Study on the Realization of Indium Point

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Jun TAMBA∗, and Masaru ARAI∗

Abstract: Indium point cells are fabricated using ingots of various forms from a variety of sources (manufacturers). Using these cells, newly built indium point furnaces are evaluated and their reliability is confirmed. The indium point realizations based on the single solid-liquid method (SSL method) and multi solid-liquid method (MSL method) are evaluated. The effect of impurities in the ingots is evaluated from the dependency of the slope of the freezing curve on the change in furnace temperature, the indium point depression based on the impurity analysis, and the cell comparison. The results show equality among the cells. Based on the results obtained, the uncertainty in realizing the indium point using the described indium point cells and indium point furnaces is estimated. The new uncertainty budget introduces uncertainties coming from plateau repeatability and chemical impurity derived by the present work, the values of which are significantly lower than those adopted in the current calibration service.

Key Words: fixed-point, fixed-point cell, freezing-point, freezing curve, cell comparison.

1. Introduction

The internationally recognized primary temperature standard in thermometry is based on the International Temperature Scale of 1990 (ITS-90) [1]. Between the triple point of equilibrium hydrogen (13.8033 K) and the freezing point of silver (961.78°C), the temperature following the ITS-90, usually denoted T0, is defined by means of platinum resistance thermometers calibrated at some metal fixed points and using an interpolating function. The authors are engaging in the dissemination of temperature standards at a range between the triple point of water (0.01°C) and the freezing point of silver by means of long stem standard platinum resistance thermometers (SPRTs). At that range, the metal fixed points, at which the SPRTs are calibrated, are the freezing points for indium, tin, zinc, aluminum and silver. The method of realizing the fixed points has already been reported in the Supplementary Information for the ITS-90 [2].

In relation to the realization of the fixed points, impurities have been among the most important topics. Material impurities cause a temperature departure from that of the pure material. This departure produces significant uncertainty in the realization method also has applicability for evaluating impurity uncertainties coming from plateau repeatability and chemical impurity derived by the present work, the values of which are significantly lower than those adopted in the current calibration service.

The following sections outline the cell fabrication and related temperature measurements. Evaluation of the impurity effect on the indium point realization is also presented.

2. Apparatus

2.1 Fixed Point Cell

The fixed point cell consists of a graphite crucible assembly, in which the fixed-point metal is contained, a sand-blasted quartz thermometer-well for inserting a standard platinum resistance thermometer (SPRT), graphite wool as a thermal insulator, a sand-blasted quartz cylinder as a container for these parts, and a cylinder cap equipped with an argon gas port for sealing the quartz cylinder. The argon gas port is connected to an argon gas supply-system that includes an argon gas container, a vacuum pump and a pressure gauge. The argon gas supply-system maintains the inner pressure of the cell. The graphite crucible assembly consists of graphite-made parts, namely, a crucible, a crucible cap, a thermometer well (thermowell) and a thermowell holder. The graphite well, used for impurities. In such a situation, it is difficult to adequately assess the influence of impurities on the fixed-point realization [6].

Continuing to the authors’ studies concerning the development of new techniques for fabricating fixed-point cells including aluminum, zinc, tin and silver points, along with their measurements [7]–[9], indium point cells have been newly fabricated. Fabrication is followed by temperature measurements done in the following conditions: 1) during a solid-liquid coexistence within indium point cells, where the indium fixed-point is determined, and 2) between cells realizing the indium fixed-point. Temperature measurements at condition 1) are based not only on the fixed-point realization method recommended in reference [2], but also on a proposed method that may prevent a measuring thermometer from experiencing rapid quenching during realization. Besides such advantages, the proposed realization method also has applicability for evaluating impurity effect on fixed point without destructing the cell.

The graphite crucible assembly consists of graphite-made parts, namely, a crucible, a crucible cap, a thermometer well (thermowell) and a thermowell holder. The graphite well, used...
for installing the quartz well, is fixed to the crucible cap by a graphite well-holder to overcome the buoyant force from melted fixed-point metal (indium in this case) during fixed point realization. All graphite-made parts were baked under vacuum at 980°C for at least 100 h before the fixed-point cell fabrication. Except the graphite wool, the graphite materials are 5N grade carbon (Toyo Tanso). Set up of the fixed point cell is illustrated in Fig. 1.

Four cells were newly fabricated: one using indium ingots, one using indium shots, one using the blend of indium ingots and shots, and one using an indium cylinder. The method of filling indium sample into its crucible follows that reported elsewhere [10], namely, a set of graphite weights was used to insert a graphite thermowell into a graphite crucible, where a fixed-point metal was melted, under a pressurized argon gas within a closed quartz cylinder.

The new as well as the existing cells are listed in Table 1. Cell TR0205E, a commercial one, is used at present as the acting national standard. Except cell TR0228, the indium cells have no detailed impurity analysis data. The impurity analysis of cell TR0228 was conducted by the supplying manufacturer (Nippon Mining and Metals Co., Ltd.).

Fig. 1 Set-up of indium point cell.

2.2 Fixed-Point Furnace

Three fixed-point furnaces, each of which was consisted of three zone heaters were used here for the realization of indium point. One fixed-point furnace was commercial one and customized only for use with cell TR0205E. The other fixed-point furnaces were utilized for the other cells. Each zone heater was equipped with a control unit for controlling the output of the heater in accordance with the target temperature. A thermocouple was installed in each zone heater as sensor. Thermal isolator wrapping the heaters was used for minimizing the heat leakage from the heaters. The temperatures of the zone heaters were adjusted in advance of an indium point realization so as to produce the best immersion profile in the thermowell.

Table 1 Indium cells evaluated in the present study.

<table>
<thead>
<tr>
<th>cell code</th>
<th>mass of ingots/g</th>
<th>Initial condition</th>
<th>nominal purity</th>
<th>immersion depth/mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>TR0205E</td>
<td>unknown</td>
<td>unknown</td>
<td>6N</td>
<td>160</td>
</tr>
<tr>
<td>TR0219</td>
<td>1100</td>
<td>ingots</td>
<td>6N</td>
<td>175**</td>
</tr>
<tr>
<td>TR0220</td>
<td>1200</td>
<td>shots+ingots</td>
<td>6N</td>
<td>192**</td>
</tr>
<tr>
<td>TR0221</td>
<td>1200</td>
<td>shots</td>
<td>6N</td>
<td>195**</td>
</tr>
<tr>
<td>TR0228</td>
<td>1200</td>
<td>cylinder</td>
<td>6N</td>
<td>187**</td>
</tr>
</tbody>
</table>

Table 1 Indium cells evaluated in the present study.

Fig. 2 Schematic diagram of the experimental apparatus: Ar: argon gas tank; B: resistance bridge; C: fixed-point cell; DCV1-DCV3: DC voltage source for upper, middle, lower zone-heaters; F: heat insulator; H1-H3: upper, middle, lower zone-heaters; P: pressure gauge; PID1-PID3: digital PID controller for upper, middle, lower zone-heaters; R(S): standard resistor; SPRT: standard platinum resistance thermometer; TC: thermo-sensor for zone-heater; V: voltage meter and DMM scanner; Vac: vacuum pump.

Fig. 3 Temperature stability of fixed-point furnace.

In order to measure the heat consumption during the indium point realization, a multimeter was introduced to monitor the voltage of each zone. Since the resistance of each zone heater is known, the heat added to or extracted from the indium sample, as well as the heat needed to maintain the indium sample at a certain temperature, can be calculated from the measured
voltage and the known resistance. This measurement was referred to our previous work on tin [11] and silver [12]. Figure 2 shows schematically the experimental apparatus.

Optimizing and setting of the fixed-point furnace were conducted to obtain best temperature control, each by measuring temperature using an SPRT and an indium point cell installed within. Conditions for the temperature measurements were: (1) when the SPRT was fixed at a position and the temperature at a fixed value, (2) when the SPRT was set at various positions while the temperature at a fixed value, (3) when the SPRT was fixed at a value while the temperature was changed to various setting values.

Temperature measurements at condition (1) are shown in Fig. 3, where $t$ denotes time. The fixed-point furnace is shown to realize successfully temperature stability within 1 mK for at least 4 h.

![Graph showing temperature measurements](image)

**Fig. 3** Temperature stability within 1 mK for at least 4 h.

Results of temperature measurements at condition (2) are shown in Fig. 4, where $h$ shows the height of SPRT sensor from the well bottom. As shown in Fig. 4, up to 170 mm from the well bottom, which corresponds to immersion depth of most cells, temperature of the thermowell was homogeneous within 2 mK.

![Graph showing temperature along the thermowell](image)

**Fig. 4** Temperature along the thermowell.

The response of the fixed-point furnace due to programmed temperature setting, as condition (3), was evaluated, and the result is depicted in Fig. 5, where the broken line shows the temperature setting, while the data plots the temperature measured. Except at the point where temperature setting was changed, and although a twenty-minute delay in response was detected, the fixed-point furnace realized satisfactorily the temperature program.

![Graph showing response of furnace](image)

**Fig. 5** Response of furnace to programmed temperature setting.

The above temperature program was adjusted for minimizing overshooting by the furnace, from which a smooth freezing curve would be obtained. Preceding the freezing, indium melting was done at various $T_{\text{setting}}$. In the case of melting, $T_{\text{setting}}$ was set above the indium point. From the melting curves, it is possible to determine the melting time, namely time between

### 3. Fixed Point Realization

The fixed point of indium is defined as a freezing point, namely, a point when an infinitely small solid is formed in a liquid indium under atmospheric pressure. In practice the first solid has a certain volume. The formation of the first solid in the liquid indium is conducted by a nucleation process. There are some methods used for this process. One of the methods is already given in the Supplementary Information for the ITS-90 [2], namely, by inserting cold rod into the thermowell while the furnace temperature is set below the indium freezing point. The insertion of the cold rod creates solid layer around the outer wall of the thermowell (inner mantle). Since the furnace temperature is set below the indium freezing point, solid layer is also expected to be formed on the inner wall of graphite crucible. This will be referred to as a multi solid-liquid surface method (MSL method) in this paper.

The second method is by extracting the fixed point cell out from the furnace for some minutes and re-inserting it into the furnace. This method is especially adopted for fixed point metal that has deep supercooling temperature.

The third method is only by lowering the temperature of the fixed-point furnace. Solid layer is expected from this method to be formed homogeneously on the inner wall of graphite crucible (outer mantle). This will be referred to as a single solid-liquid surface method (SSL method) in this paper.

The MSL method is recommended especially for fixed-point furnace, the temperature control of which has less performance, where solidification would possibly happen uniformly across the crucible. Forming solid layer around the thermowell stabilizes the temperature read by the SPRT. When the fixed-point furnace has sophisticated temperature control system, the SSL method is applicable.

In this paper, except the commercial one, the fixed-point furnaces has satisfactory temperature control systems as previously described. Such these furnaces allow us to realize the indium point based on both the MSL and the SSL methods.

For MSL, quartz rods were used to create solid layer in the outer wall of the thermowell, while the furnace temperature is set some degree below the indium freezing point. The SSL was realized in the present study through a series of furnace temperature settings as follows.

1. Keep the temperature at $T_{\text{In}}+3\text{K}$, where $T_{\text{In}}$ denotes the freezing point of indium.
2. Decrease the temperature to $T_{\text{In}}-8\text{K}$ at 0.2°C/min then keep at this temperature for 15 min.
3. Increase the temperature to $T_{\text{In}}-0.8\text{K}$ at 0.02°C/min then to the desired final temperature, $T_{\text{setting}}$, at 0.02°C/min.

The above temperature program was adjusted for minimizing overshooting by the furnace, from which a smooth freezing curve would be obtained. Preceding the freezing, indium melting was done at various $T_{\text{setting}}$. In the case of melting, $T_{\text{setting}}$ was set above the indium point. From the melting curves, it is possible to determine the melting time, namely time between
the point where the first liquid drop appears and the melt-off point. These points were determinable from the change in voltage acquired by the multimeter described previously. Relying on satisfactory performance of the present fixed-point furnaces described by Figs. 3–5, it is also possible to calculate the solid fraction formed during the nucleation process, using which the freezing time can also be derived.

Figure 6 shows the time required for melting and for freezing; time for freezing has been corrected for nucleation process, at various $T_{\text{setting}}$, where $\Delta T_{\text{setting}}$ in abscissa is $|T_{\text{ln}} - T_{\text{setting}}|$, and the ordinate the time for phase change (melting or freezing). Since cell TR0205E has significantly smaller ingot than the rest of cells, the time required for phase change, as shown in Fig. 6 by broken line, is much shorter accordingly. Similarly, as the ingot of cell TR0219 is slightly smaller than cell TR0220, TR0221 and TR0228, the time for phase change is slightly shorter, as shown by a broken dot line in Fig. 6. This slight difference is more visible at lower $\Delta T_{\text{setting}}$ (right part of Fig. 6).

Figure 7 shows typical temperature change during indium freezing realized using both the SSL (○) and MSL (□) in this work. The temperatures were plotted after recalescence from supercooling. The abscissa is time progressing, while the ordinate the ratio of SPRT resistance to its value at water triple point. In the MSL, temperature fluctuation happens during temperature recalescence, after which the temperature decreases slightly along with the progressing solid mantle, and decreases drastically when some part of the solid mantle makes contact with the thermowell. Calibration of an SPRT based on the MSL method is usually conducted after the above described temperature fluctuation ends over.

On the other hand, in the SSL method, supercooling takes more time but with relatively less temperature fluctuation. Almost constant temperature range is formed soon after the supercooling. Along this constant temperature range, an SPRT can be calibrated. Since the fraction of solid formed by the SSL method is greater than that by the MSL method, the freezing time of the SSL would be shorter, and the peak temperature lower. If the end point of the curve obtained by the SSL is adjusted to that of the MSL, as shown in Fig. 7 (+ plot), both curves would agree on each other. Difference in the peak temperature between the MSL and SSL methods was 0.1 mK, as represented by the gap between broken line and broken dot line.

Figure 8 depicts peak temperature of freezing curve taken at various $\Delta T_{\text{setting}}$ based on both the MSL and the SSL methods. Peak temperature for the MSL method is determined as highest point in freezing curve soon after temperature fluctuation due to supercooling ends over. Since, unless cell TR0205E, the rest of cells have similar specification and only slight difference in ingot, for detail investigation on the different realization methods based on the peak temperature measurement, cell TR0228 is used. For this purpose, an SPRT was used commonly so that the peak temperature can be compared directly from the obtained resistance ratio. A limited number of measurements were done for MSL method, from which a relatively larger dispersion of data is obtained. For the SSL method, measurements were done before and after that for the MSL method to confirm the stability of the method. Results in Fig. 8 are consistent with those in Fig. 7, where due to larger solid fraction from supercooling, the peak temperature of the SSL method is lower than that of the MSL method.

Freezing curve is often expressed in terms of $1/F$, where $F$ denotes the fraction of liquid during the phase change. Since the heater temperature was set at constant value during the phase change, heat would constantly be transferred to or from...
One of freezing curves obtained is shown in Fig. 9 in terms of 1/F. A dotted tangential line is drawn in Fig. 9 to represent slope of the freezing curve around the peak temperature. If such the slopes taken for all cells in the present work are organized in terms of \( \Delta T_{\text{setting}} \), Fig. 10 is obtained. The ordinate, \( \partial T / \partial (1/F)_{\text{peak}} \), of Fig. 10 shows the slope of freezing curve around the peak point, and the abscissa, \( \Delta T_{\text{setting}} \), the rate of solidification. Also shown in Fig. 10 is the freezing point depression, ♦ symbol along with its uncertainty, arrow line, calculated from the impurity analysis that will be described later.

Since as shown in Table 1, except cell TR0205E, the rest of cells were from the same specification, cells TR0219 with slightly smaller ingot and TR0228 with ingot being nearly as much as cells TR0220 and TR0221 were selected for freezing curve evaluation under different realization methods.

As shown in Fig. 10, slopes of most of the cells form a band having a width from 0.02 mK to 0.1 mK. Slight differences in the slopes derived by the SSL and the MSL methods, especially for cell TR0228, are obtained, where the slopes by the MSL method are steeper than those by the SSL method. The fact shown in Fig. 7 that the 1/F of peak temperature of the MSL method is smaller than that of the SSL method, may imply that the slope becomes steeper as the 1/F gets smaller, by which the slope at 1/F = 1, which may correspond to zero solidification rate or thermally equilibrium condition, would be the steepest.

The slope of the freezing curve is often used to evaluate the quality of fixed point cell in relation with impurities that may be contained during the production of the ingot, and/or contaminations that may be occur during the cell fabrication. Related description will be given in the next section. Slopes of cells in Fig. 10 reflect that most of cells have similar level of purity, and would accordingly realize indium point at same level. Cell TR0221, while the same purity-level ingot as the rest of cells did, has slopes slightly lower than the other. This may imply a possibility of contamination during the cell fabrication, and thus a possibility of realizing slightly lower indium point would be predicted.

Using cell TR0219, measurements using the MSL method were done twice (‘earlier’ and ‘later’ in Fig. 10), intercepted by a series of measurements using SSL method. The later results are in excellent agreement with the earlier ones, showing the reliability of the system.

### 4. Impurity Analysis

Most of impurities in fixed point metal bring effect of depressing the freezing point temperature. The information of impurities of indium ingot used for realizing the indium point is, therefore, essential, especially for estimating the related indium point uncertainty. The need for impurity information increases this recent time as a recommendation has been published by the

<table>
<thead>
<tr>
<th>element</th>
<th>( m_i )</th>
<th>( \partial T / \partial c_{ij} )</th>
<th>( k_{ij} )</th>
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<tbody>
<tr>
<td>Li</td>
<td>&lt; 0.01</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>&lt; 0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>&lt; 0.01</td>
<td>0.13</td>
<td>1.2</td>
</tr>
<tr>
<td>Mg</td>
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<td>0.11</td>
<td>2.2</td>
</tr>
<tr>
<td>Al</td>
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<td>Si</td>
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<tr>
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<tr>
<td>Cl</td>
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<td>K</td>
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</tr>
<tr>
<td>Ca</td>
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</tr>
<tr>
<td>Ti</td>
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<tr>
<td>V</td>
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<tr>
<td>Cr</td>
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<tr>
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<tr>
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<tr>
<td>Th</td>
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<tr>
<td>U</td>
<td>&lt; 0.0001</td>
<td></td>
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</tr>
</tbody>
</table>

...
CCT [13]. The impurity information of cells fabricated earlier is nearly impossible to obtain, because fixed point metal ingots were usually purchased with only nominal purity information without any chemical assay. Some were equipped with specified impurities information obtained from method whose reliability was questionable. Analyzing ingot of already fabricated cell requires destruction of the valuable cell. To avoid such the destruction, a cell whose impurities of its ingot has been analyzed in advance, is used to calibrate the earlier cells through cell comparison.

In this work, cell TR0228 is the one that has impurity analysis based on the glow discharge mass spectrometer (GDMS). GDMS has recently gained much attention in thermometry for its ability to analyze extensive elements by only one operation run. Two data sheets from different GDMSs were provided by the ingot manufacturer [14]. Tables 2 and 3 show the result of the analysis, where according to Table 2 no detected element is obtained from cell TR0228, while according to Table 3 some elements are detected. The unit of concentration in Table 2, mass fraction, is different to that in Table 3, atomic fraction. Unifying the unit will show the consistency of the result, namely, those undetected by high-grade GDMS are also undetected by the low-grade GDMS. It should be noted that the analysis was done by the manufacturer far before the cell fabrication. Based on this fact, possible contamination during the cell fabrication is considerable.

Fixed point depression due to impurities can be derived from the dependence of the observed temperature, \( T_{\text{obs}} \), on the fraction of liquid, \( F \), given by Eq. (1), where \( T_{\text{pure}} \) stands for, in this case, the fixed point of ideally pure indium, \( c_{\text{li}} \), \( \partial T/\partial c_{\text{li}} \), and \( k_{0,i} \), the element \( i \) concentration in equilibrium solid, \( c_{\text{si}} \), over \( c_{\text{li}} \).

\[
T_{\text{obs}} - T_{\text{pure}} = \sum_{i} c_{i} \left( \frac{\partial T}{\partial c_{i}} \right) \left( 1 - k_{0,i} \right)
\]

For \( F=1 \) where the fixed point is defined, Eq. (1) yields to Eq. (2) showing a total sum of elemental effects that called the sum of individual estimates (SIE) [13]. The standard uncertainty of the SIE, \( \mu(\Delta T_{\text{SIE}}) \), is given by Eq. (3).

\[
\mu(\Delta T_{\text{SIE}}) = \sum_{i} \left[ \mu(c_{i}) \left( \frac{\partial T}{\partial c_{i}} \right) \right]^{2} + \left[ c_{i} \mu \left( \frac{\partial T}{\partial c_{i}} \right) \right]^{2}
\]

Since at low concentration the relationship \( \partial T/\partial c_{\text{li}} = -\frac{1}{A} \) may be used (\( A \) is cryoscopic constant; for indium \( A=0.00213 \text{ K}^{-1} \)), for special condition where \( k_{0,i} \approx 0 \), Eq. (2) yields to Eq. (4), which is also known as the Raoult’s law. In thermometry, the estimation for impurity effect based on Eq. (4) is called the overall maximum estimate (OME). Although, as shown in Table 2, the real binary alloy has \( k_{0,i} > 0 \), the OME is often used for estimating uncertainty in thermometry because it usually produces the maximum fixed point depression.

\[
\Delta T_{\text{OME}} = T_{\text{obs}} - T_{\text{pure}} = -\frac{\sum c_{i}}{A}
\]

The standard uncertainty of \( \Delta T_{\text{OME}}, \mu(\Delta T_{\text{OME}}) \), is as follows.

\[
\mu(\Delta T_{\text{OME}}) = -\frac{\sum \mu(c_{i})}{A}
\]
From Eq. (1), slope of freezing curve at $1/F=1$ can be derived as given by Eq. (6).

$$\frac{\partial (T_{obs} - T_{pure})}{\partial (1/F)} = - \sum_{j=1}^{n} c_j (k_{0j} - 1) \frac{\partial T}{\partial c_j}$$

(6)

By comparison, it is found that Eq. (6) differ from Eq. (2) by a factor of $-(k_{0j} - 1)$. For $k_{0j}=0$ system, called Raoult’s system for convenience, the slope of freezing curve reflects the SIE. Assuming high purity indiums of say 6N level have typical dominant impurity elements, comparison in the slope of freezing curve among the indium cells can also be used to evaluate the difference in quality among the cells. Highly pure ingot will produce shallower slope than the less pure one. Such this evaluation was already described in the previous section as shown in Fig. 10.

Using the impurity analysis and Eq. (1), the SIE for ingot used in cell TR0228 can be calculated. Values for $\partial T/\partial c_0$, and $k_{0j}$ are taken or derived from reference [15]. Since, as shown in Tables 2 and 3, not all elements have data for $\partial T/\partial c_0$, Eq. (4) is also introduced to combine the SIE and the OME for estimating the indium point depression. For estimating uncertainty of the indium point depression, Fellmuth and Hill [16] proposed a method taking half of the concentration values or half of the detection limit as the uncertainties of the analysis results, $u(c_{li})$. For $\partial T/\partial c_0$, a relative uncertainty of order 30%, which comes from typical difference among reported values, can be adopted.

<table>
<thead>
<tr>
<th>Table 4</th>
<th>Indium point depression.</th>
</tr>
</thead>
<tbody>
<tr>
<td>cell</td>
<td>$\Delta T_{\text{indium}}$ (mK)</td>
</tr>
<tr>
<td>TR0228</td>
<td>-0.007</td>
</tr>
</tbody>
</table>

Equation (5) was adopted for estimating standard uncertainty of the OME method. The maximum concentration values from Table 2 and Table 3 are taken as the input data. The indium point depression, $\Delta T_{\text{indium}}$, and its standard uncertainty, $u(\Delta T_{\text{indium}})$, obtained using the above procedure, are given in Table 4.

The uncertainty range tabulated in Table 4 is represented in Fig. 10 as a solid line and denoted in the legend as SIE range. Compared to its indium point depression, the experimental slopes of cell TR0228 have slightly lower values. Most of their average, however, is still within $u(\Delta T_{\text{indium}})$. Concerning the other cells, except cell TR0221, since their slopes scatter within the same band as cell TR0228, it is expected that those cells would have same level of indium point depression, or in other words, would produce the same indium point value.

5. Cell Comparisons

To confirm whether the cells produce the same indium point or not, comparison measurements among some of the cells were conducted. Such the cell comparison can also be used to evaluate the impurity effect of a cell relative to the other cell having different purity ingot. In thermometry it is termed estimate based on representative comparison (ERC). As transfer in this comparison, cell TR0205E was used, while the participating cells are cells TR0220, TR0221 and TR0228. The selection of TR0205E as transfer was based on the fact that this cell was participated in the key comparison CCT KC-3 [17], so that comparison on the regards of this cell will connect the cells TR0220 and TR0221 to the key comparison reference value of the CCT KC-3.

Measurements were conducted using two systems each of which consisted of a platinum resistance thermometer (PRT) connected to a resistance bridge (ASL F18) and standard resistor. The cell comparisons were done during freezing at the furnace temperature $\Delta T_{\text{setting}}=0.4$K. PRT resistance measurements at each cell were done using two currents; for each current twelve data were acquired in 20 second interval. From the results at two currents, correction due to self heating of the PRT was calculated and the PRT resistance at zero current derived. In the case of cell TR0228 only one system was introduced.

In cell comparison a measuring thermometer is moved at indium point from one cell, where measurement has been done, to the other cell, whose indium point is to be measured. During the cell-to-cell moving, the thermometer is cooled by surrounding air, and then heated again by the indium cell when it is inserted into the cell. On the other hand, when the cool thermometer enters the cell, heat is extracted from the cell causing the indium ingot around the outer wall of graphite thermometer well to freeze. At least two solid mantles exist in indium ingot: that on the inner wall of graphite crucible and the one on the outer wall of the graphite thermometer well. An MSL method has been conducted. Cell comparison is a practice of the MSL method. To obtain longer plateau, from which extensive cell-comparison measurement is aimed, a rod is introduced for initiating solidification in the present participating cells.

The results of cell comparison are represented in Fig. 11. The ordinate is temperature deviation of participating cell from cell TR0220. Two systems are used in comparisons using cell TR0110 and cell TR0221, each denoted by bracket in the legend. Solid line, broken line and dotted line correspond to the average of cell TR0220, cell TR0221 and cell TR0228, respectively.

It can be seen from Fig. 11 that two measuring systems used for the comparison of a pair of cells produce similar results, im-

Fig. 11 Indium point difference among cells in terms of cell TR0205E.
Table 5 Results for cell comparisons.

<table>
<thead>
<tr>
<th>cell pair</th>
<th>$\Delta T_{ERC}$ (mK)</th>
<th>$\sigma(\Delta T_{ERC})$ (mK)</th>
<th>$u(\Delta T_{ERC})$ (mK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TR0220-TR0205E</td>
<td>0.050</td>
<td>0.049</td>
<td>0.013</td>
</tr>
<tr>
<td>TR0221-TR0205E</td>
<td>-0.024</td>
<td>0.040</td>
<td>0.011</td>
</tr>
<tr>
<td>TR0228-TR0205E</td>
<td>-0.027</td>
<td>0.040</td>
<td>0.017</td>
</tr>
</tbody>
</table>

The uncertainty determined in this work is significantly smaller than the value used in our present calibration service. The effort to build highly reliable fixed-point furnaces and fixed point cells has led to more reliable fixed point realization as reflected by the significant reduction in uncertainties due to plateau repeatability and chemical impurity. Both uncertainties are dominant in our present calibration service.

7. Conclusion

Indium point cells were fabricated using ingots of various forms from a variety of sources (manufacturers). Using these cells, newly built indium point furnaces were evaluated and their reliability was confirmed. The indium point realizations based on the SSL and MSL were evaluated. The effect of impurities in the ingots was evaluated through the dependency of the slope of the freezing curve on the change in furnace temperature, the indium point depression based on the impurity analysis, and the direct cell-comparison. The results showed equality among the cells.

Based on the results obtained, uncertainty in realizing indium point using the described indium point cells and indium point furnaces was estimated. The new uncertainty budget introduced uncertainties coming from plateau repeatability and chemical point realization was calculated as shown in Table 6.

First row of Table 6 denotes the source of uncertainty, the second row, $u_i$, is its standard uncertainty. The estimation in Table 6 follows the Guide to the Expression of Uncertainty in Measurement (GUM) [18]. Plateau repeatability is based on measurements at 8 plateaus during the cell comparison TR0205E vs. TR0228. Chemical impurity is taken as standard uncertainty in Table 4. Plateau variability is considered from the possible temperature drop during indium point measurement in a plateau; 0.1 mK with rectangular distribution is adopted here. Pressure correction is reflected from 0.1 kPa uncertainty in correcting the pressure of the cell. Temperature distribution shows the deviation of temperature gradient within the thermowell from that defined by the ITS-90 based on the indium hydrostatic head. Self-heating correction is uncertainty in extrapolated resistances taken at two different currents to zero current. Bridge stability is the long term stability of the bridge, while short term stability of resistance measurement shows short time fluctuation. Temperature difference repeatability reflects the stability of SPRT used for comparing indium point cell. Excluded this term, the uncertainty budget stands for an indium point realization.

The uncertainty determined in this work is significantly smaller than the value used in our present calibration service. The effort to build highly reliable fixed-point furnaces and fixed point cells has led to more reliable fixed point realization as reflected by the significant reduction in uncertainties due to plateau repeatability and chemical impurity. Both uncertainties are dominant in our present calibration service.

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Based on the results obtained, uncertainty in realizing indium point using the described indium point cells and indium point furnaces was estimated. The new uncertainty budget introduced uncertainties coming from plateau repeatability and chemical
impurity derived by the present work, the values of which were significantly lower than those adopted in the current calibration service.

References