Innovations in Thermal Metrology - Improvements at the Copper Point

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Abstract:

At NCSLi 2009 a new and novel combination of fixed point cell, heat siphon and immersion compensator was described being suitable for indium, tin, zinc or aluminium.

Research has continued to try and extend the concept to other ITS-90 fixed points, in particular silver and copper. In developing a solution to these two higher temperature fixed points (silver melts at 961.78°C and copper at 1084.62°C), solutions were sought that did not involve the use of quartz glass which is both fragile and porous at these temperatures.

In order to accurately measure the copper point a new and novel thermometer was designed and produced.

This report presents results obtained with the metal clad cells and as an aside describes the performance of the new very high temperature thermometers.

1. Three Copper Cells, 3 New Thermometers

One Silver and three Copper Cells were made and tested in a new and novel desktop apparatus designed specially to melt and freeze Silver and Copper Metal Clad Cells.

To measure the Cells a new design of thermometer was realised. 3 such thermometers were used. The thermometer design is described elsewhere.

2. Results Summary

The Silver Cell had a melting range of 3 milliK and 50% of the freeze was flat. Melt and freeze were coincident within 50 microK

Copper Cell 1 was contaminated during the development phase of the project.

It had a melt range of 18 milliK and a freeze range of 6 milliK.

Copper Cell 2 had a manufacturer's certificate claiming the purity was 6N9.

The measured melt range was 9 milliK; the 50% freeze was 4 milliK.

Copper Cell 3 was made from copper shot with a comprehensive independent impurity analysis totalling 85ppb. The main impurity was Iron at 63ppb; this will elevate the Cell's temperature by 0.1 milliK

The 80% melt range was 3 milliK; the 50% freeze was flat.

The 3 thermometers were stable within 0.1 milliK per hour or better at the Copper Point after 100 hours of stabilisation.

The first thermometer had a quartz mandrel and was unstable at RWTP.

The second and third thermometer had mandrels of synthetic sapphire and these were stable at RWTP.

The third Copper Cell associates to ITS-90 within ±1 milliK. The Synthetic Sapphire HTSPRT's are able to follow the melt and freeze curves within a fraction of a milliK.

3. Introduction

Part One [1] of this sequence described the development of a novel combination of Cell, Apparatus and Immersion Compensation for the ITS-90 Fixed Points of Indium, Tin, Zinc and Aluminium.

It had always been the intention to extend the range to Silver and Copper.

4. Description

One objective in extending the range to Silver and Copper is to eliminate the use of quartz glass that traditionally surrounds these cells. The glass is not only fragile and untransportable except by hand, but the glass is porous to ions such as Nickel, Chromium and Iron for example. The glass also softens and deforms especially at the Copper point and easily devitrifies.

Solutions already exist in Radiation Pyrometry for the Copper and Silver points which do not rely on glass.

Pyrometry has to use open cells where the graphite surrounding the metal is exposed so that it can be viewed by optical pyrometers.

This is achieved by flushing the cell assembly with 6N0 pure Argon. The cell assembly is supported at these temperatures inside a sodium isothermal liner. A typical copper point furnace is illustrated in Supplementary Information for ITS-90 [2].

In pyrometry the cells are horizontal, whereas in Contact Thermometry the cells are mounted vertically.

5. Construction of the Siphonic Cell

The cell was housed in a heat syphon in the shape of a Dewar, with extended inner tube as shown in Figure 1. A removable lid with re-entrant tube and Argon supply tube was fitted above the cell.

A heated metal collar was used to compensate for the stem conduction of the test thermometer.

6N0 grade Argon was used to blanket the cell with a flow of 0.2l/m.

Argon is heavier than air and so quickly displaces the air in the cell.

To measure the temperature at the Silver and Copper point a new thermometer was designed and used.

The new thermometer differs from existing models in a number of novel ways.

Described elsewhere, it has an alumina rather than a quartz sheath to provide rigidity at these high temperatures.

Readings were made using a microK 100 with an external Tinsley 1 ohm resistor held at 20°C.

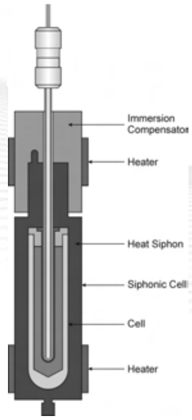


Figure 1. Siphonic Cell & Immersion Compensator.

6. Results at the Silver Point

The apparatus above was built - see picture 1, and a series of melts and freezes were performed on the cell.

A typical Silver melt and freeze are shown in Figures 2 & 3.

The three hour melt had an 80% slope of 3mK whilst the first 50% of the 3 hour freeze was flat.

Melt and freeze were coincident.

Picture 1. High Temperature Isothermal Tower.

Figure 2. Silver Cell Melt Curve

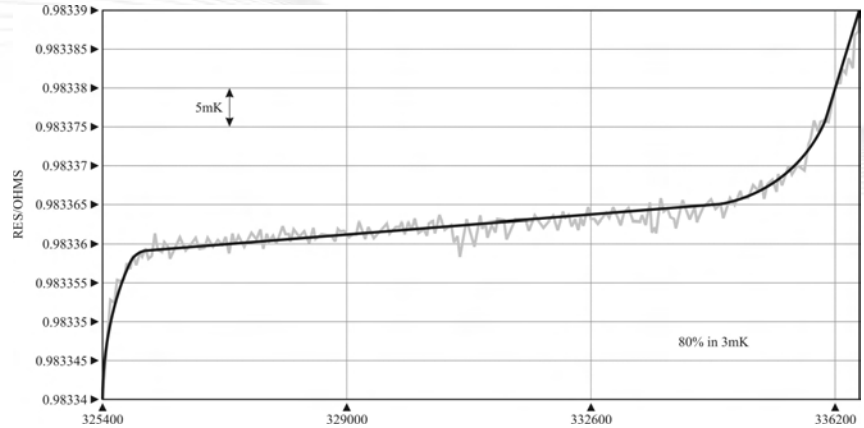
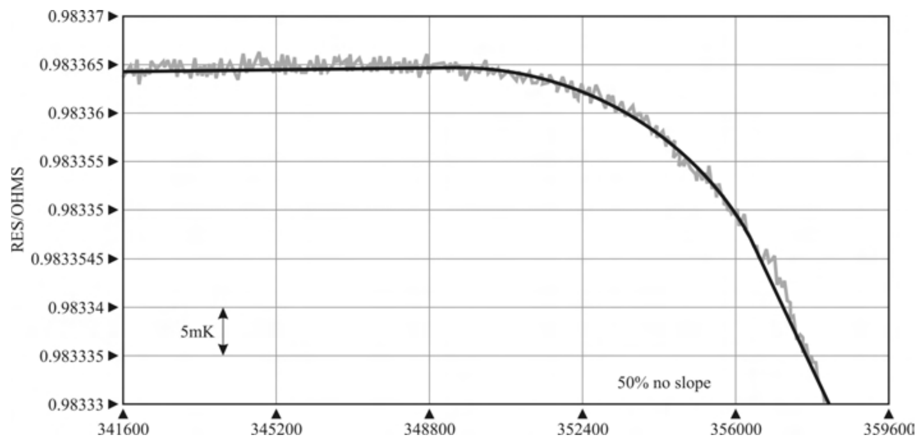


Figure 3. Silver Cell Freeze Curve



7. Discussion of Silver Point results

The Silver cell was constructed in early June 2009 and the total time at temperature some 200 hours, during which it was cycled a number of times through its melt/freeze curves, probably remaining molten for 80 hours of the total test time.

During the whole test sequence the cell was within the metallic heat siphon with 0.2l/m of 6N0 Argon flux around it.

A small amount of corrosion of the first sacrificial graphite washer was observed.

Regarding the performance of the cell its curves remained consistent with other cells made with this lot of Silver having quartz encapsulation.

Regarding the model 108462/s thermometer, it remained very stable during the tests including being removed from the cell and reinserted during the cold rod process.

These results are encouraging; suggest little or no contamination over a 200 hour period of either the cell or its monitor thermometer.

8. Introduction - The Copper Point

To assess the quality of a copper cell. Firstly its purity is important.

Cells 1 & 2 in this report had a manufacturer's certificate indicating impurities of Iron of 0.1 ppm.

Cell 3 was made from shot having a much more comprehensive analysis from an independent laboratory. These impurities totalled 85ppb.

Next a series of melts and freezes were performed on the Cell, monitored by stable thermometers, the melts and freezes were plotted and then analysed.

The three Copper Cells described in this sequence of tests were housed in a metallic cladding and so the melts and freezes were analysed to see if the Copper was becoming contaminated - contamination shows as an increased melt and freeze slope.

During the testing of the 3 Copper Cells, three thermometers, developed for this project were used. The first had a quartz mandrel supporting the winding. The second and third have a synthetic sapphire mandrel.

Oxygen is reported as being a problem with Copper. 1ppm of oxygen can depress the Copper's temperature by 5mK.

At the end of testing Cell 2, it was taken to 1100°C for 24 hours under vacuum.

The change in its measured temperature was less than 1mK.

9. Copper Cell No. 1

This development Cell was made in March 2009 and was tested using a Type R Thermocouple. The apparatus was developed and improved and the first of a new range of thermometers was developed. It had a quartz mandrel and an alumina sheath. In November a +9V charge was added to the thermometer. The rest of the measuring system was a microK 400 and internal Vishay 1 ohm resistor.

Results - April: ±15mK on melts R T/C

Table 1 - Melts & Freezes of Copper Cell 1 using 108462/001 Thermometer with a Quartz Mandrel

Date	Slope of Melt or Freeze in mK			Thermometer Reading in Ω
October 14	20 Hr	M, 80%	5mK	1.061,555Ω
October 15	12 Hr	F, 50%	8mK	1.061,545Ω
October 16	2 Hr	M, 80%	15mK	1.061,527Ω
October 17	6 Hr	F, 50%	0	1.061,521Ω
October 18	10 Hr	M, 80%	20mK	1.061,525Ω
Mean Melt = 17mK, Mean Freeze = 4mK, Drift 30mK				

Table 2 - Melts & Freezes of Copper Cell 1 using 108462/001 Thermometer with a Quartz Mandrel

Date	Slope of Melt or Freeze in mK			Thermometer Reading in Ω
November 9	3 Hr	M, 80%	20mK	1.061,520Ω
November 10	22 Hr	F, 50%	10mK	1.061,525Ω +9V
November 11	9 Hr	M, 80%	16mK	1.061,540Ω +9V
November 12	21 Hr	F, 50%	5mK	1.061,525Ω +9V
November 13	3 Hr	M, 80%	20mK	1.061,535Ω +9V
November 14	21 Hr	F, 50%	10mK	1.061,525Ω +9V
Mean Melt = 19mK Mean Freeze = 8mK Drift = 5mK				

Summary of Results for Copper Cell 1

Means of all measurements on Cu 1
80% Melt = 18mK 50% Freeze = 5mK

10. Copper Cell 2

Of the same purity copper as Cell 1, Cell 2 was made early in December 2009.

First measurements were made with the same measuring system as Cell 1.

At the end of December 2009 a new thermometer with synthetic Sapphire coil support became available. The microK 400 was replaced by a microK 100 and a Temperature Controlled 1Ω Tinsley AC/DC resistor.

Table 3 - Melts & Freeze of Copper Cell 2 using 108462/001 Thermometer with a Quartz Mandrel

Date	Slope of Melt or Freeze in mK			Thermometer Reading in Ω
December 10	3 ½ Hr	M, 80%	10mK	1.061,562Ω
December 11	4 Hr	F, 50%	5mK	1.061,560Ω
December 12	17 Hr	M, 80%	10mK	1.061,560Ω
December 13	3 Hr	F, 50%	5mK	1.061,560Ω
Mean Melt = 10mK Mean Freeze = 5mK Drift = 2mK				

Table 3 Equipment used: microK 400, Int. Vishay 1Ω, 108462/001 +9V

Table 4 - Melts and Freezes of Copper Cell 2 using 108462/S/002 Thermometer with a Sapphire Mandrel

Date	Slope of Melt or Freeze in mK			Thermometer Reading in Ω
December 30	3 Hr	M, 80%	5mK	1.092,387Ω
January 1	9 Hr	F, 50%	5mK	1.092,362Ω
January 2	4 Hr	M, 80%	15mK	1.092,350Ω
January 3	8 Hr	F, 50%	0	1.092,308Ω
Mean Melt = 10mK Mean Freeze = 3mK Drift = 80mK				

Table 4 Instrument upgrade: microK 100 ext Tinsley 1Ω new Sapphire Thermometer 108462/S/002

Table 5 - Melts and Freezes of Copper Cell 2 using 108462/S/002 Thermometer with a Sapphire Mandrel

Date	Slope of Melt or Freeze in mK			Thermometer Reading in Ω
January 8	1 Hr	M, 80%	7mK	1.092,310Ω
January 8	4 Hr	F, 50%	3mK	1.092,302Ω
January 9	2 Hr	M, 80%	8mK	1.092,300Ω
January 10	3 Hr	F, 50%	4mK	1.092,299Ω
Mean Melt = 8mK Mean Freeze = 4mK Drift = 11mK				

Table 5 Instrument Upgrade: microK 100 ext Tinsley 1Ω new Sapphire Thermometer 108462/S/002

Table 6 - Melts & Freezes Copper Cell 2 using 108462/S/002 Thermometer with a Sapphire Mandrel

Date	Slope of Melt or Freeze in mK			Thermometer Reading in Ω
January 30	3 Hr	M, 80%	8mK	1.092,298Ω
January 31	6 Hr	F, 50%	4mK	1.092,294Ω

Table 7 - Melts & Freezes Copper Cell 2 using 108462/S/002 Thermometer with a Synthetic Sapphire Mandrel

Date	Slope of Melt or Freeze in mK			Thermometer Reading in Ω
February 2	8 Hr	M, 80%	10mK	1.092,293Ω
February 3	8 Hr	F, 50%	5mK	1.092,287Ω
February 6*	x 4 Hr	M,80%	8mK	1.092,287Ω
February 7*	x 4 Hr	F, 50%	Failed	1.092,283Ω
Mean Melt = 9mK Mean Freeze = 5mK Drift = 10mK				

*After 24 hours at 1100°C under vacuum

Summary of Results for Copper Cell 2

Mean of all measurements on Cu2 80% Melt = 9mK 50% Freeze = 4mK

11. Copper Cell 3

This cell constructed in February 2010 was made from 7N pure Copper.

The first measurement was made with the first Synthetic Sapphire thermometer whilst the last sequence was performed with a second Synthetic Sapphire thermometer.

Results:-
Last reading of 108462/S/002 in Cell 2.
Melt 1.092,287Ω
Freeze 1.092,283Ω (see previous page)

Tables 8 - Melts & Freeze Copper Cell 3 using 108462/S/002 Thermometer with a Synthetic Sapphire Mandrel

Date	Slope of Melt or Freeze in mK			Thermometer Reading in Ω
February 23	1 Hr	F, 50%	0mK	1.092,287Ω
February 24	5 Hr	M, 80%	3mK	1.092,285 Ω
February 25	4 Hr	F, 50%	0mK	1.092,280 Ω

Table 9 - Melts & Freeze Copper Cell 3 using 108462/S/001 Thermometer with a Synthetic Sapphire Mandrel

Date	Slope of Melt or Freeze in mK			Thermometer Reading in Ω
February 27	2 Hr	F, 50%	0mK	1.099,557Ω
February 28	2½ Hr	M, 80%	3mK	1.099,553 Ω
Mean Melt = 3mK Mean Freeze = 0mK				

Figure 4 - Copper IsoTower Melt Plateau 24th February 2010 – Cell 3

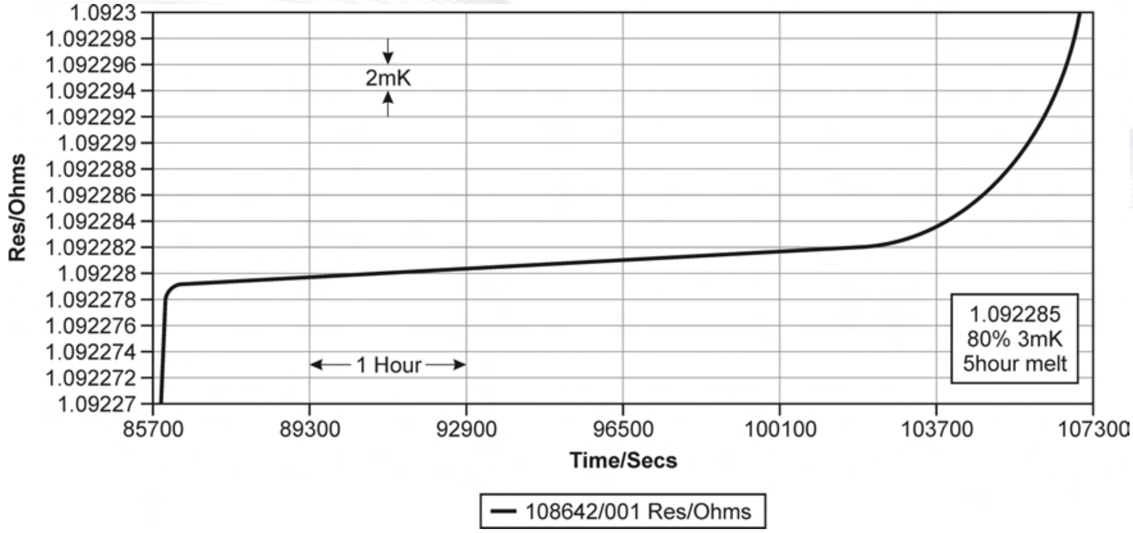


Figure 5 - Copper IsoTower Freeze Plateau 25th February 2010 – Cell 3

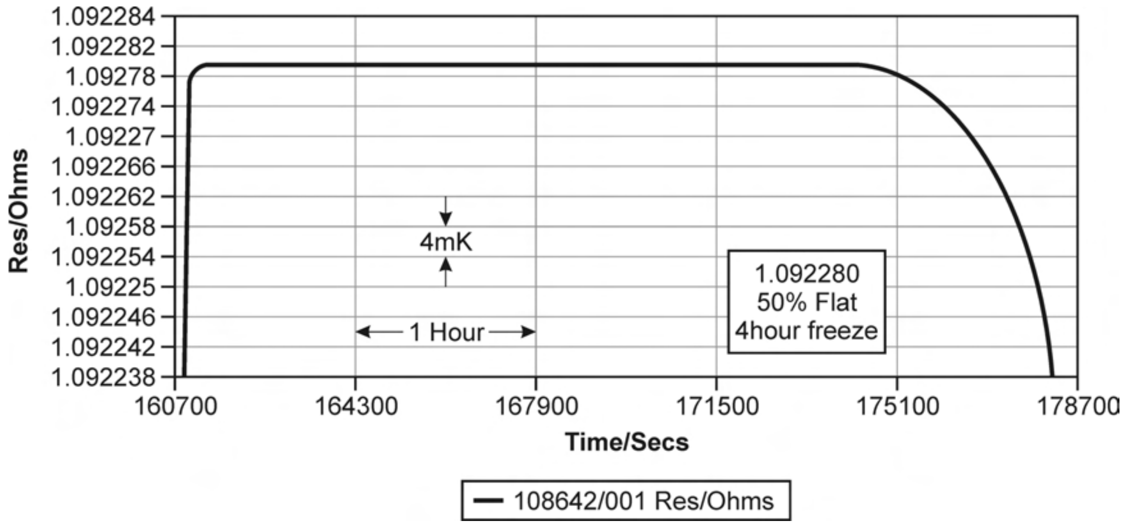


Table 10 - Means of All Measurements

Cu	80% Melt	50% Freeze
Cell 1	18mK	6mK
Cell 2	9mK	4.2mK
Cell 3	3mK	0mK

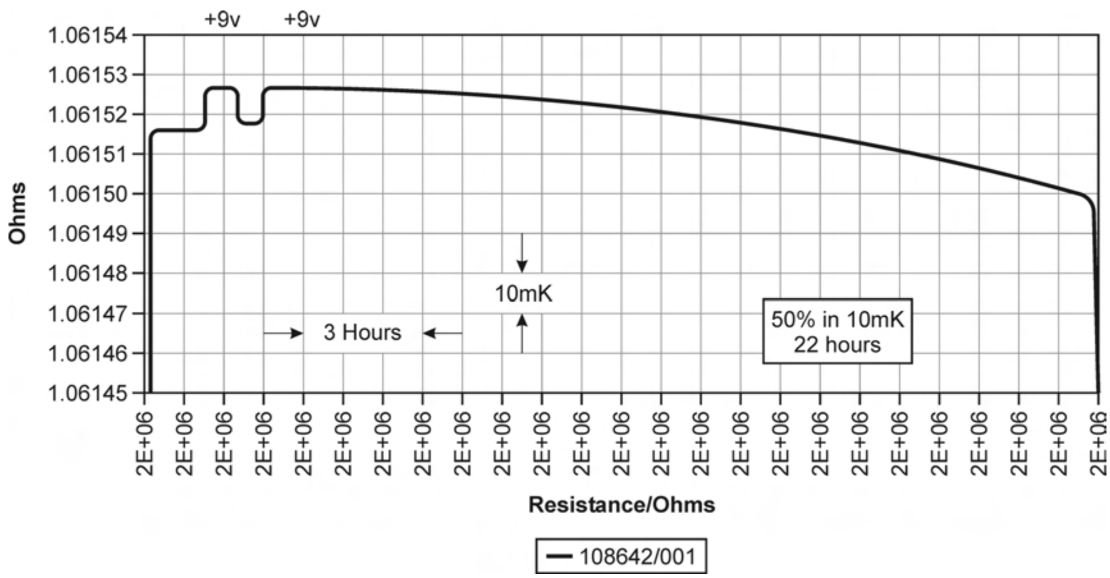
Table 10 - Summary of results for Copper Cells 1, 2 & 3 plus the Silver Cell

Silver Cell	3mK	0mK

12. Electrical Bias

On the freeze dated 10th October 2009 a +9V dc bias was added to the thermometer with quartz mandrel, its resistance increased by the equivalent of 7mK. The battery was disconnected then permanently connected. The Sapphire reduced the offset to 2mK.

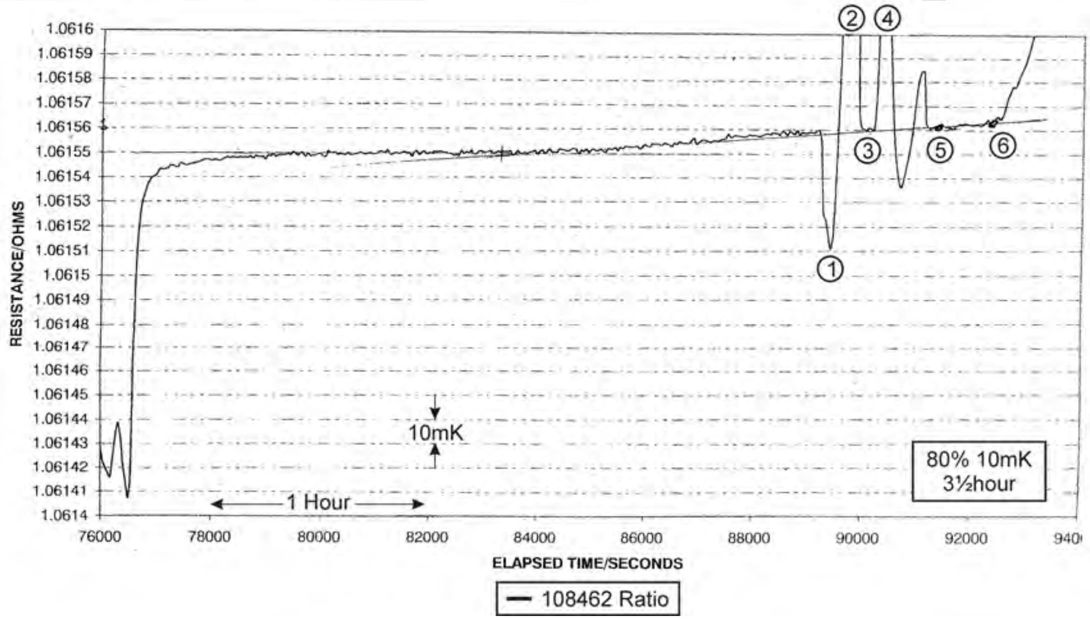
Figure 6 - Copper 10th October 2009 showing effect of Electrical Bias



13. Immersion

On the melt dated 10th December 2009 the heated block above the cell is being optimized. The monitor is raised 100mm (1) and the temperature drops. The blocks temperature is raised (2) the monitor is re-inserted (3) and raised again 100mm (4) the heated block is adjusted until there is no gradient over the 100mm (5) the monitor is reinserted and the melt is completed (6).

Figure 7 - Copper 10th December 2009 showing Immersion Compensation



14. Discussion

3 Copper Cells of increasing purity have been evaluated using 3 thermometers designed specifically for this project.

Thermometer drift after the initial 100 hours of use settled to less than 0.1mk per hour enabling accurate melts and freezes to be plotted and analysed.

No trace of oxygen was found in the Cells.

Cells 2 & 3 had similar temperatures with Cell 3 perhaps 2mK higher in temperature than Cell 2.

The purity (7N) and melt/freeze slopes (3mK & 0mK) suggest that Cell 3 is within 1mK of its ITS-90 temperature. (See graphs dated 24th February and 25th February 2010).

No reduction in purity of the Copper Cells was noted during testing.

15. Conclusion

A Copper Cell and Apparatus with association of 1mK to the ITS-90 value has been produced. Using a new design of thermometer the Cells performance can be measured to within 1mK per 10 hours or better.

My laboratory has a reference standard that can be used to certify other Copper Cells of our manufacture.

16. Future Work

To work within UKAS we are required to intercompare our cell with a National Standard. At present this will add 30mK to our uncertainties.

We need to find a National Laboratory interested in reducing its uncertainties with purer Copper and better thermometers.

References

[1] Improvements Relating to the Calibration of Thermometers, John P. Tavener, NCSLi 2009.

[2] Supplementary Information for the ITS-90, page 67, ISBN 92-822-2111-3