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Establishment of NIMT Zinc Fixed-Point Cell

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Abstract One of the research programs for the Thermometry Metrology Department at the National Institute of Metrology (Thailand), NIMT, is establishment of its own fixed-point cells. Among the fixed-point cells adopted for the realization of the International Temperature Scale of 1990 (ITS-90), NIMT has chosen the zinc fixed point to start the program. The fabrication and the initial evaluation of the zinc fixed-point cell were conducted at the National Metrology Institute of Japan, NMIJ. The cell fabrication was following the design and procedures developed by the NMIJ. In the cell fabrication, a 6N nominal purity zinc metal cylinder ingot was used. The metal ingot was collected in a graphite crucible under an argon gas atmosphere. The new fixed-point cell was compared with the old fixed-point cells already owned by NIMT, namely, one open-type cell and one sealed-type cell by direct cell comparisons. Since the ingot was equipped with a detail impurity element analysis, it is possible to calculate the effect coming from the existence of the impurities based on, for example, the sum of individual estimates (SIE) method. This effect can then be used to correct for the influence impurities on the realization of the temperature fixed point.

Keywords Fixed point · ITS-90 · Zinc fixed-point cell

1 Introduction

Phase transitions of pure substances are employed to underpin the International Temperature Scale of 1990, ITS-90, as defined fixed points [1]. NIMT has two sets of

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fixed-point cells for each fixed point, one open-type cell and one sealed-type cell, in the range of 234.3156 K (−38.8344 °C) to 1234.93 K (961.78 °C). All the fixed-point cells were commercial items. For the purpose of improving the capability to establish and maintain its own primary standards, NIMT has started a program of fabricating its own fixed-point cells. The zinc point is chosen as the first attempt. The newly fabricated zinc cell was open type, the fabrication of which was conducted at the National Metrology Institute of Japan (NMIJ/AIST). The cell was compared with the existing zinc cells in the present study. The methodology and the results are discussed in the present paper.

2 Measurement Apparatus

2.1 Fixed-Point Cell

In addition to two zinc-point cells already owned, one is sealed while another is open type; another open-type zinc-point cell is newly fabricated for this work. The zinc material used for the new cell is a 6N nominal purity cylinder ingot. Prior to assembling the fixed-point cell, the material was analyzed by the manufacturer using a glow-discharge mass spectrometry (GDMS). The cell design and fabrication procedure follow those reported by Widiatmo et al. [2].

Figure 1 shows schematically the newly fabricated cell. The cell consists of the graphite parts: a crucible, which contains the ingot, and its crucible cap, a thermometer well, and its thermometer-well holder. These parts are enclosed in a quartz cylinder together with a quartz thermometer well and some layers of graphite wool as a thermal insulator, and a sealer equipped with a gas port seals the quartz cylinder. Through the gas port, evacuation and pressurization of the cell become possible. A gas supply system maintains the inner pressure of the cell. Before being used, all graphite parts were baked at 980 °C under vacuum for 120 h. Table 1 lists the specification of the cells introduced in this work.

2.2 Fixed-Point Furnace

Three commercial fixed-point furnaces are used for measurements in this work. Two heat-pipe furnace are used exclusively for cells Zn 127 and Zn 3, while three-zone-heater furnaces are used for cell 26057. Before being used for the zinc-point realization, the zone heaters are optimized so that the vertical temperature uniformity is improved. For the optimization, a cell is set inside the furnace and temperatures at various heights along the thermometer well are measured whenever a combination of zone-heater temperature settings is determined. As a result, for heights from the bottom of the thermometer well up to 100 mm, the temperature is uniform within 10 mK. Table 2 shows the specification of the furnaces.

2.3 Measurement System

Measurements throughout this work are carried out using standard platinum resistance thermometers (SPRTs) connected to an AC bridge (ASL Model F18). The SPRTs have

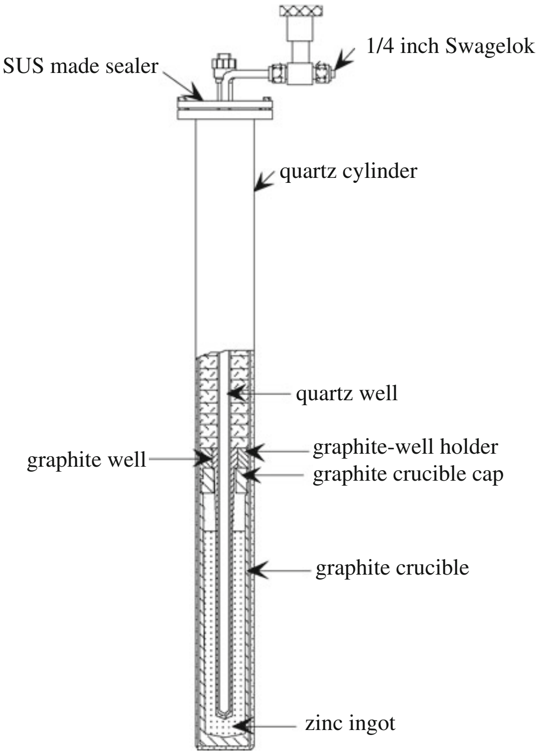


Fig. 1 Zinc open fixed-point cell

Table 1 Zinc-point cells studied in this work

Cell	Nominal purity	Type	Immersion height (mm)	Supplier
Zn 127	6N	Sealed	195	Isotech
26057	6N	Open	235	FHS[a]
Zn 3	6N	Open	195	NMIJ[b]

[a] Fluke Hart Scientific
[b] Built in this work under cooperation with National Metrology Institute of Japan, AIST

Table 2 Specification of fixed-point furnaces

Manufacturer	Model	Type	Corresponding cell
Hart Scientific	9114	Three-zone heater	26057
Hart Scientific	9115	Heat pipe	Zn 3
Isotech	ITL-M-17671	Heat pipe	Zn 127

a resistance of about 25 Ω at the triple point of water. A 100 Ω standard resistor is connected to the bridge. For cell comparison measurements, currents of 1 mA and $\sqrt{2}$ mA are used, based on which compensation for the self heating is determined. At each current, 30 readings are acquired.

3 Zinc-Point Realization

The zinc point here is realized from the freezing of a melted zinc ingot. The initiation of freezing is done by inserting quartz rods into the thermometer well. Melting of the ingot is done by raising the furnace temperature to realize a temperature 2 °C above the predicted zinc point at a rate of 3 °C · min^{-1}. After the ingot is completely molten, it is kept at the temperature for several hours. As a first step for initiating freezing, the furnace temperature is set at 5 °C below the predicted zinc point, during which supercooling occurs. At this point, the SPRT is removed and two quartz rods are inserted into the thermometer well, each for 1 min to induce an inner mantle. The furnace temperature is then set at the desired final temperature. For this work the final temperature is 0.8 °C below the predicted zinc point. The freezing realized by this setting lasts over a period of time of approximately 20 h, as shown in Fig. 2. The scattered data form a band of 1 mK width on the freezing plateau.

For zinc materials used in open cells, namely, cells 26057 and Zn 3, the manufacturers provide the elemental analyses. From such analysis results, the uncertainty due to the effect from the impurity existence can at least be estimated. The estimation follows [3]:

$$\Delta T_{\mathrm{SIE}} = \sum_i c_{\mathrm{l}i} \left(\frac{\partial T}{\partial c_{\mathrm{l}i}} \right) \tag{1}$$

$$u^2 \left(\Delta T_{\mathrm{SIE}} \right) = \sum_i \left[\left[u \left(c_{\mathrm{l}i} \right) \left(\frac{\partial T}{\partial c_{\mathrm{l}i}} \right) \right]^2 + \left[c_{\mathrm{l}i} u \left(\frac{\partial T}{\partial c_{\mathrm{l}i}} \right) \right]^2 \right] \tag{2}$$

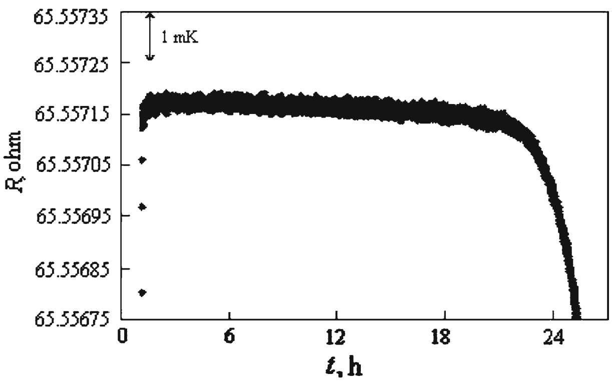


Fig. 2 Zinc freezing curve

ΔT_{SIE} stands for the deviation of the realized zinc point from the ITS-90, while $u(\Delta T_{\mathrm{SIE}})$ is its standard uncertainty. $c_{\mathrm{l}i}$ and $(\partial T/\partial c_{\mathrm{l}i})$ are the concentration of impurity i in the equilibrium liquid and the slope of the liquidus line in the phase diagram with respect to $c_{\mathrm{l}i}$, respectively. $u(c_{\mathrm{l}i})$ and $u(\partial T/\partial c_{\mathrm{l}i})$ are their respective uncertainties. $(\partial T/\partial c_{\mathrm{l}i})$ can be determined from those reported by Ancsin [4] and/or estimated from compilations by Masaalski [5], while $u(\partial T/\partial c_{\mathrm{l}i})$ is 35 %, which is the average difference between values reported by Ancsin [4] and Masaalski [5]. $u(c_{\mathrm{l}i})$ is taken as 50 % of the reported value for detected elements and 50 % of the detection limit provided for other elements. Table 3 lists the corresponding values for cells 26057 and Zn 3. Table 4 shows the results of calculation using Table 3 and Eqs. 1 and 2.

Since the analysis for cell 26057 is about ten times that for cell Zn 3, the estimated uncertainty is also larger, accordingly. Table 4 may show from the viewpoint of chemical analysis that any difference among the zinc points realized by both cells would be within 1.33 mK.

4 Cell Comparison

Cell comparisons are conducted to confirm the reliability of the cell newly fabricated. The comparison includes two pairs of cells, namely, cells Zn 127 and Zn 3, and cells 26057 and Zn 3.

Procedures for melting and initiating freezing are those already described in the previous section. Measurement is started in a cell (starting cell, A) 1 h after the temperature recovery from supercooling. The measuring SPRT is then moved to the counter-part cell (B), and 20 min later the measurement at that cell is conducted. After completing the measurement at B, the SPRT is moved back to A, and 20 min later, measurement at A is done. This cycle is repeated to form a sequence A–B–A–B–A–B.

Figure 3 shows the resistance ratio obtained during comparisons between cells Zn 127 and Zn 3, after being corrected for the immersion depth, where (a) is for a system with an AC bridge and (b) with a DC bridge. From measurements using those two measurement systems, cell Zn 127 is found to have a higher temperature than cell Zn 3. The average difference is 0.43 mK.

The result of cell comparisons between cells 26057 and Zn 3 is represented in Fig. 4. The ordinate is the resistance ratio obtained after being corrected for the immersion depth. Only one system, the one for Fig. 3a, has been used for this comparison. The result shows that the temperature difference between cell 26057 and cell Zn 3 is not significant. The average temperature difference is 0.02 mK, with cell Zn 3 higher.

For a simple comparison among the three cells under study, since the cell comparison given in Fig. 3a and that in Fig. 4 are done using the same system, Fig. 5 is constructed. It is shown that the data scatter, represented by data for Zn 3, in a cell comparison for the Zn 127–Zn 3 pair is wider than that in the Zn 3–26057 pair. The difference may partly come from the gas pressure of cell Zn 127, which may exceed atmospheric.

Because cell Zn 127 was the one calibrated by the other NMIs, the calibration data can be used to check the reliability in terms of changes of its long-term calibration data. Three NMIs have been involved in the calibration of the cell. Figure 6

Table 3 Impurities in zinc-point cells

Element	Cell 26057 w_i (mass ppm)	Cell Zn 3 w_i (mass ppm)
Li		<0.01
Be	<0.1	
B	<0.1	<0.01
Mg	<0.1	<0.01
Al	<0.1	<0.01
Si	<0.5	<0.01
P	<1	<0.01
K		<0.01
Ca	<0.1	<0.01
Ti	<0.1	<0.01
V	<0.1	<0.001
Cr	<0.1	<0.01
Mn	<0.1	<0.001
Fe	<0.1	0.05
Co	<0.1	<0.01
Ni	<0.1	<0.01
Cu	<0.1	<0.05
Ga	<0.1	
Ge	<0.5	
As	<0.5	<0.01
Se		<0.01
Sr	<0.1	
Zr	<0.1	<0.01
Mo	<0.1	<0.01
Pd	<0.1	
Ag	<0.1	<0.05
Cd	<0.1	<0.05
In	<0.5	
Sn	<0.5	
Sb	<1	<0.01
Te	<5	
Ba	<0.1	
W		<0.01
Pt	<0.5	
Au	<0.1	<0.05
Hg	<0.5	
Tl	<0.5	
Pb	<0.5	0.24
Bi	<1	<0.01

Table 4 ΔT_{SIE} and $u(\Delta T_{SIE})$ for zinc-point cells

Cell	ΔT_{SIE} (mK)	$u(\Delta T_{SIE})$ (mK)
Cell 26057	–	1.33
Cell Zn 3	−0.09	0.06

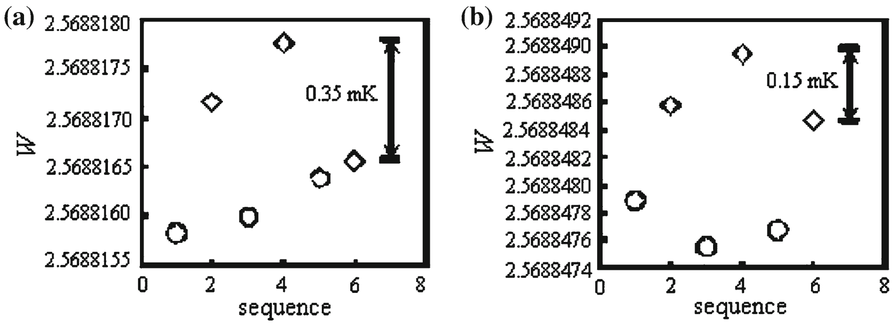


Fig. 3 Temperatures measured during direct cell comparison using (a) SPRT1 and Bridge 1 system with arrow of 0.35 mK and (b) SPRT2 and Bridge 2 system with *arrow* of 0.15 mK: ◇ in cell Zn 127; ◯ in Zn 3

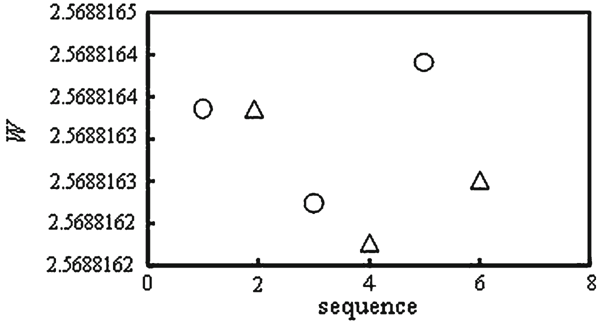
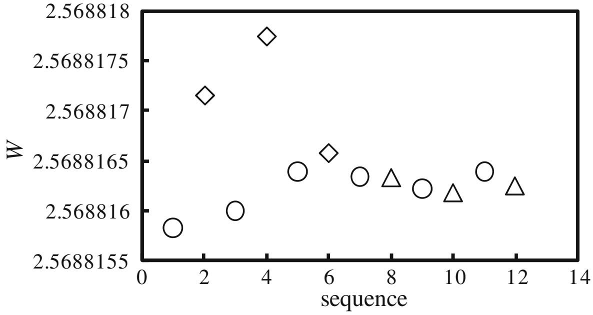


Fig. 4 Temperatures measured during direct cell comparison: ◇ in cell 26057; ◯ in Zn 3

Fig. 5 Temperatures measured during direct cell comparison: ◇ in cell Zn 127; ◯ in Zn 3; △ in cell 26057



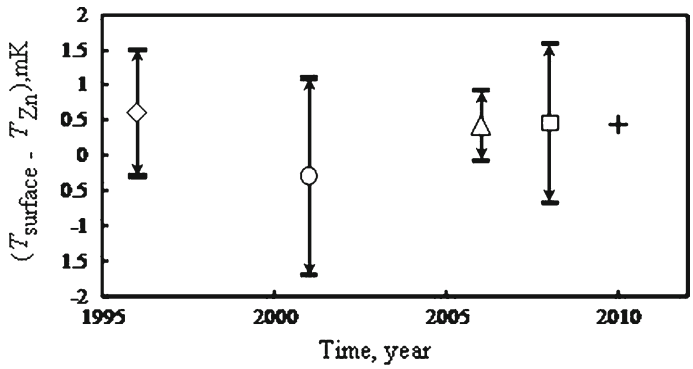


Fig. 6 Direct cell comparison between cell Zn 127 and: ◇ standard cell owned by NMI 1; ○ standard cell owned by NMI 2; △ standard cell owned by NMI 3; □ cell 26057; + cell Zn 3

summarizes the change in temperature determined at the metal surface of cell Zn 127. The ordinate is given as the temperature deviation of the metal-surface temperature of cell Zn 127, $T_{surface}$, from the metal-surface temperature of the calibrating zinc cell, T_{Zn}. The comparison of cell Zn 127 and cell 26057 has been reported elsewhere [6].

As represented in Fig. 6, the temperature calibrated is stable within the claimed uncertainty. For the present value, the uncertainty estimation needs accumulation of measurements that will be done in the near future.

5 Conclusions

A zinc fixed-point cell (coded Zn 3) was newly prepared in this study using 6N nominal purity zinc. A direct cell comparison between this cell and an existing sealed cell (coded Zn 127) resulted in a temperature difference of 0.43 mK (Zn 127 was higher) while that between this cell and an existing open cell (coded cell 26057) was 0.02 mK (Zn 3 was higher). The sum of individual estimates (SIE) of cell Zn 3 and cell 26057 were derived using their impurity analyses, the results of which showed that the aforementioned cell difference was within the estimated uncertainties. Compared to a previous study on cell comparisons between cell Zn 127 and cell 26057, which resulted in a temperature difference of 0.46 mK (Zn 127 was higher), the present results showed good consistency and satisfactory reliability. Based on this fact, therefore, cell Zn 3 is considered applicable as a national reference cell for disseminating a temperature standard in Thailand. The present results also motivate further fabrication of fixed-point cells for other fixed points.

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