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NMIA Realization of the ITS-90 Based on Fixed-Point Cell Ensembles

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Abstract NMIA has recently moved from an ITS-90 realization based on single cells of each fixed point to one based on ensembles of up to five cells of each fixed point from argon to silver. It has been suggested that relying on Raoult's law to estimate the concentration of impurities in fixed-point cells, and to thereby estimate the likely shift introduced to the temperature of the melting or freezing phase transition, is inadequate. Measurements of NMIA's present set of 36 cells confirm that using Raoult's law alone is inadequate, and underestimates the temperature depression of some cells. Material purity assays are usually available for the metals (or gases); however, this will not include contamination introduced during the cell construction process or in-use impurity migration into the sample. At NMIA, we have (1) established ensembles of up to five cells of each fixed point and (2) established techniques and uncertainties for comparisons of cells at the 0.2 mK level. It is concluded that, at the sub-mK accuracy level, fixed-point cells should be considered as artifacts requiring calibration or validation to confirm their suitability as intrinsic reference standards.

Keywords Thermometry · Primary-standards · Fixed-points · Impurities · Cell-comparison · Freezing-point-depression

1 Introduction

In 1995, the General Conference on Weights and Measures (CGPM) [1] resolved to initiate a process toward formal recognition by national metrology institutes (NMIs)

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Table 1 First cryoscopic constant, A, for ITS-90 fixed-point substances, and expected temperature depression caused by 1 molar ppm of impurities

Substance	Ar	Hg	Ga	In	Sn	Zn	Al	Ag
A (K^{-1})	0.0203	0.00502	0.00732	0.00213	0.00329	0.00185	0.00149	0.000891
Depression (mK)	0.05	0.20	0.14	0.47	0.30	0.54	0.67	1.12

of each other's primary standards and a series of international comparisons of primary standards was commenced. In the 1997 Consultative Committee for Thermometry's Key Comparison 3 (CCT-K3) [2], the National Metrology Institute of Australia's (NMIA) indium- and tin-point results were approximately 1.19 mK and 0.68 mK low, respectively, although the freezing and melting curves showed no evidence of cell contamination, and the manufacturer's assay of the source materials indicated $>$99.9999 % purity. In 2000–2003, NMIA piloted the regional equivalent comparison APMP-K3, and both NMIA and the Korea Research Institute of Standards and Science (KRISS), who provided the link to the CCT-K3 comparison, had experienced cell breakages in the interval between the CCT and Asia Pacific Metrology Programme (APMP) key comparisons. In this case, both laboratories had good direct comparison data between their old and new reference cells, enabling a satisfactory link between the CCT-K3 and APMP-K3 to be made, albeit with greater uncertainty.

Prior to CCT-K3, NMIA, like many other NMIs, had relied upon the use of methods based on Raoult's law (such as examination of the flatness and the agreement of melting and freezing curves) to validate our fixed-point cells. The CCT-K3 results prompted NMIA to establish a set of five tin cells for comparison, and the results [3] confirmed the inadequacy of techniques based on Raoult's law. NMIA then commenced a program to establish sets of cells for the other ITS-90 [4] fixed points with the aim of better validating the cell uncertainty estimates based on material-purity assays, and ensuring that a firm, low-uncertainty link to key comparison data was maintained.

2 Freezing-Curve Analysis

Raoult's law of dilute solutions states that the depression of the freezing point of a dilute solution is proportional to the concentration of the impurity. The proportionality constant, called the first cryoscopic constant, is given in Table 1 together with the depression expected from Raoult's law from a 10^{-6} mol (1 ppm mole fraction) impurity concentration. In a slowly freezing sample, the solid insoluble impurities would be expected to become increasingly concentrated in the remaining liquid-phase material, thereby depressing the freezing-point temperature proportionally to $1/F$, where F is the liquid fraction of the freezing metal. Estimation of the purity of a fixed-point cell metal sample from analysis of the freezing and melting curves has been undertaken by many authors, who have demonstrated the limitations of the technique.

In two of the seminal works in this field, McLaren and Murdock [5,6] performed detailed analysis of freezing and melting curves to identify the main physical processes occurring in thermometric fixed-point cells, examining the geometry of the freezing interface and the sensitivity of the melting and freezing curves to certain impurities. They were able to identify samples sufficiently pure for thermometric use by analysis of the freezing and melting curves, including both a "Raoult's law analysis" and "melt following fast and slow freeze analysis".

Strouse and Moiseeva [7] performed an extensive melting and freezing analysis on a batch of tin to establish its suitability for use as a standard reference material (SRM), and found discrepancies between the use of Raoult's law and the purity assay data.

Lee and Gam [8] examined the melting and freezing behavior of indium, aluminum, and silver samples, and concluded that by using (1) the difference between the maximum of the freezing curve and the average of the melting curve and (2) the melting range after different freezing methods, the purest samples could be identified, although no clear quantitative relationship was established. The authors also found that both techniques failed to identify some types of impurity.

Ancsin [9,10] examined the effects of the addition of known amounts of a range of different impurities on the melting and freezing curves of pure tin.

Widiatmo et al. [11] examined freezing curves for several samples of aluminum of various purities. They determined that by varying the freezing rate, and extrapolating to adiabatic conditions, the purest aluminum samples could be identified. However, they were unable to obtain quantitative agreement between the predictions of Raoult's law and the measured freezing points.

Connolly and McAllan [12] examined the effect of trace impurities of the freezing points of tin and zinc. Experimental results and consideration of the binary phase diagram led to the conclusion that eutectic and peritectic binary phases confuse the simple analysis suggested by Raoult's law.

The Consultative Committee for Thermometry has also extensively discussed this issue: Fellmuth [13] discussed the magnitude of the expected errors in estimation of impurities using Raoult's law, Strouse[14] discussed several independent techniques for impurity analysis, and Moisseeva [15] discussed the implications of impurity analysis for the formal mechanism of traceability.

Hill and Rudtsch [16] opened a debate in the thermometric community about whether the thermometric fixed-point materials would be better considered as certified reference materials, and linked directly to the field of chemical metrology.

In [17], Fellmuth and Hill used detailed GDMS analysis, and the distribution coefficients of each impurity, to compare the expected and measured melting and freezing behavior of real Sn cells under a variety of freezing and melting conditions and histories.

In summary, although a rough overestimate, the "overall maximum estimate" (OME), of the temperature error compared to the pure material can be obtained from the first cryoscopic constant and the overall molar impurity level, a detailed analysis requires knowledge of the binary phase diagrams for each impurity. It is also very important to note that while a "sloping" freezing curve indicates the presence of impurities, a "flat" freezing curve is not necessarily indicative of a pure sample. For example, materials with similar solubility in the solid and liquid phases (minimal segregation) will generally exhibit “flat” freezing curves displaced in temperature relative to that of the pure substance (e.g., argon in oxygen).

3 NMIA Fixed-Point Ensembles

At NMIA, over the range from Ar to Ag, only Ga and water-triple-point (WTP) cells are purchased in the form of manufactured cells. For the other cells, metals (or gases in the case of argon) with impurity concentrations ≤1 ppm are purchased and fixed points constructed from the samples. Within each batch of cells, we have attempted to source the materials from a range of manufacturers, and cells are manufactured from different material lots to randomize any possible systematic errors. The total impurity estimates are those given by the metal suppliers, supported by either ICPMS or spectrographic analysis. Details of the cells used by NMIA are given in Tables 2 and 3. The graphite crucibles are manufactured by Carbone of America with a claimed impurity concentration below 5 ppm, and are held in quartz tubes. The crucibles are baked in vacuum for 24 h prior to filling, while all quartz are steam-cleaned for several days, and then baked in vacuum. The crucibles are filled iteratively (no filling crucible is used). All NMIA melting-point (MP) and freezing-point (FP) cells are of the “open” design, and are kept under a 99.999 % argon atmosphere, held about 100 Pa above atmospheric by a simple “bubbler” arrangement.

Table 2 Construction details of reference cells of each ensemble used in the study

Substance	Ar	Hg	Ga	In	Sn	Cd	Zn	Al	Ag
Ingot mass	16 g	3.8 kg	0.5 kg	1.1 kg	0.9 kg	1.0 kg	0.9 kg	0.5 kg	1.9 kg
Well base to metal surface (mm)	130	216	230	175	175	175	177	240	240

Table 3 Typical values for the uncertainty components in cell temperature comparisons at NMIA, together with the expanded combined uncertainties

(mK)	Ar	Hg	Ga	In	Sn	Cd	Zn	Al	Ag
Conduction errors (DUT), semi-range	0.15	0.1	0.05	0.1	0.1	0.15	0.15	0.2	2
Conduction errors (REF), semi-range	0.15	0.1	0.05	0.1	0.1	0.15	0.15	0.2	2
Bridge differential linearity, semi-range	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
Hydrostatic depth (DUT), semi-range	0.03	0.07	0.01	0.03	0.02	0.05	0.03	0.02	0.05
Hydrostatic depth (REF), semi-range	0.03	0.07	0.01	0.03	0.02	0.05	0.03	0.02	0.05
Self-heating, (DUT), semi-range	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Self-heating, (REF), semi-range	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Type-A (SD of 10 differences)	0.3	0.08	0.06	0.1	0.07	0.2	0.1	0.27	3
Uc ($k = 2$)	0.32	0.21	0.10	0.19	0.18	0.29	0.26	0.38	3.83

Note that the dominant components are the measured standard deviations of the repeated cell-difference measurements and the estimated errors due to conduction effects

4 Cell-Comparison Technique

The experimental equipment and techniques used for cell comparisons are given in detail in [18]; however, a brief summary is given below.

For the triple point of argon, as realized for standard platinum resistance thermometers (SPRTs), NMIA uses a small cell inside a vacuum cryostat immersed in a liquid nitrogen bath. Approximately 15 g of argon can be condensed into the cell from one of four G-sized ultra-high-purity argon bottles from different suppliers. A new sample is condensed for each measurement, and between samples the cell is warmed and pumped to below 10^{-4} torr. The SPRT is not removed from the cell between samples to minimize any mechanically induced calibration shifts. A typical melting plateau lasts 14 h using small electrical heat pulses applied to the cell at 40 min intervals.

For Hg cells, a maintenance bath 40 cm × 40 cm × 72 cm deep and filled with a 50 % ethanol/water mixture stirred by a N_2 gas bubbler is used to achieve a uniformity of a few mK. Two layers of Perspex with a small gap act as a thermal cover and prevent condensation of water into the bath. Up to four Hg cells, each held in a 50 mm diameter Perspex tube with a stagnant layer of fluid between the cell and bath as a thermal impedance, can be held in the bath simultaneously. Melt and freeze plateaux of typically 3 h duration are used for cell comparisons.

Up to four Ga cells can be maintained in a small commercial “viscometry” bath, which achieves a uniformity and stability of a few mK. Cells are placed on a small polystyrene spacer into glass tubes immersed 40 cm into the bath, with polystyrene insulation covering the top of the cell.

For the In and Sn cells, a custom-built version of the Hart Scientific 6022 oil bath is used. Two stainless-steel tubes of 53 mm ID are immersed 35 cm into the Dow Corning 210H silicone oil, which is stirred to achieve a uniformity and stability of a few mK. Pairs of In and Sn cell assemblies can be placed into the bath and simultaneously melted and frozen.

For Cd and Zn cells, 2 three-zone furnaces (Model K23 from Pond Engineering) are used, while for Al and Ag cells, two Hart Scientific Model 9115 furnaces using a 37 cm long sodium-filled heat-pipe furnace liner are used.

For realizations of the Ag freezing point, conduction losses from the top of the crucible were found to be excessive because of the long crucibles used. An additional top heater, constructed of ceramic-insulated Kanthal wire wound around a 10 cm long Inconel tube placed vertically on top of the Na heat-pipe furnace liner and supplied with approximately 140 W, significantly improved the temperature uniformity in the cell assembly.

For measurements of temperature differences of cells from Ar to Al, measurements using two different 25 Ω quartz-sheathed SPRTs were used. For the Ag cell, because of the need to ensure that apparent temperature differences between cells did not arise from electrical shunting effects within the SPRT, three different 0.25 Ω quartz-sheathed SPRTs were used. The SPRT resistances were measured using an ASL F18 AC resistance bridge, with data logged to a computer. Self-heating-corrected resistances were obtained from 10 measurements at each of 1 mA, $\sqrt{2}$ mA, and 1 mA measurement currents for 25 Ω SPRTs (10 mA for 0.25 Ω SPRTs), and resulted in a typical electrical noise of 1 μΩ to 2 μΩ for the 25 Ω SPRTs. 100 Ω and 1 Ω reference resistors for the resistance bridge were kept in a temperature-controlled oil bath with mK-level uniformity and stability.

The procedure adopted for the work here is the same as that used for NMIA's service for the calibration of fixed-point cells against a nominated NMIA reference cell. Cells are compared directly by realizing the appropriate phase transition as per the International Temperature Scale of 1990 (ITS-90) [19] (for example, by nucleating inner and outer liquid–solid interfaces) in both cells, and measuring the self-heating-corrected resistance of an SPRT alternately between the two cells.

For MPs and FPs, the same argon gas system is used for both cells, to reduce any possible errors in the difference due to pressure. Typically, three to six measurements are made on each cell per melt or freeze, taking 1 h to 1.5 h, with furnace or bath settings chosen to limit phase transitions to a 3 h to 5 h duration. In some cases the heat transfer to the two cells is slightly different, so the furnace settings are adjusted to give plateaux of similar duration to ensure that cell differences are measured over the central "maximum" part of the plateau for each cell. Cells are then melted and re-frozen appropriately, and the process repeated to give data on at least three separate realizations. To assess the uncertainty arising from stray heat fluxes, the temperature-immersion profile over the bottom 60 mm of the fixed-point well is measured and compared to the theoretical hydrostatic pressure-induced temperature gradient. Measurement of a cell-to-cell difference and its uncertainty typically takes several days of laboratory time.

5 Uncertainty Analysis

The calculation of the uncertainty in temperature of a fixed-point cell includes the contributions from the uncertainty of the reference cell, such as impurity-induced temperature errors, together with the uncertainty in determining the *difference* between the reference and test cell. The following uncertainty contributions to these cell–cell temperature differences and their methods of assessment are given below:

1. Conduction: Stray heat fluxes in *both* the reference and test cell are assessed as the maximum deviation over the bottom 40 mm of each thermometer well from the theoretical relationship (the SPRT sensor is approximately 40 mm in length).
2. Bridge differential non-linearity: measured using an AEONZ RBC resistor network as less than 3 μΩ (0.03 mK) for a 25 Ω SPRT with a 100 Ω reference resistor.
3. A nominal 10 mm uncertainty in the depth of metal above the midpoint of the SPRT in *both* the reference and test cells, leading to an uncertainty in hydrostatic head correction, is applied (not relevant to the Ar cell, since the gas is condensed onto many horizontal baffles within the cell).
4. Self-heating: The uncertainty, taken in *both* cells, due to any error in the $\sqrt{2}$ measurement current ratio; assessed as 0.1 % of the typical 0.5 mK to 1 mK self-heating correction, based on the maximum deviation of the measured ratio over several years (this component is negligible).
5. Random variations (Type A): This is taken as the standard error of the mean of the 12 to 15 individual cell-to-cell temperature differences, and by experimental design is thought to implicitly include:

   (a) any short-term instability of the SPRT, for example due to movement or Pt oxidation state,
   (b) any instability in the reference resistor,
   (c) electrical noise and measurement resolution,
   (d) repeatability of the phase-transition realization, and
   (e) in the case of the Ag cell, the use of three SPRTs in the data set randomizes any effects due to shunting.

6. Plateau identification: If the measured data indicate that, over the central 50 % of the phase transition, the temperature drift is statistically significant compared to the measurement reproducibility (item 5), then the statistical assumption that they are independent and uncorrelated measurements is incorrect. In this case, we take an additional uncertainty with a rectangular distribution with full width equal to that of the middle 50 % of the plateau.

The uncertainty components for typical comparisons between cells are given in Table 3. In most cases, the dominant uncertainties are the error in tracking the theoretical hydrostatic temperature gradient and the variance of the repeatedly measured differences. Note that the term due to "plateau identification" is significant only for cells with significant contamination (i.e., several mK depression).

6 Results and Discussion

Table 4 and Fig. 1 summarize the measurement results for NMIA's ITS-90 fixed-point cells. Note that each data point and associated uncertainty represents several days' laboratory effort with 12 to 15 differences over up to four separate plateaux. Where a cell was also measured in the 1997–2001 CCT-K3 [2] comparison, the measured difference to the comparison reference value "ARV", generated after CCT-K3 by Strouse [20], is also plotted in Fig. 1, together with its combined uncertainty.

In the case of Hg, Ga, In, and Sn, the cells used in the CCT-K3 comparison were still available for direct comparison to other cells in the ensembles. However, the higher-temperature cells Cd, Zn, Al, and Ag used in K3 and K4 were broken (mostly due to rapid-freezing events such as power failures) before direct cell comparisons were conducted, and the linkages had to be based on a number of SPRTs used for the NMIA calibration facility that had been calibrated in the old and new cells. In these cases, the uncertainties are larger due to the instability of the SPRTs.

Generally, the dispersion of cell-temperature differences within each fixed-point set is consistent with that expected from the material purity and cell-difference measurement uncertainty. However, some specific observations can be made on each of the sets of cells (the following uncertainties are given at $k = 2$ or approximately 95 % confidence level).

1. Ar: The CCT-K3 and immediately following sample of 99.999 % purity gas from two different suppliers showed a significant depression, although not as large as determined in CCT-K3. The three 99.9999 % purity argon samples exhibit a 0.2 mK range. The uncertainty of the cell differences, typically 0.4 mK, is dom-

Table 4 Cells used at NMIA to realize the ITS-90, giving (i) the cell serial number, (ii) the source material manufacturer and total purity estimate, (iii) the difference in mK to the reference cell and its uncertainty as measured in the work presented in this article, and (iv) the difference and combined uncertainty to the CCT-K3 or CCT-K4 reference value for the cell used in that comparison

Ar97/1	**ArLinde2006/1**	ArScott06/1	ArBOC06/1	ArBOC06/2
Linde, 5N5	**Linde IL3008AR, 6N**	Scott K020653, 6N	BOC AS776555, 6N	BOC W209, 5N
	0 (ref cell)	-0.17 0.43	0.027 0.5	-0.625 0.5
K3: -2.21 +/-1.06				

HgI	HgII	HgIII
NMI, twice dist.	NMI, twice dist.	NMI, twice dist.
0 (ref cell)	-0.16 0.32	0.17 0.2
K3: -0.01+/-0.51		

GaYSI	Ga(o)-395	Ga 43072	8062
YSI, 6N	Isotech, 7N	Hart,6N	Pond, 7N
0 (ref cell)	-0.01 0.17	0.01 0.18	0.03 0.16
K3: -0.12+/-0.51			

In96/1	**In00/1**	In2006/1	In2006/2
Cominco, 6N	**Arconium, 6N**	In. Corp. 6N5	In. Corp. 6N5
-0.6 0.22	**0 (ref cell)**	0.06 0.15	0.17 0.19
K3: -1.19+/-1.05			

Sn95/1	SnUnk	SnXI	Sn2004/1	Sn2006/1
Cominco, 6N	contaminated cell	unknown	JM, 6N	JM, 6N
0 (ref cell)	-1.34 0.39	-0.32 0.25	-0.02 0.21	-0.01 0.16
K3: -0.68+/-0.58				

Cd95/1	**Cd02/1**	Cd2006/1	Cd2007/1
Cominco, 6N	**JM, 6N**	Honeywell, 6N	Honeywell, 6N
0.21 0.54	**0 (ref cell)**	0.37 0.41	0.41 0.52
K3: -1.13+/-1.21			

Zn98/2	**Zn02/2**	Zn98/1a	Zn03/1	Zn2006/1	Zn2006/2
Cominco, 6N	**JM, 6N**	Cominco, 6N	JM, 6N	Honeywell, 6N	Honeywell, 6N
0.26 0.46	**0 (ref cell)**	0.72 0.26	-0.18 0.37	0.18 0.71	0.02 0.36
K3: 0.04+/-0.36					

Al98/1	**Al2006/2**	Al05/1	Al06/1	Al2007/1	Al2007/2
JM, 6N	**Honeywell, 6N**	Honeywell, 6N	Honeywell, 6N	Honeywell, 6N	Honeywell, 6N
1.38 3.17	**0 (ref cell)**	-1.658 0.35	-0.46 0.68	0.8 0.79	0.87 0.96
K3: 0.56+/-1.85					

Ag93/1	**Ag2006/1**	Ag2006/2
JM, 6N?	**Honeywell, 6N**	Honeywell, 6N
	0 (ref cell)	3.74 5.94
K4: -13.0+/-12.9		

Note that the reference cells are highlighted in bold (JM = Johnson Matthey, and 6N is 99.9999 %, etc.)

inated by the reproducibility of the SPRT, which shifted slightly due to thermal cycling between −189 °C and ambient as the gas samples were changed.

2. Hg: Cell differences can be determined with an uncertainty of 0.2 mK and the three cells agree within a 0.3 mK range consistent with the CCT-K3 results. However, the same facility and source material were used for the three distillations of Hg into the cells, so the three cells are not entirely independent.
3. Ga: The four cells in this study differed by less than 0.04 mK and are in agreement with the CCT-K3 results.
4. In: The NMIA In cell used in the CCT-K3 comparison was found to be 1.2 mK low. As a result, NMIA constructed three new cells, which were in agreement

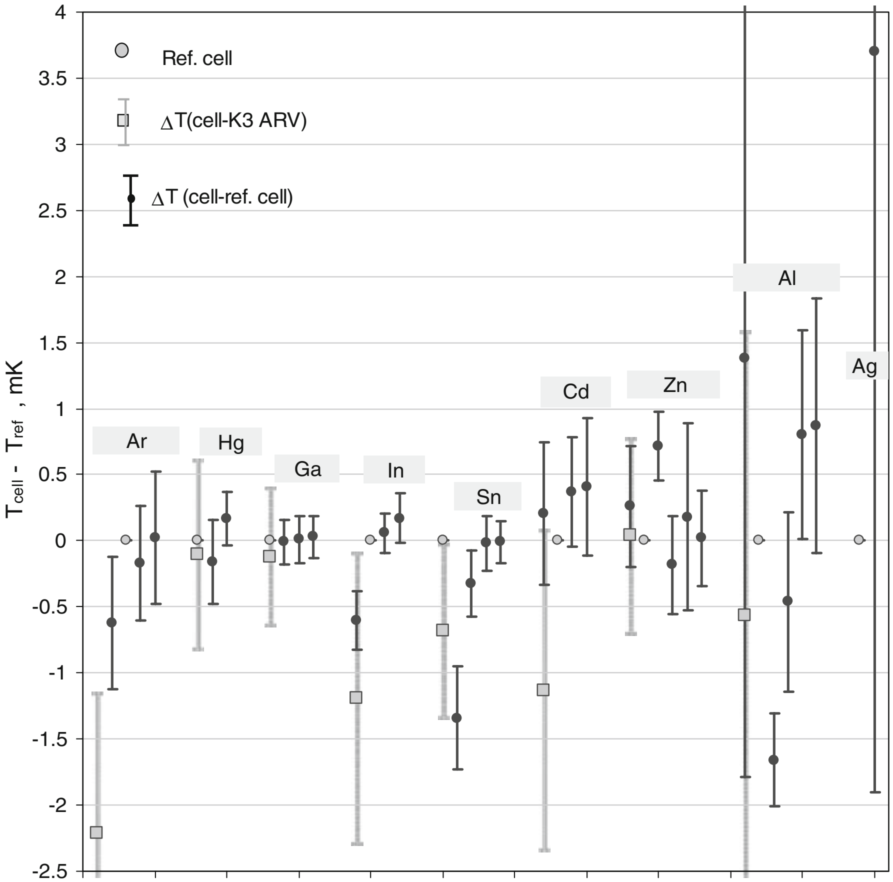

Fig. 1 Graph of the present status of NMIA ITS-90 fixed points. Temperatures are plotted as differences from the NMIA reference cell, denoted by an *open circle*. *Open squares* denote the difference to the "average reference value", or ARV, found for that cell in the CCT-K3 comparison. Error bars (95 % CL) reflect only the uncertainty of the cell–cell difference measurements

within our comparison uncertainty level of 0.2 mK. The measurements show the In cell used in CCT-K3 to be 0.6 mK low with respect to these new cells, consistent with the CCT-K3 results. This is despite the melting and freezing curves and melt–freeze agreement for this cell (Fig. 2) being similar to the other cells, typically within a range of 0.1 mK.

5. Sn: In the CCT-K3, the NMIA cell was found to be (0.68 ± 0.65) mK low. As a result, several new cells were constructed, and the differences measured between them (with an uncertainty as low as 0.2 mK) were within a range of 0.3 mK, only just consistent with the K3 result. A fifth cell of unknown origin, and repaired after a well breakage, was also measured, and found to be about 1.3 mK below the other Sn cells, despite exhibiting very good melt–freeze agreement and a freezing range (Fig. 3) of 0.35 mK over 50 % of the plateau.

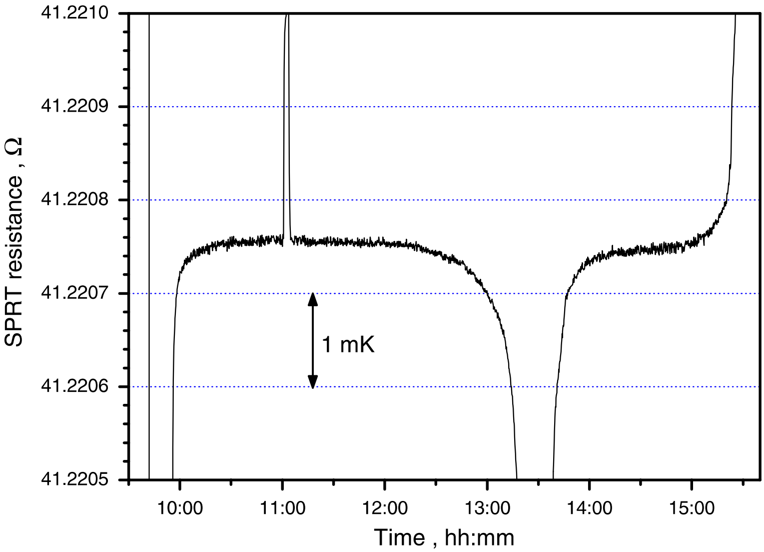

Fig. 2 Melting and freezing plateaux for cell In 96/1 showing good melt–freeze agreement despite 0.6 mK depression in freezing temperature (*Note*: the "spike" on the freezing plateau is due to the $\sqrt{2}\times$ measurement current for the self-heating measurement)

6. Cd: The three new cells agree within a 0.4 mK range. However, the cell used in the CCT-K3 comparison was broken before linking to a replacement, so no direct link is available; however, indirect linkage via several SPRTs shows the cell used in CCT-K3 to be equivalent to the other three cells.
7. Zn: Four of the Zn cells in the ensemble agree within 0.54 mK, but one cell is 0.7 mK higher than the others. However, for this cell the freezing plateau and the melt–freeze agreement show evidence of contamination in the cell. Only indirect (SPRT) measurements are available for the cell used in the CCT-K3 comparison, which was broken prior to direct comparison. The results indicate that this cell is equivalent to the three newer cells.
8. Al: Four of the cells agree within ±0.7 mK; however, the fifth cell is 1.7 mK lower than the others. Examination of the melt–freeze agreement and freeze plateau for this cell showed contamination. Only indirect (SPRT) measurements are available for the cell used in CCT-K3; however, the results are consistent with those in CCT-K3, within the rather large uncertainty arising from the instability of the SPRTs.
9. Ag: The two NMIA cells agree within 3.5 mK; however, an unresolved problem with electrical noise limits the accuracy of the cell comparison to about 5 mK.

The temperatures of most cells lie within the combined uncertainty of the estimated 1 ppm OME range and cell–cell difference uncertainty. However, there is one cell in each of the In, Sn, Zn, and Al ensembles with a temperature difference larger than can be explained by either impurities or comparison errors. In the case of Zn and Al, each discrepant cell shows a large freezing range and can thus be discarded; however, for

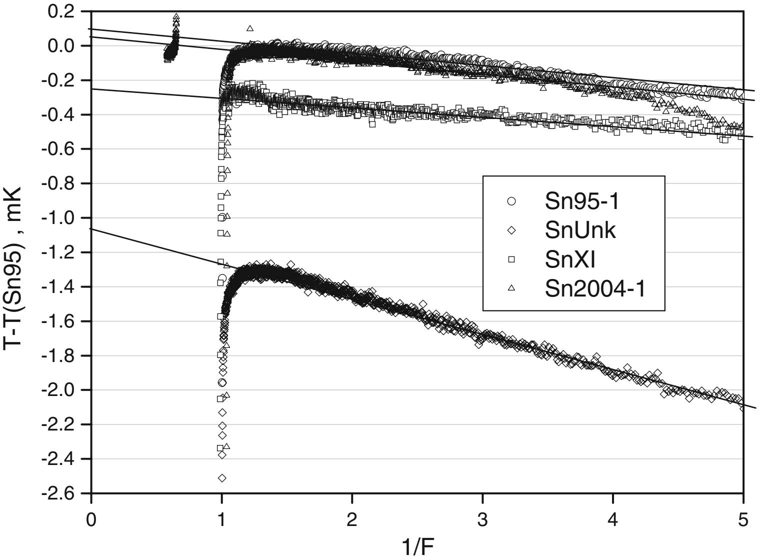

Fig. 3 Freezing plateaux for four NMIA Sn cells plotted against $1/F$, where F is the calculated remaining liquid fraction. Cells Sn95/1 and Sn2004/1 are made with 99.9999 % purity material; however, cells SnUnk and SnXI are old cells that were recovered after well breakage, which may have introduced impurities at an unknown level. The extrapolated values at $1/F = 0$ are the liquidus temperatures for a "pure sample" based on the assumptions of Raoult's law and complete impurity segregation, showing that these assumptions are not satisfied

In and Sn there is no evidence from the freezing curves to suggest contamination—it can only be identified by comparison with other cells.

7 Conclusion

Fixed-point cells should not be regarded as intrinsic primary standards because, once a cell is made, measurements of the melting and freezing characteristics of the cell alone cannot provide sufficient evidence of the purity of the reference material in the cell. Because of the risk of contamination of the reference material during the cell construction process and the difficulty in sampling a cell once constructed, comparisons of cells are required to confirm estimates of its purity. Comparisons and, in particular, the Mutual Recognition Arrangement (MRA) Key Comparisons, provide confirmation of the purity of the specific cell used by the NMI for the comparison, but this information will be lost if this cell is broken before transferring its systematic error to other reference cells. Because of the risk of cell breakage (for the high-temperature cells in particular), it is essential to ensure that each cell is linked to other cells held in the laboratory prior to participation in a key comparison. NMIA has successfully established sets of fixed-point cells as well as facilities and methods for the comparisons of these cells at sub-mK uncertainty levels. This now provides NMIA with internal comparison data (1) to validate the "as-filled" temperature uncertainty estimates based on the total impurity estimates of the source materials provided by the suppliers and (2) to provide a secure link to the MRA key comparisons.

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