FIXED POINTS FOR SECONDARY LEVEL CALIBRATIONS

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ABSTRACT

Fixed-point calibrations have many advantages over comparison calibrations. The unsuitability of traditional fixed-point apparatus for secondary and industrial calibrations is discussed. New kinds of fixed points have been developed for secondary and industrial calibrations.

A miniature cell for the triple point of water (TPW) and a self-operating TPW apparatus have been developed for secondary and industrial calibrations. Built-in programming in the apparatus makes its operation extremely simple. Typical freezing curves are shown. A comparison between the new device and a traditional TPW cell shows a difference between them less than 0.2 mK.

A permanently sealed gallium cell is discussed. The procedure for realizing its melting point is described in detail. Its melting plateau typically lasts from ten days to two months. Three cells were intercompared using five SPRTs. The differences among them were well within 0.1 mK.

Miniature cells for the freezing points of pure metals and a portable apparatus for these mini cells are introduced. Many freezing and melting curves were realized from the mini cells. A comparison between these mini fixed-point cells and their traditional-size counterparts shows differences within 1.0 mK for the freezing points of tin and zinc. The benefits of using the melting point technique instead of the freezing point technique for secondary calibrations are discussed. These include lack of supercool, longer plateaus, simplicity, and increased efficiency.

1. INTRODUCTION

Fixed-point calibrations provide many advantages over comparison calibrations. 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, 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 unit 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. Some attempts in the past at simplified designs of traditional fixed points have provided inaccurate calibration results. Until now, almost all secondary and industrial calibrations have been performed using the comparison method.

Techniques we have developed in recent years [1-5] have made it possible to advance new kinds of fixed-point cells for secondary and industrial applications. A number of features were included in our designs of these cells that distinguish them from traditional fixed points.

Of course, for traditional fixed points, achieving the lowest possible uncertainty has always been the most important consideration. For our new fixed-point cells, high productivity, ease of 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 reference platinum resistance thermometers (PRTs), industrial-grade RTDs, 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.

2. A PORTABLE SYSTEM FOR REALIZING 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. A solution of water and alcohol 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

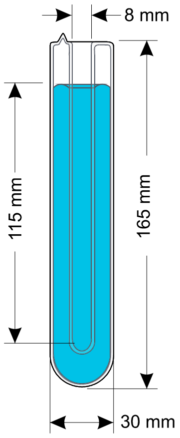
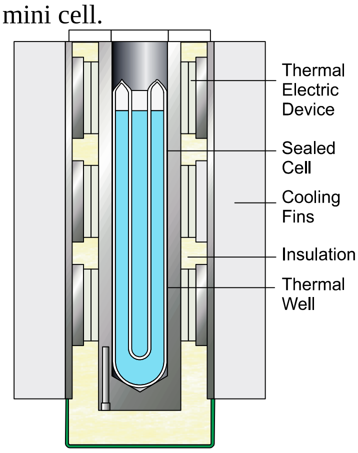


Figure 2. A portable automated apparatus for realizing the TPW, using a mini cell.



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.

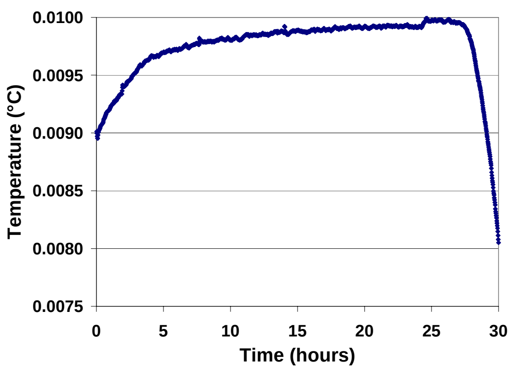
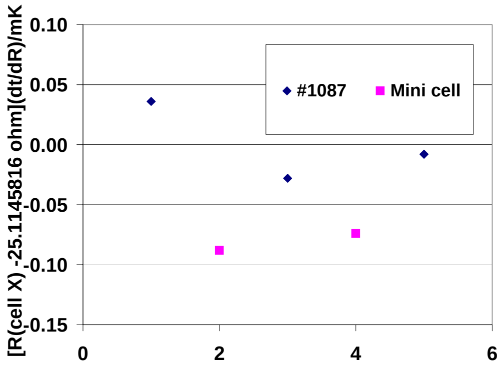


Figure 4. Comparison between equilibrium temperatures in a mini TPW cell with a portable apparatus and a regular TPW cell (S/N 1087).



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 a standard platinum resistance thermometer (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.

3. THE MELTING POINT OF GALLIUM

A permanently sealed gallium cell (Fig. 5) was developed for our research using a Teflon vessel and an outer Pyrex shell. The Teflon vessel allows for the 3.1% expansion of gallium upon solidification. The purity of the gallium used is greater than 99.99999%. The total immersion depth (from the inner bottom of the central well to the upper surface of pure gallium) is approximately 150 mm. The well of the gallium cell should be filled with distilled water to improve the heat transfer between the thermometer and the gallium.

This sealed cell design has many advantages. One of these is avoiding the use of a vacuum and filling system, thereby making the gallium cell much easier to use, particularly for secondary and industrial calibrations. No drift has been found in these cells over a six-year period. Probes as short as 270 mm can be calibrated in this cell and it can be used in a bath with a depth of only 300 mm (Figure 6). A portable apparatus for the sealed gallium cell is currently being developed.

Figure 5. A permanently sealed gallium cell.

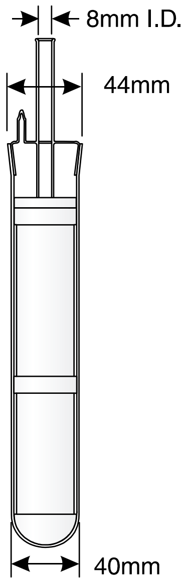
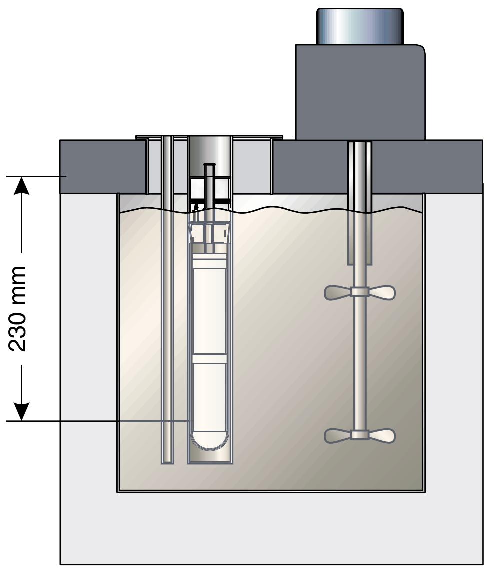


Figure 6. The sealed gallium cell in a bath



Realization of the melting point of gallium using the sealed cell is quite simple. Before beginning, be sure the gallium in the cell is completely solidified. Put the cell into a water bath at a temperature approximately 0.5°C below the melting point of gallium (29.7646°C) and place an 8-watt heater (turned off) in the cell. Increase the bath’s temperature to 1.0°C above the melting point at a rate of 0.1°C per minute and keep the bath at this temperature for twenty minutes. Turn on the 8-watt heater during the last four minutes. A little more than 10% of the gallium in the cell will melt during this period. Decrease the bath’s temperature to anywhere from 0.01°C to 0.1°C above the melting point.

The melting curve will last for about ten days if the water bath remains stable at approximately 0.1°C above the melting point. A typical melting curve obtained in this way is shown in Figure 7. The temperature of the cell is stable well within 0.1 mK during most of its melting plateau. If the bath’s temperature is stable at approximately 0.01°C above the melting point, the melting curve will last for about two months. A large number of thermometers can be calibrated during a single melting curve with very little manual maintenance of the cell required.

Our gallium cell design was tested using the same technique we used to test our miniature triple point of water cells. Using five SPRTs, we compared three cells. The results are shown in Figure 8. The differences among the cells were all within 0.1 mK. The equilibrium temperatures of the three cells were measured with an SPRT (S/N 1031) which was calibrated by NIST. The differences between the measured values and the ITS-90 assigned value (29.7646 °C) are all within 0.2 mK.

Figure 7. A typical melting curve of gallium

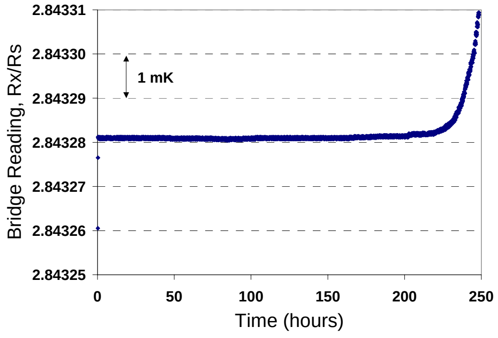
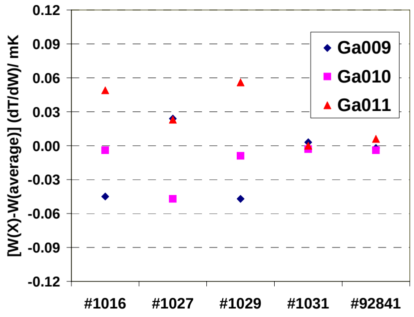


Figure 8. Comparison of three gallium cells, using five SPRTs.



4. MELTING AND FREEZING POINTS OF PURE METALS

A mini fixed-point cell (Figure 9) was developed for secondary and industrial calibrations. The design and manufacturing techniques have been described in detail elsewhere [5]. The purity of the metals used is greater than 99.9999%. The total length of the cell is much shorter than traditional fixed-point cells so that probes as short as 200 mm may be calibrated with it. Mini cells can be used in baths below 500°C (Figure 10) or in traditional fixed-point furnaces [5].

A small, portable furnace (Figure 11) has been developed for using mini 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 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.

Figure 9. A mini fixed-point cell.

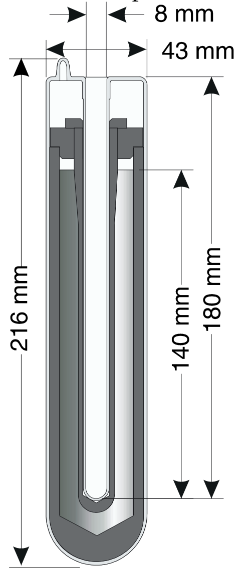
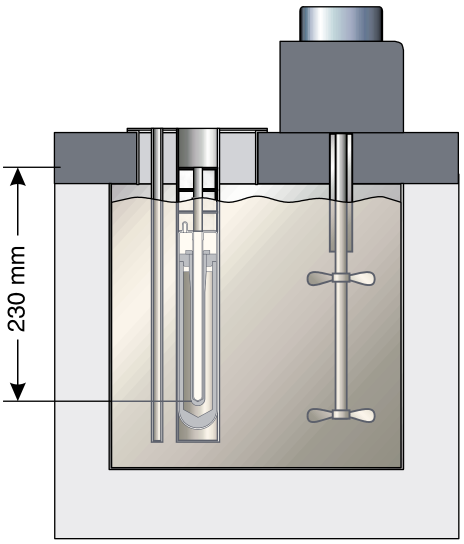


Figure 10. A mini cell in a salt bath.



A number of freezing and melting curves were obtained using mini cells. Figure 12 shows a melting curve of tin in a salt bath. Similar baths are commonly found in many secondary laboratories. The melting plateau lasted for more than 75 hours and the change in temperature during 92% of the plateau was within 0.6 mK. 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.

Equilibrium temperatures realized in mini cells were compared with those of traditional freezing-point cells. Some of these results are summarized in Table 1 and Table 2. The differences in equilibrium temperatures between the mini cells and the traditional cells were found to be easily within 1.0 mK at the freezing points of tin and zinc.

Table 1. Comparison between a mini 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	Mini	2.56891310	0.00000056	0.16
The results were measured by using an SPRT, S/N 5681-5-1016				

Table 2. Comparison between a mini 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	Mini	1.89269920	0.00000053	0.14
The results were measured by using an SPRT, S/N 5681-5-1027				

Figure 11. A mini cell in a portable furnace.

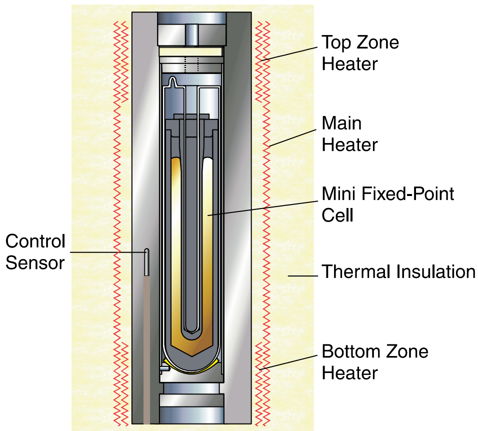


Figure 12. A melting curve of tin, using a mini cell.

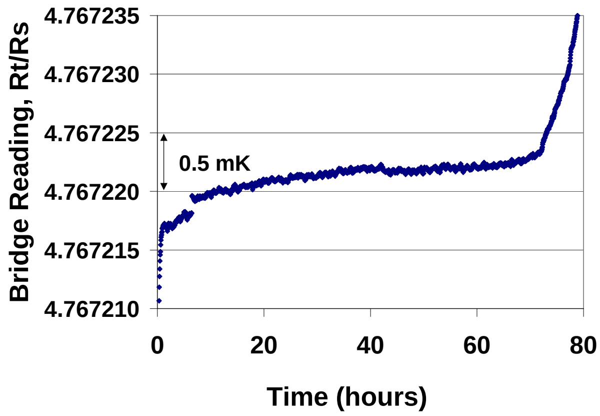
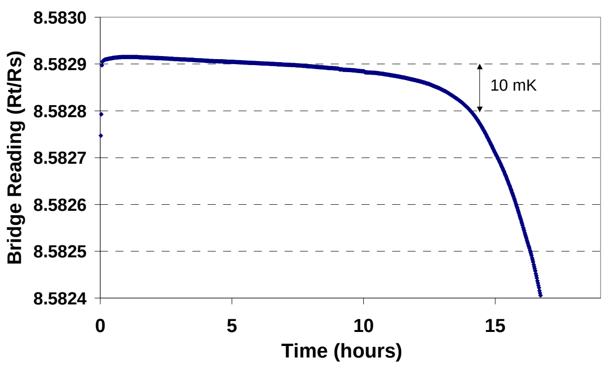


Figure 13. A freezing curve of aluminum, using a mini cell.



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.

5. DISCUSSION

The uncertainty components of the fixed points described in the paper are listed in table 3. 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 3. 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 mini cells are used in the portable apparatus described in the paper for all points except gallium, which uses a bath.

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