SLIM CELLS – AN INTERNATIONAL INTERCOMPARISON

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Abstract

In the early days, when realizations of defining thermometric fixed points were done only in National and University Laboratories, the cells in which the metals were contained were open to the atmosphere, and were protected from oxidation and contamination by scrupulous care in use. As the requirements for more fundamental calibration capability in-house developed in science and industry, sealed fixed-point cells, containing a proper atmosphere and invulnerable to chance contamination, were developed.

The special requirements of immersion depth, plateau duration, etc. required for the calibration of SPRT's may not be necessary in laboratories charged with calibrating industrial resistance thermometers, thermocouples and thermistors, but mobility and cost may be more important. "Slim cells" is a name given to another category of cell, which are somewhat slimmer, slightly shorter, and lower in price. Slim cells are built using the same materials, techniques and purity of metal as the larger cells, but the uncertainties associated with them are somewhat larger, not because of the cells but precisely because their properties cannot be measured with SPRT's, and transfer thermometers must be employed in qualifying them.

In consequence of their smaller size, smaller, lighter-weight apparatus (bench-top or cart-mounted furnaces) may be used to melt and freeze the metal in these cells.

During the 1990's a careful series of intercomparisons were made at the Northern Temperature Primary Laboratory in England. The results gave an insight into the uncertainties to be expected when using slim cells. In these experiments the slim cells were clad in glass. In the latter part of the 1990's sufficient evidence was available to indicate that slim cells could be clad in metallic housings without contamination. Recent slim cells have been supplied with metallic housings.

During 2002 the DKD accredited laboratory of KK applied for an improvement in their accreditation to the slim cells and bench top apparatus that they were using, PTB evaluated the cells and apparatus against their National Standards.

This paper presents the results of the original primary laboratory intercomparisons and the more recent intercomparisons of PTB. The results show that the slim cells and apparatus offer good agreement with Primary and National Standards.

1. Introduction

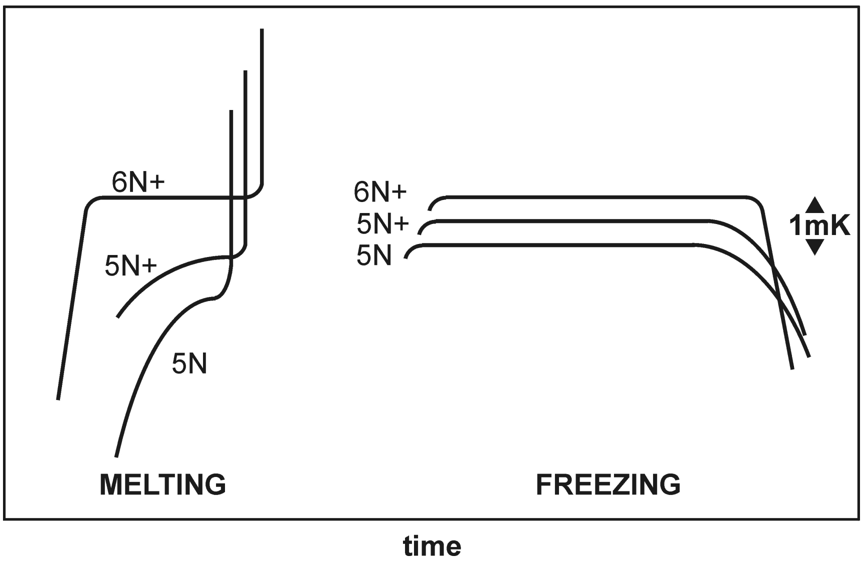
ITS-90 is defined in terms of a number of temperatures at which pure substances such as water, mercury, tin etc. melt or freeze. [1] Supplementary information to ITS-90 [2] and more recently CCT/2000-13 describe the optimal realizations of ITS-90 i.e. the very best that can be made.

The exacting requirements of national laboratories may not be necessary for laboratories charged with calibrating industrial resistance thermometers, thermocouples and thermistors. Mobility and cost may be more important. For these laboratories smaller (thinner and shorter) cells may be of most use. Slim cells therefore are built using the same materials, techniques and purity of metal as the larger cells but the uncertainties are somewhat larger, not because of the cells but because their properties cannot be measured to the same precision as large cells. In consequence of their smaller size, smaller lightweight apparatus can be used to melt and freeze the metal in the cells.

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 0.2 mK. 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 20 mK and 50% of its freeze will occur over 1 to 2 mK.

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. Slim Cells are all $6N^+$ pure so that the melt curve is very flat.

2. 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.

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°C 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 before measurements can be made.
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°C above the cell's temperature before it comes out into ambient air.

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

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°C and then giving it a shake. Shaking the cell initiated nucleation and sufficient water turned to small ice crystals to bring the cells temperature up to +0.01°C. This method has been adapted for use in portable apparatus.

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

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

4. The Gallium Point

The melting temperature of Gallium can also be created as described below: -

A small gallium melt point cell is placed inside the apparatus; the temperature was set so that the block was 2 to 3°C 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 5cm^3 of warm water was introduced in the re-entrant tube to melt a sheath around the reentrant tube, and the temperature of the apparatus was reduced to 0.5 °C above the melt temperature. The thermometer read within 0.3 mK of the calibrated gallium point after 20 minutes and remained within 0.3 mK of the expected melt value for over 48 hours (Graph. 2).

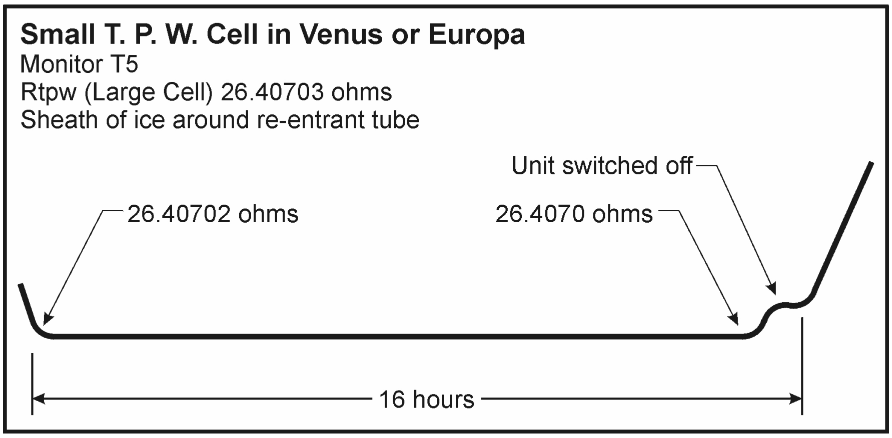
The portable apparatus is not self-protecting, thus after melting, it is necessary to remove the cell and freeze the gallium from the bottom up. This is because gallium expands 3% as it freezes. Freezing is easily accomplished by placing the cell in 30 to 50 mm of cold water, or onto a bed of ice cubes.

The same portable apparatus as used with water and gallium can also be used with a Slim Mercury Triple Point Cell as follows:

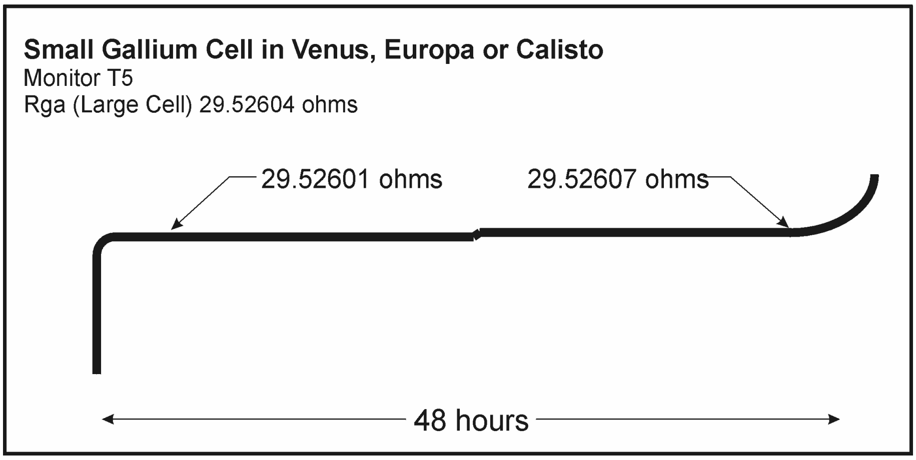
After placing the cell into the well of the apparatus its control temperature is set to –45°C, the cell is cooled, supercooled, nucleates and quickly comes onto its freeze plateau. At this time the set point is raised to 0.5°C below the freeze temperature and calibration can begin. Again: the more sensors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

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 0.3 mK or better.

Graph 1

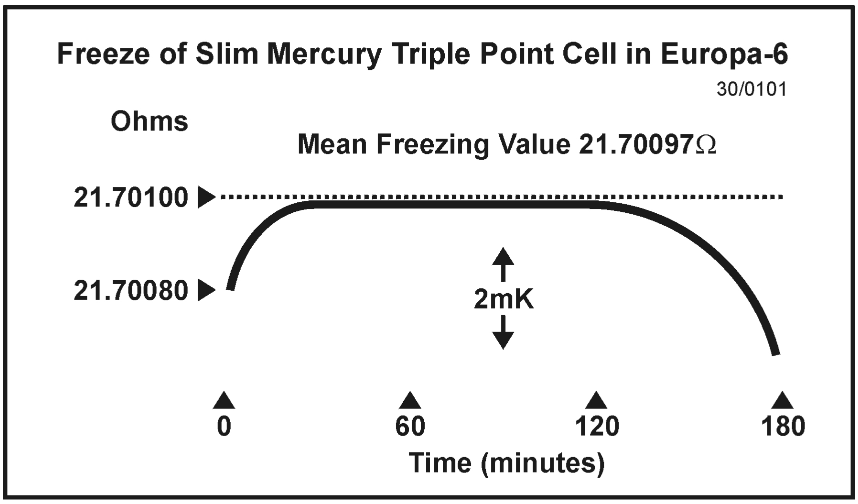


Graph 2

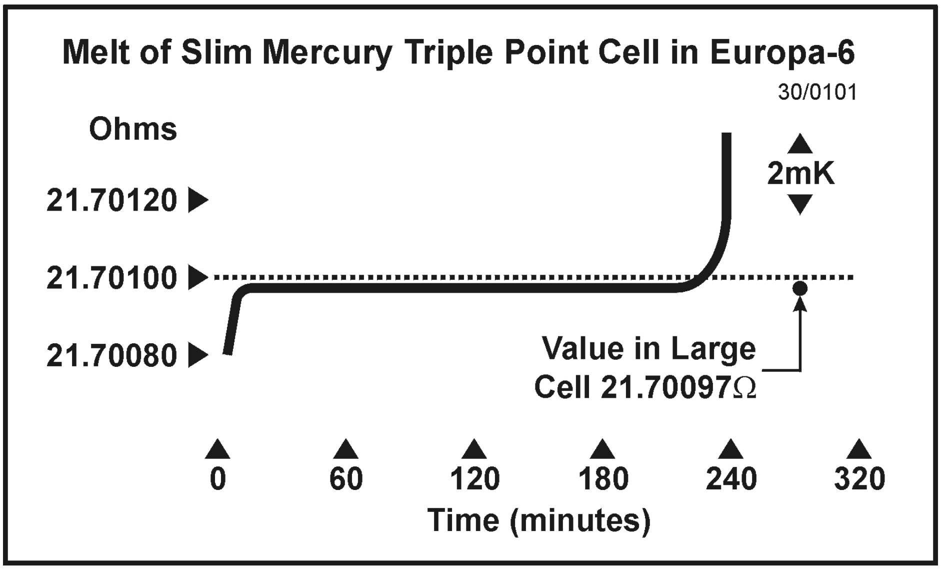


The Europa-6 and Slim Mercury Triple Point Cell give accurate realization of the ITS-90 value.

Graph 3



Graph 4



Above gallium at a temperature of 29.7646°C there are indium at 156.598°C, tin at 231.928 °C and zinc at 419.527 °C.

A bench top apparatus can be used with indium, tin and zinc. Operation is very simple; the controller of the apparatus is set to a temperature 0.5 °C 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 apparatus is used only 1 fixed point can be created in a day. If 3 apparatus are available it is possible by use of a timer in each to have indium, tin, zinc melt temperatures available all day, every day.

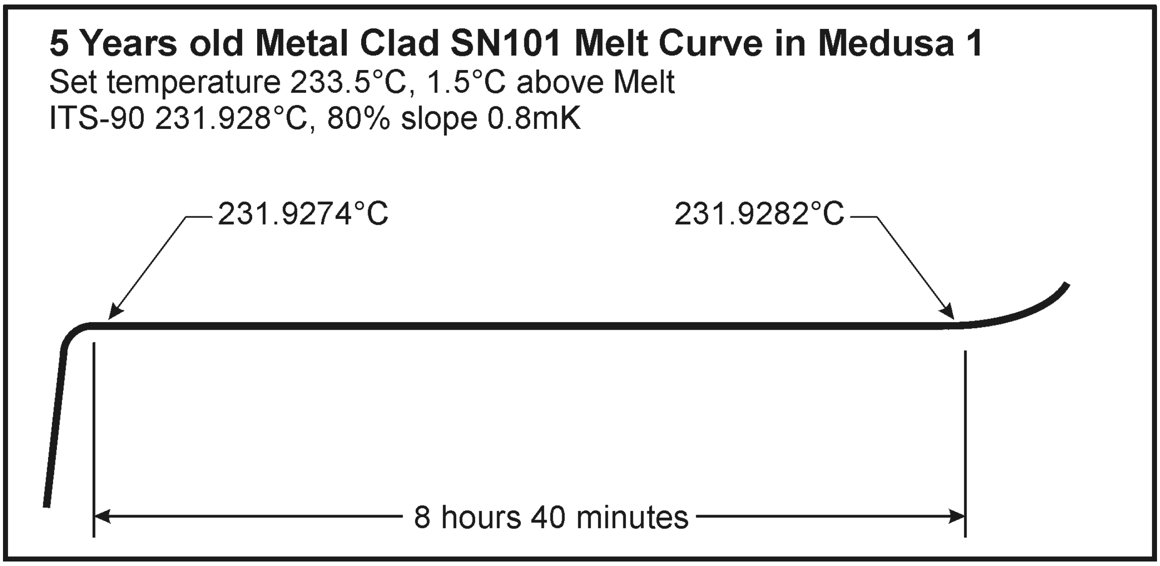
The melt curves attached are actual results taken regularly on a UKAS accredited slim cell fixed point system. The slim cells themselves are metal clad for rugged use, and the cells are 5 years old, and in use most days of the year.

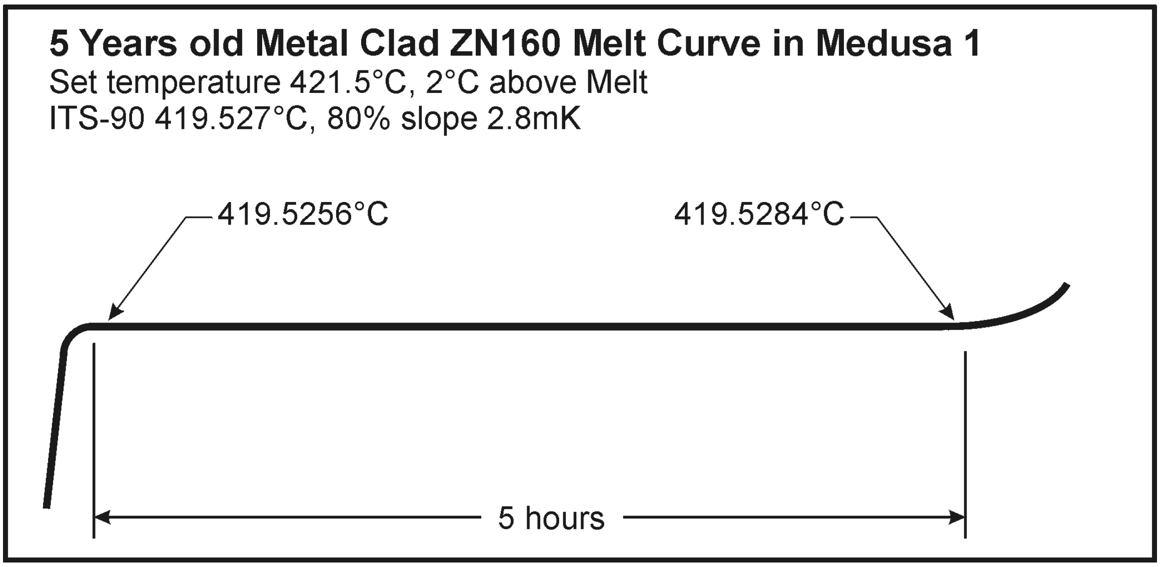
The zinc cell, Serial No. Zn 160 began its melt just 1.4mK below the ITS-90 value and ended just 1.4mK above the ITS-90 value. This is within the uncertainty of calibration of the SPRT used.

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°C 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 °C difference gives a 5 hour melt a 1 °C difference will give a 10 hour melt.*





5. Summary Chart of the Results Obtained

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
Slim Tin Cell in Medusa	±0.6mK
Slim Zinc Cell in Medusa	±1.4mK

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	-1.6	2
Sn 132	+1.4	2
Zn 64	+0.3	3
Al 160	+1	2

All temperature deviations were within the uncertainties assigned by PTB!

References

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