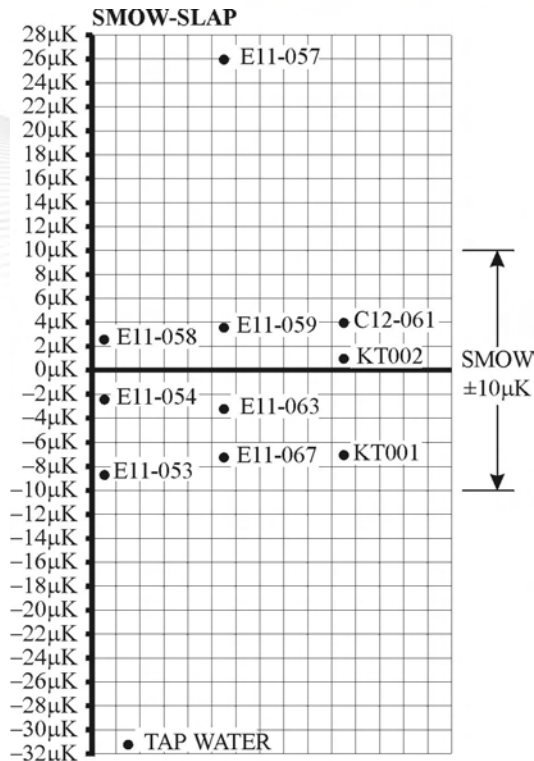
Shows the deviation of some production cells Isotopic analysis compared to SMOW.

Graph 3

Shows the 3 designs of cell KT001 and KT002, All-2127 and ref standard NMI 119 intercompared on two separate occasions.

All results show the 4 cells to be within 13µk.

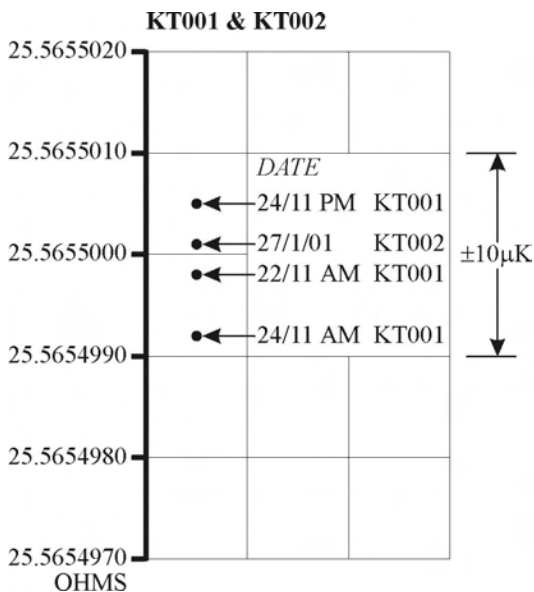
These preliminary results confirm that the NTPL reference cells are indeed very close to the assumed ITS-90 value. Which has improved NTPL's confidence in its water triple point cell measurements and has incidentally produced a new design of water triple point cell that can be directly related to ITS-90.



SMOW = Standard Mean Ocean Water
SLAP = Standard Laboratory Analysis Procedure

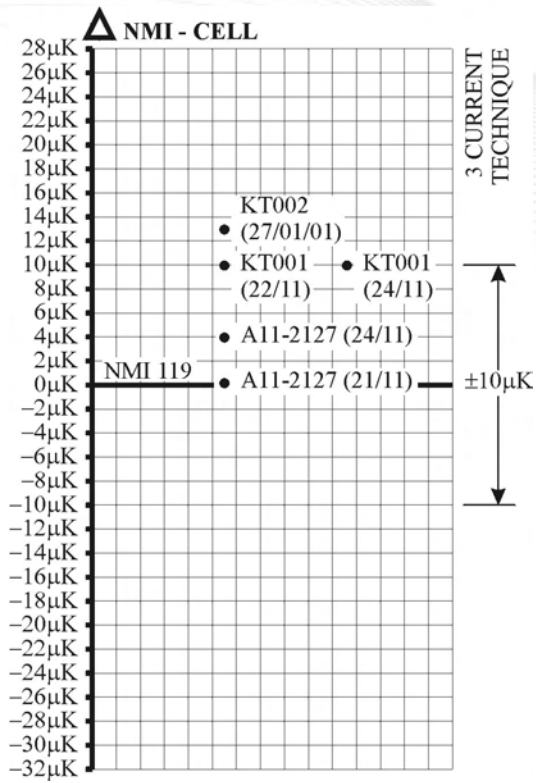
Graph 2

This graph shows the results of 10 cells produced from the new Isotech still compared to SMOW. E11-057 was made to have a very high Isotopic content.



Graph 1

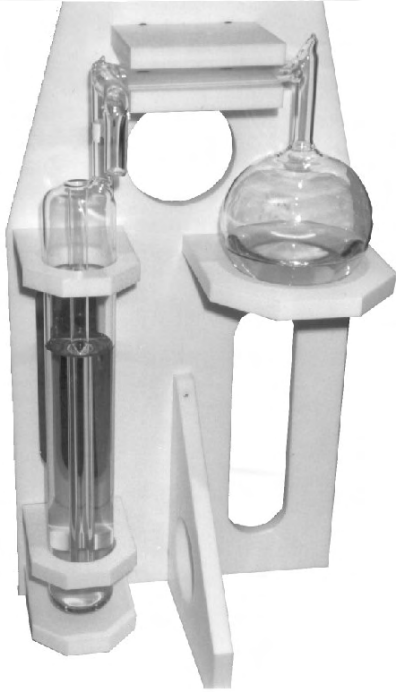
Resistance of YSI III in KT001 on 4 separate measurements over a period of 3 days in November 2000 and on KT002 in January 2001.



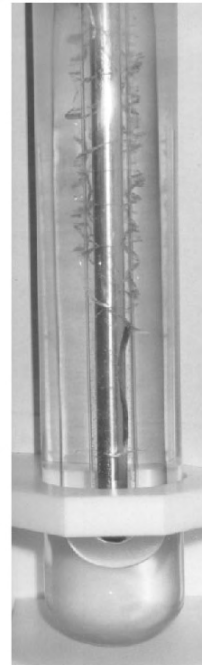
Graph 3

This graph shows KT001 and A11-2127

intercompared with Reference Cell NMI 119.



1 K.T.002
Optimal Water Triple Point Cell & Support



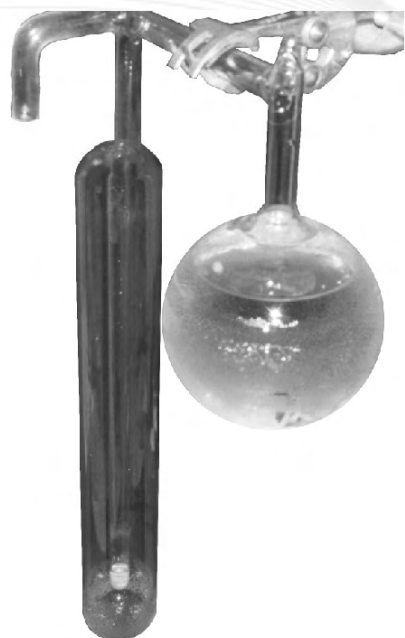
2 K.T.002
The Ice Mantle
The Concentrated colour around the Ice Mantle is due to the Ice rejecting the impurities in the water.



3 K.T.001
After testing the cell
The water can be transferred to the flask, leaving behind the pure ice mantle.



4 K.T.001
A close-up of the Melting Ice Mantle



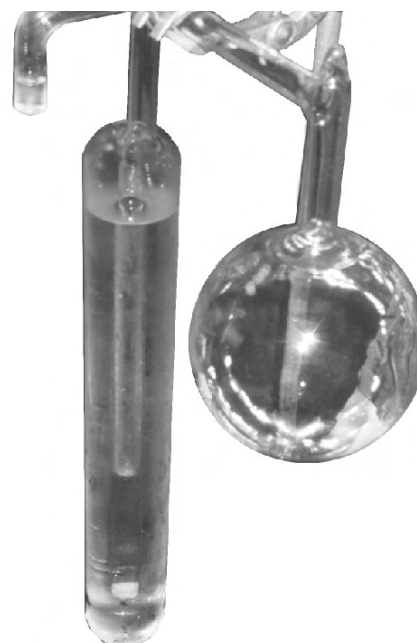
5 K.T.001
All the liquid is now in the flask attached to the cell.
 The McLeod gauge can be clearly seen in the top left.



6 K.T.001
The Liquid is quietly distilled back into the cell
 By placing the cell in crushed ice and leaving the flask at room temperature.



7 K.T.001
The Flask half empty during the distillation process



8 K.T.001
The Cell is full of the water distilled over from the Flask