Evaluation

Fixed Points for the Thermal Calibration Laboratory
(Celebrating 10 years of Slim Cell Production)

Introduction

The advantage of fixed point calibration is the small uncertainties associated with the method.

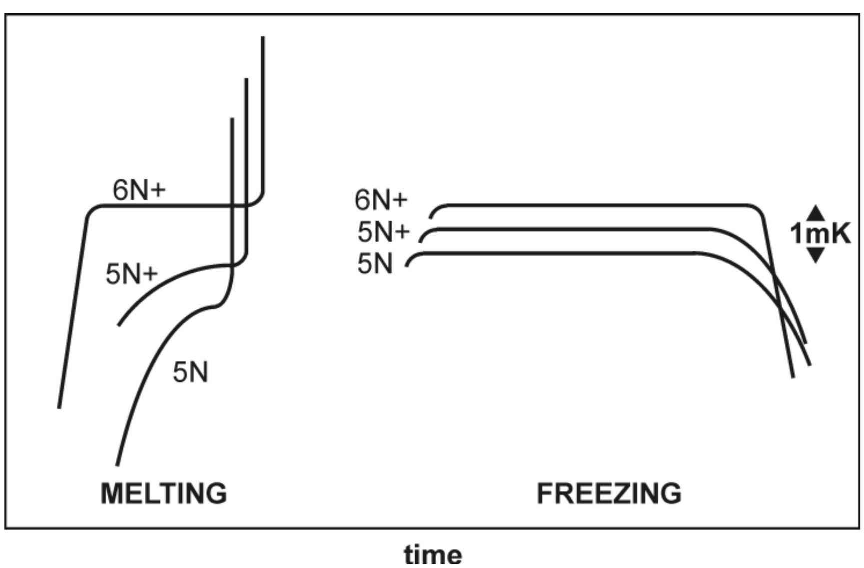
The very pure fixed point substance can be melted or frozen to produce an absolute temperature for calibrating temperature sensors.

The figure below shows the changes in slope and absolute temperature that occur for various purities.

Typically a 6N pure cell will melt 80% of its contents over 2mK and its contents will freeze 50% in between 0.1 and 0.2mK. The above is the accepted method of specifying the purity of a fixed point – *see references 1 and 2 for more details.*

A 5N pure cell will melt 80% of its contents over 20mK and 50% of its freeze will occur over 1 to 2mK.

Typical Melting & Freezing Curves of Metals of Three Levels of Purity



For all but Primary Laboratories, it is quicker, simpler and easier to use fixed point cells during their melt. Isotech's Slim Cells are all $6N^+$ pure so that the melt curve is very flat.

Small or 'Slim' Fixed Point Cells

These cells contain less of the metal contained in cells designed to fully realize the ITS-90 Scale. By reducing the size (both diameter and length) the slim cells can be fitted into much smaller pieces of apparatus. The negative side of such a design concept is that thermometers being calibrated are not so deeply immersed. This may, or may not be a problem, as we shall show later in this evaluation.

The melt plateau has the following advantages over the freeze:-

1. It can be automated. A simple timer switches on the apparatus 1 to 2 hours before it is needed its controller set to 1℃ above the melt. The cell then automatically comes onto its melt, which will last all day. Over night the timer re-freezes the cell ready for the next day. To freeze a cell means melting it first and most of the day is lost.

2. As thermometers are calibrated (at the rate of about 1 per 20 minutes) each one re-freezes a little of the melted cell causing the melt to lengthen i.e. the more calibration is performed the longer the plateau.

3. Stem conduction is minimized. This is because the sensor being calibrated passes through the apparatus, which is 1℃ above th e cell's temperature before it comes out into ambient air.

Summary Chart of the Results Obtained in this Evaluation

Slim cells in small apparatus compared to large cells in large apparatus

Slim Mercury Triple Point Cell in Europa	±0.1mK
Slim Water Triple Point Cell in Europa or Venus	±0.3mK
Slim Gallium Cell in Europa, Venus or Calisto	±0.3mk
Small Indium Cell in Calisto	±0.5mK
Slim Tin Cell in Medusa	±0.6mK
Slim Zinc Cell in Medusa	±1.4mK
Slim Aluminum Cell in Oberon	±5mK

Experimental Results

The following results at various fixed points were all performed in the same way.

A Standard Platinum Resistance Thermometer was calibrated in a large cell in a large apparatus. The thermometer was then transferred to the smaller cell in a large apparatus to check out the cell's purity.

Lastly the smaller cell was placed in the portable apparatus and the difference (if any) gives a measure of the stem conduction error due to the portable apparatus.

For convenience I will group the cells into 3.

Group 1 comprises the Triple Point of Mercury, the Triple Point of Water and the Gallium Cell.

1 piece of apparatus can create the conditions to melt or freeze any of group 1 cells. Called Europa, this piece of apparatus can create temperatures around the cells from –45℃ to +140℃.

The most complex temperature to create is the Triple Point of Water, and so this will be described first.

In 1982 a paper was presented at the 5th Conference of Temperature by Cox & Vaughn in which was described a slush method for creating the Triple Point of Water. Briefly the method comprised of supercooling the water cell to –7℃ and then giving it a shake. Shaking the cell initiated nucleation and sufficient (about 30%) water turned to small ice crystals to bring the cells temperature up to +0.01℃.

This method has been adapted for use in the Europa, or Venus.

A Small Triple Point of Water Cell was placed inside the Europa apparatus the temperature adjusted to cool the water cell to –6℃ or –7℃ it was then shaken to create a slush of ice and water. After a further 30 minutes at –7℃ the Europa was reset at 0℃. To gauge the accuracy of this approach a 25.5ohm quartz sheathed Standard Platinum Resistance Thermometer was calibrated in a Large Triple Point of Water Cell. Next it was transferred to the small cell in Europa. A plateau lasting longer than 16 hours was obtained with the thermometer reading within 0.3mK of its calibrated value (Graph 1).

Such a system, using RS232 link can be automated (with the exception of the shake) to provide a economically priced Triple Point of Water temperature all day every day.

The Gallium Point

Either by changing cells, or by having a second Europa apparatus the melting temperature of Gallium can also be created as described below:-

A small gallium melt point cell is placed inside the Europa, the temperature was set so that the block was 2 to 3℃ above the gallium melt point. A thermometer was placed in the reentrant tube of the cell and the warm-up and arrival on the plateau are observed. Once the gallium begins to melt, 5cc of warm water was introduced in the re-entrant tube to melt a sheath around the reentrant tube, and the temperature of the Europa was reduced to 0.5℃ above the melt temperature.

The thermometer read within 0.3mK of the calibrated gallium point after 20 minutes and remained within 0.3mK of the expected melt value for over 48 hours, (Graph. 2)

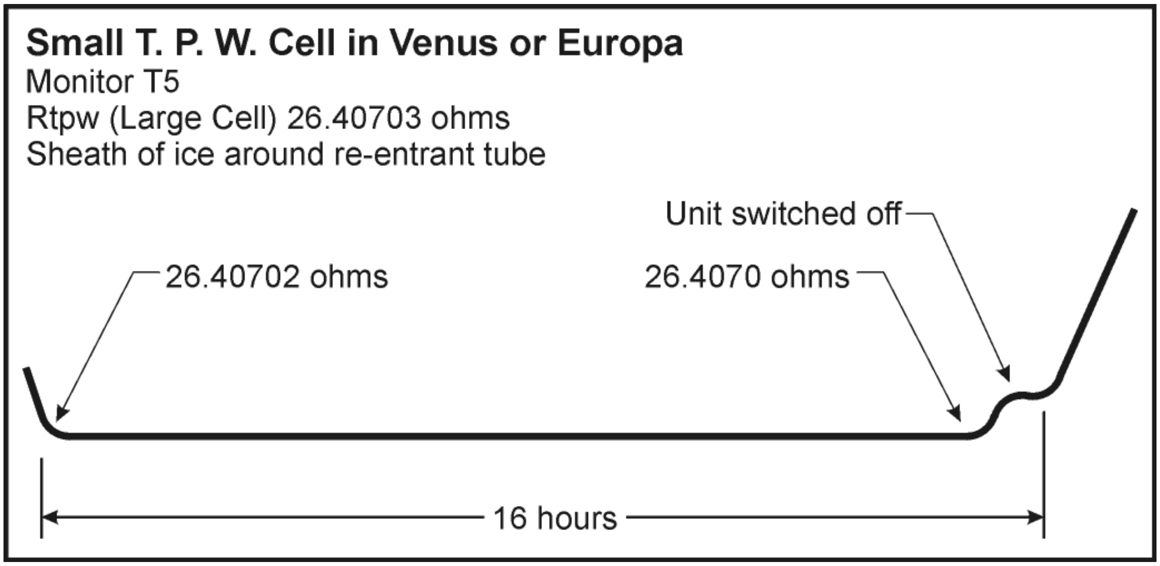
Unlike the gallium apparatus, the Europa is not self-protecting, its flexibility precludes this. Thus after melting, it is necessary to remove the cell and freeze the gallium from the bottom up. This is because gallium expands 3% as it freezes. Freezing is easily accomplished by placing the cell in 30 to 50mm of cold water, or onto a bed of ice cubes.

The Europa can also be used with a Slim Mercury Triple Point Cell as follows:-

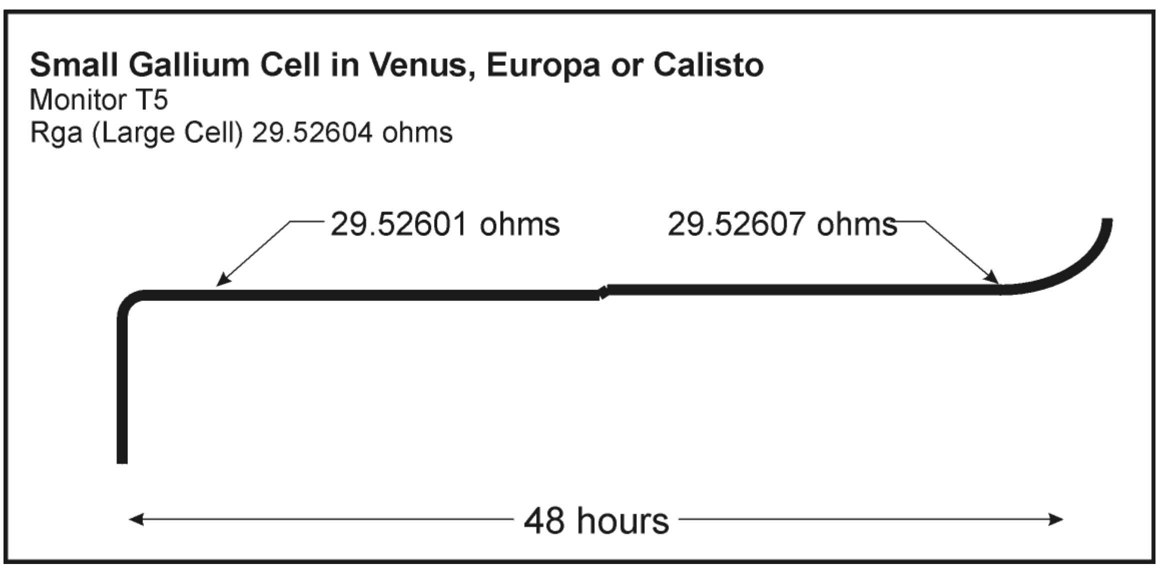
After placing the cell into the well of the Europa its control temperature is set to –45℃ the cell is cooled, supercooled, nucleates and quickly comes onto its freeze plateau. At this time the set point is raised to 0.5℃ below the freeze temperature and calibration can begin. Again the more sensors are calibrated, the longer the freeze plateau.

Thus with 1 small piece of apparatus and 3 slim cells, 3 of the most fundamental points of ITS-90 can be created and maintained for a working day or longer to an accuracy of 0.0003℃ or better.

Graph 1

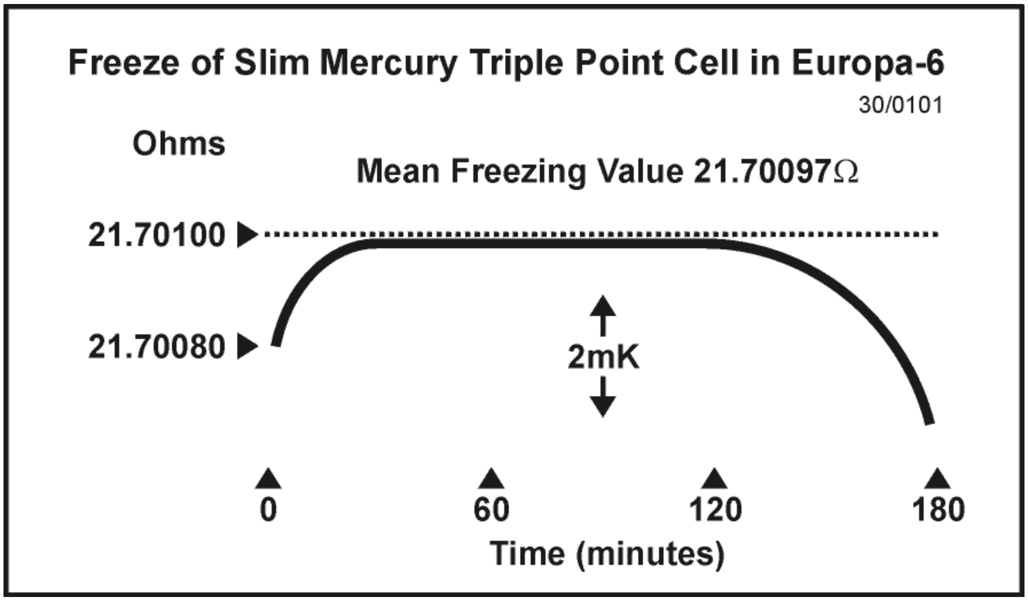


Graph 2

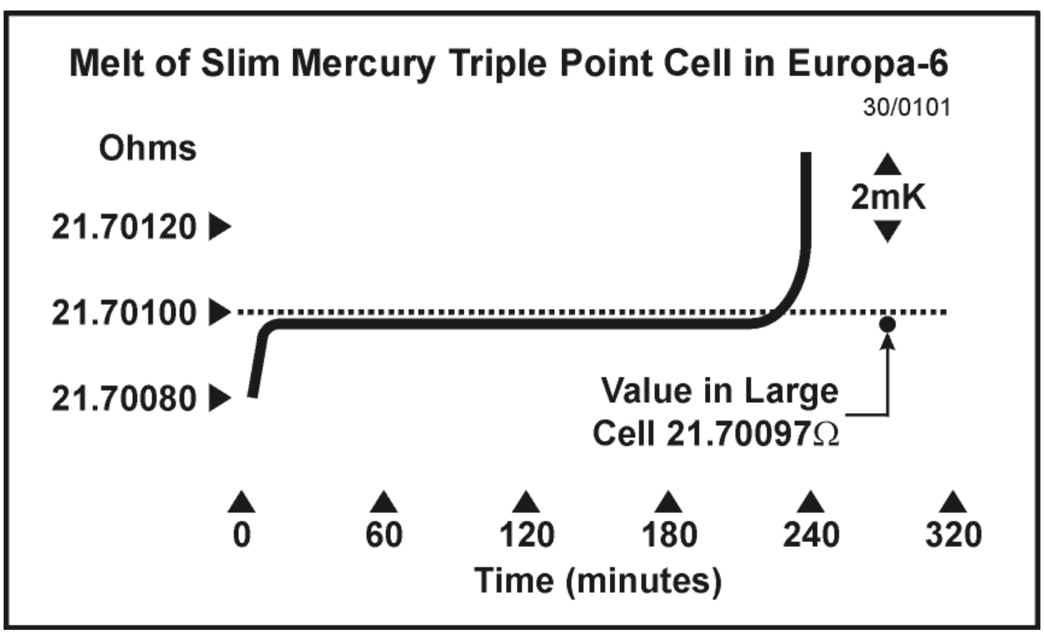


The Europa-6 and Slim Mercury Triple Point Cell give accurate realization of the ITS-90 value.

Graph 3



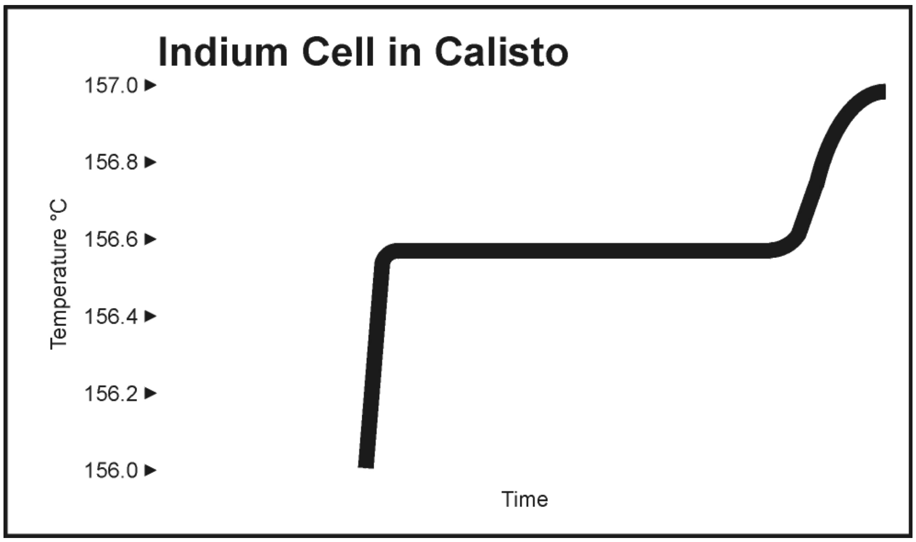
Graph 4



We can go beyond the temperatures –38.8344℃, 0.01 and 29.7646℃ with a second group of cells.

The second group of slim cells comprises Indium at 156.598℃, Tin at 231.928℃ and Zinc at 419.527℃.

Small Indium Cells can be melted in a portable apparatus called Calisto.



Indium has a phase transition of 156.5985℃. For co nvenience the cells are used with the melting point. For a short and well-defined melting point plateau the cell is place centrally into the Calisto's well. The temperature is set for 158.4, a metal ring is placed over the cell re-entrant tube and insulation is added both below and above this ring. Oil may optionally be used inside the cell for improved heat transfer to the thermometer being calibrated. Typically one hour after switch on a 2 hour plateau will be achieved, see chart.

Alternatively a bench top apparatus called Medusa 1 can be used with Indium, Tin and Zinc.

Operation is very simple, Medusa 1's controller is set to a temperature ½℃ above the melt temperature of fixed point cell. The cell will melt over a working day during which time calibrations can be performed.

If only 1 Medusa is used only 1 fixed point can be created in a day. If 2 or 3 Medusa's are available it is possible by use of a timer to have Indium, Tin, Zinc melt temperatures available all day, every day.

Because the apparatus and cells are smaller than standard cells and apparatus it is important to discover the effects of these changes. A report of Tin and Zinc points is presented below.

In the evaluation the Slim Zinc Sealed Cell was chosen because it is most sensitive to stem conduction and thermal gradients, hence it has the largest errors. This is because at lower temperature points such as Tin and Indium the gradients and stem conduction are less because the apparatus is closer to ambient.

An Isotech Model 909/25.5ohm SPRT was used for all measurements since it has a long sensing length and would show large stem conduction errors if these exist.

Method

The 25.5ohm SPRT was calibrated in a large sealed cell in furnace 17701. Values being obtained for a freeze plateau.

Subsequently the same apparatus and thermometer were used in conjunction with a Slim Sealed Zinc Cell to evaluate any difference in plateau values.

Next the same Slim Sealed Zinc Cell was placed in a Medusa I and the melt characteristics were monitored.

A similar procedure was adopted to test the Slim Tin Cell.

Discussion of Results

The melt curves attached are actual results taken regularly on our UKAS accredited Slim Cell Fixed Point System. The Slim Cells themselves are metal clad for rugged use, and the Cells are now 5 years old, and in use most days of the year.

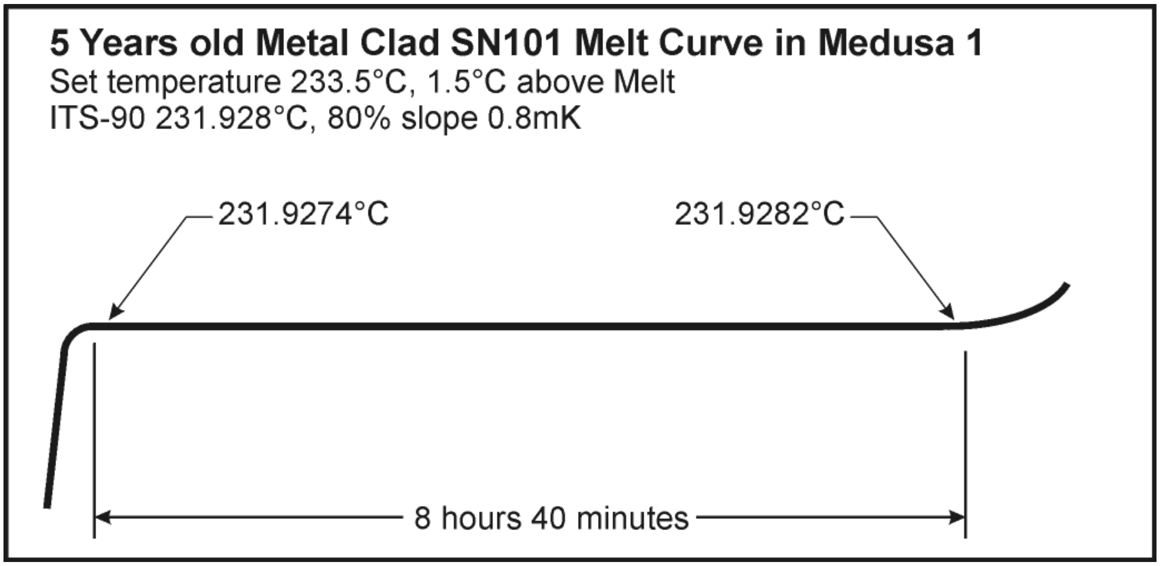
The Zinc Cell, Serial No. Zn 160 began its melt just 1.4mK below the ITS-90 value and ended just 1.4mK above the ITS-90 value. This is within the uncertainty of calibration of the SPRT used.

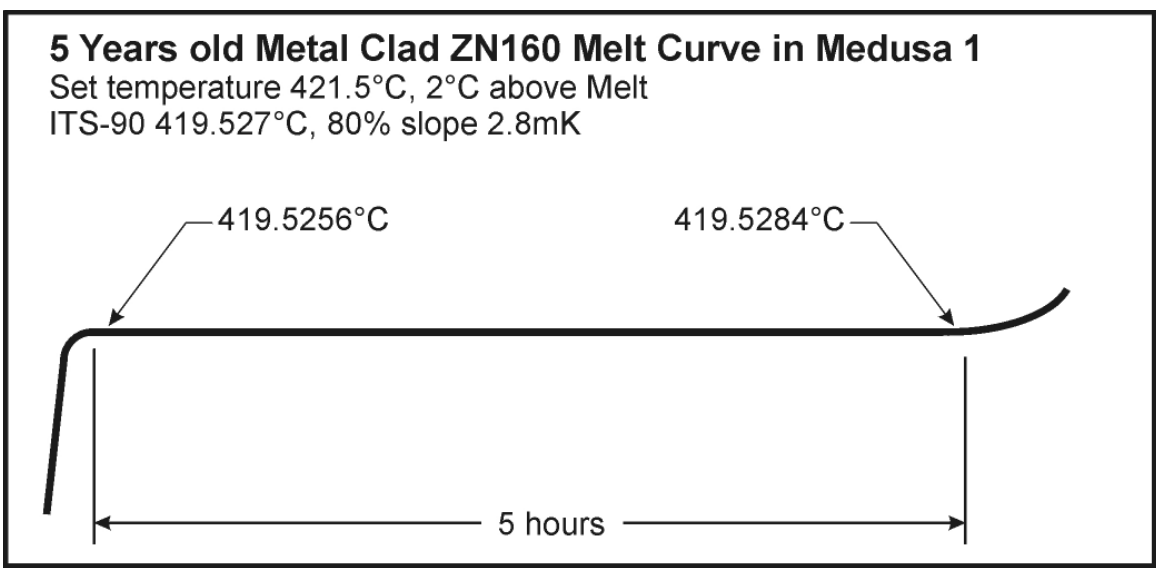
The Tin Cell Serial No. Sn 101 began its melt just 0.6mK below the ITS-90 value and ended 0.2mK above the ITS-90 value, again within the uncertainty of calibration of the SPRT used.

The set points were 1.5 to 2℃ above the melt temperature so that the melts would be complete within a working day.

By adjusting the set point closer to the melt temperature longer plateaus can be obtained.

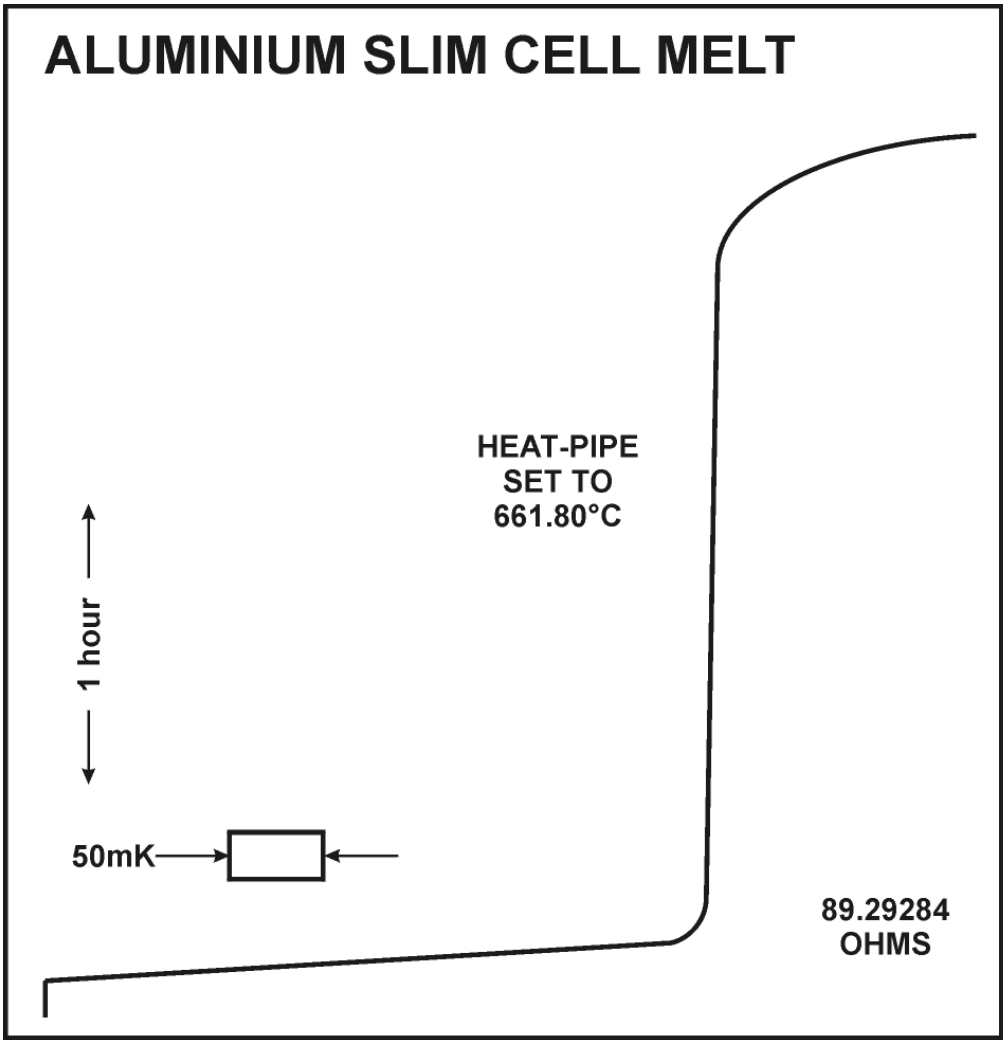
N.B. Plateau length is proportional to the difference of melt and set point temperatures i.e. if a 2℃ difference gives a 5 hour melt a 1℃ difference will give a 10 hour melt.


5 Years old Metal Clad SN101 Melt Curve in Medusa 1
Set temperature 233.5°C, 1.5°C above Melt
ITS-90 231.928°C, 80% slope 0.8mK
231.9274°C
231.9282°C
8 hours 40 minutes


5 Years old Metal Clad ZN160 Melt Curve in Medusa 1
Set temperature 421.5°C, 2°C above Melt
ITS-90 419.527°C, 80% slope 2.8mK
419.5256°C
419.5284°C
5 hours

Group 3 comprises Aluminum and Silver Slim Cells.

In order to get a long, uniform plateau from these cells it is necessary to house them in an expensive piece of apparatus containing a sodium heat pipe called Oberon, the cell/apparatus combination gives a melt plateau of 2 or more hours with a flatness of 3 to 5mK – *see graph.*



For details of Isotech's range of slim cells and apparatus ask for a free copy of Databook 2.

In 2002, a German DKD accredited laboratory applied to widen its accreditation to include a set of slim cells, mercury, water triple point, gallium, indium, tin, zinc and aluminium. The slim cells and apparatus were sent to PTB for intercomparison to the National Standards of Germany.

The results are tabulated below: -

Slim Cell	ΔT (mK)	u/c (mK)
Hg 137	0	1
Ga 123	-0.173	0.25
In 125	-1.4	2
Sn 132	+1.4	2
Zn 64	+0.3	2
Al 160	+1	3

References

1. Optimal Realization of the Defining Fixed Points of the ITS-90 that are used for Contact Thermometry.

   CCT Working Group – B.W. Mangum (retired from NIST), Chairman; P. Bloembergen (retired from VSL); M. V. Chattle (retired from NPL); B, Fellmuth (PTB); P. Marcarino (IMGC); and A. I. Pokhodun (VNIIM).

2. The Freezing Points for High Purity Metals as Precision Temperature Standards.

   Precision Measurements with Standard Resistance Thermometers; E. H. McLaren.

3. Completely Automated Fixed Points from ITS-90 for Industry – Points On The Temperature Scale (POTTS).

   John P. Tavener, Isothermal Technology Limited (Isotech), Pine Grove, Southport, England.

4. Sealed Cells, Open Cells, Slim Cells.

   Isotech Journal of Thermometry – Vol. 2, No. 1, Second Quarter 1991.