REALIZATION OF THE FREEZING POINTS OF INDIUM, TIN AND ZINC USING STAINLESS STEEL–CASED CELLS

Xumo Li, Mingjian Zhao and Deming Chen
Hart Scientific

ABSTRACT

Realization of the freezing points of indium, tin and zinc using new stainless steel–cased cells is reported. The stainless steel–cased cells were compared against classic fused silica–cased cells, and the differences between them were within 0.2 mK for all three fixed points. The long-term stabilities of the new cells were checked after about one year of use and no obvious drifts have been detected. The expanded uncertainty (k=2) was estimated to be 0.7 mK for the indium point, 0.8 mK for the tin point, and 1.0 mK for the zinc point. It was tried to simplify the fixed-point realization by using a small portable furnace and melting plateau for "secondary" calibrations with just a little larger uncertainty.

1. INTRODUCTION

More and more laboratories are using, or will use, fixed points to calibrate standard platinum resistance thermometers (SPRTs) and other temperature probes. Fused silica has been used as the 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; so a stronger material, such as stainless steel (SS), is more desirable as an outer case material for many users. The main questions are whether the case material will contaminate the pure metal in the cell, and how we can reduce, or eliminate, such contamination. The project was started about five years ago to investigate the possibility of using SS as the case material for fixed-point cells. A mini SS-cased indium cell was developed successfully three years ago, and the results obtained were very encouraging [1, 2]. Good long-term stability of such indium cells showed 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 cells for "primary" SPRT calibrations. Our goal is to have the expanded uncertainties of the new cells be the same as, or at least very close to, those for the classic fused silica–cased cells. At the same time, a great effort was made toward the simplification of the fixed-point realization with a little larger uncertainty for secondary or "industrial" calibrations in order to decrease costs and to simplify the operation. This includes using a small portable furnace instead of the classic fixed-point furnace, and using the melting plateau instead of the freezing plateau.

2. SS-CASED FIXED POINT CELL

The new cell consists of a SS outer case and a high-purity, high-density graphite crucible containing the pure metal. The purity of the metal is 99.9999+%, and the total impurities in the graphite are about 1 ppm. The detailed dimensions of the cell are shown in Fig. 1. The total length is so chosen that the cell can be accommodated into a small, portable furnace and probes as short as 230 mm can be calibrated in the cell [3].

The high-purity metal was melted into the graphite crucible in high vacuum or in a 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 argon arc-welded to the SS outer case. 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 that were a few degrees Celsius above their freezing points for indium and tin, and about 50°C below its 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. A special inner surface treatment of the SS case is critical in order to reduce possible contamination during the lifetime of the cell.

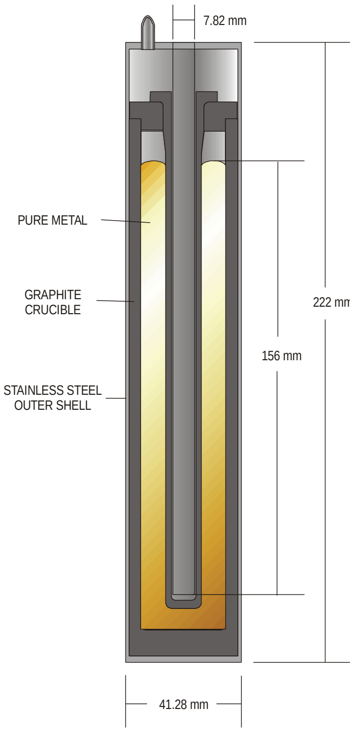

Figure 1: A SS-cased indium cell

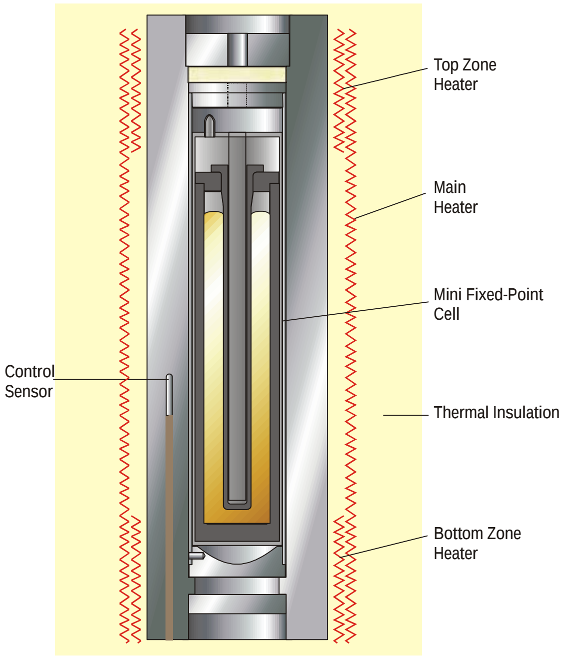

Figure 2: The SS-cased indium cell in a small, portable furnac

3. FIXED POINT FURNACE

Realization of freezing points of pure metal with high accuracy requires a strict envelopment around the fixed-point cell, where the temperatures must be very uniform, stable and accurately controlled. A three-zone furnace (Model 9114), reported in detail earlier, satisfies all of the requirements mentioned above [4]. A temperature uniformity of ± 0.01°C within a SS-cased fixed-point cell placed in the furnace is very easy to be 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 and industrial probes to be calibrated. A small, portable fixed-point furnace with lower costs is desirable for many applications, especially for secondary and industrial calibration. We reported a furnace for this purpose a few years ago [3]. Its size is much smaller than that of a classic fixed-point furnace. The small furnace has a total height of 489 mm and an outer diameter of 209 mm, and it weights about 17 kg (Fig. 2). The costs to build a small furnace are low, too—only about 40% of that for a classic fixed-point furnace. But it is much more difficult to obtain a uniform temperature around the fixed-point cell in a small furnace than in a classic fixed-point furnace. Many measures were taken to improve the small furnace's performance. Three heaters are used to obtain uniform temperatures around the fixed-point cell. Using this technique, we can achieve temperature uniformity of ±0.03°C within the cell. Vertical temperature profiles for four different heater settings at 155°C are shown in Fig. 3. When the top heater power was 56% and the bottom heater power was 82% relative to the main heater power, the temperatures in a vertical range from 0 mm to 150 mm were within ±0.03°C. Temperature stability of the furnace is better than ± 0.03°C over a few hours.

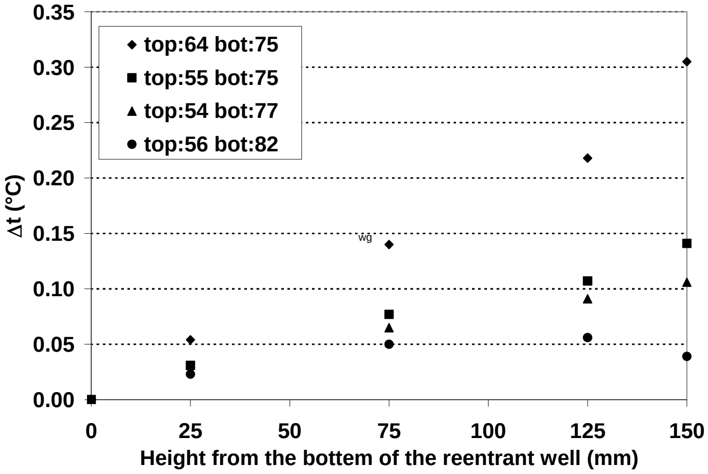

Figure 3: Vertical temperature profiles in a small, portable furnace with a SS-cased indium cell

4. REALIZATION OF THE FREEZING POINTS

For the lowest uncertainty, the following method was used to realize the freezing points. First, the temperature of the furnace was raised to a few degrees Celsius above the freezing point at a rate 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/min. 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 classic fixed-point furnace. The set temperature of the small furnace should 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 freezing plateau that typically lasts for more than twenty hours. The changes in temperature during the first ten hours were usually within 0.1 mK to 0.2 mK. A typical freezing curve of zinc obtained in a classic furnace is shown in Fig. 4. Many SPRTs or other temperature probes can be calibrated in a single freezing plateau. The operation for the tin point was a little different because of its larger “supercool.” 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.

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 secondary and industrial calibrations. The melting plateaus are easier to realize, require less training and make calibration work more efficient. 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 and industrial calibrations. The realization of a melting plateau is quite simple. The temperature of the furnace was raised to 1°C below the freezing point at a rate about 3°C/minute and left overnight. The next morning, the furnace temperature was 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 was decreased to 0.3°C above the freezing point at a rate of 0.1°C/min and maintained at the temperature during the entire melting plateau. A typical melting curve of indium obtained this way is shown in Fig. 5. The changes in temperature during 90% of the entire melting curve were within 0.8 mK.

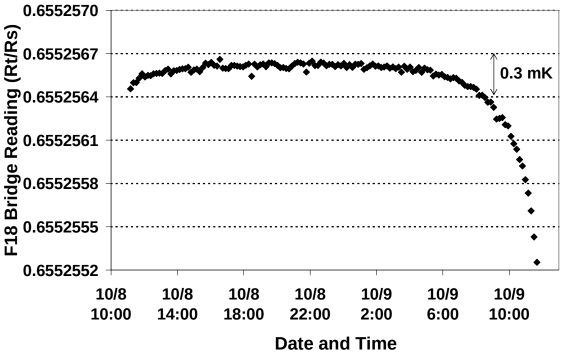

Figure 4: A typical freezing curve of zinc obtained in a classic fixed-point furnace with a SS-cased cell

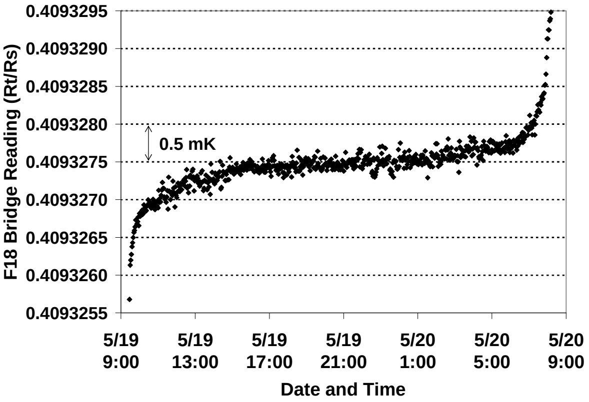

Figure 5: A typical melting curve of indium obtained in a small, portable fixed point furnace with a SS-cased cell

5. TESTS AND RESULTS

All SPRT resistance measurements were made using a DC automatic bridge (Model 6675A) except the recording freezing and melting curves was done with an F18 AC Bridge. The nonlinearity of the bridge is better than 0.02 ppm according to the manufacturer's specifications. A 10-ohm standard resistance maintained at 25°C ±0.01°C in a bath was used with the bridge. The stability of the standard resistance was better than 2 ppm per year. All resistances were measured at two currents (1 mA and 1.414 mA), so that the results can be extrapolated to values at zero power. The resistance at the triple point of water was measured immediately after a measurement at the freezing points. The resistance ratio W(t) = R(t)/ Rtp was calculated.

New SS-cased cells were compared against their counterparts of fused silica–cased cells in 2002, which were used as references to calibrate SPRTs in Hart Scientific's calibration laboratory. The fused silica–cased cells were put into classic fixed-point furnaces, and the new SS-cased cells were put into small, portable furnaces. Several SPRTs were used for the comparisons. The results obtained for the indium point are shown in Fig. 6. The average difference between the new cell #In-44002 and reference cell #5004 was 0.11 ±0.1 mK by six SPRTs. The average differences for the tin and zinc points were also within 0.2 mK (see Table 1 in detail).

The same pairs of fixed point cells were compared after about one year of use in order to check the long-term stabilities. The results are summarized in Table 1. No obvious drifts have been detected

Table 1: A summary of fixed point cells comparisons and long term stabilities

	2002	2003
In-44002 – 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

Immersion checks were made in both furnaces (classic and small furnaces) with the new SS-cased cells at all of the three points, and the results at the tin point are shown in Fig. 7. The measured values tracked the hydrostatic effect very well in a range of 20 mm from the full immersion in the small furnace at the zinc point (30 mm at the tin point and at the indium point). The tracked ranges in classic furnaces were more than double those in small furnaces. So the immersion depths in both furnaces are enough to eliminate the stem conductivity error at all three points.

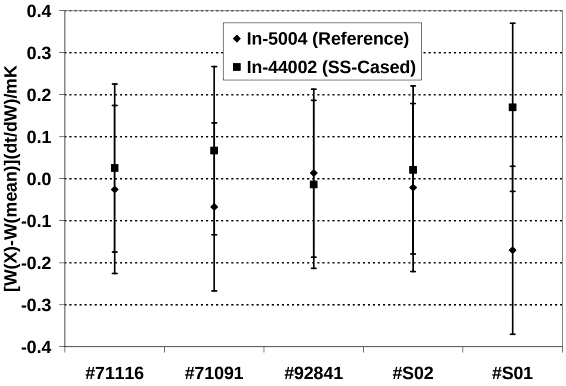

Figure 6: A direct comparison of a new SS-cased cell #In-44002 with fused silica–cased cell #In-5004 in May 2002

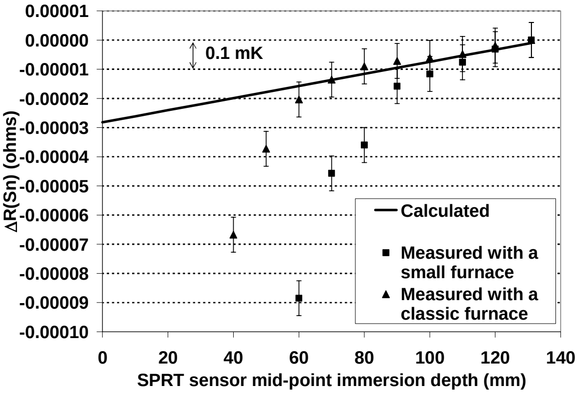

Figure 7: Immersion profiles in the new SS-cased cell during freezing plateau of tin in both furnaces (classic and small furnace)

The melting plateau was compared with the freezing plateau. Two SS-cased indium cells were used in two small furnaces. A freezing plateau was realized using cell #In-44001, and a melting plateau was simultaneously realized using cell #In-44002. Five SPRTs were calibrated on both the freezing plateau and the melting plateau. The mean difference between the melting plateau calibration and the freezing plateau calibration was -0.4 ±0.2 mK.

6. UNCERTAINTY ESTIMATION

The uncertainty components for the realization of all three points using the new SS-cased cells are listed in Table 2 and Table 3. The uncertainty associated with calibration of the cell from the national standard is not included here. Reproducibility of thermal state (Type A) and impurities (Type B) are two main uncertainty components. The difference between the classic furnace and the small furnace with a freezing plateau is very small. Actually, both provide nearly identical expanded uncertainty.

Table 2: Uncertainty budget with classic furnace

Source of uncertainty	Uncertainty Component (mK)		
	In	Sn	Zn
Resistance reading (A)	0.034	0.041	0.059
Reproducibility of thermal state (A)	0.180	0.200	0.300
Total A	0.183	0.204	0.306
Impurities (B)	0.253	0.310	0.350
Hydrostatic correction (B)	0.033	0.022	0.027
Pressure correction (B)	0.025	0.017	0.022
Immersion (B)	0.030	0.030	0.030
SPRT self heating	0.030	0.030	0.030
Propagated from TPW	0.030	0.050	0.080
Bridge non-linearity (B)	0.017	0.020	0.029
Total B	0.262	0.319	0.364
Total standard uncertainty	0.320	0.378	0.476
Expanded uncertainty (k=2)	0.640	0.757	0.951

Table 3: Uncertainty budget with small furnace

	Uncertainty Component (mK)					
	Freezing			Melting		
	In	Sn	Zn	In	Sn	Zn
Resistance reading (A)	0.034	0.041	0.059	0.034	0.041	0.059
Reproducibility of thermal state (A)	0.220	0.240	0.350	0.500	0.600	0.700
Total A	0.223	0.243	0.355	0.501	0.601	0.702
Impurities (B)	0.253	0.310	0.350	0.253	0.310	0.350
Hydrostatic correction (B)	0.033	0.022	0.027	0.033	0.022	0.027
Pressure correction (B)	0.025	0.017	0.022	0.025	0.017	0.022
Immersion (B)	0.030	0.030	0.030	0.030	0.030	0.030
SPRT self heating	0.030	0.030	0.030	0.030	0.030	0.030
Propagated from TPW	0.030	0.050	0.080	0.030	0.050	0.080
Bridge non-linearity (B)	0.017	0.020	0.029	0.017	0.020	0.029
Total B	0.262	0.319	0.364	0.262	0.319	0.364
Total standard uncertainty	0.344	0.401	0.509	0.566	0.681	0.791
Expanded uncertainty (k=2)	0.668	0.802	1.017	1.131	1.361	1.583

7. FINAL REMARKS

The performance of the new SS-cased fixed-point cells are 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 uncertainties for the new cells are almost the same as 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 cells provides many advantages compared with fused silica–cased cells: the new cells can be shipped instead of being hand-carried, they are much more robust and durable, and they are easier to use.

The new cell can be used in a small, portable furnace to obtain almost the same uncertainty as in a classic fixed-point furnace. The new cell can be used to calibrate not only SPRTs, but also 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 secondary and industrial calibrations: an absence of supercool, longer plateaus, simplicity, less training, and improved efficiency. 90% of a melting plateau can be used for calibration work compared with only about the first 40% of a freezing plateau (compare Fig. 4 and Fig. 5). A great number of probes can be calibrated on a single melting plateau.

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Address of the Author:

Xumo Li, Hart Scientific, 799 East Utah Valley Drive, American Fork, UT 84003-9775, USA, tel. 801 763 1600, fax 801 763 1600, e-mail: xumo.li@hartscientific.com, website: www.hartscientific.com