Practical Limitations Of ITS-90 From Mercury Triple Point To The Silver Freeze Point

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Abstract. The NPL published a forward to the ITS-90 text as follows:-

"The purpose of the ITS is to define procedures by which certain specified practical thermometers of the required quality can be calibrated in such a way that the values of temperature obtained from them can be precise and reproducible, while at the same time closely approximating the corresponding thermodynamic values." [1]

The paper investigates the properties of thirty four lots of 6N pure metal used to make cells conforming to ITS-90 from mercury through silver over a period of twenty years.

Three hundred individual cells are analysed by the impurities listed and supplied with each lot, melt and freeze curve slopes are also summarised for each lot and depressions calculated.

These are then compared to the slopes and depressions suggested in the Supplementary Information for the ITS-90 and in CCT/2000-13 "Optimal Realizations".

Results are summarised, tabulated and discussed.

Three lots of the thirty four were found to produce cells outside 6N expectations; however the remaining thirty one lots no matter how well or badly the accompanying certification was presented produced cells that conformed to 6N expectations as suggested in Supplementary Information to ITS-90 and CCT/2000-13.

Keywords: ITS-90, Mercury, Gallium, Indium, Tin, Zinc, Aluminium, Silver, Practical Limitations, SPRT, Calibration Uncertainties
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INTRODUCTION

One of the main purposes of ITS-90 is to specify a series of temperatures at which suitable SPRT's can be calibrated. Subranges enable SPRT performance to be optimised over a particular temperature range and documents are available that describe the uncertainties in realising the SPRT subranges of the ITS-90 [2, 3, 4]

Impurities in the ITS-90 substances are the largest source of uncertainty in fixed point realizations, and a significant contribution to the total uncertainties of ITS-90 sub-ranges.

Models have been developed of the impurity effects on ITS-90 substances, however the lack of available chemical analysis, the lack of liquidus slope data for combinations of impurities in fixed point substances have hampered this approach.

The alternative is to rely on the nominal purities indicated by the manufacturer, supported by an incomplete chemical analysis and an uncertainty model based on an overall maximum estimate of the impurity level. But is this approach reliable?

The Northern Temperature Primary Laboratory (NTPL) is accredited by UKAS for the characterisation of ITS-90 fixed points from mercury triple point through to the silver freeze point.

Over the past 20 years it has characterised over 300 fixed point cells made from 34 lots of 99.9999% pure substances. Each cells melt and freeze curve has been recorded on 3 occasions followed by two intercomparisons of actual temperature with reference cells traceable to National Standards.

There is sufficient data accumulated to try and answer the fundamental questions concerning the practical limitations of the ITS-90.

EFFECTS OF IMPURITIES

For many years the detailed work of E. H. McLaren on the melt and freeze slopes of various purity substances was the reference to which workers referred.

The first cryoscopic constant was also used to estimate the depression or elevation of a substances transition temperature caused by impurities. The Supplementary Information to ITS-90 contains estimates of the association of a 99.9999% pure substance to the assigned temperature as follows:

Hg TP ±0.1mK
Ga MP 25 to 85μK
In FP reproducible to 0.1mK for 6N pure In
Sn FP reproducible to 0.1mK for 6N pure Sn
Zn FP reproducible to 0.2mK for 6N pure Zn
Al FP reproducible to 1.0mK for 6N pure Al
Ag FP reproducible to 1.0mK for 6N pure Ag

In 2000 the CCT published CCT/2000-13 which lists "expected depressions" for 99.9999% pure substances as follows:

0.2mK for 6N pure Hg
0.1mK for 6N pure Ga
0.5mK for 6N pure In
0.3mK for 6N pure Sn
0.5mK for 6N pure Zn
0.7mK for 6N pure Al
1.1mK for 6N pure Ag

More recently the CCT published CCT/08-19/REV which describes two methods of correcting for impurities.

The SIE Method

It says *"An overall correction for impurities can be made by Summing the Individual Estimates (SIE) of the correction for each impurity.....it is not yet fully realizable for any of the metal fixed points. The method requires knowledge of all the liquidus slopes for the various impurities and complete data is not yet available for any of the metal fixed points."*

The OME Method

This is the Overall Maximum Estimate (OME) of impurity concentration.

It says *"Where suppliers' assays are incomplete i.e. lacking uncertainties or detection limits, or the list of detected elements is incomplete, often no further claim can be made beyond the nominal purity (e.g. 99.9999% by weight, metallic elements only)".*

The Methods Used In This Paper

Supplier Analysis of the 34 lots, listed between zero and sixty metallic impurities and so where possible the SIE method was used to calculate the depression, or elevation caused by each significant impurity.

In addition the melt and freeze slopes of each of the 300 cells were measured and compared to the published figures in Supplementary Information to the ITS-90 and CCT/2000-13.

The comparison indicates whether a particular lot of metal performs better or worse than expected from a 99.9999% pure metal.

Experimental Results

Over 1,800 melt and freeze graphs have been analysed to obtain their slope.

The traditional method of analysing the curves is to measure 80% of the melt and derive the increase in temperature over this part of the melt, or take the decrease in temperature over the first 50% of the freeze.

The results have been separated by metal and by lot number. To reduce the data to manageable proportions the mean melt and freeze slope has been calculated for the cells made and tested from each lot.

From the impurity analysis supplied by the metal manufacturer for each lot the depression or elevation caused by each significant impurity has been calculated from the first cryoscopic constant.

If the total impurities are 0.1ppm or less as in the case of Mercury and Gallium the slopes and analysis are so small that the differences between lots cannot be accurately measured and so the results are generalised. In the case of Indium, Tin, Zinc, Aluminium and Silver however the results have been tabulated to show the differences between lots.

Water Triple Point Cells

The water triple point cell can offer uncertainties of ±35μK (see separate paper presented at this conference titled "The Triple Point of Water, its History and Current Development").

Mercury

All the lots of Mercury used have less than 0.1ppm impurities. 25 Mercury Triple Point Cells have been certified over 20 years. The cells gave a typical 50% freeze of 0.1mK and an 80% melt of 0.2mK.

CCT/2000-13 suggests a 50% freeze depression for a 6N pure cell is 0.2mK and so all Mercury cells tested meet this requirement.

Gallium

All lots of Gallium used have less than 0.1ppm impurities. 25 Gallium cells were analysed and averaged an 80% melt slope of 0.05mK.

CCT/2000-13 suggests a slope of 0.1mK for 6N pure Gallium and so all Gallium cells analysed meet the requirement.

Indium

Table 1 contains impurity analysis along with both measured and calculated offsets from the ITS-90 assigned value. The data comes from a total of 40 ITS-90 Indium cells manufactured from four separate metal lots.

TABLE 1. Analysis of Forty Indium Cells

1	2	3	4	5	6	7	8	9
Metal Lot Ref	Significant Detected Metal Impurities ppm by weight	Source of Metal Analysis	Number of Metallic Elements Analysed	Measured 50% of Freeze mK	Measured 80% of Melt mK	Calculated Depression or Elevation mK	CCT/2000-13 mK	Number of Cells Analysed
6030	Mg°.1 Ca°.1 Si^+ .1	Supplier	36	.17	.44	.2	.5	12
1285	Mg°.1 Pb^+.2 Sn^- .3	Supplier	30	.33	1.2	-.1	.5	10
1169	Fe°.1 Ni^+.1 Pb^+ .5	Supplier	30	.4	1.1	.2	.5	17
0529	Ti° .12	NRCC	60	.14	.4	0	.5	1

The measured values were determined from the mean of three melts or freezes, from each cell analysed e.g. Lot 6030, 12 cells, each had 3 melts and freezes = 36 melts and freezes. The mean slopes of the 36 measurements are presented.

The calculated value was determined by using the first cyoscopic constant for the significant metal impurities.

The National Research Council Canada (NRCC) can analyse more impurities than the metal suppliers, detecting up to 60 elements, to smaller uncertainties.

The 50% freeze values of all forty cells met the requirements of CCT/2000-13 (0.5mK).

Tin

Here fifty cells from eight lots were analysed (Table 2). Only 1 lot, 23822, has a full NRCC certificate.

The Tin impurity analysis from the supplier shows a disturbing tendency whereby the supplier lists only the impurities detected, giving no indication of how many elements were analysed or the detection level. One lot merely has ND written on the certificate indicating that no impurities were detected.

CCT/2000-13 suggests 0.3mK as the typical depression. Three lots gave 50% freeze slopes outside the guideline. In particular lot 30915 has a large freeze and melt slope but column 7 suggests zero deviation from ITS-90.

A sample from this lot was sent to NRCC for full analysis, which suggested a copper impurity of 0.2ppm and Ag 0.1ppm giving a depression of 0.15mK (Column 7)

TABLE 2. Analysis of Fifty Tin Cells

1	2	3	4	5	6	7	8	9
Metal Lot Ref	Significant Detected Metal Impurities ppm by weight	Source of Metal Analysis	Number of Metallic Elements Analysed	Measured 50% of Freeze mK	Measured 80% of Melt mK	Calculated Depression or Elevation mK	CCT/2000-13 mK	Number of Cells Analysed
2310	N.D.	Supplier	0	.1	.9	0	.3	3
7331	Mg .1 Si .2	Supplier	2	.15	1	.1	.3	13
23823	Pb .1	NRCC	60	.18	1.2	0	.3	5
8967	B .1 Ca .2 Mg .1 Si .2	Supplier	4	.28	1.4	-.1	.3	4
9387	Ag .1 B.1 Ca .2 Cu .1 Mg .1 Si .1	Supplier	6	.45	1.7	-.26	.3	8
1707	Ag .1 Bi .1 7e .05 Mg .1 Sb .3 Si .1	Supplier	6	.43	1.25	-.1	.3	9
10782	N.D.	Supplier	0	.2	1.2	0	.3	4
30915	Si .05 Cr .05 Ni .03 Ni .03 Na .03	Supplier	16	.52	2	0	.3	3

Zinc

Forty two cells from 10 lots are included in Table 3.

The first three lots were of crystal grade Zinc at least 6N5 pure and accompanied with NRCC certificates. Freezes and melts were very good. At the other end of the scale is lot 2209 from 1991 this has a "typical analysis" not taken from the lot supplied, and is probably less than 6N pure. The other nine lots all give 50% freezes less than the 0.5mK depression suggested in CCT/2000-13.

TABLE 3. Analysis of Forty Two Zinc Cells

1	2	3	4	5	6	7	8	9
Metal Lot Ref	Significant Detected Metal Impurities ppm by weight	Source of Metal Analysis	Number of Metallic Elements Analysed	Measured 50% of Freeze mK	Measured 80% of Melt mK	Calculated Depression or Elevation mK	CCT/2000-13 mK	Number of Cells Analysed
7253	x	NRCC	60	.17	.43	0	.5	7
7232	x	NRCC	60	.16	.38	0	.5	7
7288	x	NRCC	60	.3	.45	0	.5	2
11404	Mg .2 Si .3	Supplier	2	.28	1.87	-.4	.5	3
9073	Hg .05 Fe .02	NRCC	60	.13	1.11	0	.5	5
2209	1 (Typical)	Supplier		.7	2.75	-	.5	12
7568	B .1 Mg .2 Pb .2 Si .1	Supplier	5	.1	.8	-.45	.5	1
27615	N.D.	Supplier	0	.1	.8	0	.5	3
5817	Ag .1 Cu .1	Supplier	2	.1	.5	.1	.5	1
30982	Si .1	Supplier	14	.3	1	0	.5	1

X = Crystal grade (at least 6N5)
Lot 2209 analysis is "typical", and probably not 6N

Aluminium

There are thirty eight Aluminium Cells in table 4, from five lots, three have NRCC certificates. Lot 6502 is a special ingot from Pechiney in France certified 6N5. It is significantly better than the other lots.

The other two lots with NRCC certificates meet the 0.7mK depression suggested by CCT/2000-13, the two with suppliers certificates do not.

These results suggest that the supplier analysis is conservative.

TABLE 4. Analysis of Thirty Eight Aluminium Cells

1	2	3	4	5	6	7	8	9
Metal Lot Ref	Significant Detected Metal Impurities ppm by weight	Source of Metal Analysis	Number of Metallic Elements Analysed	Measured 50% of Freeze mK	Measured 80% of Melt mK	Calculated Depression or Elevation mK	CCT/2000-13 mK	Number of Cells Analysed
4913	Fe 1.4 Si .17 Ti .05 Cr .07 In .085 Mn .06	NRCC	60	.65	1.8	-.5	.7	7
9904	Mg .16 Si .42 7e .22 Cu .23	NRCC	60	.66	2.7	-.5	.7	15
10086	Mg .2 Si .5	Supplier	2	.9	3.2	-.5	.7	11
1858	Mn .1 Si .3 Ca .1 Cu .3 Mn .1	Supplier	5	.78	2.3	-.4	.7	4
6502	Mg .06 Si .1 Sc .04 Mn. 03 V .04 Ti .02 Cr.06	NRCC	60	.3	.3	-.1	.7	1

Silver

Silver, nineteen cells are analysed from seven lots, one has NRCC analysis the rest suppliers (see Table 5)

All but lot 26306 meet CCT/2000-13 suggested 1.1mK depression. Uniquely lot 6238 performed better than the calculated depression of 1.9mK.

TABLE 5. Analysis of Nineteen Silver Cells

1 Metal Lot Ref	2 Significant Detected Metal Impurities ppm by weight	3 Source of Metal Analysis	4 Number of Metallic Elements Analysed	5 Measured 50% of Freeze mK	6 Measured 80% of Melt mK	7 Calculated Depression or Elevation mK	8 CCT/2000-13 mK	9 Number of Cells Analysed
1948	Mg .1 Si .1	Supplier	2	.9	2.7	-.9	1.1	5
4947	Mg .1	Supplier	1	.8	2.4	-.5	1.1	4
6238	Ca .1 Mg .1 Si .3	Supplier	3	.5	2.4	-1.9	1.1	2
19998	7e 0.24 As .22 Se 0.4 Sn .12 Sb .1 Hg .52	NRCC	60	1	5	-.9	1.1	1
11787	N.D.	Supplier	0	1	3	0	1.1	3
19082	Mg .1	Supplier	1	.3	4.2	-.5	1.1	2
26306	7e .66 S .04 Sb .06 Te .07 Ag .05	Supplier	55	2.1	4.2	-.3	1.1	2

Analysis of Results

In calibrating SPRT's to the highest accuracy the first 25% of the freeze is used and so the 50% freeze depression can be halved.

Mercury and gallium are commercially available in purities that give association to ITS-90 within 0.1mK.

- For the forty Indium Cells analysed from 4 lots all were within ±0.25mK for the first 25% of the freeze irrespective of the source of analysis and whether the impurities formed Eutectics or Peritectics.
- For the fifty Tin cells analysed from 8 lots all were within ±0.26mK for their first 25% of the freeze.
- For the forty two Zinc cells analysed from 10 lots, all were within ±0.25mK (excepting lot 2209) for the first 25% of the freeze.
- For the thirty eight Aluminium cells analysed all were within - ±0.45mK for 25% of freezes.
- For the nineteen Silver cells analysed all were within ±0.55mK (except lot 26306) for the first 25% of the freeze.

TABLE 6. Mean 25% freeze depression in mK of thirty one lots analysed in Tables 1 to 5 compared to CCT/2000-13 of typical depressions for 6N pure metals

Metal	25% Freeze in mK	CCT/2000-13 depression for 6N Pure (mK)
Hg	0.1	0.2
Ga	0.05	0.1
In	0.25	0.5
Sn	0.26	0.3
Zn	0.25	0.5
Al	0.45	0.7
Ag	0.55	1.1

Lots Zn 2207, Sn 30915 and Ag 26306 are omitted for the reasons described in the text

TABLE 7. 25% freeze depressions in mK for those lots with NRCC analysis

Metal	25% Freeze in mK
In	0.1mK
Sn	0.1mK
Zn	0.15mK
Al	0.35mK
Ag	0.5mK

TABLE 8. 25% freeze depressions in mK – the best lot selected from each metal.

Metal	25% Freeze in mK
In	0.07mK
Sn	0.05mK
Zn	0.05mK
Al	0.15mK
Ag	0.25mK

TABLE 9. Those lots accompanied with NRCC certificate – 50% freeze depression compared to the calculated depression using the first Cyroscope constant

Lot	50% Freeze Depression	Calculated Depression†
In 0529	0.14mK	0
Sn 23823	0.18mK	0
Zn 7253	0.17mK	0
Zn 7232	0.16mK	0
Zn 7288	0.3mK	0
Zn 3073	0.13mK	0
Al 4913	0.65mK	-0.5mK
Al 9904	0.66mK	-0.5mK
Al 5602	0.3mK	-0.1mK
Ag 19998	1mK	-0.9mK

†Using impurities 100ppb and above.

Clearly, even at 6N purity metals vary from lot to lot. For calibrating SPRT's most lots, whether well certified by an organisation such as NRCC, or poorly certified with a manufacturers certificate stating "no impurities detected", give adequate accuracy over the first 25% of freeze to calibrate the best SPRTS.

However where further investigation of a cell is required it is essential that the lot be analysed by the best laboratory available to the smallest uncertainties.

In general, those lots with the lowest amount of impurities detected, by whatever source give the flattest freezes and melts.

CONCLUSION

ITS-90 specifies a number of fixed temperatures for the calibration of suitable SPRT's and other temperature sensors.

In practice the embodiments of the ITS-90 fixed points are not ideal and although they are specified as being 6N pure (99.9999%), each lot is slightly different from the others.

By analysis of the impurities, and measuring the melt and freeze slopes of three hundred cells from thirty four lots of 99.9999% pure metals over twenty years it is concluded that in practice the performance of the fixed points of ITS-90 are adequate for the uncertainties associated with SPRT calibration.

Authors Note

We are indebted to all those customers who asked for UKAS certificates to accompany their Fixed Point Cells which enabled us to gather the data for this article.

In 2009 CIPM issued CIPM-2009-24 "Traceability in CIPM MRA". Since when the requests for UKAS certification has stopped and in consequence so has our ability to continue this detailed research.

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