Quality Control of Fixed-Point Cells During Manufacturing

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Abstract

The quality of fixed-point cells is influenced by several factors during the manufacturing process, such as metal purity, vacuum control, and temperature control. It is important to evaluate the cells after they are manufactured to ensure quality. Most of the possible quality problems coming from the manufacturing process can be detected by cell testing and evaluation. Procedures for testing the freezing plateau as a quality check is described in the paper, including comparing against reference cells. A method for calculating metal purity from the test data is discussed. Calculations of metal purity were verified by chemical analysis, and the results are presented in the paper.

1. Introduction

The quality of metal fixed-point cells depends on such manufacturing variables as metal purity, crucible quality, argon purity, vacuum control, manufacturing duration, and temperature control. In order to minimize contamination of the metal during manufacturing, all these factors must be carefully controlled. Quality can be assessed by observing the freezing plateau when the fixed-point temperature of a metal fixed-point cell is realized. Extensive studies of freezing plateaus of metal fixed-point cells have been carried out in the past half century [1-5]. The performance of the freezing plateau of a fixed-point cell depends on several factors, including amount of impurities in the metal, the method of inducing nucleation, and the furnace maintenance temperature.

Calculation of impurity concentration in a metal fixed-point cell can be performed based on observations of the freezing curve by applying Raoult's law of dilute solution, as described by the following equation [6]:

$$T_0 - T = \frac{\Sigma x_i}{A} \tag{1}$$

Variable T_0 is the freezing point temperature of the pure sample, T is the observed realization temperature, x_i is the mole fraction of the impurity, and A is the first cryoscopic constant, which depends on the metal and can be found in reference [7].

In this paper, the method for realization of freezing plateaus of metal fixed-point cells is introduced. The performance of freezing plateaus is evaluated based on the stability and duration of freezing plateaus, and the comparison to the reference cells' freezing temperatures. The calculation method for estimation of impurities concentration of metal samples in fixed-point cells is introduced. The calculation result is compared with the experimental result.

2. Experimental methods and results

In this study, five types of classic silica-quartz-shell metal fixed-point cells were tested in five furnaces: Fluke Hart Scientific sodium heat-pipe furnace (model 9115) for silver cells and Fluke Hart Scientific three-zone freeze-point furnace (model 9114) for indium, tin, zinc, and aluminum cells. Three types of standard platinum resistance thermometers (SPRTs) were used in the testing: Fluke Hart Scientific model 5681 SPRT (25 ohm) for aluminum cells, model 5683 SPRTs (25 ohm) for indium, tin, and zinc cells, and model 5684 high temperature SPRT (0.25 ohm) for silver cells. Three resistance bridges were used to measure the resistances of the SPRTs: Guildline DC current comparator model 6675A (accuracy ±0.1ppm), Measurements International DC current comparator model 6010T (accuracy: <±0.05ppm), and ASL F18 AC thermometry bridge (accuracy: <±0.1ppm). Leeds & Northrup 1 ohm DC and Tinsley 10 ohm AC/DC standard resistors were used with the bridges. A triple point of water cell, Fluke Hart Scientific model 5901, with appropriate maintenance bath (Fluke Hart Scientific model 7312), provided the temperature comparison standard.

The influence of the induction method and the furnace maintenance temperature on the performance of freezing plateaus of metal fixed-point cells has been studied in prior research [5]. It was found that one or two room-temperature silica quartz tubes or rods can be used to induce nucleation for indium, tin, zinc, aluminum, and silver. The induction time varies from 2 minutes to 4 minutes depending on the metal. A suitable furnace maintenance temperature is 0.4 ºC below the corresponding theoretical freezing points for indium, tin, zinc, and aluminum and 0.25 ºC for silver [5]. The duration of the freezing plateau is typically in the range of 15 to 30 hours prior to a 2 mK drop. The induction methods (including induction media and induction duration), the furnace maintenance temperature, bridges, and SPRTs that were used in this study for the five different types of metal fixed-point cells are summarized in Table 1.

The general procedure for realizing freezing plateaus of metal fixed-point cells can be found in reference [5]. Before testing, the furnace temperature is initially set to 4K above the freezing temperature, and the cell's temperature is allowed to stabilize for at least two hours. To begin the freeze, the furnace is set to slowly cool to 2K below the theoretical freezing temperature at a scan rate of 0.1 K/min. As soon as recalescence occurs, recognized by a sudden rise in temperature, a room-temperature quartz glass tube or rod is inserted into the re-entrant well and left for two minutes to induce nucleation. If necessary, a second room-temperature quartz glass tube can be inserted for another two minutes after the first tube is removed. After induction, the furnace temperature is set to 0.4K (or 0.3K for silver) below the freezing temperature and maintained at that temperature during the entire testing process.

Table 1. Freezing plateau testing methods.

Fixed-point cells	Induction media	Induction duration (minutes)	Furnace maintenance temperature	Bridges	SPRTs
In	quartz tube	2	0.4	F18 or 6610T	5683
Sn	compressed air + quartz tube	2 + 2	0.4	F18 or 6610T	5683
Zn	quartz tube	2	0.4	F18 or 6610T	5683
Al	qQuartz rod	2	0.4	F18 or 6610T	5681
Ag	quartz tube	3	0.3	6675A	5684

For the tin fixed-point cell, because of its large supercooling, compressed air was used to enhance induction and accelerate nucleation. During the initial cooling scan, as soon as the temperature reaches the theoretical freezing point of the metal fixed-point cell, compressed air is blown in around the cell basket. This causes the temperature to drop more quickly. When recalescence occurs, the air is switched off and two room-temperature quartz glass tubes are inserted sequentially to induce nucleation around the re-entrant well.

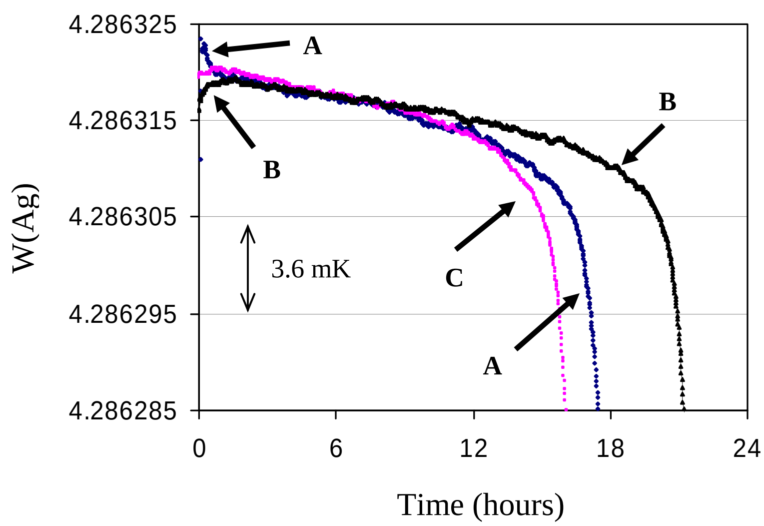


Figure 1. Silver freezing plateaus with different durations of induction
(A: 2 minutes, B: 3 minutes, C: 4 minutes).

The induction duration has a significant influence on the freezing plateau. Longer duration causes more extensive solidification, which shortens the plateau duration. A short induction time may result in failure to form a frozen mantle around the thermometer well, and a proper freezing plateau might not be obtained. Figure 1 shows freezing plateaus of a silver cell obtained by inserting the quartz glass tube into the re-entrant well for three different durations. The furnace temperature was held at 0.3 K below the freezing temperature. In plot A there is overshoot at the beginning of the plateau because the 2-minute induction duration is insufficient. When the duration is increased to 3 minutes, the freezing plateau is much better. At 4 minutes, the plateau duration is shortened by several hours.

During realization of a freezing plateau, the furnace maintenance temperature should be controlled at an optimal value in order to produce a long and stable plateau. If the furnace temperature is too low, the solidification process proceeds too quickly, resulting in a short plateau period. If the furnace temperature is too close to the freezing point, within 0.1 or 0.2 K, there is risk that drift of the furnace temperature could cause the cell to start melting again, in which case the freezing plateau would be destroyed.

Figure 2 shows freezing plateaus of a sealed fused-silica-cased silver fixed-point cell at three different furnace temperatures below the freezing point. The induction method was the same for all three. When the furnace maintenance temperature was 1.2 K below the freezing point, the plateau duration was only about 6 hours before falling 2 mK. When the furnace temperature was 0.45 K below the freezing point, the plateau duration increased to 14 hours. With the furnace temperature 0.3 K below the freezing point, the plateau duration was 17 hours.

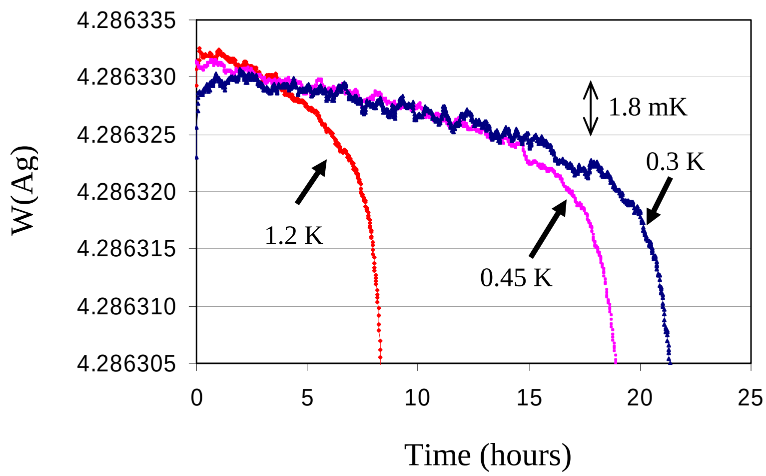
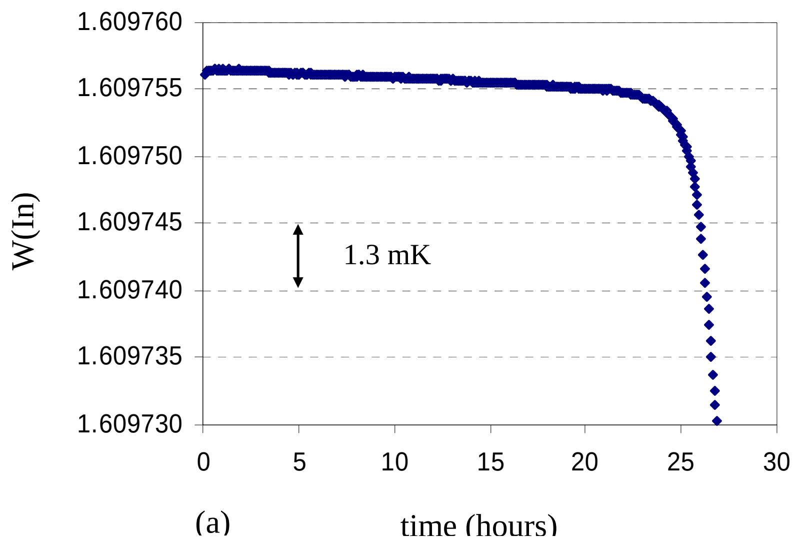
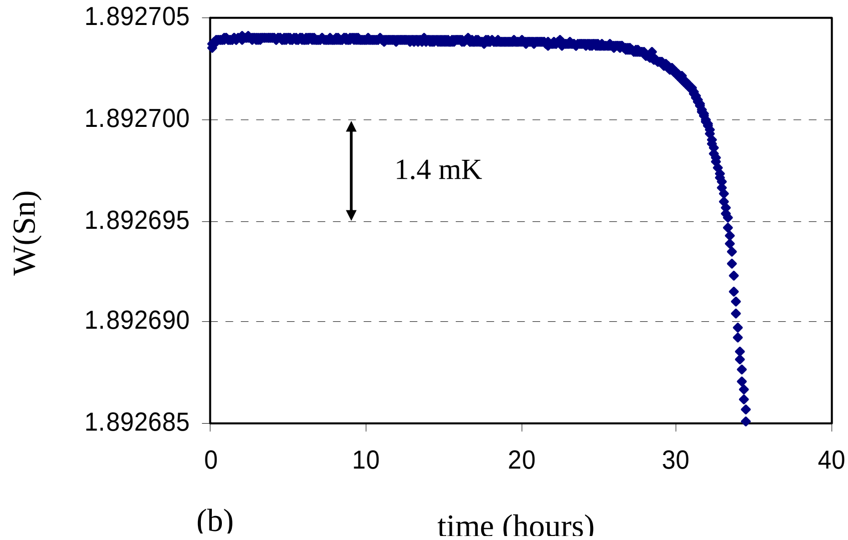


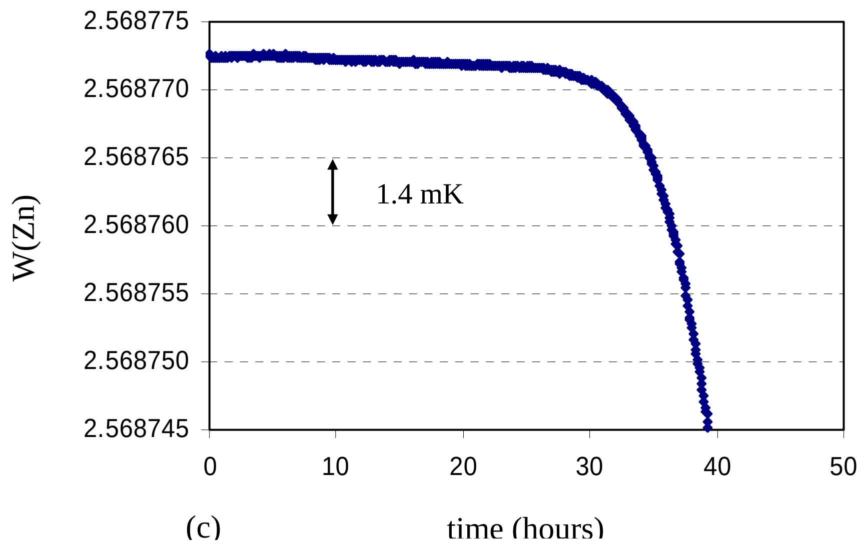
Figure 2. Freezing plateaus with various furnace temperatures.



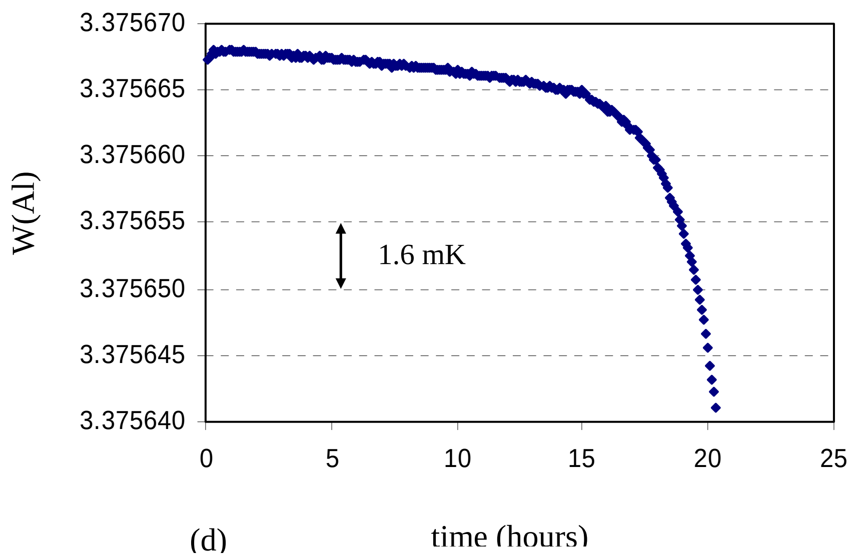
(a)


1.892705
1.892700
1.892695
1.892690
1.892685
W(Sn)
1.4 mK
0
10
20
30
40
time (hours)

(b)


2.568775
2.568770
2.568765
2.568760
2.568755
2.568750
2.568745
W(Zn)
1.4 mK
0
10
20
30
40
50
time (hours)

(c)


3.375670
3.375665
3.375660
3.375655
3.375650
3.375645
3.375640
W(Al)
1.6 mK
0
5
10
15
20
25
time (hours)

(d)

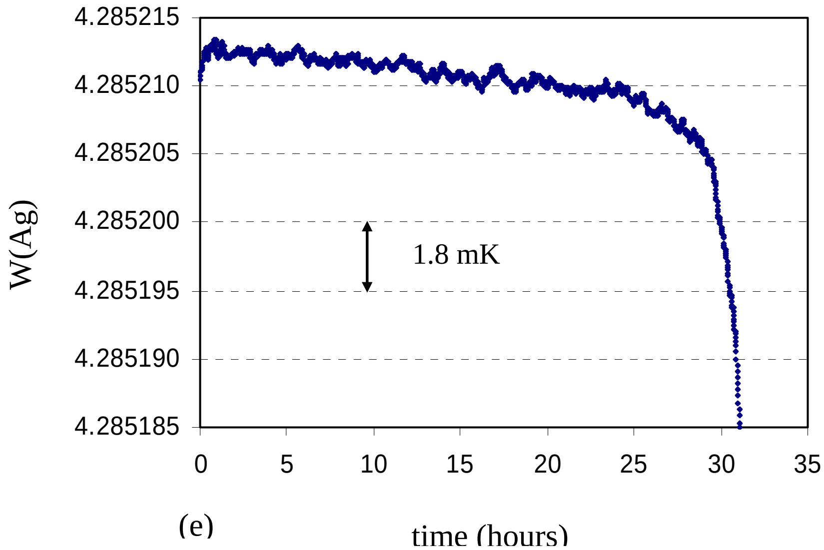


Figure 3. Typical freezing plateaus of metal fixed-point cells
(a: indium, b: tin, c: zinc, d: aluminum, e: silver).

Figure 3 (a) through (e) shows typical freezing plateaus of indium, tin, zinc, aluminum, and silver sealed fused-silica-cased metal fixed-point cells using the induction methods and furnace maintenance temperatures listed in Table 1.

3. Estimation of impurity concentration in metal fixed-point cells

The procedure for quality assessment of metal fixed-point cells based on the performance of their freezing plateaus has three steps. The first is to check the stability of the plateau. Instability (large fluctuations of apparent temperature) can come from two sources: electrical interference and instability of testing equipments (e.g. maintenance furnaces, bridges, SPRTs). If a freezing curve is not stable, the freezing curve should be re-tested after checking the equipment. Three good freezing curves are needed to properly qualify a fixed-point cell.

The second step in evaluating a metal fixed-point cell is to compare its freezing temperature to that of a calibrated reference cell. If the difference in temperatures is larger than the allowed uncertainty, the cell should be tested again to determine whether there is a problem with the test or the cell.

The third step in evaluating a metal fixed-point cell is to estimate the purity of the metal from the freezing curve. This is based on Raoult's law of dilute solution (Equation 1). Figure 4 illustrates the analysis of the freezing curve. A straight line is drawn from point E at -8 mK and point F at -10 mK on the curve. Another line is drawn from point B at 20% of the total freezing time to point D at 70%. This line intersects the ordinate at point A and intersects the first line EF at G. Point C is the midpoint of the line segment AG. In Equation 1, T_0 is set to the *y*-axis value of point A, and T is set to the *y*-axis value of the point C. The mole fraction of the total metal impurities in the fixed-point cell is then calculated.

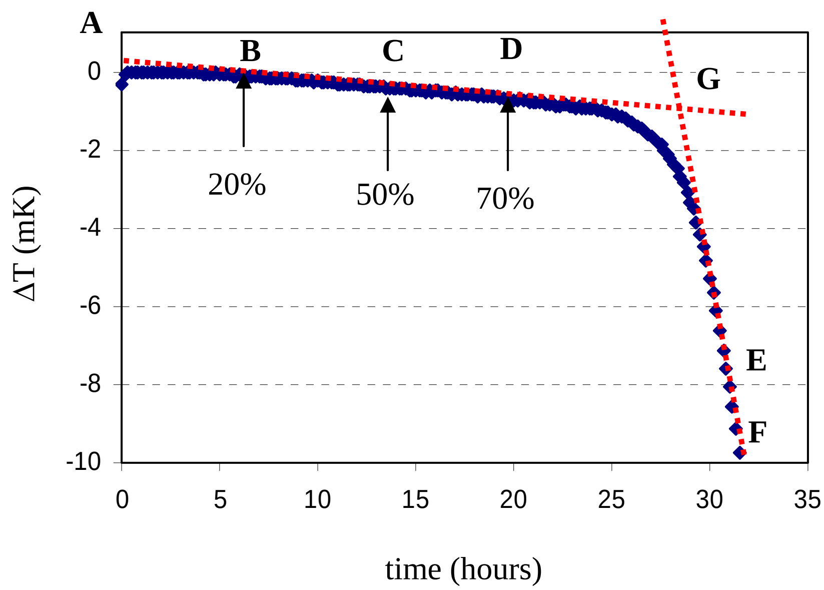
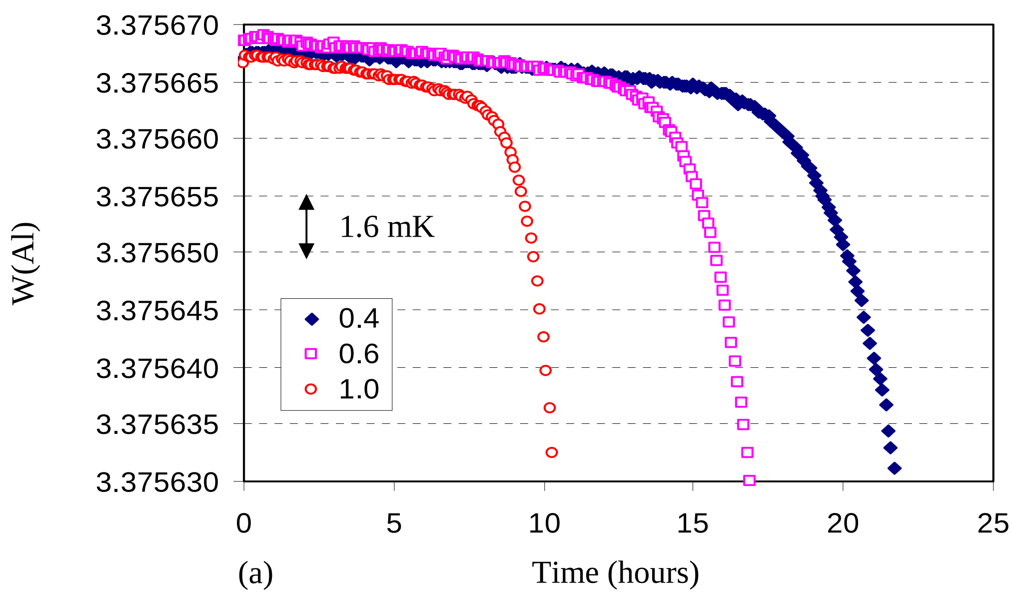


Figure 4. Calculation method for estimation of metal purity.

As an example, the calculated mole fraction of impurities in the aluminum cell of Figure 3 (d) is 1.5E-06. Mass spectrometry analysis of the same metal shows the concentration to be 1.6E-06, which is very close to the calculated value.



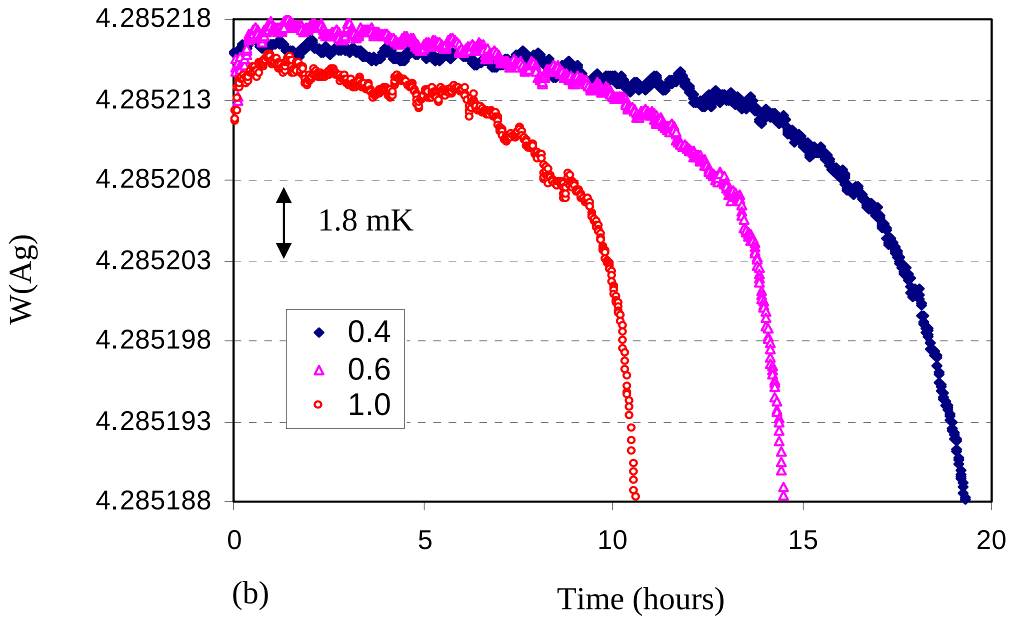


Figure 5. Freezing curves of an aluminum (a) and a silver cell (b) at different furnace temperatures.

If the method of calculating impurity concentration is accurate, results should be the same at different freezing rates. To verify this, an aluminum cell and a silver cell were tested at three different rates, determined by the furnace temperature. The resulting freezing curves are shown in Figure 5, and calculated impurity concentrations are given in Table 2. The results for the aluminum cell are consistent. But with the silver cell there are significant differences. It appears that the method needs further improvement so that it can be used to estimate impurity concentration accurately under a variety of conditions.

Table 2. Calculation of impurities at three different freezing rates.

Al		**Ag**	
Maintenance temperature (ºC)	Impurities mole fraction	Maintenance temperature (ºC)	Impurities mole fraction
0.4	8.3E-07	0.4	3.1E-07
0.6	9.0E-07	0.6	8.7E-07
1.0	9.3E-07	1.0	6.0E-07

To investigate how selection of the E and F points (see Figure 4) affects calculated impurities, the analysis was repeated with various E and F point temperatures. The furnace temperature was 0.4 ºC below the freezing point. Resulting calculated mole fractions of impurities are given in Table 3. Selection of the E and F points appears to have little effect on the results. This conclusion should hold as long as the slope of the freezing curve is constant as the temperature falls (from -4 mK to -10 mK).

Table 3. Calculation of impurities with different E and F point temperatures.

Al		**Ag**	
E, F points	Impurities mole fraction	E, F points	Impurities mole fraction
-4, -6 mK	8.3E-07	-4, -6 mK	5.1E-07
-6, -8 mK	8.3E-07	-6, -8 mK	4.4E-07
-8, -10 mK	8.3E-07	-8, -10 mK	3.1E-07
-10, -12 mK	8.3E-07	-10, -12 mK	5.7E-07

4. Summary

A metal fixed-point cell must not be contaminated during manufacture. It is important to check the final purity of the metal to ensure quality. Methods used at Fluke Hart Scientific for evaluating the quality of manufactured metal fixed-point cells were presented. This involves calculating impurity concentration based on characteristics of the freezing plateau. Results of impurity calculations agreed well with the mass spectrometry analysis. But some discrepancy was observed when different freezing rates were used, suggesting some need for further improvement.

References

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