A procedure for estimating ideal freezing temperatures using the gradient of the freezing plateau

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Background

Impurities in the sample of material in a fixed-point cell are a significant source of error and uncertainty in the realisation of melting and freezing points [1]. The temperature may be depressed or elevated and, due to segregation of the impurities, the melting or freezing plateau will not be entirely flat. In principle, a correction should be made to obtain the desired ideal transition temperature, T_0, but this strictly requires a complete analysis of the material and a knowledge of the relevant cryoscopic constants. This note describes an empirical method of establishing the correction for the impurity effect, which may be applied at any point on the plateau, using the gradient of the plateau at that point.

The method is an implementation of the 'Gulliver-Scheil' [2-4] model for a slow-freeze, which has been used by Hunt [5] to provide an estimate of the ideal freezing temperature independent of a detailed impurity analysis. It requires only an estimate of the (effective) equilibrium distribution coefficient $k = C_S/C_L$, where C_S and C_L are the solid and liquid impurity concentrations, respectively.

The Scheil model

The key assumptions of the model are that the freeze is slow enough that mixing in the liquid phase is complete, and that there is no diffusion in the solid phase. Under those conditions, the solute rejected into the liquid during an incremental change in liquid fraction, δg_L, is equal to the change in liquid composition at that point in the freeze, $g_L \delta C_L$. Thus

$(C_S - C_L)\delta g_L = g_L \delta C_L$, or

$$\delta g_L / g_L = (\delta C_L / C_L)/(k-1). \quad \ldots(1)$$

On integrating along the freeze, this gives the Scheil equation $C_L = C_O g_L^{(k-1)}$ ...(2)

At any particular time the departure from the pure material freezing point, ΔT, is given by multiplying the liquid impurity concentration by the slope of the liquidus curve, $m = \mathrm{d}\Delta T/\mathrm{d}C_L$, which is linear at least in the dilute limit. Thus:

$\Delta T = mC_L = mC_O g_L^{(k-1)}$.

The gradient on the freezing or melting curve is

$\dfrac{d\Delta T}{dg_L} = \dfrac{(k-1)}{g_L} mC_O g^{(k-1)} = \dfrac{(k-1)}{g_L}\Delta T$, so we have

$$\Delta T = \frac{d\Delta T}{dg_L}\frac{g_L}{(k-1)} \qquad \ldots(3)$$

Thus at any point on the freeze, the departure from the ideal temperature can be estimated from the slope $d\Delta T / dg_L$ *at the liquid fraction* g_L, *and a value for k.*

Implementation

The method is illustrated in Figure 1, which shows a Scheil freeze, and the constructions at solid fractions of 0.2, 0.5 and 0.8, each giving an estimate of T_0. The beauty of the method is that *we can consider the freeze to start at any point*, *i.e.* treat the rest of the freeze (the remaining liquid) as a new sample. Thus g_L at any point is taken to be 1, and the tangent is extrapolated from that point to $g_L = 0$ (solid fraction = 1). From Equation 3, the freezing point depression is simply given by the drop in temperature along the tangent, divided by (k - 1).

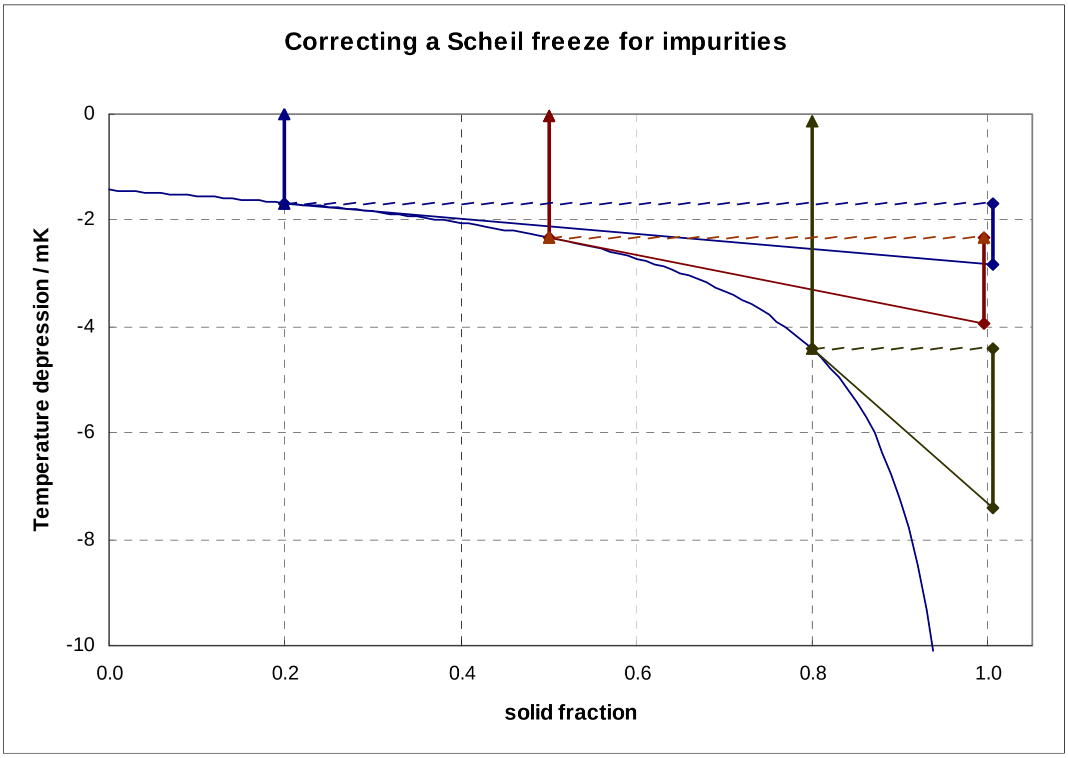

Figure 1: Scheil freeze, illustrating the constructions to correct for impurities. The curve is derived for an initial slope of 1 mK over the complete freeze, and $k = 0.3$.

The corrected temperatures in Figure 1 accord well with the ideal freezing point (zero depression), but this is of course to be expected, as the model has been used both to derive the freezing curve and to make the corrections. The purpose of the figure is therefore only to show the constructions to be used, and the question is to what extent a real freeze follows the Scheil model. Real examples are given later.

Assumptions and requirements

The key assumption, that the solute is fully mixed in the liquid phase, is less reliable in the initial stages (for practical reasons the freezing curve is anyway not well established until a significant fraction of solid has formed, but the exact amount is not important in this analysis). The criterion is that the distance left to freeze (thickness of the liquid sample) is smaller than *D/V*, where *D* is the diffusion coefficient and *V* is the velocity of the interface. If the freezing rate is 1 mm/hr, then $V \sim 3 \times 10^{-7}$ m s^{-1}, and for $D = 3 \times 10^{-9}$ m^{2} s^{-1}, the relevant distance is ~10 mm. At that rate mixing is near complete when ~5 mm is left and a reasonable answer might be achieved before that [5]. Clearly for a slower freeze a larger fraction would behave as Scheil, but some uncertainty from this source will remain.

In the later stages it becomes more important to identify the point of 100% frozen correctly. One can see from Figure 1 that the uncertainty in the end-point of the extrapolated the tangent becomes more significant, but in the early stages, where the curve is less steep, this is not a problem. In practice one would look for consistency among corrected values taken at several points on the freeze, and expect the errors and uncertainties to increase as the solidus point is approached.

In a real case where many different solutes are present, each should behave in a Scheil manner so we have

$\frac{d\Delta T}{dg_L} = \sum_i \frac{(k_i - 1)}{g_{Li}} \Delta T_i$, and a total depression of $\Delta T = \sum_i \Delta T_i$.

The largest effects will occur for $k = 0$ (Raoult's law, complete rejection of the impurity into the liquid), because then the liquidus slope is large and negative and the depression is also large. Conversely, when $k > 1$ the liquidus slope is always small and positive and the error is small.

In fact, the biggest effect on the corrections calculated using Equation 3 is in the value of the slope, which is measured, rather than in the value of k, which is assumed. Clearly, to avoid the singularity one should not take $k \sim 1$, but for a sample in this regime the plateau would anyway be rather flat and the corrections correspondingly small. Since impurities with low values of *k* create the largest effects, the choice of the effective distribution coefficient is biased toward $k \to 0$. In most cases it is realistic to choose a low value, and the exact value is not critical.

The remaining proviso is that the freeze must be regular: effects due to fluctuating furnace temperatures (irregular heat flows) must be small, and the freezing interface should follow a cylindrical profile in the ingot. Imperfections in the thermal conditions have a greater effect on the quality of the plateau as the solidus point is approached, and corrections based on earlier stages of the freeze are likely to be more reliable.

While it is clear that the errors and uncertainties are greater for poorer samples and conditions, the method offers useful advantages in all cases, from the point where the freeze becomes firmly established until the limitations of the practical realisation become apparent. One further assumption in a practical implementation is that the time axis is well correlated with the solid fraction.

Examples of the corrections for real freezing curves

To test the model and its application, several freeze curves have been examined. In all cases the data were logged continuously, with readings every 12 s or 17 s, and the total freeze times (> 10 hr, and typically ~20 hr) were large enough for the model to be applied. The traces were plotted, with no averaging, and the plateaux were divided into five or more segments from which the slopes were derived from linear fits. The corrections were then calculated to estimate the ideal freeze values.

We first apply the method to a tin cell which was degraded and no longer in use. It was measured as found, and then after doping with 5.5 ppm and 7.4 ppm of cobalt [6]. The freezes are shown in Figures 2-4. Corrections were calculated with $k = 0$ and with estimated solidus points at 18, 53 and 20 hours from the start, respectively. The corrected values are plotted, and are seen to be relatively constant over half or more of the freezes: the mean corrected temperatures for the first four points were 231.9274 °C, 231.9284 °C and 231.9278 °C, for the three freezes, respectively. Considering the magnitude of the corrections, the consistency obtained is encouraging and indicates the potential of the method, even though irregularities are found in the second half of the freezes. (Note that although in this example the bridge readings have been converted to temperatures, this should not be taken to mean that that the 'correct' value should be 231.928 °C as in the ITS-90.)

The next example is for two freezes of an indium cell which show a modest slope on the plateau, see Figures 5 and 6. The first freeze was comparatively short at 11 hr, but produces corrections which are small and consistent within 0.05 mK. The second (17 hr) freeze was less regular, but the first four corrections are consistent within 0.24 mK and the average corrected value agrees within 0.03 mK with the average for the first freeze.

The third example is of freezes for two tin cells, Figures 7 and 8. In the first, the plateau is quite flat, and the corrections are small. Although there is a downward trend, the first four corrected values are within 0.05 mK. The freeze for second cell is more sloped, but the first four corrected values are within 0.16 mK.

These examples show the advantages of the method for both good and degraded cells. Worthwhile corrections can be applied whether they are large or small, and in many cases the uncertainties may be in the region of 10 to 20%, based on corrections from 50% or more of the freeze.

Summary of advantages and disadvantages

In conclusion, the advantages of the method are:

- It is based on experimental freezes rather than extensive, but incomplete and uncertain, analyses of the materials
- Corrections are simply obtained from experimentally-determined slopes of the freezing plateaux, assuming only a value for the effective distribution coefficient, k_{eff}
- Realistic values of k_{eff} are likely to be small, in which case the results are not sensitive to the exact value adopted
- Consistent corrected freezing point temperatures can be achieved over more than half of the freeze, with uncertainties in the region of 10-20%.
- The initiation process is not important, provided that it produces at least one quasi-cylindrical solid-liquid interface
- There is no requirement to estimate the solid fraction at the start of the plateau. At any point, it is only the remainder of the freeze which is important
- The method can be applied to good and degraded cells
- It can be used to re-validate a cell which may have become contaminated after a period of use.

Some disadvantages or conditions are:

- The freeze must be slow enough that the impurities are effectively diffused in the liquid
- The end point of the freeze must be estimated, though uncertainties in this are less important early in the freeze
- The thermal conditions must be controlled well enough that the freeze follows the Scheil model. Departures form this condition will show up as inconsistent or divergent corrected values, especially in the second half of the freeze.

A fuller exposition of the Scheil model and its application, including the possibility of executing best-fits to all or part of the freeze to deduce T_0, k_{eff}, etc, is to be published [7].

References

1. *Uncertainties in the realisation of the SPRT sub-ranges of the ITS-90*, Document CCT/08-19/rev, Section 2.3, BIPM (2008) http://www.bipm.org/cc/AllowedDocuments.jsp?cc=CCT
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6. P. Petchpong, PhD Thesis, Brunel University, 2009
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Figure 2

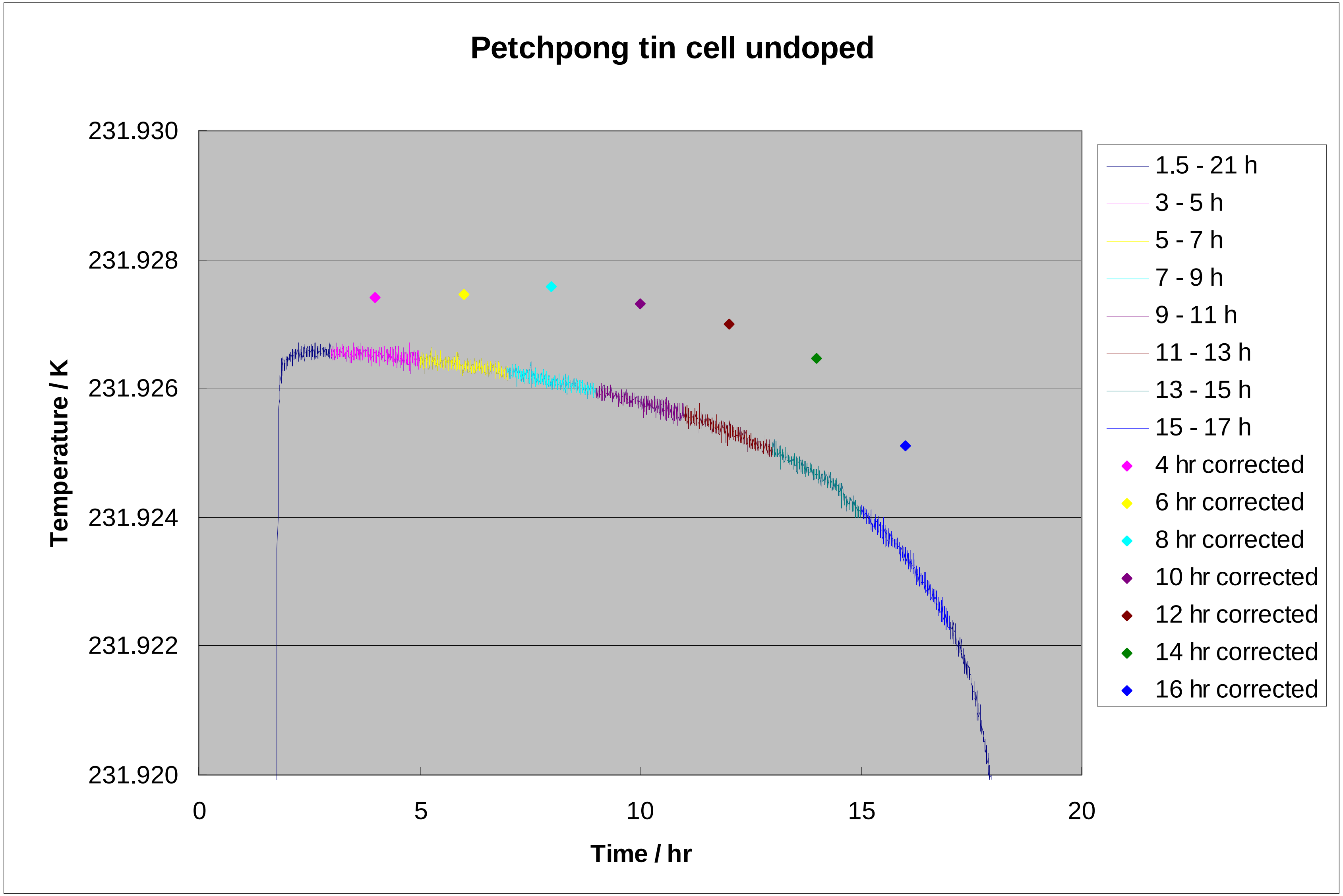

Petchpong tin cell undoped
231.930
231.928
231.926
231.924
231.922
231.920
Temperature / K
0
5
10
15
20
Time / hr
1.5 - 21 h
3 - 5 h
5 - 7 h
7 - 9 h
9 - 11 h
11 - 13 h
13 - 15 h
15 - 17 h
4 hr corrected
6 hr corrected
8 hr corrected
10 hr corrected
12 hr corrected
14 hr corrected
16 hr corrected

Figure 3

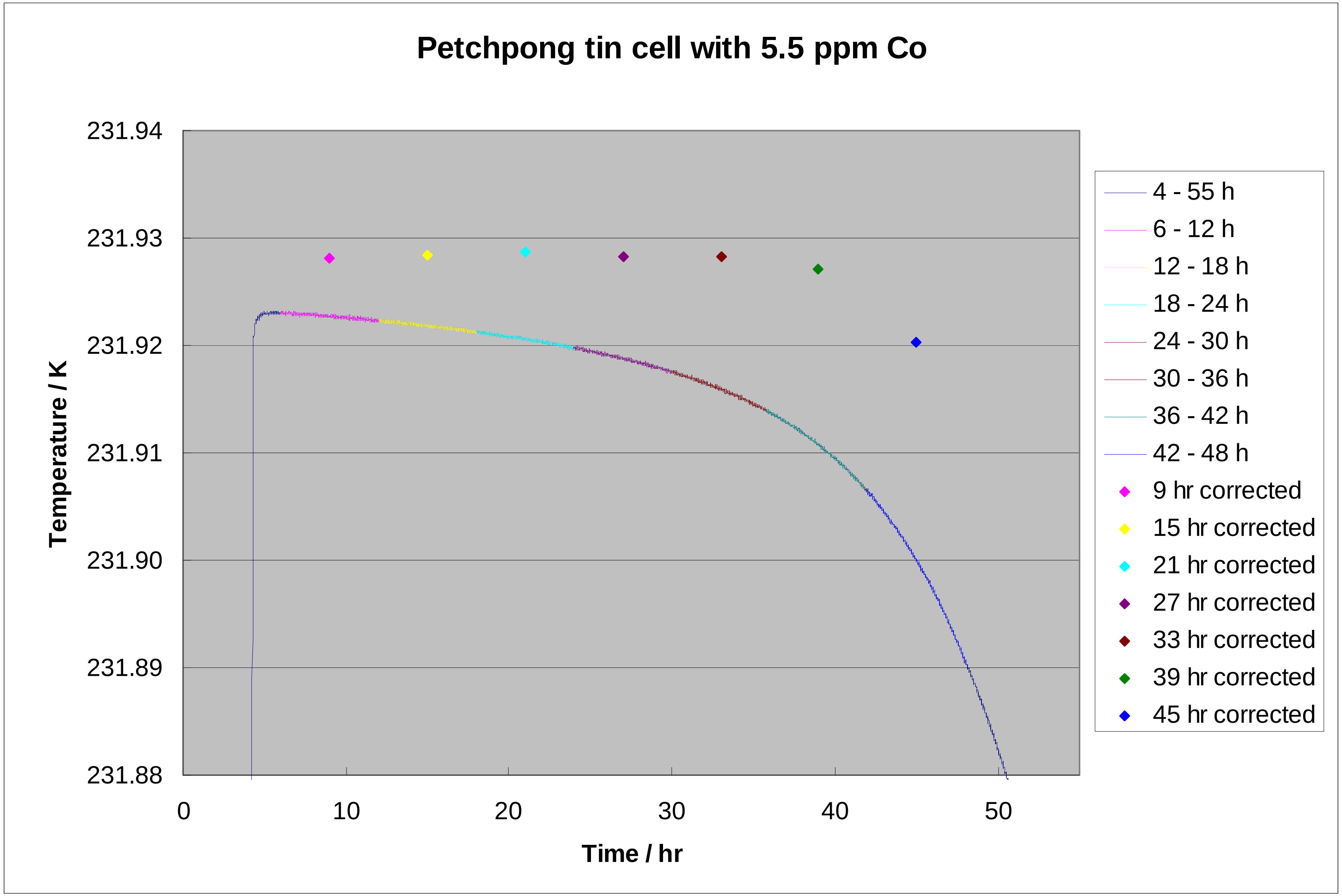

Petchpong tin cell with 5.5 ppm Co
231.94
231.93
231.92
231.91
231.90
231.89
231.88
Temperature / K
0
10
20
30
40
50
Time / hr
4 - 55 h
6 - 12 h
12 - 18 h
18 - 24 h
24 - 30 h
30 - 36 h
36 - 42 h
42 - 48 h
9 hr corrected
15 hr corrected
21 hr corrected
27 hr corrected
33 hr corrected
39 hr corrected
45 hr corrected

Figure 4

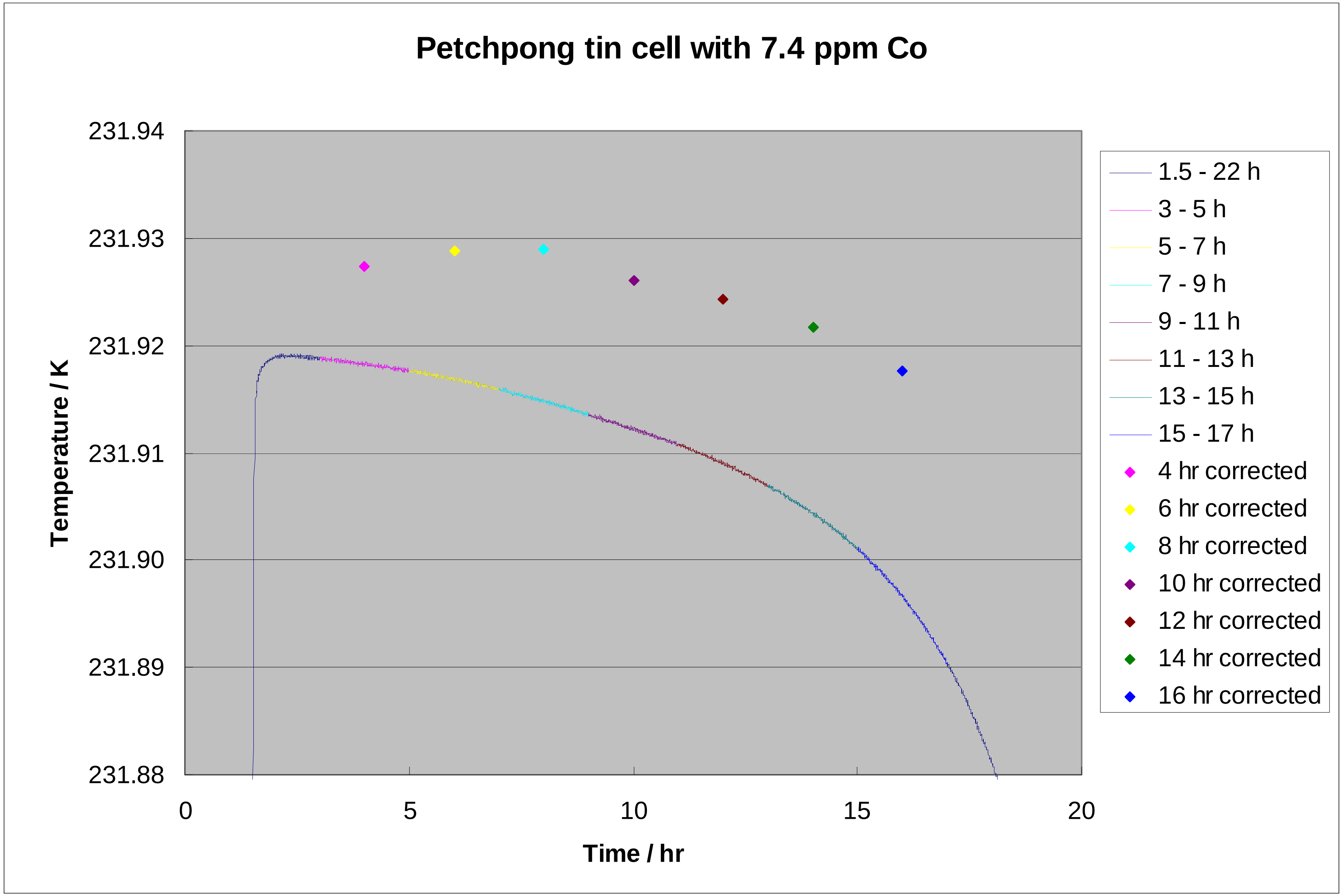

Petchpong tin cell with 7.4 ppm Co
231.94
231.93
231.92
231.91
231.90
231.89
231.88
Temperature / K
0
5
10
15
20
Time / hr
1.5 - 22 h
3 - 5 h
5 - 7 h
7 - 9 h
9 - 11 h
11 - 13 h
13 - 15 h
15 - 17 h
4 hr corrected
6 hr corrected
8 hr corrected
10 hr corrected
12 hr corrected
14 hr corrected
16 hr corrected

Figure 5

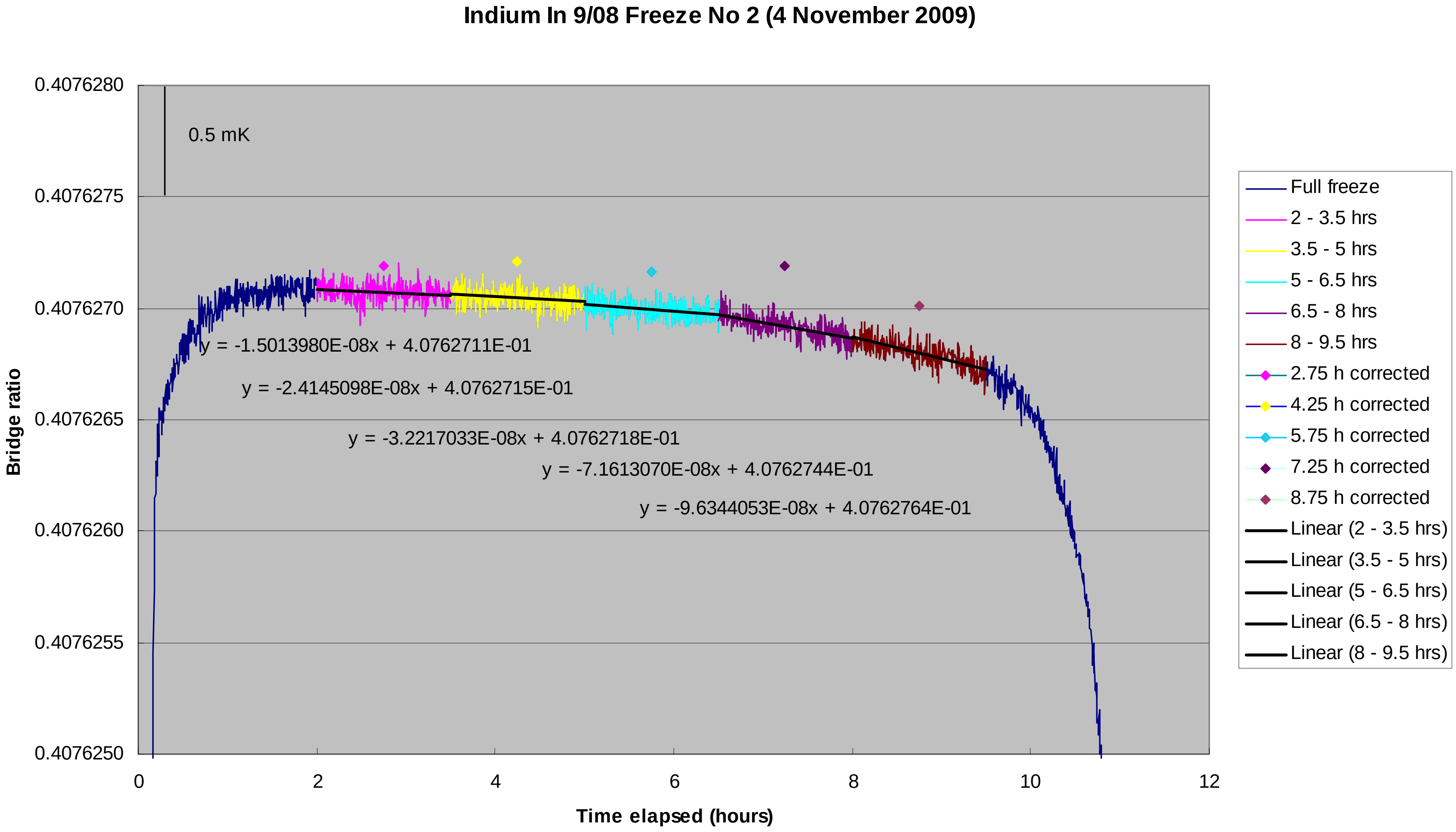

Indium In 9/08 Freeze No 2 (4 November 2009)
0.4076280
0.4076275
0.4076270
0.4076265
0.4076260
0.4076255
0.4076250
Bridge ratio
0
2
4
6
8
10
12
Time elapsed (hours)
0.5 mK
y = -1.5013980E-08x + 4.0762711E-01
y = -2.4145098E-08x + 4.0762715E-01
y = -3.2217033E-08x + 4.0762718E-01
y = -7.1613070E-08x + 4.0762744E-01
y = -9.6344053E-08x + 4.0762764E-01
Full freeze
2 - 3.5 hrs
3.5 - 5 hrs
5 - 6.5 hrs
6.5 - 8 hrs
8 - 9.5 hrs
2.75 h corrected
4.25 h corrected
5.75 h corrected
7.25 h corrected
8.75 h corrected
Linear (2 - 3.5 hrs)
Linear (3.5 - 5 hrs)
Linear (5 - 6.5 hrs)
Linear (6.5 - 8 hrs)
Linear (8 - 9.5 hrs)

Figure 6

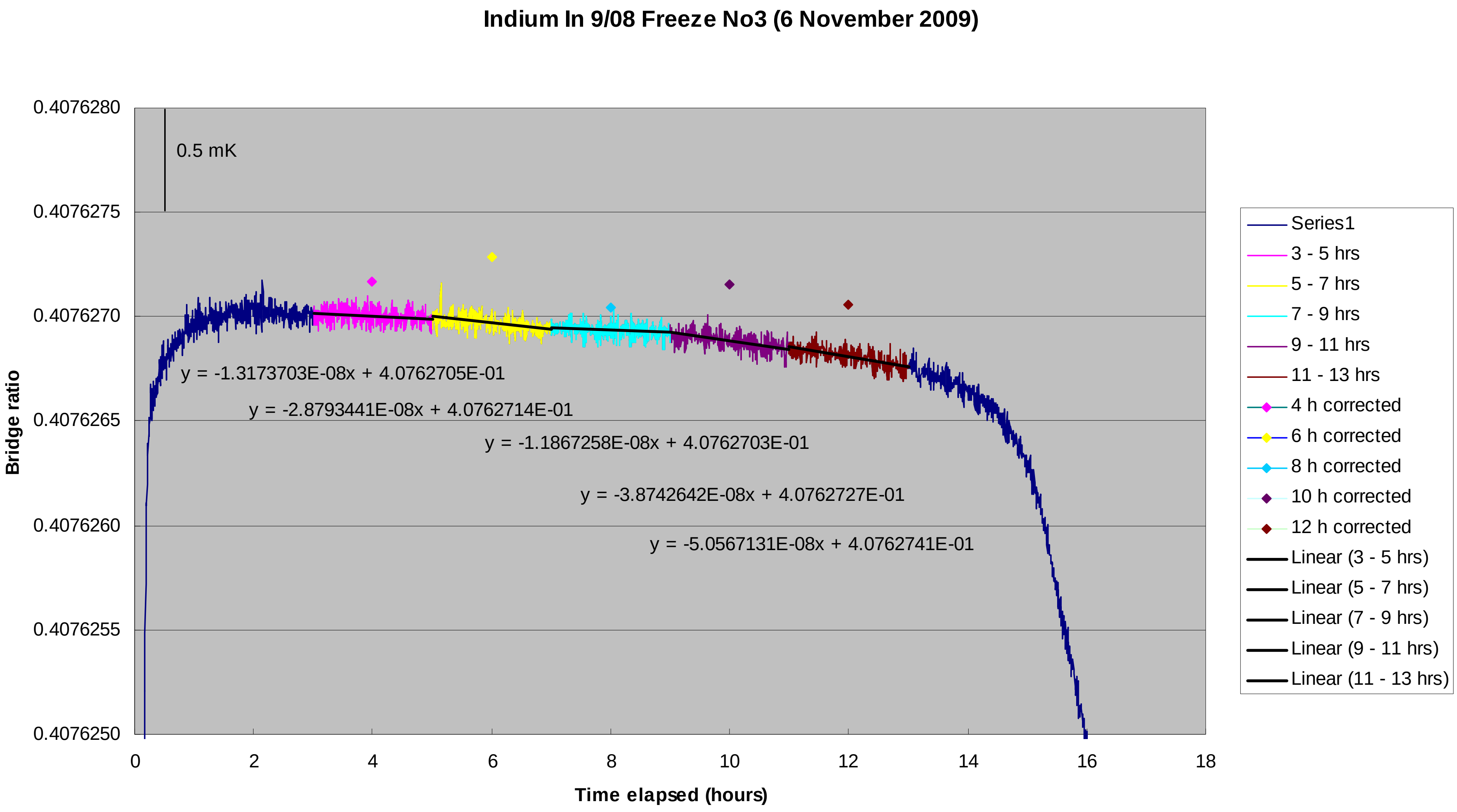

Indium In 9/08 Freeze No3 (6 November 2009)
0.4076280
0.4076275
0.4076270
0.4076265
0.4076260
0.4076255
0.4076250
Bridge ratio
0
2
4
6
8
10
12
14
16
18
Time elapsed (hours)
0.5 mK
y = -1.3173703E-08x + 4.0762705E-01
y = -2.8793441E-08x + 4.0762714E-01
y = -1.1867258E-08x + 4.0762703E-01
y = -3.8742642E-08x + 4.0762727E-01
y = -5.0567131E-08x + 4.0762741E-01
Series1
3 - 5 hrs
5 - 7 hrs
7 - 9 hrs
9 - 11 hrs
11 - 13 hrs
4 h corrected
6 h corrected
8 h corrected
10 h corrected
12 h corrected
Linear (3 - 5 hrs)
Linear (5 - 7 hrs)
Linear (7 - 9 hrs)
Linear (9 - 11 hrs)
Linear (11 - 13 hrs)

Figure 7

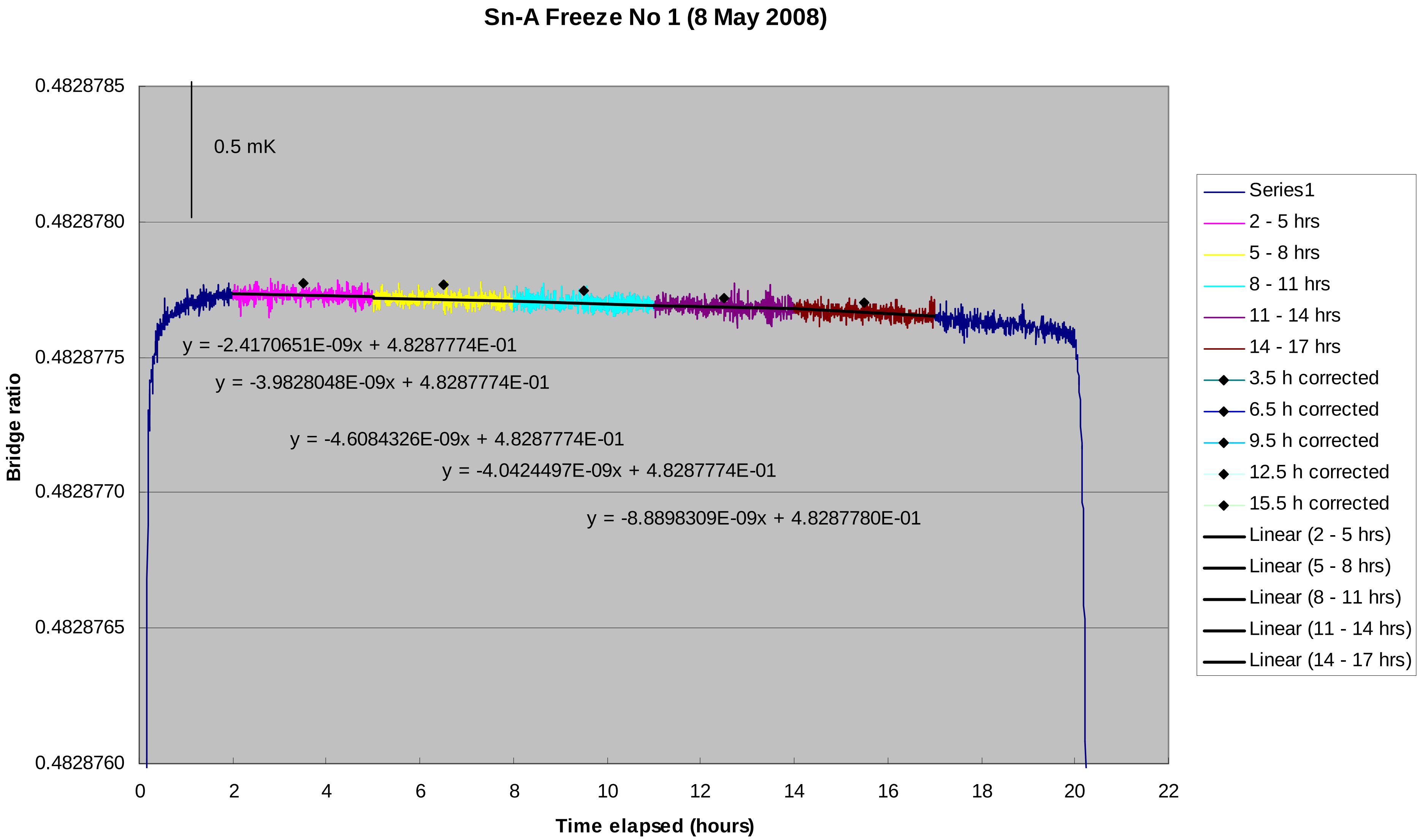
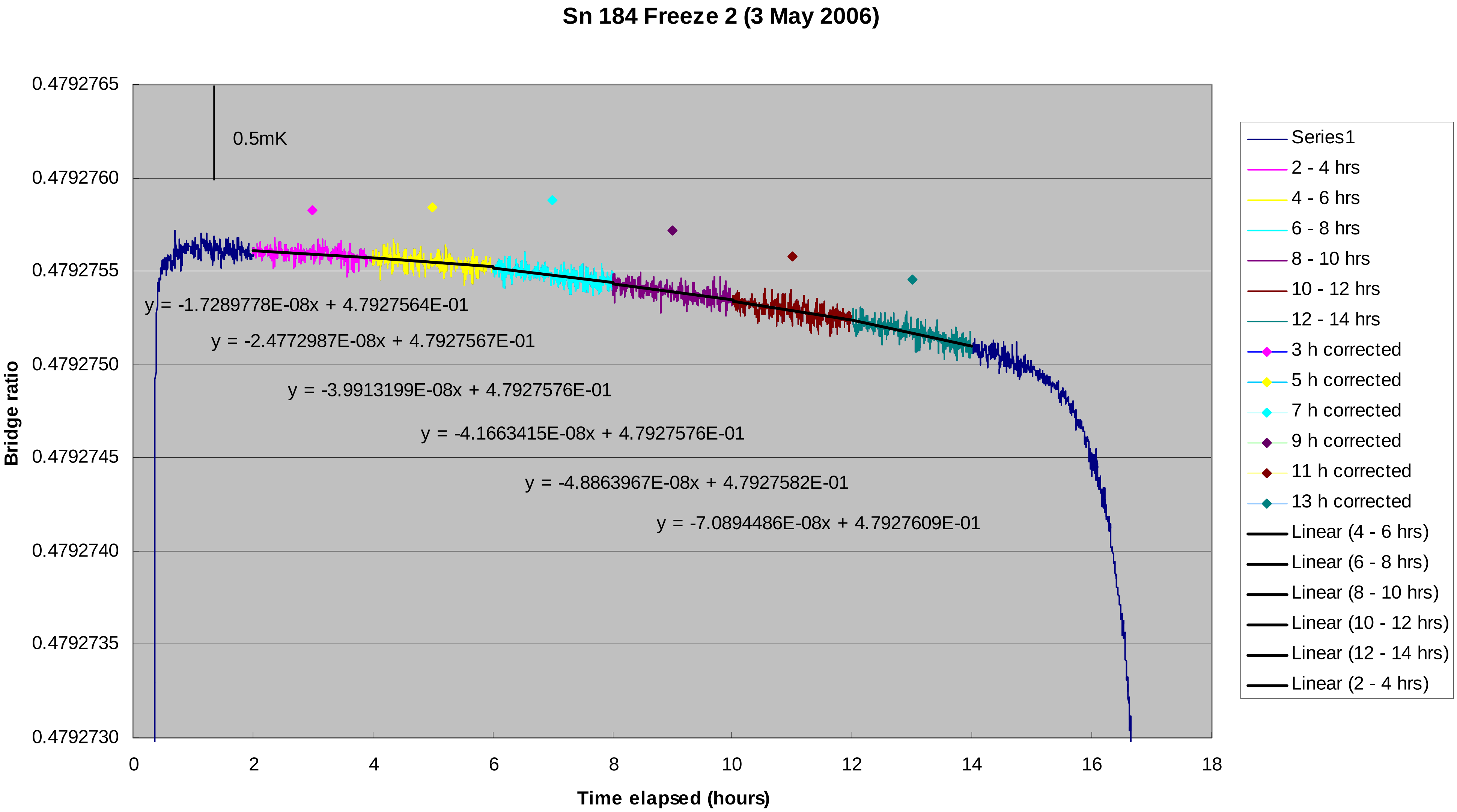

Sn-A Freeze No 1 (8 May 2008)
0.4828785
0.4828780
0.4828775
0.4828770
0.4828765
0.4828760
Bridge ratio
0.5 mK
y = -2.4170651E-09x + 4.8287774E-01
y = -3.9828048E-09x + 4.8287774E-01
y = -4.6084326E-09x + 4.8287774E-01
y = -4.0424497E-09x + 4.8287774E-01
y = -8.8898309E-09x + 4.8287780E-01
0
2
4
6
8
10
12
14
16
18
20
22
Time elapsed (hours)
Series1
2 - 5 hrs
5 - 8 hrs
8 - 11 hrs
11 - 14 hrs
14 - 17 hrs
3.5 h corrected
6.5 h corrected
9.5 h corrected
12.5 h corrected
15.5 h corrected
Linear (2 - 5 hrs)
Linear (5 - 8 hrs)
Linear (8 - 11 hrs)
Linear (11 - 14 hrs)
Linear (14 - 17 hrs)

Figure 8


Sn 184 Freeze 2 (3 May 2006)
0.5mK
y = -1.7289778E-08x + 4.7927564E-01
y = -2.4772987E-08x + 4.7927567E-01
y = -3.9913199E-08x + 4.7927576E-01
y = -4.1663415E-08x + 4.7927576E-01
y = -4.8863967E-08x + 4.7927582E-01
y = -7.0894486E-08x + 4.7927609E-01
Bridge ratio
0.4792765
0.4792760
0.4792755
0.4792750
0.4792745
0.4792740
0.4792735
0.4792730
Time elapsed (hours)
0
2
4
6
8
10
12
14
16
18
Series1
2 - 4 hrs
4 - 6 hrs
6 - 8 hrs
8 - 10 hrs
10 - 12 hrs
12 - 14 hrs
3 h corrected
5 h corrected
7 h corrected
9 h corrected
11 h corrected
13 h corrected
Linear (4 - 6 hrs)
Linear (6 - 8 hrs)
Linear (8 - 10 hrs)
Linear (10 - 12 hrs)
Linear (12 - 14 hrs)
Linear (2 - 4 hrs)