# NIST Methods of Estimating the Impurity Uncertainty Component for ITS-90 Fixed-Point Cells from the Ar TP to the Ag FP

Gregory F. Strouse
National Institute of Standards and Technology
Gaithersburg, Maryland USA

**Abstract.** The NIST Platinum Resistance Thermometry Laboratory uses International Temperature Scale of 1990 (ITS-90) fixed-point cells to calibrate standard platinum resistance thermometers as ITS-90 defining standards. One important component of uncertainty in the realization of ITS-90 fixed-point cells is the effect of sample purity on the realized temperature. Four different methods of analysis (mole fraction sum of impurity components, freezing curve, direct comparison, and 1/*F* realization curve) are used to both estimate and crosscheck the value used for the impurity uncertainty component. The crosschecks provided by the multiple methods are an integral part of our quality assurance. The paper applies each method and the subsequent crosscheck analysis to four different samples of In.

## Introduction

The NIST Platinum Resistance Thermometry (PRT) Laboratory, which realizes the International Temperature Scale of 1990 (ITS-90) from the Ar TP (83.8058 K) to the Ag FP (1234.93 K), uses four methods to estimate and validate the impurity uncertainty component value for an ITS-90 fixed-point cell [1]. As an overview, Table 1 gives five methods in order of priority. A detailed description with examples of four different samples of In for each method is described later in the document. Further background information on the five methods is found in references 2-5.

Table 1. Overview of the methods used by the NIST PRT Laboratory to estimate and validate the impurity uncertainty component of an ITS-90 fixed-point cell.

| Method of Analysis | Application |
|---|---|
| mole fraction sum of impurity components | sample assay used prior to fabrication of fixed-point cell |
| freezing curve | consistency check with mole fraction sum of impurity components method, after fabrication of fixed-point cell |
| direct comparison | consistency check with freezing curve and mole fraction sum of impurity components methods, after fabrication of fixed-point cell |
| 1/*F* realization curve | alternative to freezing curve method; consistency check with mole fraction sum of impurity components methods after fabrication of fixed-point cell |
| total impurity concentration | not for use by an NMI; typically used by industry with no sample assay available to end user, prior to fabrication of fixed-point cell |

The estimated impurity uncertainty component value is taken as the standard uncertainty and is not considered a rectangular distribution and is **not** divided by root three [6,7]. The estimated impurity uncertainty component value is treated as a symmetric uncertainty, though the effect is most likely asymmetric.

It is important to remember that NIST manufactures all of its own fixed-point cells (except water) and purchases the fixed-point cell materials from precious metal refiners. Purification and analysis of the fixed-point samples are performed by the refiners. As a minimum, three fixed-point cells are fabricated using the same sample lot and are tested at the same time. Table 2 gives the NIST PRT Laboratory current requirement for the minimum purity level (wt %) for each fixed-point sample used to make fixed-point cells. A sample assay for the specific sample lot is required from the refiner.

Table 2. Minimum sample purity currently required from refiner for use by NIST PRT Laboratory in the manufacture of ITS-90 fixed-point cells.

| ITS-90 fixed-point sample | Minimum purity, wt % | ITS-90 fixed-point sample | Minimum purity, wt % |
|---|---|---|---|
| Ar | 99.9999 | Sn | 99.9999 |
| Hg | 99.999 999 | Zn | 99.9999 |
| Ga | 99.999 995 | Al | 99.9999 |
| In | 99.999 99 | Ag | 99.9999 |

**Methods of Analysis**

**1. Mole fraction sum of impurity components – pre-fabrication of fixed-point cell**

The refiner that purifies and directly sells the fixed-point samples also supplies a sample assay for each sample lot. The refiner sample assay is used to determine which impurities are present and the concentration of each impurity that exists in the fixed-point sample.

As given in tables 3-6, the impurity concentrations (wt %) are converted to mole fraction concentrations and summed to determine the total mole fraction impurity concentration in the fixed-point sample. Using the total mole fraction impurity concentration contained in the fixed-point sample and the first cryoscopic constant, the impurity uncertainty component value is estimated using Raoult's Law of Dilute Solutions. With the distribution coefficient ($k$) of each impurity set at zero, such that the impurities are only soluble in the liquid sample, the equation simplifies to:

$$\Delta T = T_0 - T = \frac{x_2}{A} \qquad (1)$$

where $T_0$ is the freezing point temperature of the 100% pure sample, $T$ is the observed realization temperature, $x_2$ is the mole-fraction impurity concentration, and $A$ is the first cryoscopic constant. Values of the first cryoscopic constants for the ITS-90 fixed-points materials are found in reference 8. The dilute amount of impurities present in the fixed-point sample are assumed to be colligative, such that the mole-fraction impurities may be summed

and used with the first cryoscopic constant for the fixed-point sample in equation 1 to estimate the impurity uncertainty component value [3].

Table 3. Calculation of total mole fraction impurity concentration for Arconium† 79 In (lot S2739) for estimating the impurity uncertainty ($k$=1, Type B, normal distribution) component value prior to fabrication of a fixed-point cell.

**Mole fraction sum of impurity components method**

Glow Discharge Mass Spectroscopy assay of Arconium 79 In (lot S2739)

NIST cells In 96-4, In 96-5, and In 96-6

| assay element | impurity, wt % | atomic weight | number of atomic weight atoms | mole fraction, % |
|---|---|---|---|---|
| Sn | 5E-08 | 118.7 | 4E-10 | 4.84E-08 |
| Pb | 2E-08 | 207.2 | 1E-10 | 1.11E-08 |
| Fe | 5E-09 | 55.85 | 9E-11 | 1.03E-08 |
| Ni | 4E-09 | 58.69 | 7E-11 | 7.82E-09 |
| Al | 4E-09 | 26.98 | 1E-10 | 1.70E-08 |
| Na | 1E-08 | 22.99 | 4E-10 | 4.99E-08 |
| Si | 7E-09 | 28.09 | 2E-10 | 2.86E-08 |
| In | 0.9999999 | 114.8 | 9E-03 | |
| | | | mole fraction sum of impurity concentrations | 1.73E-07 |
| | | | 1st cryoscopic constant for In | 0.00213 |
| | | | Estimated impurity uncertainty component value, mK | 0.08 |

Table 4. Calculation of total mole fraction impurity concentration for Arconium 79 In (lot S2552) for estimating the impurity uncertainty ($k$=1, Type B, normal distribution) component value prior to fabrication of a fixed-point cell.

**Mole fraction sum of impurity components method**

Glow Discharge Mass Spectroscopy assay of Arconium 79 In (lot S2552)

NIST cells In 96-1, In 96-2, and In 96-3

| assay element | impurity, wt % | atomic weight | number of atomic weight atoms | mole fraction, % |
|---|---|---|---|---|
| C | 1.2E-09 | 12.01 | 1E-10 | 1.15E-08 |
| N | 7E-09 | 14.01 | 5E-10 | 5.74E-08 |
| O | 1.8E-09 | 16 | 1E-10 | 1.29E-08 |
| Al | 3E-10 | 26.98 | 1E-11 | 1.28E-09 |
| Si | 8E-09 | 28.09 | 3E-10 | 3.27E-08 |
| Cl | 2E-09 | 35.45 | 6E-11 | 6.48E-09 |
| Ni | 2E-10 | 58.69 | 3E-12 | 3.91E-10 |
| Ga | 3.5E-10 | 69.72 | 5E-12 | 5.76E-10 |
| Sn | 7E-09 | 118.7 | 6E-11 | 6.77E-09 |
| Tl | 5E-10 | 204.4 | 2E-12 | 2.81E-10 |
| Pb | 3.8E-08 | 207.2 | 2E-10 | 2.11E-08 |
| Bi | 5E-10 | 209 | 2E-12 | 2.75E-10 |
| In | 0.9999999 | 114.8 | 9E-03 | |
| | | | mole fraction sum of impurity concentrations | 1.52E-07 |
| | | | 1st cryoscopic constant for In | 0.00213 |
| | | | Estimated impurity uncertainty component value, mK | 0.07 |

Table 5. Calculation of total mole fraction impurity concentration for Indium Corp. of America 69 In (lot SG-1156) for estimating the impurity uncertainty ($k$=1, Type B, normal distribution) component value prior to fabrication of a fixed-point cell.

**Mole fraction sum of impurity components method**
Emission spectrographic assay of Indium Corp. of America 69 In (lot SG-1156)
NIST cells In 93-1, In 93-2, In 93-3

| assay element | impurity, wt % | atomic weight | number of atomic weight atoms | mole fraction, % |
|---|---|---|---|---|
| Fe | 3E-07 | 55.85 | 5E-09 | 6.17E-07 |
| Pb | 1E-07 | 207.2 | 5E-10 | 5.54E-08 |
| Mg | 1E-07 | 24.31 | 4E-09 | 4.72E-07 |
| In | 0.9999995 | 114.8 | 9E-03 | |
| | | | mole fraction sum of impurity concentrations | 1.14E-06 |
| | | | 1st cryoscopic constant for In | 0.00213 |
| | | | Estimated impurity uncertainty component value, mK | 0.54 |

Table 6. Calculation of total mole fraction impurity concentration for Indium Corp. of America 69 In (lot SG-907) for estimating the impurity uncertainty ($k$=1, Type B, normal distribution) component value prior to fabrication of a fixed-point cell.

**Mole fraction sum of impurity components method**
Emission spectrographic assay of Indium Corp. of America 69 In (lot SG-907)
NIST cells In-1, -2, -3

| assay element | impurity, wt % | atomic weight | number of atomic weight atoms | mole fraction, % |
|---|---|---|---|---|
| Fe | 3.00E-07 | 55.85 | 5E-09 | 6.17E-07 |
| Pb | 2.00E-07 | 207.2 | 1E-09 | 1.11E-07 |
| Sn | 1.00E-07 | 118.7 | 8E-10 | 9.67E-08 |
| Mg | 1.00E-07 | 24.31 | 4E-09 | 4.72E-07 |
| In | 0.9999993 | 114.8 | 9E-03 | |
| | | | mole fraction sum of impurity concentrations | 1.30E-06 |
| | | | 1st cryoscopic constant for In | 0.00213 |
| | | | Estimated impurity uncertainty component value, mK | 0.61 |

## 2. Freezing curve – post-fabrication of fixed-point cell

The freezing-curve method is used to check for consistency with the mole fraction sum of impurity components method used to estimate the impurity uncertainty component value of the fixed-point sample prior to fixed-point cell fabrication. This consistency check is done with all newly fabricated fixed-point cells to make sure that no additional impurities were added to the fixed-point sample during fabrication of the fixed-point cell.

As given in figures 1-4, the freezing curves used for the freezing-curve method are plotted as a function of fraction frozen, $F_X$, so that the duration of the realization is not evident. The $F_0$ value is chosen to be the point in time of sample recalescence and the $F_1$ value is chosen to be the point in time when the realized temperature is 10 mK below the peak temperature, $T_{peak}$, of the freezing curve. A linear regression is performed from $F_{0.2}$ to $F_{0.7}$ to determine the slope and intercept of freezing curve. The temperature difference from fit for $\Delta T(F_{0.5} - F_0)$ is used in conjunction with the first cryoscopic constant to estimate the mole fraction impurity concentration in the fixed-point cell sample.

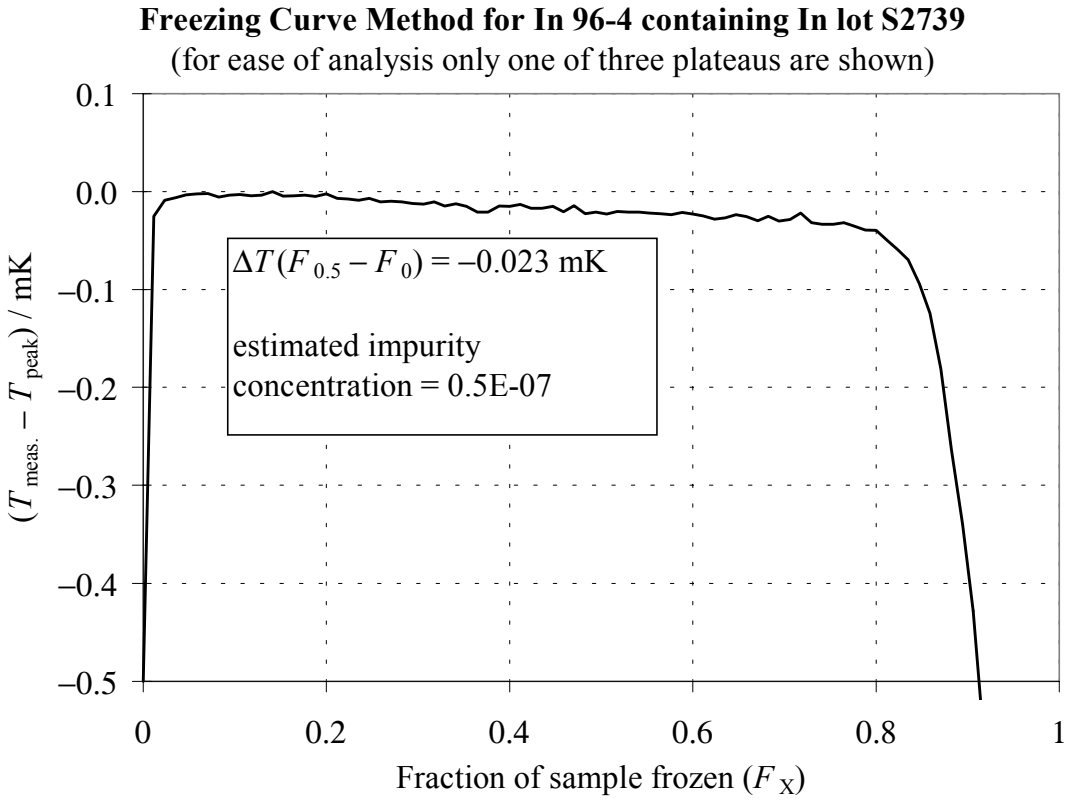


Figure 1. Example of the freezing-curve method for fixed-point cell In 96-4.

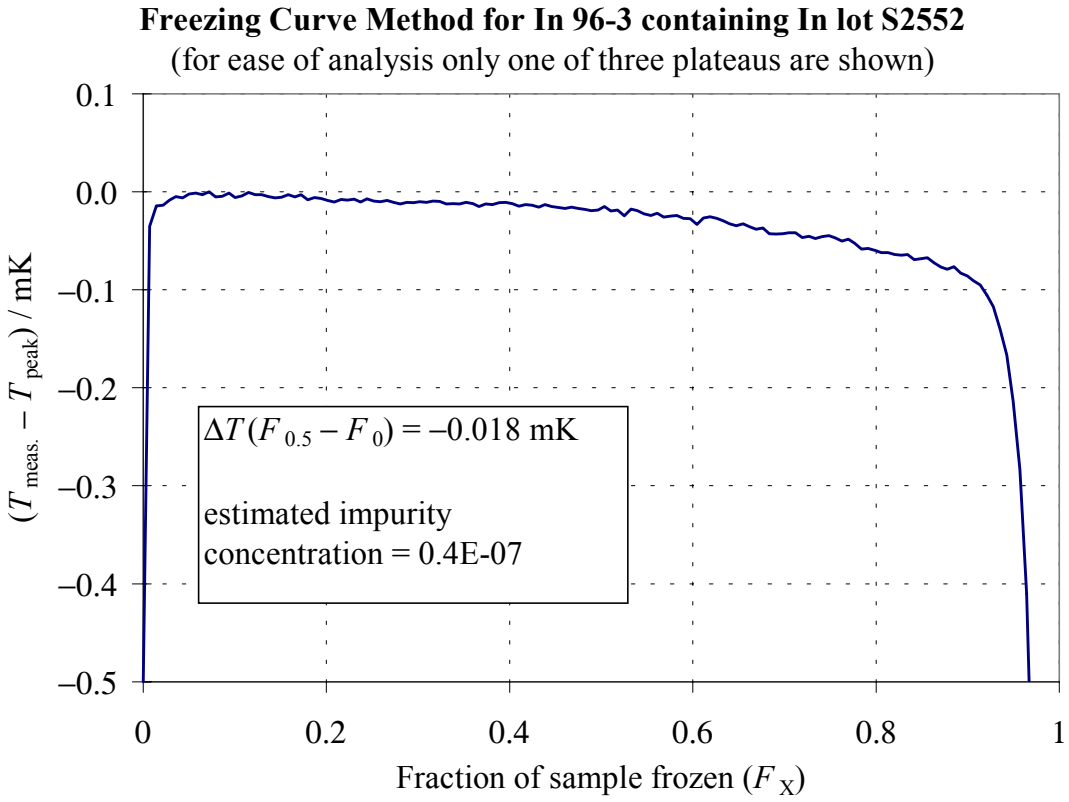


Figure 2. Example of the freezing-curve method for fixed-point cell In 96-3.

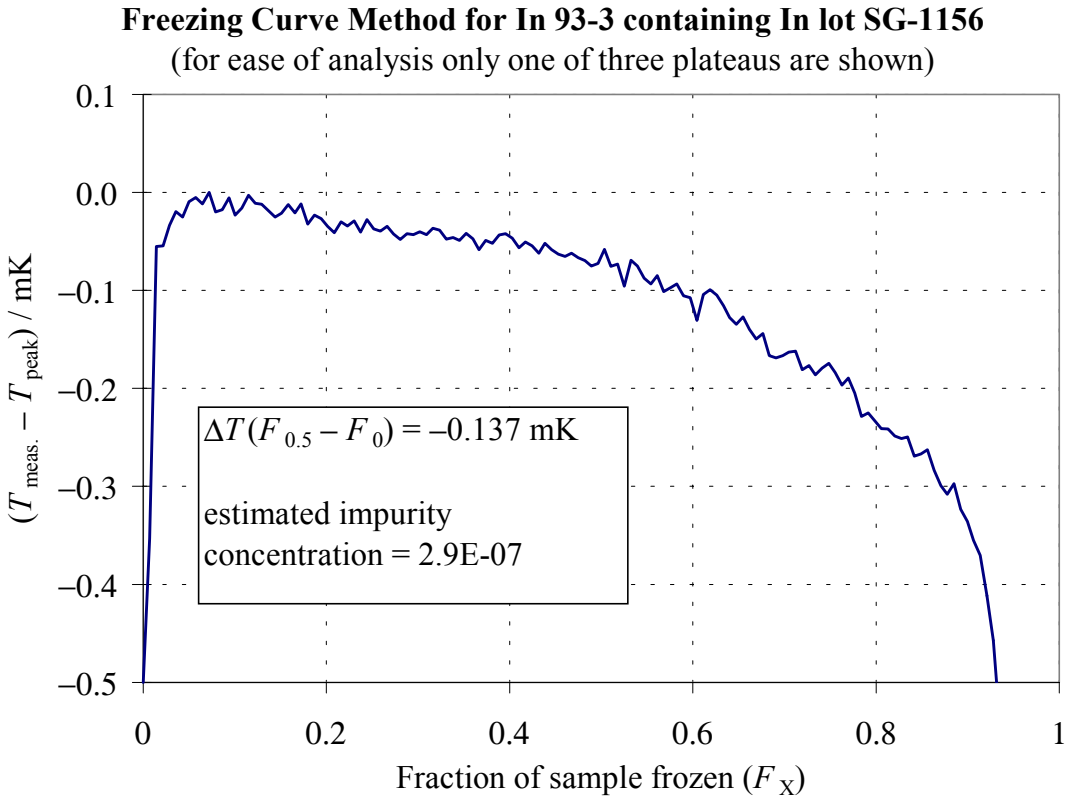


Figure 3. Example of the freezing-curve method for fixed-point cell In 93-3.

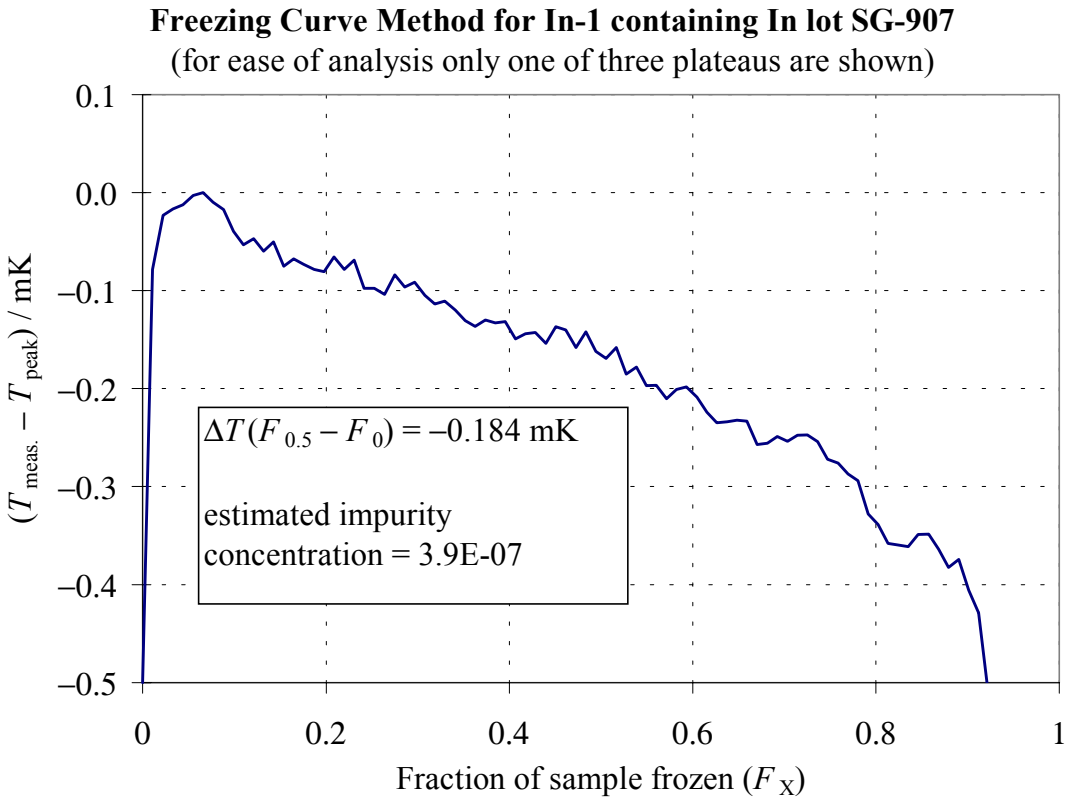


Figure 4. Example of the freezing-curve method for fixed-point cell In-1.

Table 7 gives the results of the crosscheck between the freezing-curve method with the mole fraction sum of impurity components method. It is expected that the two methods will give similar results.

If the freezing-curve method gives a larger value than that of the mole fraction sum of impurity components method, then the $\Delta T(F_{0.5} - F_0)$ value is used to estimate the impurity uncertainty component value of the fabricated fixed-point cell. A larger value from the freezing-curve analysis method may mean that fixed-point sample was contaminated during the fabrication of the cell or the refiner sample assay under-estimated the amount of impurities.

If the freezing-curve method gives a smaller value than that of the mole fraction sum of impurity components method, then the mole fraction sum of impurity components method is used to estimate the impurity uncertainty component value of the fixed-point cell. A smaller value from the freezing curve analysis method may mean that the refiner sample assay over-estimates the amount of impurities or the distribution coefficients of one or more of the impurities approaches one. An impurity with a distribution coefficient of one will not affect the slope of the realization curve, but will affect the realization temperature of the fixed-point cell.

It is important to note that there is a strong interaction between the fixed-point cell, maintenance system, and standard platinum resistance thermometer (SPRT) during the realization of the fixed point. For the analysis to be valid, the freezing curve must last at least ten hours to reduce the heat-flux effects of the furnace on the slope of the freezing curve. Additionally, during a separate heat flux/SPRT immersion test the SPRT used in the measurements must be able to track hydrostatic head effect over the bottommost 3 cm of the reentrant well.

Table 7. Results of the crosscheck between the freezing curve method with mole fraction sum of impurities method for estimating the value of the impurity uncertainty component of the fixed-point sample prior to cell fabrication.

| **Arconium 79 In (lot S2739), NIST cell In 96-4** | | |
|---|---|---|
| **Method** | **Estimated impurity concentration** | **Estimated impurity uncertainty component, mK** |
| mole fraction sum of impurities | $1.7 \times 10^{-7}$ | 0.08 |
| freezing curve | $0.5 \times 10^{-7}$ | 0.02 |
| **Arconium 79 In (lot S2552), NIST cell In 96-3** | | |
| **Method** | **Estimated impurity concentration** | **Estimated impurity uncertainty component, mK** |
| mole fraction sum of impurities | $1.5 \times 10^{-7}$ | 0.07 |
| freezing curve | $0.4 \times 10^{-7}$ | 0.02 |
| **Indium Corp. of America 69 In (lot SG-1156), NIST cell In 93-3** | | |
| **Method** | **Estimated impurity concentration** | **Estimated impurity uncertainty component, mK** |
| mole fraction sum of impurities | $11.4 \times 10^{-7}$ | 0.54 |
| freezing curve | $2.9 \times 10^{-7}$ | 0.14 |
| **Indium Corp. of America 69 In (lot SG-907), NIST cell In-1** | | |
| **Method** | **Estimated impurity concentration** | **Estimated impurity uncertainty component, mK** |
| mole fraction sum of impurities | $13.0 \times 10^{-7}$ | 0.61 |
| freezing curve | $3.9 \times 10^{-7}$ | 0.18 |

## 3. Direct comparison of fixed-point cells – post-fabrication of fixed-point cell

As described above, a minimum of three new fixed-point cells are fabricated using the same sample lot and tested at the same time. These three new fixed-point cells are directly compared with the existing NIST PRT Laboratory reference fixed-point cell to determine the relative realization temperature differences between the test and reference fixed-point cell. The direct comparison is obtained by realizing simultaneous realizations for the test and reference cells in two separate but nearly identical furnaces and making three sets of alternate measurements, at equal time intervals, on their realization-curve plateaus, using an SPRT. Ideally, the equivalent realization temperature difference between measurements of each of the pairs is identical. However, due to small differences in fixed-point sample purity, only the first of the three pairs of measurements on the cells are used for the comparison. Each test fixed-point cell is directly compared three times with the reference fixed-point cell.

Figures 5-7 give three examples of the direct comparison of fixed-point cells containing either 79 In or 69 In with a reference fixed-point cell containing either 79 In or 69 In. Table 8 gives the results of the crosscheck between the relative temperature difference as determined from direct comparison of a fixed-point cell with a reference fixed-point cell with the mole fraction sum of impurity components method for the fixed-point cells containing either 79 In or 69 In.

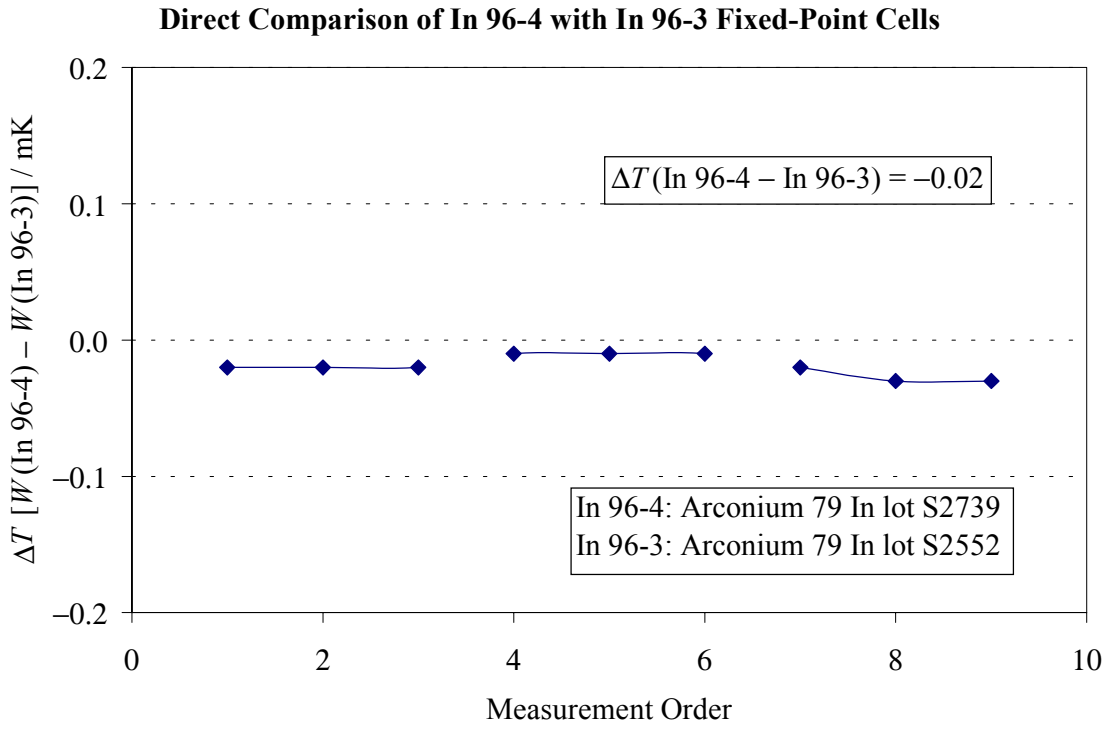


Figure 5. Direct comparison of two In fixed-point cells containing Arconium 79 In from different lots [In 96-4 (lot S2739) and In 96-3 (lot S2552)].

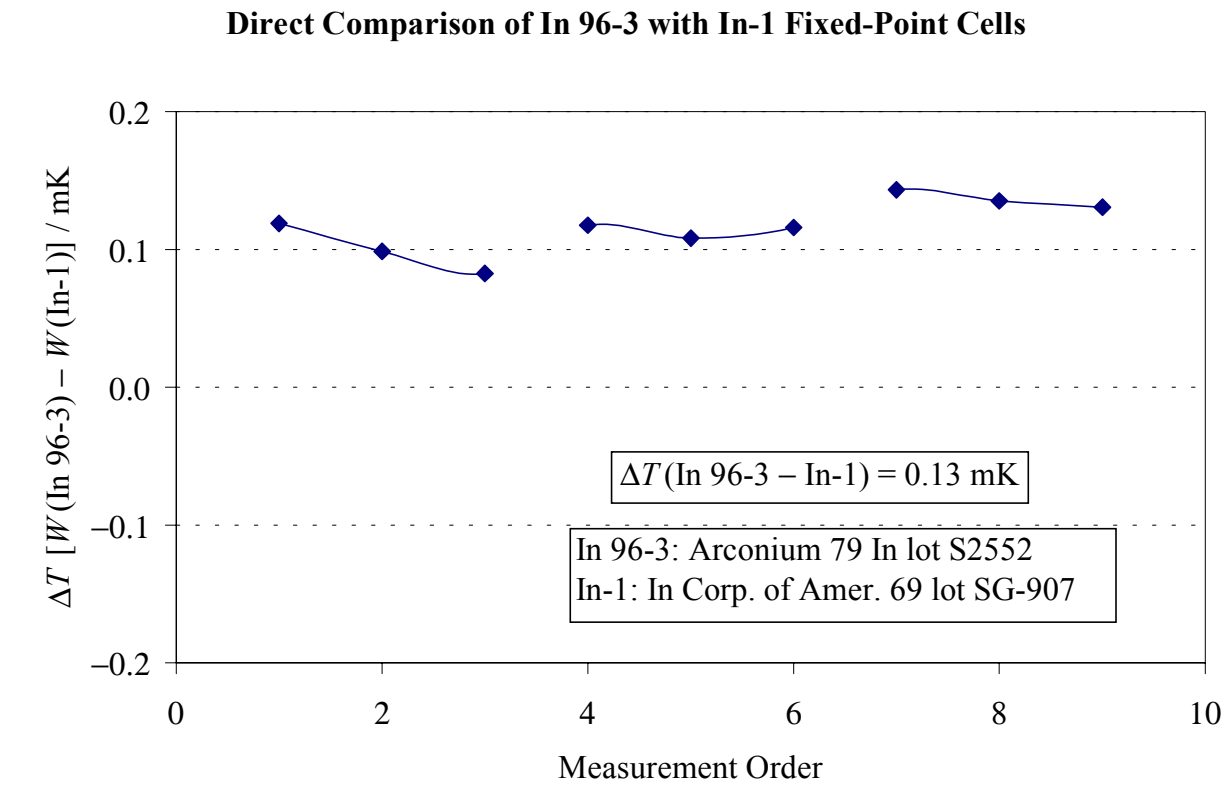


Figure 6. Direct comparison of one In fixed-point cell containing Arconium 79 In [In 96-3 (lot S2552) and one In fixed-point cell containing Indium Corp. of America In [In-1 (lot SG-907)].

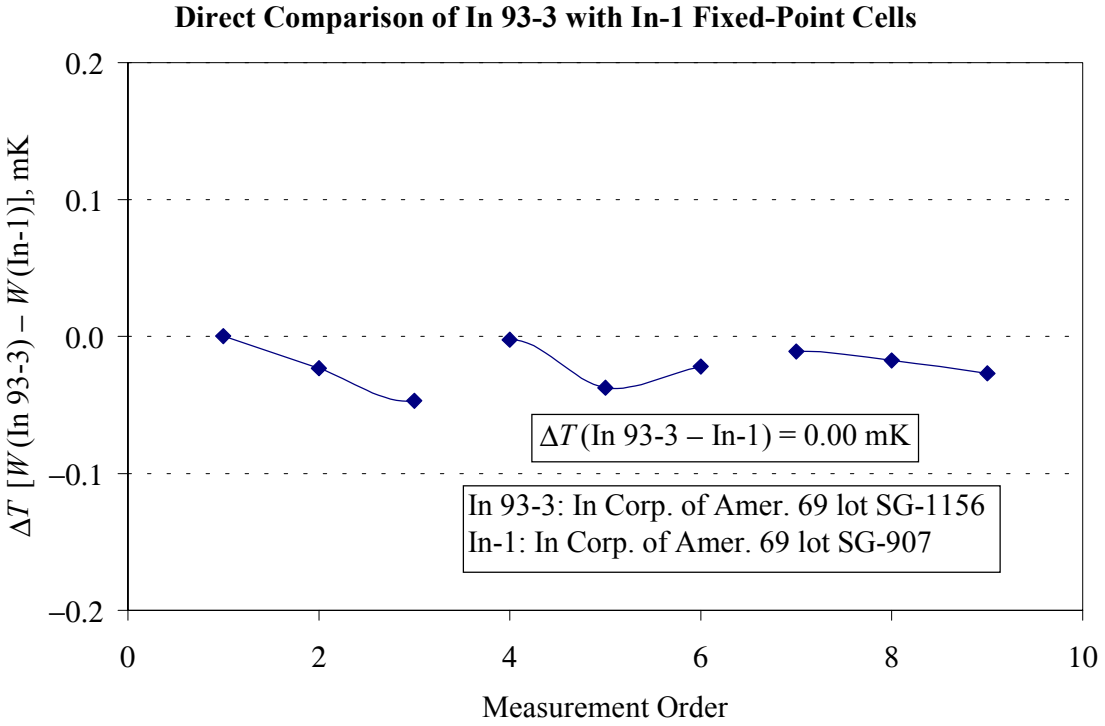


Figure 7. Direct comparison of two In fixed-point cells containing Indium Corp. of America 69 In from different lots [In 93-3 (lot SG-1156) and In-1 (lot SG-907)].

Table 8. Results of the crosscheck between the relative temperature difference as determined from direct comparison of a fixed-point cell with a reference fixed-point cell with the mole fraction sum of impurity components method.

| Δ (Fixed-point cells) | Estimated temperature difference from mole fraction sum of impurity components, mK | Relative temperature difference from direct comparison of fixed-point cells, mK |
|---|---|---|
| In 96-4 – In 96-3 | –0.01 | –0.02 |
| In 96-4 – In-1 | 0.54 | 0.13 |
| In 93-3 – In-1 | 0.07 | 0.00 |

If the freezing curve method shows that no unexpected contamination was added to the fixed-point sample during fabrication of the fixed-point cell, then it is expected that all three new test fixed-point cells will give consistent realization temperature differences with the reference fixed-point cell. Additionally, if the new fixed-point cell and the reference fixed-point cell contain different sample lots, then the realization temperature difference between the new fixed-point cell and the reference fixed-point cell should be consistent with the different impurity concentrations as calculated from the mole fraction sum of impurity components method to within the measurement uncertainty.

It is important to note that there is a strong interaction between the fixed-point cell, maintenance system, and SPRT during the realization of the fixed point. For the direct comparison method, it is useful to have the realization curve last at least sixteen hours, so that the measurements may be made over the first twenty percent of the realization. Additionally, during a separate heat flux/SPRT immersion test the SPRT used in the measurements must be able to track hydrostatic head effect over the bottommost 3 cm of the reentrant well.

## 4. 1/*F* realization curve – post-fabrication of fixed-point cell

As an alternative to the freezing curve method, either the freezing or melting curve plotted as $\Delta T$ as a function of the reciprocal fraction frozen or melted ($1/F$) may be analyzed. This method is useful with the Ga MP as a freezing curve is difficult to obtain. A linear regression from a $1/F$ value of 1.5 (denoted $1/F_{1.5}$) to $1/F_5$ is used to determine the slope of the $1/F$ plot. The $\Delta T(1/F_1 - 1/F_0)$ value from the fit in conjunction with the first cryoscopic constant is used to estimate the mole fraction impurity concentration in the fixed-point cell sample.

Figures 8-11 give three examples of melting curve plotted as $\Delta T$ as a function of the reciprocal fraction frozen or melted ($1/F$) for the fixed-point cells containing either 79 In or 69 In. Table 9 gives the results of the crosscheck between $1/F$ realization curve method with the mole fraction sum of impurity components method for the fixed-point cells containing either 79 In or 69 In.

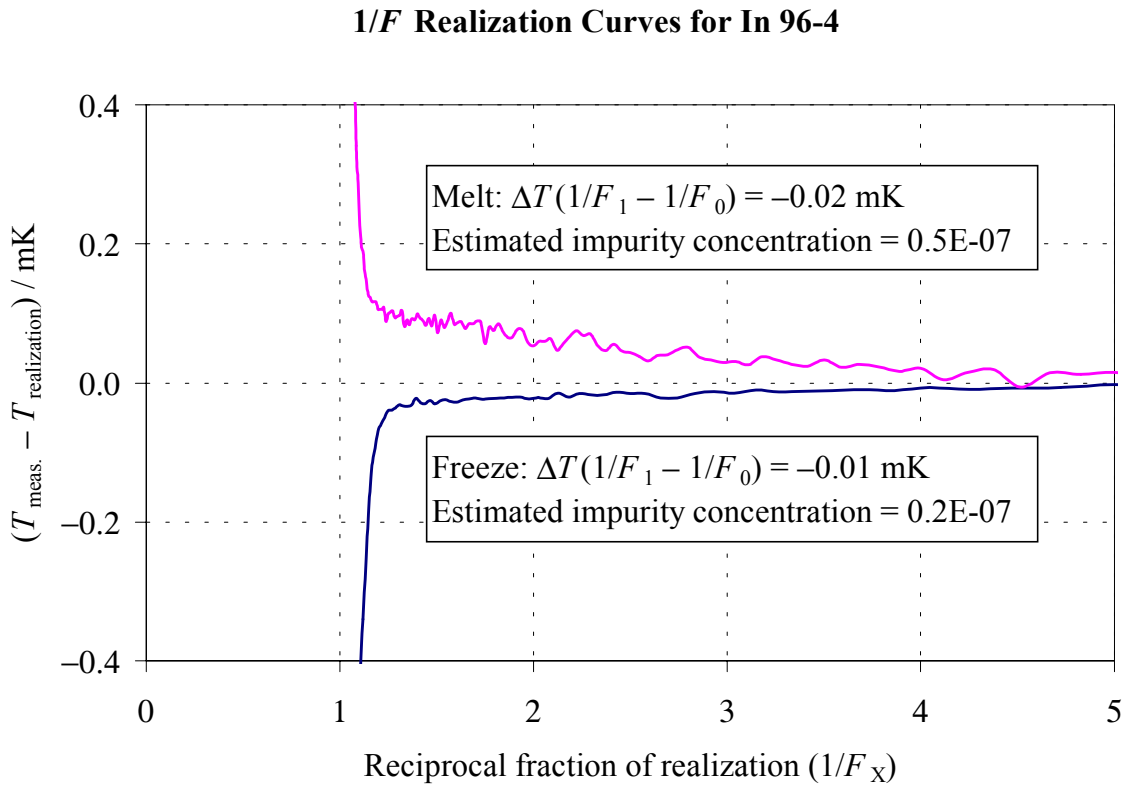


Figure 8. Example of the 1/F realization-curve method for In 96-4.

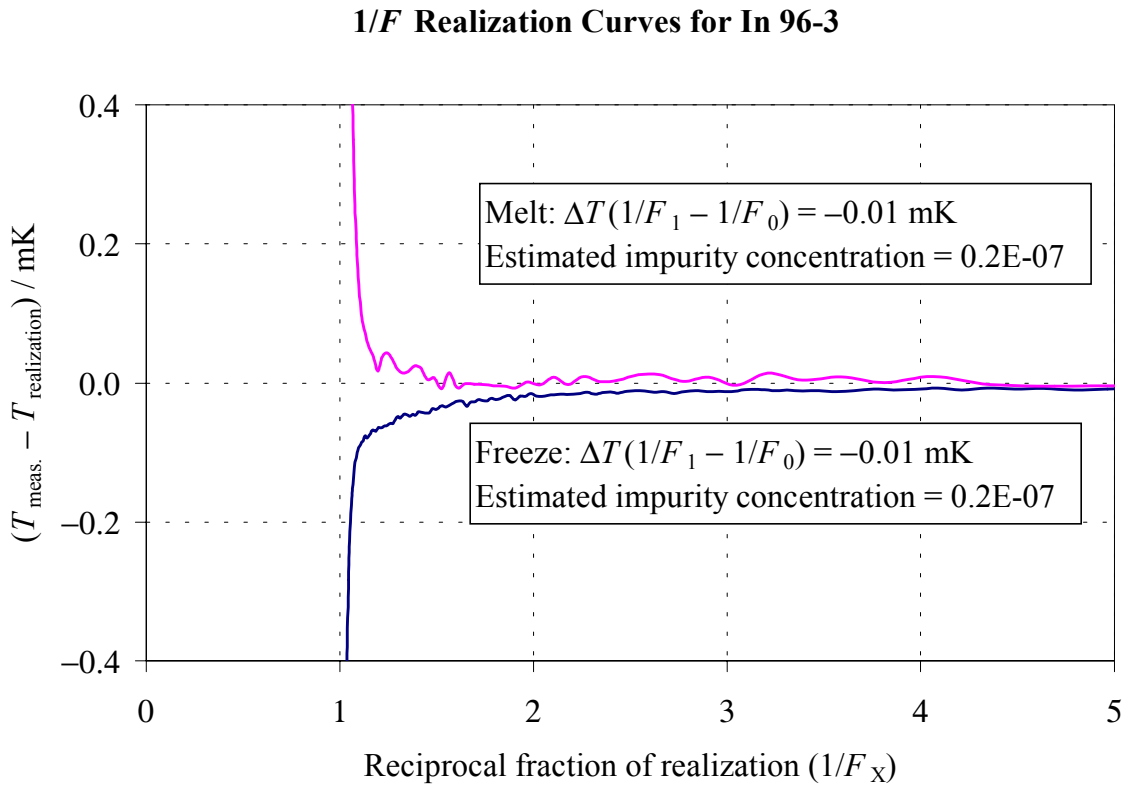


Figure 9. Example of the realization-curve method for fixed-point cell In 96-3.

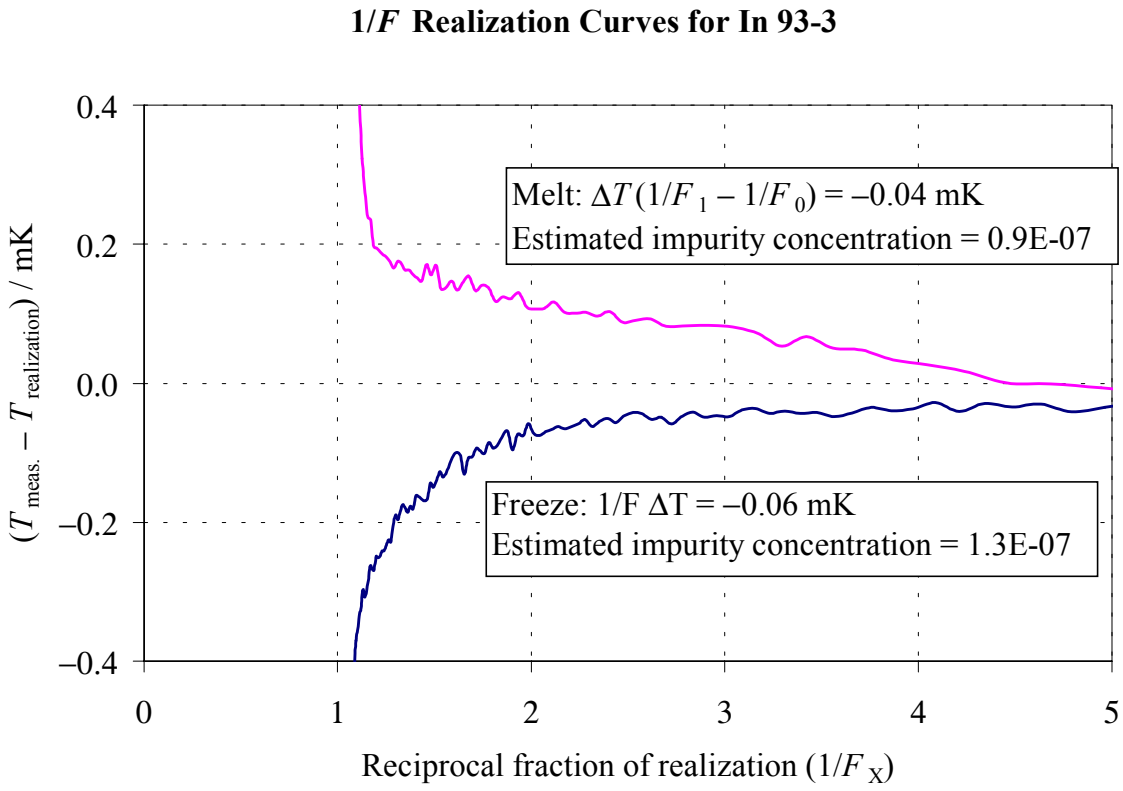


Figure 10. Example of the realization-curve method for fixed-point cell In 93-3.

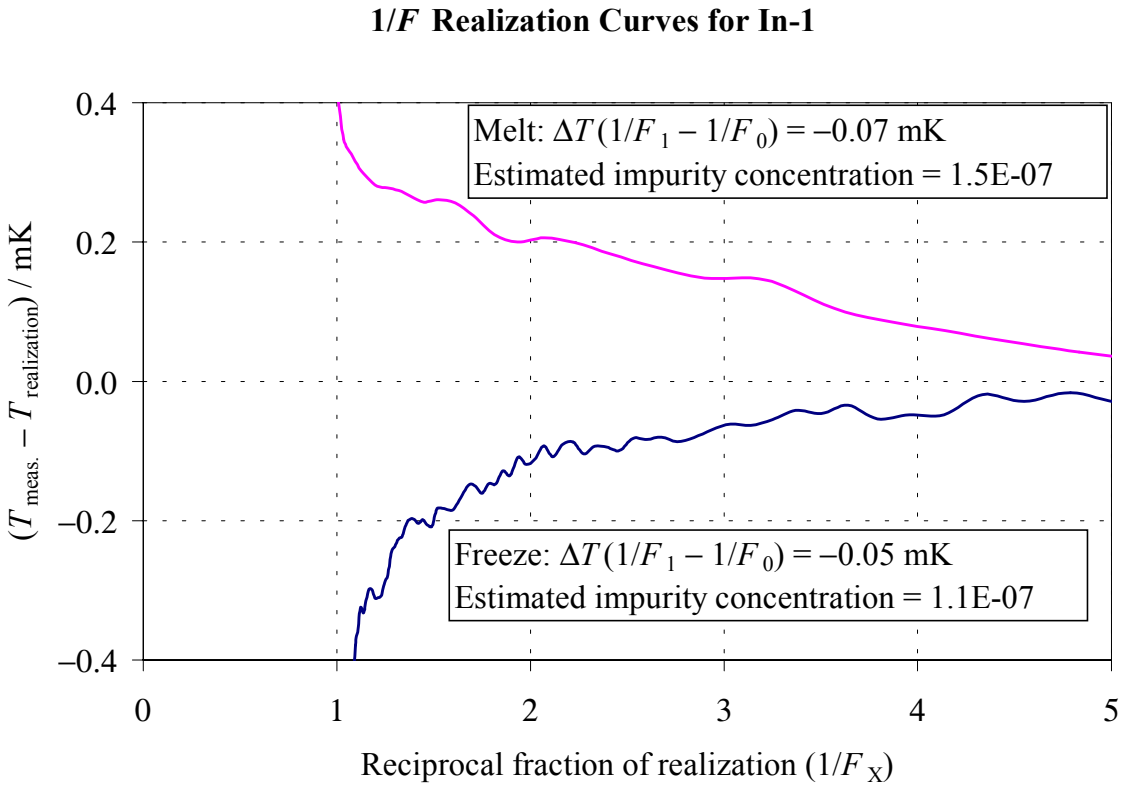


Figure 11. Example of the realization-curve method for fixed-point cell In-1.

Table 9. Results of the crosscheck between the 1/F realization-curve method with the mole fraction sum of impurity components method.

| **Arconium 79 In (lot S2739), NIST cell In 96-4** | | |
|---|---|---|
| **Method** | **Estimated impurity concentration** | **Estimated impurity uncertainty component, mK** |
| 1/*F* (freeze) | $0.2 \times 10^{-7}$ | 0.01 |
| 1/*F* (melt) | $0.5 \times 10^{-7}$ | 0.02 |
| mole fraction sum of impurities | $1.7 \times 10^{-7}$ | 0.08 |
| freezing curve | $0.5 \times 10^{-7}$ | 0.02 |
| **Arconium 79 In (lot S2552), NIST cell In 96-3** | | |
| **Method** | **Estimated impurity concentration** | **Estimated impurity uncertainty component, mK** |
| 1/*F* (freeze) | $0.2 \times 10^{-7}$ | 0.01 |
| 1/*F* (melt) | $0.2 \times 10^{-7}$ | 0.01 |
| mole fraction sum of impurities | $1.5 \times 10^{-7}$ | 0.07 |
| freezing curve | $0.4 \times 10^{-7}$ | 0.02 |
| **Indium Corporation of America 69 In (lot SG-1156), NIST cell In 93-3** | | |
| **Method** | **Estimated impurity concentration** | **Estimated impurity uncertainty component, mK** |
| 1/*F* (freeze) | $1.3 \times x\ 10^{-7}$ | 0.06 |
| 1/*F* (melt) | $0.9 \times 10^{-7}$ | 0.04 |
| mole fraction sum of impurities | $11.4 \times 10^{-7}$ | 0.54 |
| freezing curve | $2.9 \times 10^{-7}$ | 0.14 |
| **Indium Corporation of America 69 In (lot SG-907), NIST cell In-1** | | |
| **Method** | **Estimated impurity concentration** | **Estimated impurity uncertainty component, mK** |
| 1/*F* (freeze) | $1.1 \times 10^{-7}$ | 0.05 |
| 1/*F* (melt) | $1.5 \times 10^{-7}$ | 0.07 |
| mole fraction sum of impurities | $13.0 \times 10^{-7}$ | 0.61 |
| freezing curve | $3.9 \times 10^{-7}$ | 0.18 |

It is expected that a crosscheck of the 1/*F* realization curve method with the freezing curve method will give consistent results. As in the freezing curve analysis method, the following is considered when analyzing the results:

If the 1/*F* realization curve method gives a larger value than that of the mole fraction sum of impurity components method, then the $\Delta T(1/F_1 - 1/F_0)$ value is used to estimate the impurity uncertainty component value of the fixed-point cell. A larger value from the 1/*F* realization

curve method may mean that fixed-point sample was contaminated during the fabrication of the cell or the refiner sample assay under-estimated the amount of impurities.

If the $1/F$ realization curve method gives a smaller value than that of the mole fraction sum of impurity components method, the mole fraction sum of impurity components method is used to estimate the impurity uncertainty component value of the fixed-point cell. A smaller value from the $1/F$ realization curve method may mean that the refiner sample assay over-estimates the amount of impurities or the distribution coefficients of one or more of the impurities approaches one. An impurity with a distribution coefficient of one will not affect the slope of the realization curve, but will affect the realization temperature of the fixed-point cell.

It is important to note that there is a limitation in using a melting curve to estimate the purity of the metal using the $1/F$ realization curve method, because the slope of a melting curve will depend upon the history of the previous freezing of the sample in the fixed-point cell. A slow freeze (>10 h) causes the impurities ($k$<1) to be segregated by zone refining, which in turn causes a large melting range (slope of melting curve is maximized). A fast freeze (<30 min) creates a homogenous mixture of the impurities within the fixed-point sample, which in turn causes a small melting range (slope of melting curve approaches zero).

There is a strong interaction between the fixed-point cell, maintenance system, and SPRT during the realization of the fixed point. For the analysis, the freezing curve must last at least ten hours to reduce the heat-flux effects of the furnace on the slope of the freezing curve. Additionally, during a separate heat flux/SPRT immersion test the SPRT used in the measurements must be able to track hydrostatic head effect over the bottommost 3 cm of the reentrant well.

## 5. Total impurity concentration method

The total impurity concentration method is **not** used at NIST to determine or validate the impurity uncertainty component value used for the fixed-point cell. Since this method of calculation typically uses wt % instead of mole fraction, the individual contributions of the impurity component concentrations as a function of atomic weight are not taken into account. This usually leads to an impurity uncertainty component value that is too low.

However, it is useful to perform this calculation to get an idea of the magnitude of error in this method of estimating the impurity uncertainty value. Some end users that purchase original equipment manufacturer (OEM) fixed-point cells do not receive a fixed-point sample assay and use this method prior to a direct comparison with an NMI reference cell. The total impurity concentration method is **not** recommended for estimating the impurity uncertainty component value.

Table 10. Results of using total impurity concentration to estimating the impurity uncertainty component value for the fixed-point cell. The total impurity concentration method is **not** recommended for estimating the impurity uncertainty component value.

| Sample | Estimated impurity concentration, wt % | Estimated impurity uncertainty component, mK |
|---|---|---|
| 79 In (lot S2739) | $0.1 \times 10^{-7}$ | 0.05 |
| 79 In (lot S2552) | $0.07 \times 10^{-7}$ | 0.03 |
| 69 In (lot SG-1156) | $0.6 \times 10^{-7}$ | 0.27 |
| 69 In (lot SG-907) | $0.7 \times 10^{-7}$ | 0.33 |

## Remarks

As shown in the discussion above, at NIST we do not rely on a single method for checking the impurity level of our fixed-point cells. The crosschecks that we perform are an integral part of our quality assurance.

We have observed in other work that it is quite easy for fixed-point cells to be contaminated in the fabrication process. Relying on the manufacturer's or any independent laboratories assay, or even an assay with a "margin of safety" is not sufficient.

We agree with the statement made by others that the freezing-curve slope is inadequate by itself, but we see this method as very valuable in verifying that the cell construction did not add appreciable impurities.

Direct comparisons of cells are additional critical insurance that the cells have not been contaminated in the fabrication process. These comparisons do not need to be Key Comparisons. In fact, the comparisons can be direct comparisons of fixed-point cells within one laboratory. Advantages of single-laboratory comparisons are: 1) many effects other than cell variations are maintained constant and are not inappropriately interpreted as "cell impurities," and 2) because the cost is less, it is feasible to test many more cells. At first glance, a multiple-laboratory comparison may appear to be a more representative test of cell reproducibility across many laboratories. However, this will only be the case if the laboratories independently fabricate their fixed-point cells from different lots of fixed-point and crucible materials.

## References

† Certain commercial companies are identified in this paper in order to adequately identify the different fixed-point samples. Such identification does not imply recommendation or endorsement by the NIST, nor does it imply that the identified commercial sources are necessarily the best available for the purpose


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