Stainless Steel-Cased Fixed-Point Cells and Their Applications

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Abstract

Fused silica has been used as an envelope material for fixed-point cells for many years. It has been proven to be an excellent material because no contamination to the pure metal of fixed-point cells has ever been found from fused silica. In the past, fixed-points were mainly used in national laboratories. Now the situation has changed greatly, and more and more calibration laboratories have adopted the use of fixed-points in their work. These laboratories desire a stronger material, such as stainless steel (SS), instead of fused silica, for the outer case material of fixed-point cells. Several SS–cased fixed-point cells for the freezing points of indium, tin, and zinc were built and tested. New SS-cased fixed-point cells were compared against traditional fused silica–cased cells. The long-term stabilities of the new cells were checked, and no obvious drift was detected. The expanded uncertainties were estimated, which are small enough for the calibration of most standard platinum resistance thermometers. Applications of the new SS-cased fixed-point cells for secondary level and industrial calibrations are discussed.

1. INTRODUCTION

A half centenary ago, fixed-points were used only in a few national laboratories as national or world temperature standards, but that situation has been changing. More and more laboratories are using (or will use) fixed points to calibrate standard platinum resistance thermometers (SPRTs), standard thermocouples, and other temperature probes. Fused silica has been used as an outer envelope material of fixed-point cells for many years, especially in national laboratories. While being an excellent material for national laboratory applications, fused silica is too fragile for many other users. A stronger material, such as stainless steel (SS), is more desirable as an outer case material for many users. About five years ago, we began to investigate the possibility of using SS as the case material for fixed-point cells. The main concern is whether SS will contaminate the pure metal in the cell and how we can reduce or eliminate such contamination. A mini SS-cased indium cell was successfully developed four years ago, and the results obtained were very encouraging [1, 2]. Good long-term stability of such indium cells suggested that the pure indium in these cells was not contaminated by SS. The experiences accumulated in the work encouraged us to develop SS-cased fixed-point cells for SPRT calibration. Our goal for the expanded uncertainties of the new cells is for it to be the same as, or at least very close to, those for the traditional fused silica–cased cells. Applications for the new SS-cased cells were investigated, especially for secondary and industrial calibrations.

2. SS-CASED FIXED-POINT CELLS

A mini SS-cased indium cell is shown in Fig. 1. 304 SS is used as the outer case material. An inner gas-tight vessel is made of virgin PTFE, which separates the high-purity indium from the SS to avoid contamination (Fig. 1). The total length of the cell is 127 mm (5”), so it can be used in dry-wells or mini furnaces. The immersion depth into the cell’s indium is about 75 mm. Because of the relatively short immersion depth, a close fit between the probe and the reentrant well of the cell is extremely important. The diameter of many PRT probes in North America is 6.35 mm (1/4”), while the diameter of many popular metal sheath SPRTs is 5.56 mm (Rosemount 162CE and Hart 5699). Therefore, two inner diameter (ID) sizes of reentrant wells are used for these probes—6.64 mm for 6.35 mm probes and 5.84 mm for 5.56 mm probes.

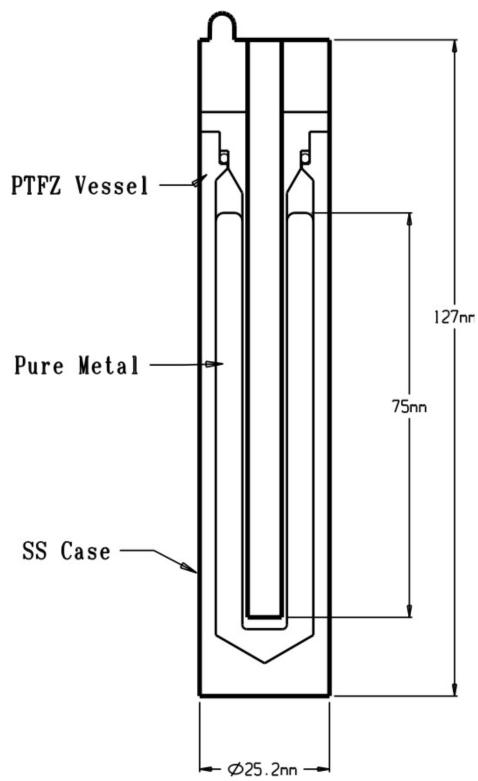

Figure 1. A mini SS-cased indium cell.

The design of the mini SS-cased indium cell can not be used for metals with higher freezing points, such as zinc and tin, because of the upper temperature limit of PTFE (about 200°C or a little higher). Furthermore the strict requirement for a tight fit between the probe and the reentrant well of the cell limits the usage of this cell to only special applications. For broader application, a new SS-cased fixed-point cell was developed. The dimensions of the new cell are much larger than those for the mini indium cell. The new cell consists of a SS outer case and a high-purity, high-density graphite crucible containing the pure metal (Fig. 2). The purities of the metals are 99.99995+%, and the total impurities in the graphite are about 1 ppm. The diameter of the cell is 41.3 mm and the total length is 222 mm. The immersion depth from the bottom of the reentrant well to the upper surface of the pure metal is 156 mm, more than double that of the mini indium cell. The total length is chosen so that the cell can be accommodated into a small portable furnace and probes as short as 220 mm can be calibrated in the cell [3].

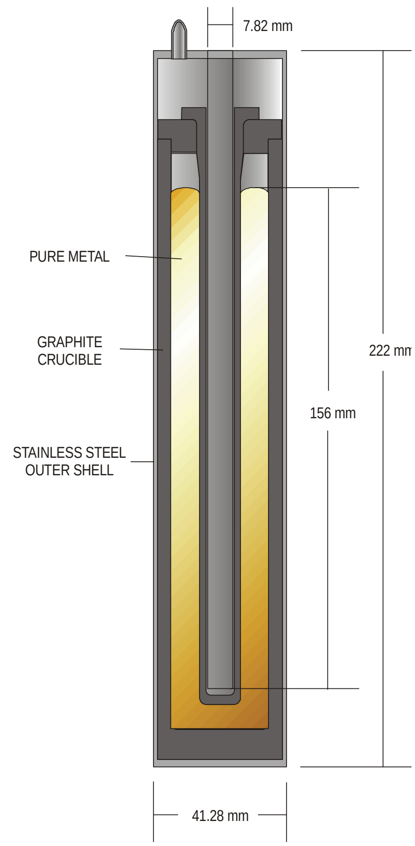

Figure 2. A SS-cased fixed-point cell.

The high-purity metal was melted into the graphite crucible in high vacuum or in a dry pure-argon atmosphere. The graphite crucible was subjected to a high-temperature, high-vacuum treatment just before loading the pure metal. The assembled graphite crucible containing the high-purity metal was inserted into the SS outer case, and the SS cap with the reentrant well was arc-welded to the SS outer case. A special inner surface treatment of the SS case is critical for reducing possible contamination during the lifetime of the cell. A special cooling jacket was used during welding to avoid overheating. The SS-cased cell was then connected to a high vacuum system and pumped down to a pressure as low as 10^{-5} Pa (8 X 10^{-8} torr). The cells were pumped for at least 100 hours at temperatures a few degrees Celsius above their freezing points for indium and tin and about 50°C below the freezing point for zinc. During this period, the cell was repeatedly purged with 99.999% pure argon. Finally, the cell was filled with pure argon and sealed permanently at a pressure close to 101.325 kPa during a freezing plateau. The actual pressure was recorded so that a correction could be made for the phase equilibrium temperature to adjust for the pressure difference from the standard atmosphere.

3. Fixed-point Furnaces

High-accuracy realization of freezing points of pure metal requires a strict environment around the fixed-point cell, where the temperatures must be very uniform, stable, and well controlled. Three types of furnaces were used with SS-cased fixed-point cells in the investigation. A three-zone furnace (Hart Model 9114), reported in detail earlier, satisfies all of the requirements mentioned above [4]. The furnace was originally designed for use with fused silica–cased cells. A temperature uniformity of ± 0.01°C within a SS-cased cell placed in the furnace is easily obtained by adjusting the top and bottom settings. Temperature stability of the furnace is better than ± 0.01°C over a few hours.

Temperature probes shorter than 420 mm cannot be calibrated in the above-mentioned furnace. There are many such short secondary level and industrial probes needing calibration. A smaller, more portable fixed-point furnace with lower costs is desirable for many applications, especially for the secondary level and industrial calibrations. We reported on a furnace for this purpose a few years ago [3]. Its size is much smaller than that of a traditional fixed-point furnace. The small furnace has a total height of 489 mm and an outer diameter of 209 mm, and it weighs about 17 kg (Fig. 3). The costs to build a smaller furnace are lower, only about 40% of the costs of a traditional fixed-point furnace. But it is much more difficult to obtain a temperature uniform area around the fixed-point cell in a smaller furnace. Many measurements were taken to test and improve the performance of the smaller furnace. Three heaters are used to produce uniform temperatures around the fixed-point cell. The main heater covers the furnace’s entire length, while the top and bottom zone heaters cover only the upper and lower parts of the furnace, respectively. Software within the unit’s controller is used to adjust the ratios of the three heaters. Using this technique, we can achieve temperature uniformity of ±0.03°C within the cell. Temperature stability of the furnace is better than ±0.03°C over a few hours. A dry-well with a depth of 127 mm was used with the mini indium cell.

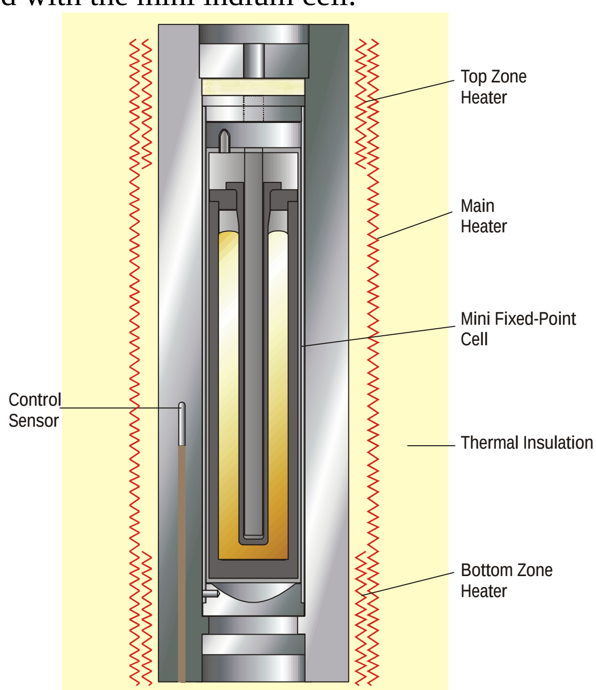

Figure 3. The SS-cased cell in a small, portable furnace.

4. Tests and Results

4.1 Realization of the Freezing Points and Freezing Curves

The following method was used to realize the freezing points with lowest uncertainties using SS-cased fixed-point cells. First, the temperature of the furnace was raised to a few degrees Celsius above the freezing point at a rate of about 3°C/minute. After the pure metal was completely melted, the furnace was set at a stable temperature about 1°C above the freezing point and left overnight. The next morning, the furnace temperature was decreased to 1°C below the freezing point at a rate of 0.5°C/minute. An SPRT was inserted into the cell to monitor the temperature. Immediately after recalescence, the thermometer was removed from the furnace and two fused-silica rods were inserted into the fixed-point cell in succession, each in the cell for two minutes. Then the preheated SPRT to be calibrated was inserted into the cell. Meanwhile, the furnace was set to a stable temperature of 0.3°C below the freezing point for the traditional fixed-point furnace. The set temperature of the small furnace needed to be a little higher, about 0.2°C below the freezing point, to obtain a long freezing plateau. This procedure provides a very stable, long, and flat freezing plateau that typically lasts for more than twenty hours if the purity of the metal in the cell is above 99.99999+% (6N+). The changes in temperature during the first ten hours were usually within 0.1 mK to 0.2 mK. Many SPRTs or other temperature probes can be calibrated during a single freezing plateau. The operation for the tin point was a little different because of its larger supercools. When the temperature indicated by the monitoring SPRT decreased to the freezing point, the SPRT was removed and a SS rod was inserted into the fixed-point cell for two minutes, followed by a fused silica rod for two minutes.

A very stable and flat freezing curve symbolizes high quality of a fixed-point cell. The purities of the metals we used are 99.99995% (6N5). It is not an easy task to maintain purity during the entire manufacturing process and the lifetime of the cell. An easy and direct way to check the quality of a fixed-point cell is to obtain and analyze its freezing curve. All of the new SS-cased fixed-point cells we developed have very stable and flat freezing curves. Two examples obtained are shown in Fig. 5 and Fig. 6. Fig. 5 shows a typical freezing curve of indium and Fig. 6 shows a typical freezing curve of zinc. The changes in temperature during the first 40% of the freezing curves were usually within about 0.2 mK.

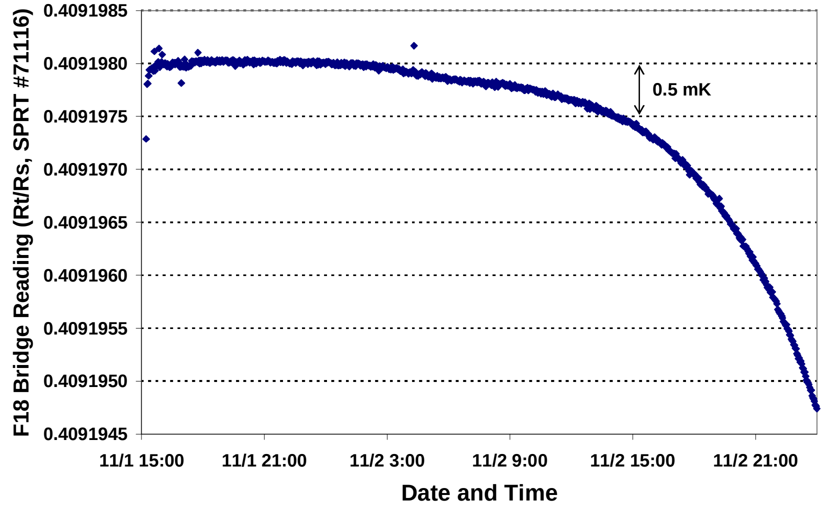

Figure 5. A typical freezing curve of indium obtained in a traditional fixed-point furnace with a SS-cased cell.

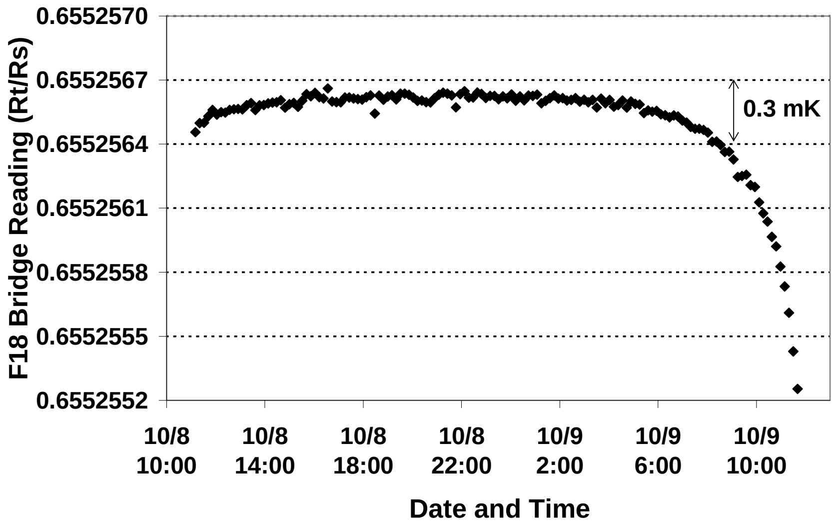

Figure 6. A typical freezing curve of zinc obtained in a traditional fixed-point furnace with a SS-cased cell.

4.2 Melting Curve

Results obtained in the laboratory in recent years show that the melting plateau is much more attractive than the freezing plateau for many calibration applications, especially for the secondary level and industrial calibrations. The melting plateaus are easier to realize, require less training, and make calibration work more efficient. Because it is easy to obtain a very long melting plateau, it can be used in a similar manner to the triple point of water. Whenever one wants to calibrate a probe, one inserts it into the fixed-point cell in the furnace during a melting plateau. The uncertainty of the melting plateau might be a little larger than that of the freezing plateau, but it is still much better than the requirements for secondary level and industrial calibrations. The realization of a melting plateau is quite simple. The temperature of the furnace is raised to 1°C below the freezing point at a rate of about 3°C/minute and left overnight. The next morning, the furnace temperature is raised to 1.5°C above the freezing point and maintained at this temperature for 30 minutes to start a melting plateau. Then the furnace temperature is decreased to 0.3°C above the freezing point at a rate of 0.1°C/minute and maintained at that temperature during the entire melting plateau. A typical melting curve of indium obtained this way in a small, portable furnace is shown in Fig. 7. The changes in temperature during 90% of the entire melting curve were within 0.8 mK. Fig. 8 shows a typical melting curve of tin.

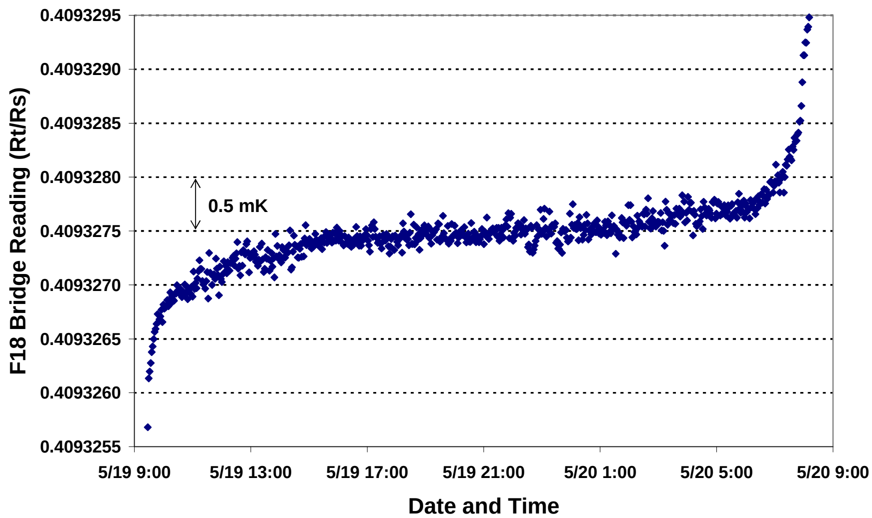

Figure 7. A typical melting curve of indium obtained in a small, portable fixed-point furnace with a SS-cased cell.

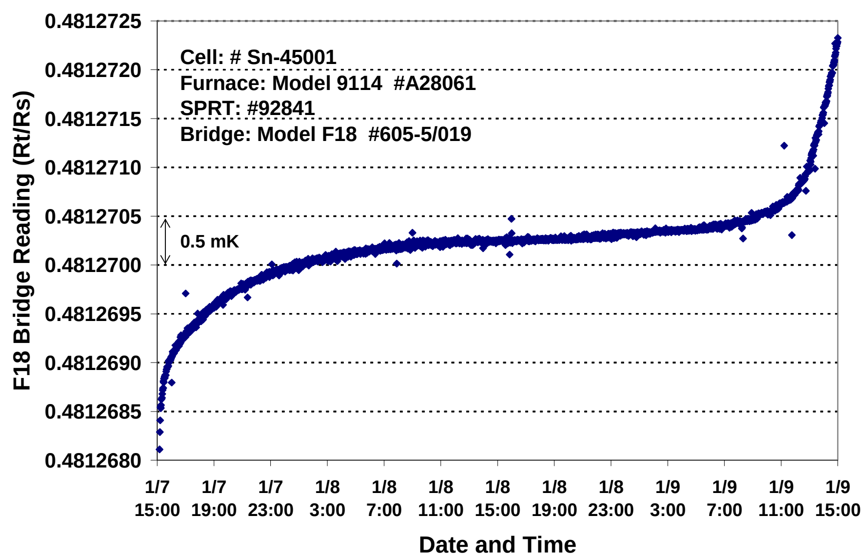

Figure 8. A typical melting curve of tin obtained in a traditional fixed-point furnace with a SS-cased cell.

4.3 Multiple Cells Comparisons

Multiple new SS-cased cells were compared with each other in small, portable fixed-point furnaces. Several 25.5-ohm SPRTs were used for the comparisons. Freezing plateaus were realized using two cells simultaneously. Each SPRT was measured in two cells successively. The resistances of the SPRTs at the freezing points were measured using an automated DC bridge (Model 6675A). The nonlinearity of the bridge is better than 0.02 ppm according to the manufacturer's specifications. A 10-ohm standard resistor maintained in a bath at 25°C ± 0.01°C was used with the bridge. The stability of the standard resistor was better than 2 ppm per year. All resistances were measured at two currents (1 mA and 1.414 mA) so that the results could be extrapolated to values at zero power. The resistance at the triple point of water was measured immediately after measurements at the freezing points using the same equipment. The resistance ratio W(t) = R(t)/Rtp was calculated for each cell. The comparison results obtained are shown in Fig. 9, Fig. 10, and Fig. 11. The mean difference between two cells was 0.07 mK for the indium cells, 0.11 mK for the tin cells, and 0.13 mK for the zinc cells. These differences were well within the reproducibility of the realizations of these fixed-points with small, portable furnaces.

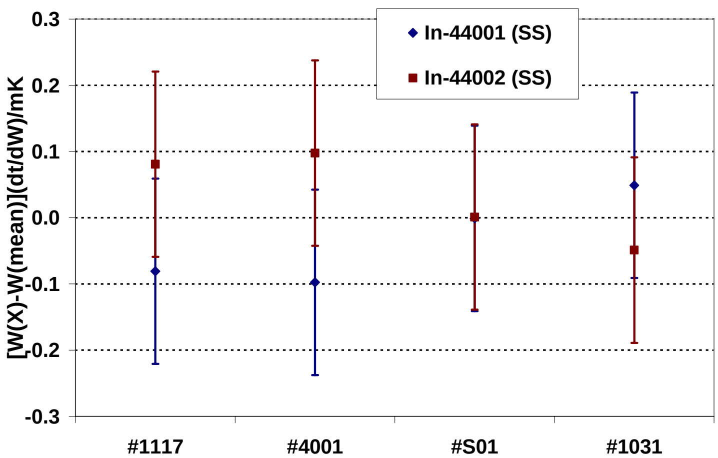

Figure 9. Comparison between two SS-cased indium cells.

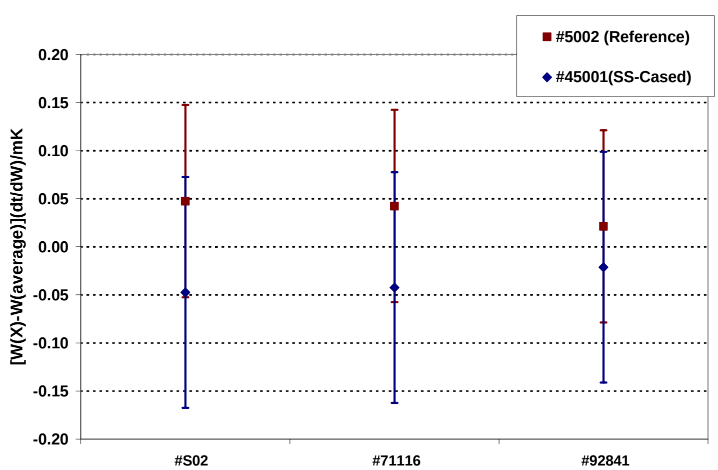

Figure 10. Comparison between two SS-cased tin cells.

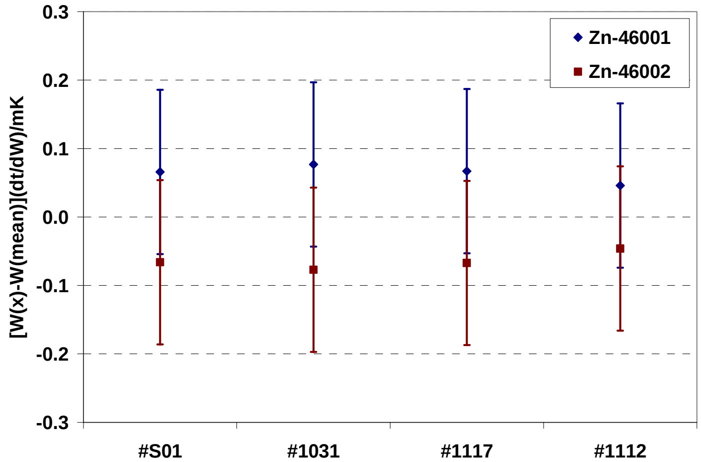

Figure 11. Comparison between two SS-cased zinc cells.

4.4 Comparisons of the SS-Cased Cells against the Reference Cells

The differences in the freezing temperatures among new SS-cased cells at all of the three fixed-points were well within 0.2 mK. Considering that all of these cells have the same design and similar manufacturing technique, it is interesting to compare these new cells against the reference fused silica–cased cells. Three fused silica–cased cells used in Hart calibration laboratory as standards to calibrate SPRTs were chosen as references in the comparisons. The purities of the metals in these cells were 99.9999+%. The serial numbers of the three reference cells are In-5005, Sn-5002, and Zn-5006. The comparison procedures and equipment used in the comparisons were the same as those used in the multiple SS-cased cell comparisons mentioned above except traditional fixed-point furnaces were used with reference fused silica cells instead of small, portable furnaces. The comparison results are shown in Fig. 12, Fig. 13, and Fig. 14. The measured average difference between the new SS-cased cells and the reference fused silica–cased cells was 0.11 mK at the indium point, - 0.07 mK at the tin point, and 0.05 mK at the zinc point.

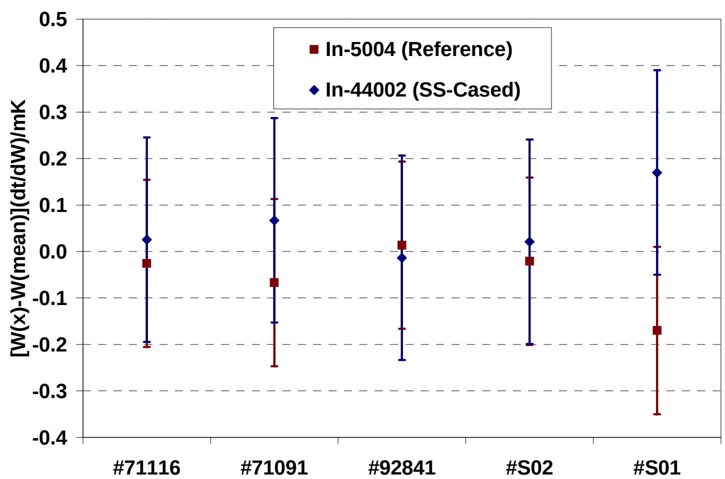

Figure 12. A direct comparison of a new SS-cased cell #In-44002 with reference fused silica–cased cell #In-5005 in May 2002.

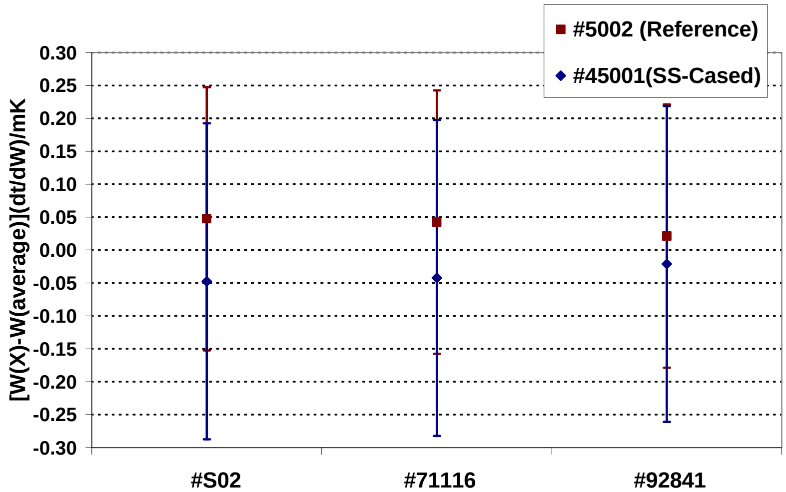

Figure 13. A direct comparison of a new SS-cased cell #Sn-45001 with reference fused silica–cased cell #Sn-5002 in June 2002.

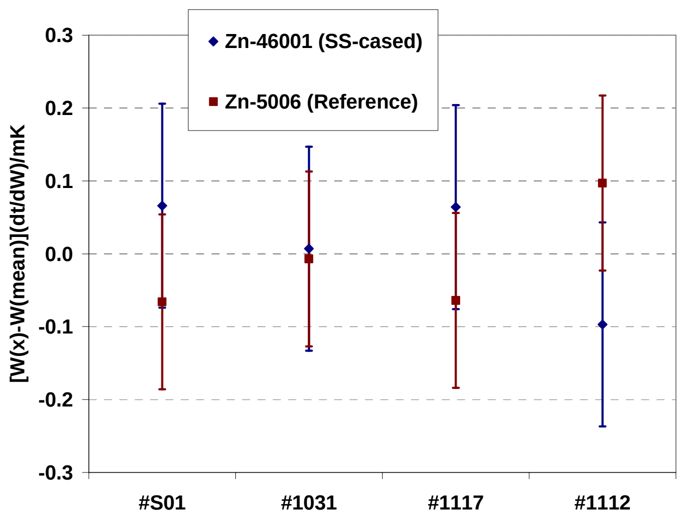

Figure 14. A direct comparison of a new SS-cased cell #Zn-46001 with reference fused silica–cased cell #Sn-5006 in July 2003.

4.5 Long Term Stability of the New SS-Cased Cells

In order to check long-term stability, the three SS-cased cells were compared against the three reference cells after about one year of use. The results of the two-year comparison are summarized in Table 1. No obvious drifts were detected.

Table 1. Two-year comparisons between SS-cased cells and reference cells.

	2002	2003
In-45002 – In-5004	0.11 mK	0.13 mK
Sn-45001 – Sn-5002	-0.07 mK	-0.08 mK
Zn-46001 – Zn-5006	0.05 mK	0.02 mK

4.6 Immersion Check

Conductivity along an SPRT sheath might possibly be an important uncertainty component in a fixed-point calibration. If a thermometer is sufficiently immersed into a fixed-point cell and there is no change in indicated temperature with a small change in immersion depth, such conductivity error can be considered to be negligible. So the immersion check is very important for verifying the fixed-point design and for estimating the uncertainty. Immersion checks were made at all three fixed-points with the SS-cased fixed-point cells in both furnaces (traditional and small furnaces) by using an SPRT with a fused silica sheath. The results are shown in Fig. 15, Fig. 16, and Fig. 17. The measured values tracked the hydrostatic effect very well in a range of 20 mm from full immersion in the small furnace at the zinc point and 30 mm at the tin point and indium point. The tracked ranges in traditional furnaces were more than double of that in small furnaces. The immersion depths in both furnaces are enough to eliminate the stem conductivity error at all three points.

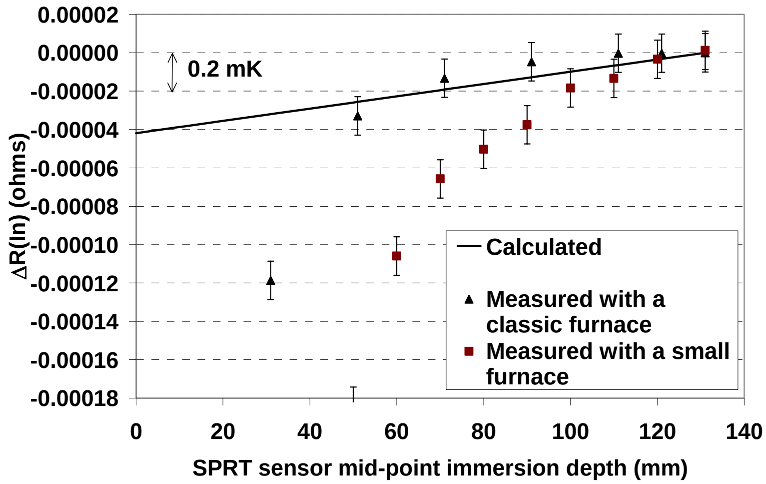

Figure 15. Immersion profiles in the new SS-cased cell at the freezing point of indium in both furnaces (traditional and small).

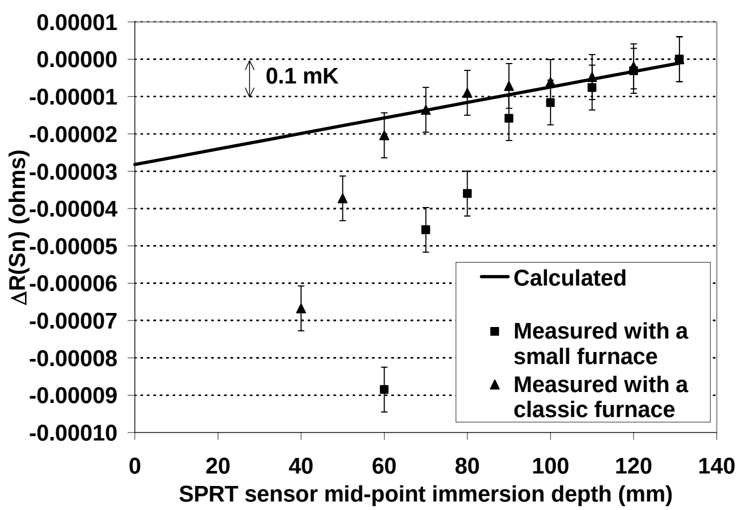

Figure 16. Immersion profiles in the new SS-cased cell at the freezing point of tin in both furnaces (traditional and small).

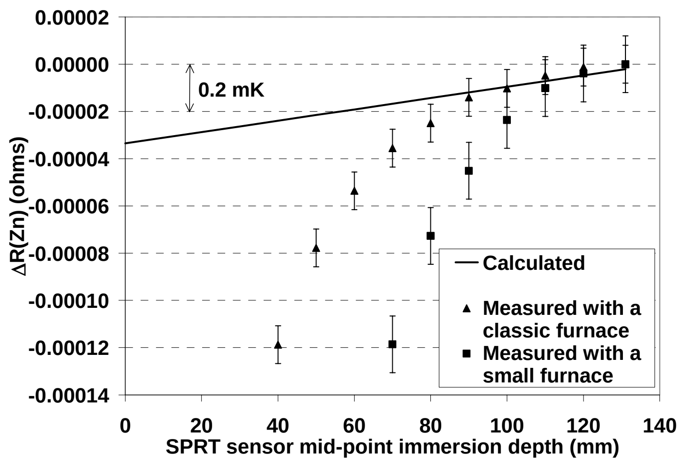

Figure 17. Immersion profiles in the new SS-cased cell at the freezing point of zinc in both furnaces (traditional and small).

5. Uncertainty Estimation

The uncertainty components for the realization of the freezing points of indium, tin, and zinc using the new SS-cased cells are listed in Table 2, Table 3, and Table 4. Three different situations are considered here: using a traditional fixed-point furnace with a freezing plateau, using a small, portable furnace with a freezing plateau, and using a small, portable furnace with a melting plateau. Reproducibility of the thermal state (Type A) and impurities (Type B) are two main uncertainty components. The difference between the traditional furnace and the small, portable furnace with a freezing plateau is very small. Actually, both provide very close expanded uncertainty.

Table 2. Uncertainty budget for the freezing point of indium using a SS-cased cell.

Source of uncertainty	Uncertainty Component (mK)		
	Traditional furnace F. P.	Small furnace F. P.	Small furnace M. P.
Resistance reading (A)	0.034	0.034	0.034
Reproducibility of thermal state (A)	0.180	0.220	0.500
Total A	0.183	0.223	0.501
Impurities (B)	0.253	0.253	0.253
Hydrostatic correction (B)	0.033	0.033	0.033
Pressure correction (B)	0.025	0.025	0.025
Immersion (B)	0.030	0.030	0.030
SPRT self heating	0.030	0.030	0.030
Propagated from TPW	0.030	0.030	0.030
Bridge non-linearity (B)	0.017	0.017	0.017
Total B	0.262	0.262	0.262
Total standard uncertainty	0.320	0.344	0.566
Expanded uncertainty (k=2)	0.640	0.688	1.131

Table 3. Uncertainty budget for the freezing point of tin using a SS-cased cell.

Source of uncertainty	Uncertainty Component (mK)		
	Traditional furnace F. P.	Small furnace F. P.	Small furnace M. P.
Resistance reading (A)	0.041	0.041	0.041
Reproducibility of thermal state (A)	0.200	0.240	0.600
Total A	0.204	0.243	0.601
Impurities (B)	0.310	0.310	0.310
Hydrostatic correction (B)	0.022	0.022	0.022
Pressure correction (B)	0.017	0.017	0.017
Immersion (B)	0.030	0.030	0.030
SPRT self heating	0.030	0.030	0.030
Propagated from TPW	0.050	0.050	0.050
Bridge non-linearity (B)	0.020	0.020	0.020
Total B	0.319	0.319	0.319
Total standard uncertainty	0.378	0.401	0.681
Expanded uncertainty (k=2)	0.757	0.802	1.361

Table 4. Uncertainty budget for the freezing point of zinc using a SS-cased cell.

Source of uncertainty	Uncertainty Component (mK)		
	Traditional furnace F. P.	Small furnace F. P.	Small furnace M. P.
Resistance reading (A)	0.059	0.059	0.059
Reproducibility of thermal state (A)	0.300	0.350	0.700
Total A	0.306	0.355	0.702
Impurities (B)	0.350	0.350	0.350
Hydrostatic correction (B)	0.027	0.027	0.027
Pressure correction (B)	0.022	0.022	0.022
Immersion (B)	0.030	0.030	0.030
SPRT self heating	0.030	0.030	0.030
Propagated from TPW	0.080	0.080	0.080
Bridge non-linearity (B)	0.029	0.029	0.029
Total B	0.364	0.364	0.364
Total standard uncertainty	0.476	0.509	0.791
Expanded uncertainty (k=2)	0.951	1.017	1.583

6. Results and Discussion

The performance of the new SS-cased fixed-point cells is identical to that of the traditional fused silica-cased cells. The differences between the new SS-cased cells and the reference fused silica–cased cells were well within 0.2 mK. The expanded uncertainty for the new cell with a traditional fixed-point furnace was estimated to be 0.64 mK at the indium point, 0.76 mK at the tin point, and 0.95 mK at the zinc point. The uncertainties of the new SS-cased cells are almost the same as those of the fused silica–cased cells. The new SS-cased fixed-point cells can be used instead of the fused silica–cased cells for most calibration applications. The stainless steel is less fragile than fused silica, so the new cell provides many advantages compared with fused silica–cased cells: the new cell can be shipped instead of being hand-carried, it is much more robust and durable, and it is easier to use. Furthermore, the new SS-cased cell can be used in a small, portable furnace with much lower costs to obtain almost the same uncertainty as in a traditional fixed-point furnace. So the combination of SS-cased cells and small, portable furnaces provide a new low-cost and easy way to calibrate SPRTs for many laboratories.

The new cell can be used to calibrate not only SPRTs, but also the secondary level PRTs and industrial probes, including probes as short as 220 mm (9 inches). Melting plateaus provide many benefits compared to freezing plateaus for the secondary and industrial calibrations: an absence of supercool, longer plateaus, simplicity, less investment in training, and improved efficiency. Ninety percent of a melting plateau can be used for calibration work compared to only about the first 40% for a freezing plateau (compare Fig. 5 and Fig. 7). A great number of probes can be calibrated on a single melting plateau. The expanded uncertainties with melting plateaus are a litter larger than those with freezing plateaus, but they are still much better than what the secondary level calibrations require. Many secondary level and industrial calibrations are still performed using the comparison technique. But the new SS-cased fixed-point cells with melting plateaus provide many advantages over comparison calibration techniques, such as eliminating the need for reference thermometers, much improved uncertainty levels, better reliability, long-term stability, ease of use, and portability. For all these reasons, these new SS-cased fixed-point cells with small furnaces are extremely attractive for secondary and industrial calibrations.

Acknowledgments

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