Fixed Points for Secondary Level and Industrial Calibration

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Abstract

A new technique for the realization of fixed points has been developed mainly for secondary level and industrial calibration. The new technique is distinguished from the traditional fixed-point technique with following aspects: simpler equipment, easier operation, less training required, lower cost, and higher working efficiency. Various new designs of fixed-point cells and their maintenance apparatus are described, including the triple point of water, the melting point of gallium, and many freezing points of pure metal. The test results are reported and the uncertainties are estimated for these fixed points using the new technique.

Instruction

Traditional fixed points are mainly used to realize the international temperature scale (ITS) and to calibrate high-accuracy thermometers, such as standard platinum resistance thermometers (SPRTs) and standard noble metal thermocouples. Under certain conditions, phase equilibrium temperatures of many pure materials are extremely stable and will not change with location or time. Due to the excellent reproducibility of many fixed points, fixed-point calibrations provide many advantages over comparison calibrations. Reference thermometers used to determine the temperature in the calibration are not required.

Traditional fixed points create poor productivity and require deep immersion of the thermometer under test. They are also difficult to use and require operators with significant experience and training. These and other considerations make them unsuitable for secondary and industrial calibrations. Until about six years ago, almost all secondary and industrial calibrations had been performed using the comparison method. Since then we have made great efforts to develop a new technique using fixed points for secondary and industrial calibrations [1-6].

Of course, for traditional fixed points, achieving the lowest possible uncertainty has always been the most important consideration. For our new fixed-point technique, high productivity, ease to use, reliability, and relatively low cost are equally important considerations. Also, these new fixed-point cells should accommodate a wide variety of temperature probes, including secondary platinum resistance thermometers (PRTs), industrial-grade RTDs, thermistors, reference thermocouples, and other common types of thermocouples. Frequently in secondary and industrial calibration labs, a large number of temperature probes require calibration during a working day, so high throughput capacity is vital as well. Further, the new cells need to accommodate short probes. Our research

goal is to develop new kinds of fixed points to satisfy as many of these requirements as possible.

A Portable Semi-Automatic System for the Triple Point of Water

The realization of the triple point of water (TPW) in traditional cells requires dry ice or liquid nitrogen to create an ice mantle and a fluid bath or ice Dewar to maintain the phase equilibrium state within the cell. An automated device for realizing the triple point of water would, of course, be attractive for secondary and industrial level calibration work. Furthermore, many short probes that are difficult to calibrate in traditional cells could be better served with a new apparatus.

A miniature TPW cell with an outside diameter of 30 mm and a total length of 165 mm was developed to address these issues (Figure 1). The manufacturing procedure of the mini cell is virtually identical to that of traditional TPW cells [7]. A dilute solution of ethanol in water is used in the well to provide adequate heat transfer to the thermometer. A portable, self-operating apparatus with thermo-electric cooling modules (Figure 2) was developed for automatically realizing the triple point and maintaining the phase equilibrium state in the mini cell. The total height of the apparatus is only 489 mm, the outer width is 209 mm, and the weight is about 6.6 kg.

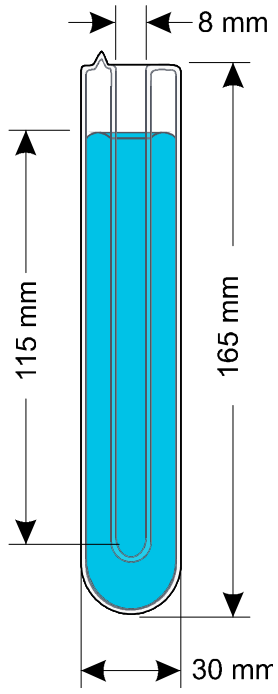

Figure 1. A mini TPW cell

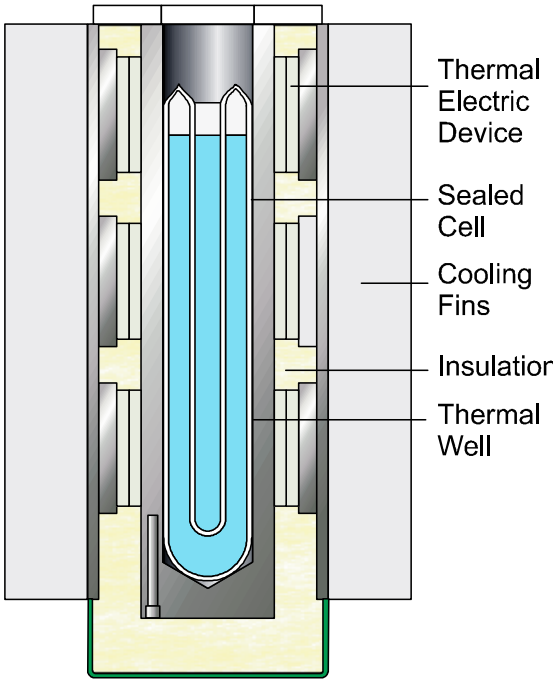

Figure 2. A portable semi-automated apparatus for realizing the TPW using a mini cell

The apparatus was designed with built-in programming for fast and easy operation. Three pre-set temperatures are built into the unit's controller: 5°C (melt mode), near 0°C (maintain mode), and -4°C (freeze mode). Operation is extremely simple. Enter the "freeze" mode through the front-panel buttons. When the apparatus alerts you (about ten to twenty minutes later), remove the mini cell from the apparatus and give the cell a light shake. The water in the cell, supercooled at a temperature of -4°C, immediately begins to freeze. Fine needle-crystals (dendrites) of ice appear uniformly throughout the cell and approximately 5% of the water freezes in a few seconds. Return the cell into the apparatus and change the program mode to "maintain."

Generally, the plateau will last for more than thirty hours. A typical freezing curve is shown in Figure 3. The temperature in a miniature TPW cell newly frozen in this manner is typically about 1 mK below the triple point of water. This low initial temperature and the subsequent gradual rising in the cell's temperature are believed to be caused by structural strains in the cell's suddenly frozen ice and the subsequent relieving of this strain over time. Creating an "inner melt" around the central well (by inserting a glass rod at room temperature) can expedite this rising process.

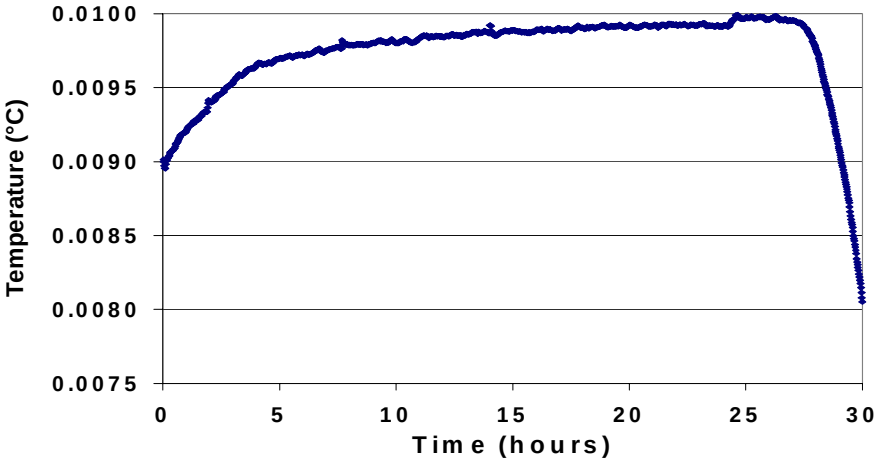

Figure 3. A typical freezing curve in a mini TPW cell

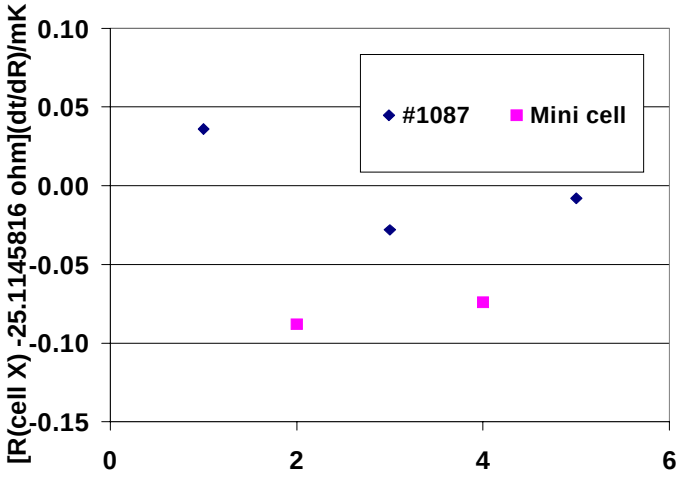

Figure 4. Comparison between equilibrium temperatures in a mini TPW cell with a portable apparatus and a regular TPW cell (S/N 1087).

The equilibrium temperature of a mini TPW cell in the above-described apparatus was compared with that of a regular TPW cell (serial number 1087) using an SPRT. The mini TPW cell was aged for ten hours after freezing the ice before the comparison began. We measured first in the regular cell, then in the mini cell, and then in the regular cell again. In total, five measurements were taken—three in the regular cell and two in the mini cell. The results are shown in Figure 4. A 0.06 mK spread in the regular cell (#1087) data was due to the reproducibility of the measuring system used. The average difference between the two cells was within 0.1 mK. If an uncertainty less than 0.5 mK is required, we suggest freezing the mini TPW cell in the late afternoon and using it the next day. If an uncertainty of 1 mK is satisfactory, the cell may be used immediately after freezing the ice in the cell.

A New Stainless Steel-Cased Gallium Cell and Its Automatic Maintenance Apparatus

The melting point of gallium (MPG) 29.7646 °C is in the range of room temperature, making it an attractive calibration point in biological engineering, life science, pharmaceuticals, environmental, oceanographic, and many other fields. Classic designs of MPG cells and apparatus require vacuum and argon filling systems, and they are too sophisticated for the secondary level and industrial calibration. Permanently sealed Pyrex-Teflon cells are much easier to use for most users [4]. While being an excellent material for standard lab applications, Pyrex glass is too fragile for many other users; so a stronger material, such as stainless steel (SS), is more desirable as the outer case material for many users. In order to eliminate the possible contamination from SS, a double sealing technique is used. The new MPG cell is shown in Fig. 5. The purity of the gallium used to fill the cell is higher than 99.99999+%. The gallium samples were melted into the Teflon crucible in a glove box containing a dry, pure argon atmosphere. Then the nylon lid with the re-entrant well was joined into the Teflon crucible by using a special epoxy. The surface of Teflon does not normally permit bonding, so a special treatment was used to change the molecular structure of the Teflon surface before the bonding. There is a port on the nylon lid so the Teflon crucible assembly can be connected to a high-vacuum system and pumped down to a pressure as low as 10^{-5} Pa to ensure a good vacuum sealing between the Teflon crucible and the nylon lid. The crucible assembly was pumped for at least 100 hours. During this period, the crucible assembly was repeatedly purged with 99.999% pure argon, and the gallium sample was completely melted and then completely frozen. Finally, during a melt plateau, the crucible assembly was filled with pure argon and sealed permanently at a pressure close to 101.325 kPa. 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.

The permanently sealed crucible assembly was inserted into the SS outer case, and the SS cap with the re-entrant well was arc-welded to the SS outer case. A special cooling jacket was used during welding to avoid damage to the crucible assembly from overheating. The welded SS case was connected to the same high-vacuum system and pumped according to a similar procedure for the crucible assembly. The SS outer case was sealed at almost the same argon pressure during a melting plateau. The gallium was first sealed into the Teflon crucible assembly as a precaution to avoid any contamination of the gallium from the SS outer case. Since Teflon and nylon can be permeable to gases and moisture, the sealed SS outer case protects the crucible assembly by maintaining a pure argon atmosphere at the same pressure as that inside the crucible assembly. The inner surface of the SS case was specially treated as a secondary precaution to avoid any contamination of the pure gallium.

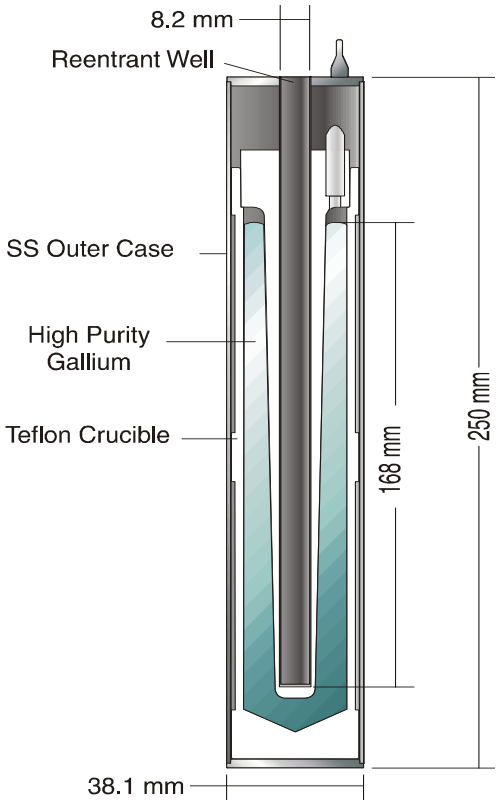

Figure 5. Schematic diagram of the new MPG cell

Realizing the MPG is not a complicated procedure for many national labs. The gallium sample is frozen completely before starting a melting curve. Because of a large amount of supercooling and a volume expansion of about 3.1% when high-purity gallium freezes, the freezing should start from the bottom of the cell upward; otherwise the volume expansion of gallium during freezing might break the cell. Good vertical temperature uniformity (±0.02°C or better) around the cell during a melting curve is also required. Many users could benefit from a fully automated maintenance apparatus for the MPG, including freezing the gallium sample in the cell automatically. We have developed such an apparatus, which is shown in Fig. 6.

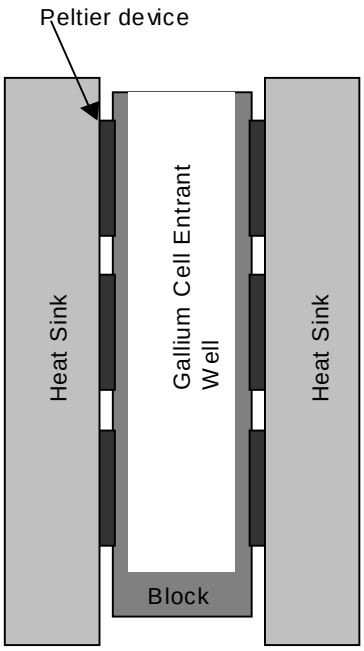

Figure 6. Cut away view of the automatic gallium apparatus

The Gallium cell is held in an aluminum block. Peltier devices are placed on the sides of the rectangular block, and they are controlled in sets at the different levels along the sides of the block. There is a bottom, middle, and top set. A PRT sensor is located in the block to provide feedback to the controller. The controller samples the resistance of the sensor and provides a closed-loop control signal to power the Peltier modules to maintain proper temperature control. The Peltier devices'

current reversal is handled by the controller to heat or cool the block during the various sections of the gallium melt/freeze cycle. The controller also controls an inner well melt heater probe that initially warms the inner well of the cell to form a liquid-solid interface around the inner well. Melting the inner wall advances the cell to the usable part of the melt plateau more quickly.

A new SS cell (#43002) was compared against our NIST certified gallium cell (#7010) in a bath. An SPRT (#61064) and a F18 bridge were used in the comparison. Three determinations on each cell were taken, and the results are shown in Fig. 7. The measured mean difference between two cells was within 0.01 mK with a standard deviation of 0.03 mK. Our reference gallium cell #7010 is an old, permanently sealed Pyrex-Teflon cell, which was originally certified by NIST. The difference between Cell #7010 and the NIST reference cell (Ga 98-1) was within 0.06 mK [8]. A typical melting curve obtained using cell #43002 in the automatic maintenance apparatus is shown in Fig. 8. The melting curve

lasted for more than seven days. The changes in temperature during 90% of the melting plateau were within 0.1 mK.

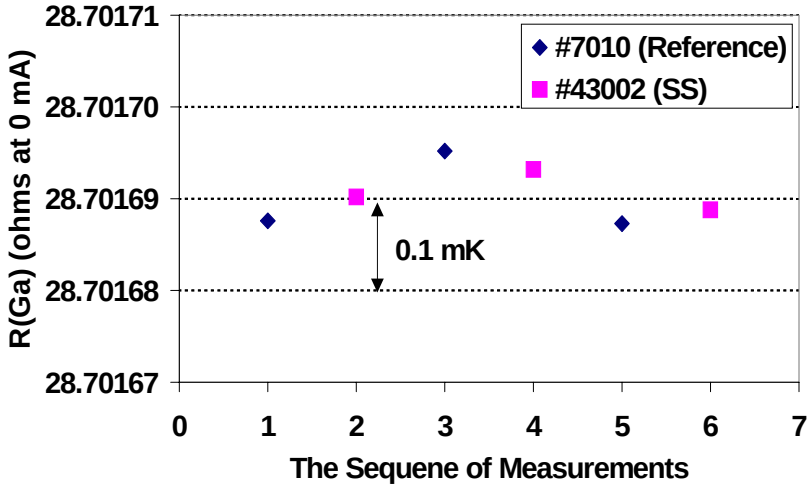

Figure 7. A direct comparison of a SS Ga cell #43002 with Hart reference Ga cell #7010

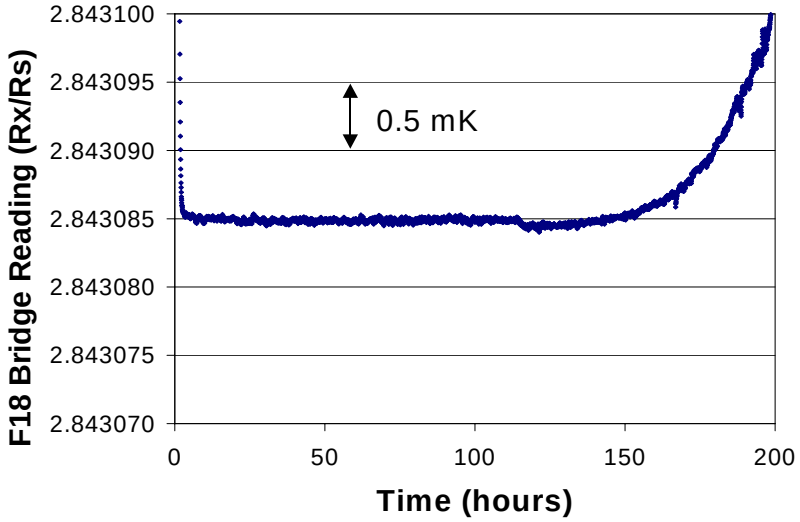

Figure 8. A typical melting curve using the new SS cell and automatic maintenance apparatus

Four new SS cells maintained by the new automatic maintenance apparatus were compared with a Pyrex-Teflon cell (#03030) in a bath. SPRT #1018 and the F18 Bridge were used for the comparison. All five of the cells started their melting curves at almost the same time. The comparison started at about the 40th hour (the third morning) from the beginning of the melting curves. The measurements started in cell #03030 and were then taken in each of the four SS cells successively. The resistance at the MPG [R(Ga)] corresponding to zero power was calculated from the data for each cell. The

measurements were repeated in the opposite sequence, i.e. from the last cell in the first run to cell #03030. The mean values of the two runs for each cell are listed in Table 1. The differences between the four cells and cell #03030 were within 0.03 mK, and the maximum difference among the five cells was within 0.05 mK.

TABLE 1. A comparison among five gallium cells

S/N of the cell	R(Ga) (ohms)	Δt (mK)
#03030	28.5363613	0.00
#43010 (SS)	28.5363596	-0.017
#43011 (SS)	28.5362639	+0.026
#43012 (SS)	25.5363591	-0.022
#43013 (SS)	25.5363596	-0.017

Pure Metal Freezing Points for Secondary and Industrial Calibration

New fixed-point cells and their maintenance apparatus have been developed for secondary and industrial calibration. A small-size fused silica (quartz glass) cell is shown in Fig. 9. The design and manufacturing techniques have been described in detail elsewhere [3]. The total length of the cell is much shorter than traditional fixed-point cells so that probes as short as 230 mm may be calibrated with it. Recently a stronger material (SS) was tried for the cell case. A SS-cased cell is shown in Fig. 10.

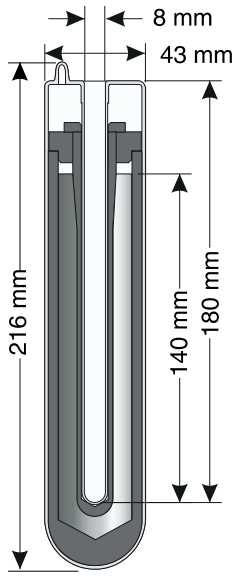

Figure 9. A small-size fused silica-cased fixed-point cell

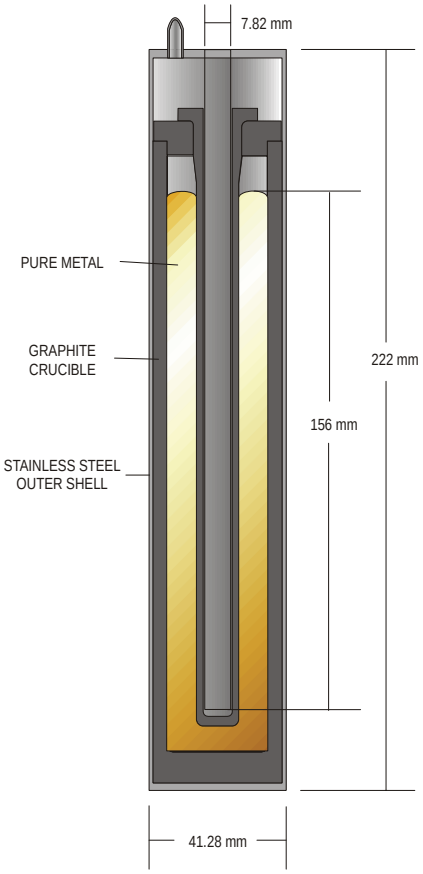

Figure 10. A SS-cased fixed-point cell

A small, portable furnace (Figure 11) has been developed for using these cells in secondary and industrial calibration applications. The furnace is much shorter than traditional furnaces and can easily be used on a table or bench. The furnace has a total height of 489 mm and an outer diameter of 209 mm, and it weights about 17 kg. Three heaters are used to obtain uniform temperatures around the mini 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 ±0.1°C within the cell. A quartz-sheath SPRT can track hydrostatic head effect when immersed in the cell to within 20 mm of full immersion for the freezing points of tin and zinc.

A number of freezing and melting curves were obtained using small-size fused silica-cased fixed-point cells. Figure 12 shows a melting curve of tin in a salt bath. The melting plateau lasted for more than 75 hours and the change in temperature during 92% of the plateau was within 0.0006°C. Many thermometers can therefore be calibrated during a single melting plateau. A freezing curve of aluminum, obtained in a portable furnace, is shown in Figure 13.

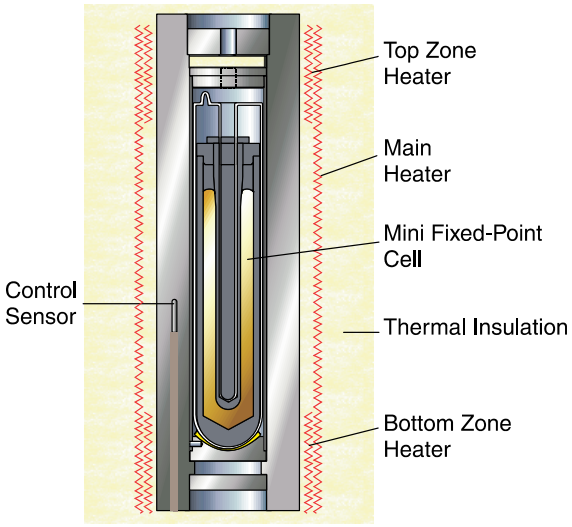

Fig. 11. A small-size fused silica-cased fixed-point cell in a portable furnace

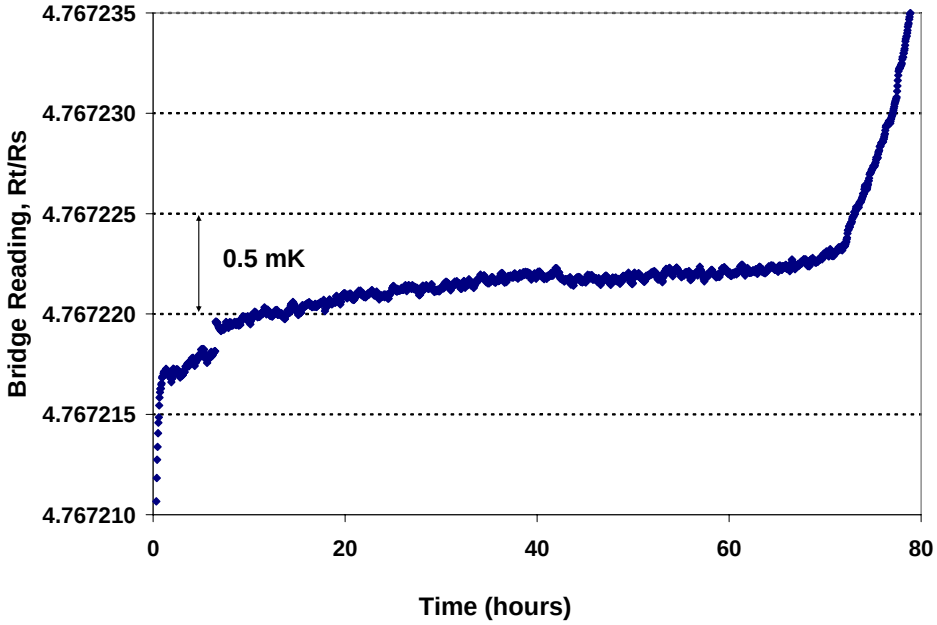

Figure 12. A melting curve of tin, using a small-size cell

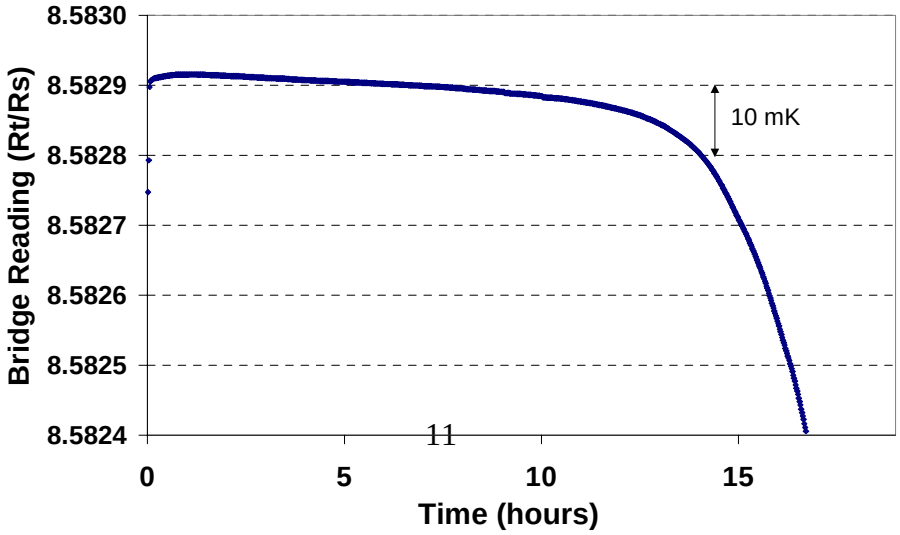

Figure 13. A freezing curve of aluminum, using a small-size cell

Equilibrium temperatures realized in small-size cells were compared with those of traditional freezing-point cells. Some of these results are summarized in Table 2 and Table 3. The differences in equilibrium temperatures between the small-size cells and the traditional cells were found to be easily within 0.001°C at the freezing points of tin and zinc.

Table 2. Comparison between a small-size zinc cell and traditional zinc cells.

S/N of cell	Type of cell	W(Zn)	ΔW(Zn) (Compared with Zn08)	Δt(Zn) (mK)
Zn07	Traditional	2.56891082	-0.00000172	-0.49
Zn08	Traditional	2.56891254	0	0
Zn-s-01	Small-size	2.56891310	0.00000056	0.16
The results were measured by using an SPRT, S/N 5681-5-1016				

Table 3. Comparison between a small-size tin cell and traditional tin cells.

S/N of cell	Type of cell	W(Sn)	ΔW(Sn) (Compared with Sn09)	Δt(Sn) (mK)
Sn08	Traditional	1.89269833	-0.00000034	-0.09
Sn09	Traditional	1.89269867	0	0
Sn-s-01	Small-size	1.89269920	0.00000053	0.14
The results were measured by using an SPRT, S/N 5681-5-1027				

Both techniques, freezing and melting, can be used for secondary and industrial calibrations. The uncertainty of a melting plateau of 99.9999+% pure metal, though a little larger than that of the freezing plateau of the same metal, is still far below the uncertainty level required by secondary-level calibrations. At the same time, the melting technique (compared to the freezing technique) has a number of clear advantages for secondary labs. These include an absence of supercool, longer plateaus, simplicity, and improved efficiency.

Discussion

The uncertainty components of the fixed points described in the paper are listed in Table 4. Obviously, the uncertainty levels can easily satisfy the typical requirements of

secondary and industrial calibration labs. These fixed points have 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. These fixed points provide excellent efficiency and can be used in a manner similar to the ice point. For all these reasons, these new fixed-point cells and apparatus are extremely attractive for secondary and industrial calibrations.

Table 4. Uncertainty budget[†]

Source of uncertainty	Value of uncertainty component (1 σ in mK)					
	TPW	Ga(7N)	In(6N)	Sn(6N)	Zn(6N)	Al(6N)
Reproducibility (A)	0.1	0.1	0.5	0.6	0.8	1.0
Impurities in the sample (B)	0.04	0.01	0.5	0.3	0.5	0.7
Hydrostatic correction error (B)	0.01	0.01	0.03	0.02	0.03	0.02
Pressure correction error (B)	< 0.01	0.02	0.05	0.03	0.04	0.07
Immersion (B)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.2
Combined	0.15	0.1	0.72	0.68	0.95	1.2

[†]This analysis assumes use of the melting (rather than freezing) technique and that small-size cells are used in the portable apparatus described in the paper.

References

1. X. Li, et al., "The Melting Point of Tin", National Conference of Standards Laboratories (NCSL) Symposium, Vol. 1, 1996, p. 419 (1996)
2. X. Li and Hirst, Mike, "The Comparison between the Freezing Point and Melting Point of Tin", 6th International Symposium on Temperature and Thermal Measurements in Industry and Science (TEMPMEKO '96), Torino, Italy, September 10-12, 1996
3. X. Li and M. Hirst, "New Generation of Fixed Points", Proceedings of 1997 NCSL Workshop and Symposium, vol. 2, pp. 567-577, 1997
4. X. Li and M. Hirst, "Fixed Points for Secondary Level Calibration", Proceedings of TEMPMEKO 99, The 7th International Symposium on Temperature and Thermal Measurements in Industry and Science, vol. 1, pp. 74-79, 1999.
5. X. Li, et al, "Mini Metal-Cased fixed-Point Cells", Proceedings of 8th International Symposium on Temperature and Thermal Measurements in Industry and Science, vol. 2, pp. 777-782, 2001.
6. X. Li, et al., "Handheld Fixed Points", NCSL International, Conference Proceeding 2002, 5B (2002)
7. X. Li, D. Chen, and M. Zhao, "Triple Point of Water Cell", 2001 NCSL International Workshop & Symposium, 5B (2001)
8. NIST, Certificate of Analysis, NIST Test No. 836/26256400, 2000