

**FLUKE**®

— **Hart Scientific**®

# ***5901 Series***

*Triple Point of Water Cells  
User's Guide*

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# Table of Contents

<b>1</b>	<b>Before You Start . . . . .</b>	<b>1</b>
1.1	Symbols Used . . . . .	1
1.1.1	Warnings . . . . .	2
1.1.2	Cautions . . . . .	2
<b>2</b>	<b>Introduction . . . . .</b>	<b>5</b>
<b>3</b>	<b>Specifications. . . . .</b>	<b>9</b>
<b>4</b>	<b>Freezing an Ice Mantle in the TPW Cell . . . . .</b>	<b>11</b>
4.1	Preparations . . . . .	11
4.2	Freezing . . . . .	11
4.2.1	Dry Ice Freezing Process . . . . .	11
4.2.2	The Heat Pipe Freezing Process . . . . .	12
4.2.3	Metal Pre-cooled In Liquid Nitrogen Freezing Process . . . . .	14
4.3	The Inner Melt. . . . .	14
<b>5</b>	<b>Maintenance and Life-Time of a TPW Realization . . . . .</b>	<b>15</b>
<b>6</b>	<b>Using the Cell . . . . .</b>	<b>17</b>
<b>7</b>	<b>Isotopic Composition. . . . .</b>	<b>19</b>
<b>8</b>	<b>Care of Your TPW Cell . . . . .</b>	<b>23</b>
<b>9</b>	<b>REFERENCES . . . . .</b>	<b>25</b>

# Figures

Figure 1	Triple point of water cell designs and dimensions . . . . .	6
Figure 2	Freeze an ice mantle using a “Quick Stick” . . . . .	13

# Tables

Table 1	International Electrical Symbols . . . . .	1
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# 1 Before You Start

## 1.1 Symbols Used

Table lists the International Electrical Symbols. Some or all of these symbols may be used on the instrument or in this manual.

**Table 1** International Electrical Symbols

Symbol	Description
	AC (Alternating Current)
	AC-DC
	Battery
	CE Complies with European Union Directives
	DC
	Double Insulated
	Electric Shock
	Fuse
	PE Ground
	Hot Surface (Burn Hazard)
	Read the User's Manual (Important Information)
	Off
	On

Symbol	Description
	Canadian Standards Association
<b>CAT II</b>	OVERVOLTAGE (Installation) CATEGORY II, Pollution Degree 2 per IEC1010-1 refers to the level of Impulse Withstand Voltage protection provided. Equipment of OVERVOLTAGE CATEGORY II is energy-consuming equipment to be supplied from the fixed installation. Examples include household, office, and laboratory appliances.
	C-TIC Australian EMC Mark
	The European Waste Electrical and Electronic Equipment (WEEE) Directive (2002/96/EC) mark.

### 1.1.1 Warnings

Always use extreme care when using liquid nitrogen. Contact with liquid nitrogen can cause frost bite or severe freezer burns.

Use extreme caution when using dry ice. Contact with dry ice can cause frost bite or severe freezer burns.

### 1.1.2 Cautions

Read section entitled “Care Of Your TPW Cell” before removing the cell from the case. Incorrect or improper handling of the cell can damage or break the cell.

**DO NOT** shake the cell.

**DO NOT** invert the cell too fast, as the cell can break due to the “water hammer” (explained in Section 8 “Care of Your TPW Cell”).

If the cell does not produce a water hammer, the cell may be broken even though there are no visible cracks.

**DO NOT** allow the entire cell to freeze, as the cell will break.

Avoid the formation of an ice bridge from the reentrant well across the surface to the outer glass cylinder of the cell while freezing the ice mantle. This may cause sufficient pressure to break the glass.

While freezing the ice mantle, the mantle should never become so thick that it comes in contact with the outer glass shell or the cell will break.

The Cell and Quick Stick (if used) need to be well supported during the freezing process, or the cell may be damaged or broken.

**DO NOT** drop probes into the reentrant well of the cell. The cell and/or probe will be damaged or broken.

It is suggested that the TPW cell be kept in the vertical position during transportation.

The cell must be transported at temperatures above 0°C.

Avoid vibration and jarring during transportation. The effect of the water hammer can break the cell.

Store the cell in temperatures above 0°C.

**DO NOT** allow the water in the cell to freeze too quickly. Rapid freezing of the water in a TPW cell will break the cell.

## 2 Introduction

The temperature of the TPW is the intrinsic temperature of pure water with the three phases of water, ice and water vapor in thermal equilibrium. The temperature of the TPW, 273.16K (0.01°C), is 0.01°C above the melting point of ice (the ice point). The ice point was historically one of the defining fixed points of the Thermodynamic Temperature Scale and the International Temperature Scale (ITS-27 and ITS-48). The equilibrium temperature of three phases of a pure material is unique. The equilibrium of three phases of a pure material can only exist at a unique pressure. Whereas the equilibrium temperature between two phases (i.e. melting point and boiling point) varies with pressure. Therefore, a special pressure must be assigned to the melting point or boiling point, which is usually standard atmospheric pressure (101.325 kPa).

The triple point of water (TPW) is the only thermometric fixed point used in definitions of both the thermodynamic temperature and the international temperature scale [1-3]. The unit of thermodynamic temperature, Kelvin, is defined as the fraction 1/273.16 of the thermodynamic temperature of the TPW. It is also a defining fixed point on the International Temperature Scale of 1990 (ITS-90). According to the ITS-90, the temperatures between 13.8033 K and 961.78°C are determined in terms of the ratio of the resistance at a temperature T ( $R(T90)$ ) and the resistance at the TPW ( $R(TPW)$ ) of a standard platinum resistance thermometer (SPRT). The ratio,  $W(T90)$  is:

$$W(T90) = R(T90) / R(TPW) \quad (1)$$

The Triple Point of Water Cell is an important instrument in temperature calibration labs. TPW cells are the most commonly used and hence one of the most important temperature fixed points. The triple point of water temperature is the most reliable and repeatable temperature point available.

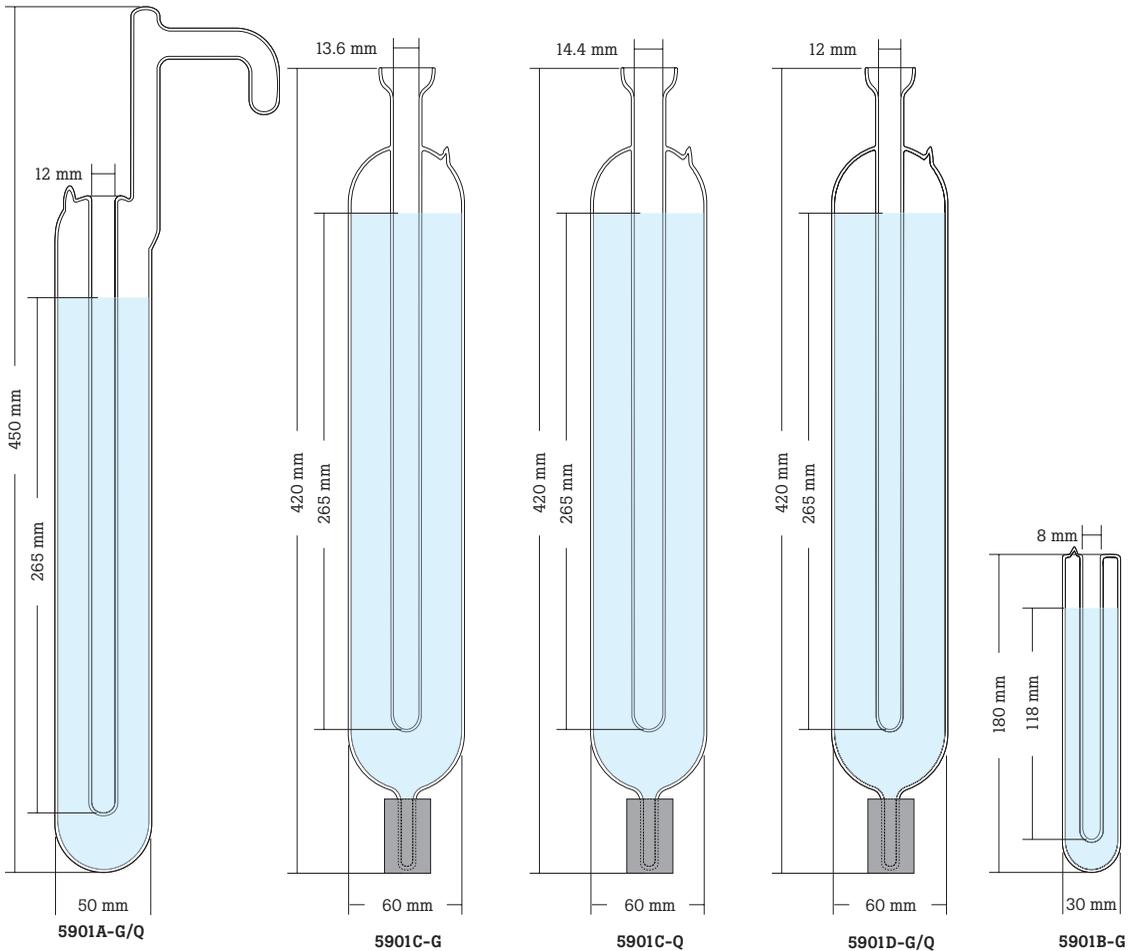
Room pressure, desolved gases in water (especially CO<sub>2</sub>), and other factors have detectable effects on the equilibrium temperature between water and ice. Therefore, it is very difficult to obtain an expanded uncertainty of 0.1 mK for the ice point. Although, it is very easy to obtain an expanded uncertainty of 0.1 mK for the TPW. The water in an ice point apparatus is easily contaminated by its surrounding environment, but the sealed TPW cell protects the water in the cell from contamination for many years. For these reasons, in 1954, CGPM (General Conference of Weights and Measures) adopted the TPW as the sole point defining the unit of Thermodynamic Temperature instead of the combination of the ice point and the boiling point of water. This is similar to the method proposed by the famous physicist W. T. Kelvin in 1848.

In order to accommodate the broad application of the TPWs, Hart Scientific has developed a series of TPW cells, including Models 5901D-G, 5901A-G, 5901B-G, 5901C-G, 5901D-Q, 5901A-Q, and 5901C-Q (Figure 1). Hart Scientific TPW cells and technology make it easy to realize the TPW. All Hart Scientific TPW cells constructed with a high-quality Pyrex envelope, or fused silica envelope are described in this User Manual. The Variations in the isotopic content of naturally occurring water can cause detectable differences in the TPW

temperature. The isotopic composition of water in Hart TPW cells is substantially the same as one of Standard Mean Ocean Water. We will discuss this issue in more detail in the manual.

Model 5901D-G and 5901D-Q Cell are of the design used by national temperature labs around the world. This design has a wide mouth to facilitate the use of crushed dry ice to freeze the mantle. The rubber foot allows the cell to rest on the bottom surface of a Dewar vessel when maintained in an ice bath or holding fixture for extra stability and protection while the cell is in use. The shell material of the 5901D-G is borosilicate glass and the shell material of 5901D-Q is fused silica glass.

Model 5901A-G and 5901A-Q Cell are designed after the original NBS cell with a glass support arm. While the arm does not impact performance in any



**Figure 1** Triple point of water cell designs and dimensions

way, some users prefer this design because it facilitates lifting and carrying the cell. The arm can be used as a hook for supporting the cell in an ice bath or used as a McLeod gauge for a strictly qualitative check of trapped air in the cell. The shell material of the 5901A-G is borosilicate glass and the shell material of the 5901A-Q is fused silica glass.

Model 5901B-G Cell is a smaller cell that is easy to handle, accommodates shorter sensors, and can be maintained in an automatic maintenance device, such as a Hart Scientific Model 9210. Despite this cell's diminutive size, it is made with the same materials and technology used to make larger cells. The 5901B has an expanded uncertainty of  $0.0002^{\circ}\text{C}$  and a reentrant well diameter of 8 mm. The shell material of 5901B-G is borosilicate glass.

Model 5901C-G and 5901C-Q cell are identical to models 5901-G and 5901-Q cells with the exception of the reentrant well diameter, which is 13.6 mm and 14.4 mm respectively, rather than the standard 12 mm. The larger reentrant well diameter is designed to accommodate larger diameter thermometers. The shell material of the 5901C-G is borosilicate glass and the shell material of the 5901C-Q is fused silica glass.

Water impurities and remnant gas are the two primary sources of error for the TPW cell; therefore Hart Scientific cells are designed to minimize the effects of these two errors. Both factors lower the equilibrium temperature within the cell. A higher equilibrium temperature in an inter-comparison usually indicates a higher quality cell.

High-quality borosilicate glass and fused silica glass are used in the construction of the shell material for TPW cells. The contamination rate of impurities from (or through) the glass into water is extremely low for these types of glass. The TPW cell must be assembled with scrupulous attention to the requirement that the water remain free of impurities. Meticulous cleaning of all parts is extremely important in the manufacture of TPW cells.

Recent research [13] shows that a decrease of 4 microK per year has been observed in borosilicate glass TPW cells due to the dissolution of glass of the cell. The borosilicate glass may be a less than ideal container as it is the most likely source of the contamination elements. As a result of this concern, Hart has introduced TPW cells with fused silica glass containers. The fused silica glass may be a more ideal container material for a TPW cell than borosilicate glass. More research results may be reported.

### 3 Specifications

	5901A-G	5901A-Q	5901C-G	5901C-Q	5901D-G	5901D-Q	5901B-G
<b>Expanded Uncertainty (k=2)</b>	< 0.0001 °C						< 0.0002 °C
<b>Reproducibility</b>	0.00002 °C						0.00005 °C
<b>Dimensions</b>	50 mm OD 12 mm ID 450 mm long	60 mm OD 13.6 mm ID 420 mm long	60 mm OD 14.4 mm ID 420 mm long	60 mm OD 12 mm ID 420 mm long	60 mm OD 12 mm ID 420 mm long	30 mm OD 8 mm ID 180 mm long	
<b>Immersion Depth (water surface to well bottom)</b>	265 mm						118 mm
<b>Material</b>	Borosilicate Glass	Fused Silica (Quartz)	Borosilicate Glass	Fused Silica (Quartz)	Borosilicate Glass	Fused Silica (Quartz)	Borosilicate Glass
<b>Water Source</b>	Ocean						
$\delta D_{VSMOW}$	$\pm 10\text{‰}$ ( $\pm 1\%$ )						$\pm 20\text{‰}$
$\delta^{18}O_{VSMOW}$	$\pm 1.5\text{‰}$ ( $\pm 0.15\%$ )						$\pm 3\text{‰}$
<b>Effect of deviation from VSMOW</b>	$\pm 7\mu K$						$\pm 14\mu K$

## 4 Freezing an Ice Mantle in the TPW Cell



**CAUTION:** *DO NOT* shake the cell or invert the cell vigorously.

To realize the triple point of water temperature, an ice mantle must be formed from the reentrant well outward.

### 4.1 Preparations

It is important that the reentrant well is cleaned and dried before attempting a freeze of the cell. If this precaution is not taken, water inside the reentrant well will freeze during the mantle formation, creating a less uniform mantle which will not last as long. A drop of alcohol in the bottom of the reentrant well before freezing will help prevent ice formation from moisture which may be introduced during the process. Remove any foreign material from the outside of the cell to prevent contamination of the bath. In order to provide more uniform mantles and reduce coolant required for freezing, pre-chill the cell by immersing it into an ice bath or maintenance bath until it is no more than a few degrees above the ice point.

### 4.2 Freezing

The cell should be frozen by refrigerating the inside of the reentrant well so that water freezes from the reentrant well outward to form a mantle of ice around the well. A variety of refrigeration methods are used to freeze a cell, such as refrigerated cold fingers, heat pipes, LN<sub>2</sub> chilled rods and dry-ice.

#### 4.2.1 Dry Ice Freezing Process

A simple and fast method of freezing an ice mantle is to pour crushed Dry Ice (solid CO<sub>2</sub>) directly into the dry reentrant well. Support the cell during freezing in a rack which will prevent breakage but allow complete visibility of the cell. Use dry ice that is ground or crushed to 2 mm diameter granules, which is the consistency of snow. Introduce small amounts into the “dry” well until a mantle is formed at the bottom and then introduce more dry ice until the level is near the top of the cell. As the dry ice sublimates, continue to refill the reentrant well so that the level is maintained at the water level. If the dry ice level becomes too low before more is added, the mantle may crack, which will require additional annealing time. Formation of an ice bridge from the reentrant well across the surface to the outer glass cylinder of the cell while freezing the ice mantle may cause sufficient pressure to break the glass. The bridging can be prevented by warming that portion of the cell with the hand while shaking it gently sideways to agitate the surface of the water and allow it to wash over the ice. The mantle should never become so thick that it comes into contact with the outer glass or breakage could occur. In the vertical position, the mantle will appear larger than it actually is due to the magnification created by the cylindri-

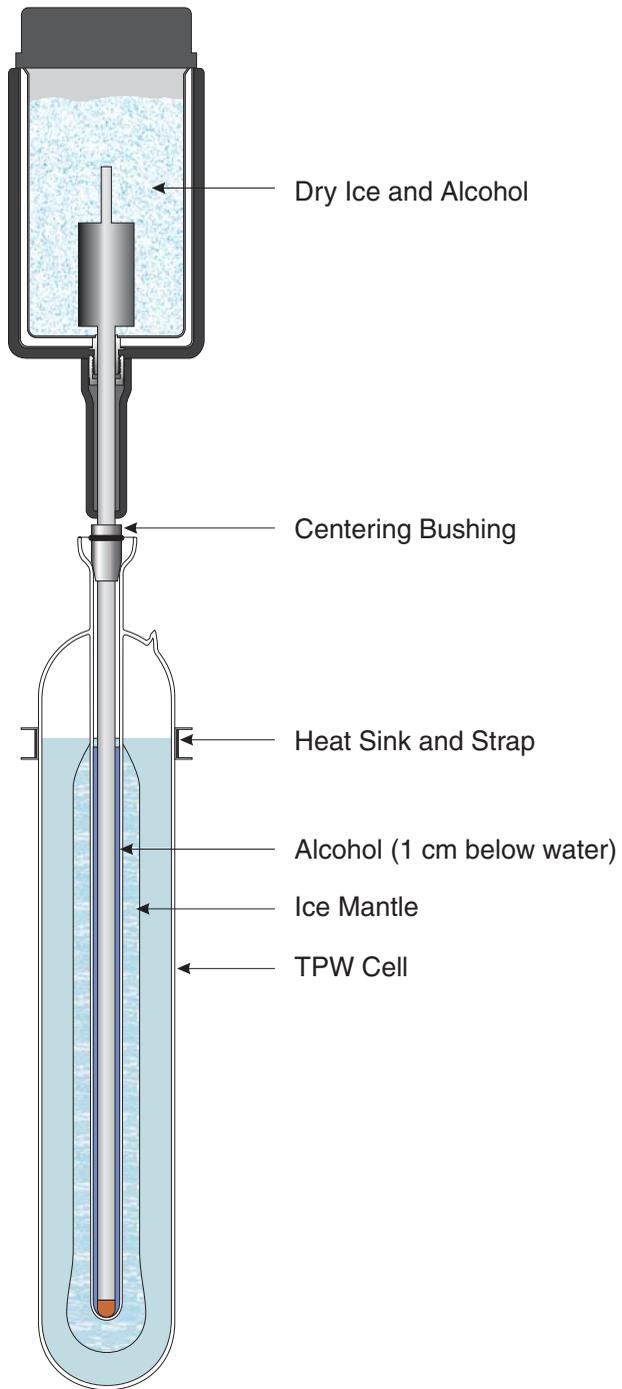
cal container and the water. If the cell is carefully inverted, the true mantle size can be observed through the portion of the cell containing only vapor. This procedure should only be performed while the mantle is still attached to the reentrant well. When the ice mantle becomes sufficiently thick (4 to 10 mm with at least 5 mm at the bottom) the cell may be carefully moved to the maintenance bath to evaporate the remaining dry ice. Allow the mantle to anneal for at least two days to remove the strains, since strains in the ice may depress the actual triple point temperature about 0.2 mK. Applications that do not require as stringent a level of accuracy will not require this delay. If the mantle cracks, it takes at least two days to anneal the mantle.

## **4.2.2 The Heat Pipe Freezing Process**

Hart Scientific has developed a “Quick Stick” to facilitate the formation of an ice mantle with greater ease. Please refer to Model 2031 Quick Stick User’s Guide for details. The instructions for use of the “Quick Stick” in the formation of an ice mantle are as follows (Figure 2):

1. Dry ice is broken into small chunks (less than ¼ inch) appropriate for fitting into the cup.
2. The TPW reentrant well is dried with alcohol and a ¼ inch of alcohol is placed into the bottom. Next approximately 2 cc of finely crushed dry ice is dropped into the bottom of the reentrant well. This helps start the freeze process and prevents super cooling of the water. A small formation of ice is frozen onto the end of the reentrant well initially before the heat pipe is inserted, which helps thicken the ice mantle at the bottom.
3. The dry ice is loaded into the Quick Stick cup and the spaces are filled with ethanol (approximately 100ml). The Quick Stick must be cooling before inserting it into the TPW. Once the cooling cycle has begun, insert it to the bottom of the reentrant well, the radius at the bottom helps center it in the well.
4. After the Quick Stick is inserted carefully into the cell, the gap is filled with ethanol until it is a little below the water level in the cell (about 1 cm). This helps to prevent ice from bridging across the top during mantle formation. A special heat sink is provided that fits around the TPW cell that also helps prevent bridging. Slide the heat sink onto the cell up to the level of the water. Room heat is absorbed and transferred to the water at the surface. Adjust the centering bushing until the heat pipe is centered in the reentrant well. The cell and Quick Stick need to be well supported during this process. Care must be taken not to break the reentrant well during this process or the cell will be ruined. The cell and Quick Stick must be supported separately. The Hart Scientific model 2067-P support kit is available for this purpose.

The freezing process takes care of itself beyond this point. Be sure that there is no ice bridging at the top. One fill of dry ice forms a good mantle in 40 to 60 minutes.



**Figure 2** Freeze an ice mantle using a "Quick Stick"



**WARNING:** Always use extreme care when using liquid nitrogen. Contact can burn skin or damage eyes.

### **4.2.3 Metal Pre-cooled In Liquid Nitrogen Freezing Process**

Pre-cool a few metal rods in liquid nitrogen. Insert the pre-cooled metal rods into the heat transfer liquid in the reentrant well successively. Several insertions will be needed to form an adequate ice mantle.

## **4.3 The Inner Melt**

A very pure ice water interface surrounding the reentrant well is formed by melting a thin layer of ice next to the well. This interface is referred to as the “inner melt”. The inner melt is formed first by pouring a small amount of pre-cooled water or alcohol (below 2°C) into the reentrant well to a level just above the top of the ice mantle. A glass rod, at room temperature, is then inserted into the reentrant well. The glass rod is left in place long enough, a few seconds, to melt the ice mantle free from the reentrant well. Test that the mantle is free by gently rotating the cell and observing that the mantle freely rotates about the axis of the reentrant well. If the mantle does not rotate, warm the rod to room temperature and repeat the process. The inner melt should be done each time the cell is used, and the test for the existence of a free mantle should be carried out regularly during the course of a use of the Cell. Once the mantle has been aged and the ice water interface created, the triple point of water cell is ready to make measurements.

## 5 Maintenance and Life-Time of a TPW Realization

After a short period of time, the ice mantle will reattach to the reentrant well. Pressure can build up in this layer and observed temperatures can be low by as much as  $0.0001^{\circ}\text{C}$ . The mantle must, of course, again be freed by the temporary insertion of a warm rod in the well as described in section 4.3.

The cell should be prepared at least two days prior to its use. The equilibrium temperature in a TPW cell is a little low ( $0.0005^{\circ}\text{C}$ ) immediately after freezing. The reason for this low initial temperature and the subsequent gradual increase during one or two days to a steady value is believed to be connected with structural strains that are produced when the ice is first frozen. Presumably, the strains are relieved with time as the ice anneals. The magnitude of the lower initial temperature and the rate of increase to a steady temperature value is dependent upon the specific technique that is employed in freezing the cell.

A TPW cell with an ice mantle can be preserved for a few months in a well controlled bath or in a Dewar filled with crushed ice with a plastic container between the Dewar and the TPW cell. The temperature uniformity and stability of the bath used to maintain TPW cells should be  $\pm 0.003^{\circ}\text{C}$  or better.

Hart's 7012 and 7312 baths are designed for this purpose. The 7012 bath can accommodate up to four TPW cells and the 7312 bath up to two. According to our experience, the bath temperature should be set at about  $0.003^{\circ}\text{C}$  below the TPW (about  $0.007^{\circ}\text{C}$ ) in order to maintain the TPW for a few months. If the bath temperature is too low, more water in the cell will freeze. If the bath temperature is too high, the ice mantle in the cell will melt gradually. During the first month a bath is used to maintain TPW cells, the ice mantle should be checked daily. Adjust the bath set temperature a little if necessary to obtain the optimal maintenance situation. If an ice bridge is found across the top surface of water in the cell, it must be melted immediately. Otherwise the pressure created from water freezing on the surface might break the cell. After initial adjustments of the bath, the TPW cells in the bath can be used for a few months with little care.

Hart's 2028 Dewar can be used to maintain TPW cell. When a TPW cell is maintained in Dewar with crushed ice, ice will form on the surface of the water in the cell as a result of heat transferred via the vapor to the cold glass, which is often at  $0^{\circ}\text{C}$ . When a cell is not disturbed for several days, the ice will freeze completely across the top surface and must be melted back (e.g. by warming with the hands) before the cell ruptures. Care must be taken to warm the water as little as possible so as not to melt too much of the mantle. The above effects are much reduced by insulating the cell from the ice bath. As mentioned above, this can be done by using a plastic container with foam spacers to ensure that there is an air gap of about 1 cm between the cell and the container wall. A cell stored in this way can be used for many months with very little attention beyond maintaining the ice bath.

## 6 Using the Cell

The following recommendations will improve accuracy and extend the life and usefulness of the cell.

### **Shock Protection**

By placing a small foam rubber sponge in the bottom of the re-entrant well, the shock created when placing the SPRT or other sensor into the re-entrant well will be reduced.

### **Heat Transfer Medium**

There should be fluid in the re-entrant well such as water or alcohol to act as a heat transfer medium from the ice and water interface to the thermometer in the well. A sufficient volume of fluid must be in the re-entrant well to bring the level above that of the cell water when the thermometer is inserted. If desired, a brass or aluminum bushing about 5 cm long may be used to increase the thermal conduction between the thermometer and the ice water interface, which will also reduce external self heating of the thermometer.

### **Thermometer Pre-cooling**

The thermometer should be pre-cooled for at least 5 minutes before insertion to avoid excessive melting of the ice mantle. Insertion into the maintenance bath or separate ice bath is an excellent way to pre-cool the thermometer. The Hart Scientific maintenance bath Models 7012, 7312, and ice bath Dewar Model 2028 have holes for pre-cooling.

### **Ambient Radiation**

Ambient room radiation to the thermometer can elevate its temperature by several tenths of a milli-Kelvin above the temperature of the inner melt even when the cell is completely packed in ice. To provide sufficient radiation shielding and to insure that the desired accuracy is obtained, use an opaque, insulated, covered container.

### **Hydrostatic Pressure Effects**

At a depth  $l$  meters below the liquid surface (where the true triple point temperature exists) the equilibrium temperature  $t$  at the solid-liquid interface is given by  $t = A + Bl$ , where  $A = 0.01^\circ\text{C}$  and  $B = -7.3 \times 10^{-4} \text{ m}^{-1} \text{ }^\circ\text{C}$ . Since the thermometer sensor is not located at the surface, the effects of hydrostatic pressure must be corrected. For example, in the case of an SPRT with the sensor at 242 mm below the surface, the correction is computed as shown below:

$$T = 0.01^\circ\text{C} + (-7.3 \times 10^{-4} \text{ m}^{-1} \text{ }^\circ\text{C}) \times 0.242\text{m} = 0.00982334^\circ\text{C}$$

## 7 Isotopic Composition

Variations in the isotopic content of naturally occurring water can cause detectable differences in the TPW temperature. A difference as large as 0.25 mK in TPW temperatures has been found between ocean water and water obtained from melted polar ice. Neither the SI definition of the Kelvin (the unit of the thermodynamic temperature as  $1/273.16$  of the thermodynamic temperature of the triple point of water) nor the official ITS texts (ITS-90 and IPTS-68) specify the isotopic composition of water for the TPW. Some suggest that documents published by BIPM, such as “Supplementary Information for the International Temperature Scale of 1990” [4] and “Supplementary Information for the IPTS and EPT-76” specify that the isotopic composition of water for TPW should be substantially the same as ocean water.

The followings excerpts are taken directly from “Supplementary Information for the International Temperature Scale of 1990”:

“An operating triple-point cell contains ice, water, and water vapor, all of high purity and of substantially the isotopic composition of ocean water.”

“Variations in the isotopic content of naturally occurring water can give rise to detectable differences in the triple-point temperature. Ocean water contains about 0.16 mmol of  $^2\text{H}$  per mole of  $^1\text{H}$ , 0.4 mmol of  $^{17}\text{O}$ , and 2 mmol of  $^{18}\text{O}$  per mole of  $^{16}\text{O}$ ; this proportion of heavy isotopes is almost never exceeded in naturally-occurring water. Continental surface water normally contains about 0.15 mmol of  $^2\text{H}$  per mole of  $^1\text{H}$ ; water coming from polar snow or glacial ice may occasionally contain as little as 0.1 mmol of  $^2\text{H}$  per mole of  $^1\text{H}$ .

The purifying of water may slightly modify its isotopic composition (distillation normally entails a decrease in the  $^2\text{H}$  content), and the isotopic composition at an ice-water interface is very slightly dependent on the freezing technique.

A decrease of 10  $\mu\text{mol}$  of  $^2\text{H}$  per mole of  $^1\text{H}$  corresponds to a decrease of temperature of the triple point of about 40  $\mu\text{K}$ ; this is the difference between the triple points of ocean water and the normally occurring continental surface water. An extreme, and quite atypical, difference in the triple-point temperatures of naturally-occurring water is about 0.25mK and is that between sea water and water obtained from melted polar ice.”

Recently D. R. White et al has made a deep investigation on the effect of isotopic content on triple-point temperature of water [12]. The follows are some information from White’s paper:

The international science community, through the International Atomic Energy Agency, uses a defined Standard Mean Ocean Water (SMOW) as a point of reference

for studies in the isotopic composition of waters. Measurements of isotopic composition are made with respect to V-SMOW (Vienna-SMOW) and SLAP (Stand Light Antarctic Precipitation), two standard reference materials (waters)

that span the isotopic range of naturally occurring waters. Absolute measurements of the isotope ratios for V-SMOW give:

$$(D/H)_{V-SMOW} = 0.00015576(5),$$

$$(^{18}O/^{16}O)_{V-SMOW} = 0.00200520(45),$$

and

$$(^{17}O/^{18}O)_{V-SMOW} = 0.0003799(8).$$

Variations in isotope ratios are conventionally reported as deviations from V-SMOW:

$$\delta^{18}O = [(^{18}O/^{16}O)_{\text{sample}} - (^{18}O/^{16}O)_{V-SMOW}] / (^{18}O/^{16}O)_{V-SMOW},$$

and similarly for  $\delta D$  and  $\delta^{17}O$ . Usually the results are in the parts-per-thousand range so are expressed as per mil (per thousand, ‰).

For isotopic compositions near V-SMOW, the effect of the isotopes can be approximated by a liner function of the delta values:

$$T_{\text{meas}} = T_{V-SMOW} + A_D \delta D + A^{17}O \delta^{17}O + A^{18}O \delta^{18}O$$

There are few measurements of the isotopic depression constants. The most precise are by Kiyosawa (1991) who measured the melting point elevation of samples of water enriched with D and  $^{18}O$ . The depression constants were found from Kiyosawa's data to be:  $A_D = 628 \pm 6 \mu\text{K}$  and  $A^{18}O = 641 \pm 23 \mu\text{K}$ . The value of  $A^{17}O$  is inferred as  $57 \mu\text{K}$ .

The delta values  $\delta D$ ,  $\delta^{17}O$ , and  $\delta^{18}O$  for precipitation (meteoric waters) are highly correlated. Approximate relationships are  $\delta D = 8 * \delta^{18}O + 0.01$ , and  $1 + \delta^{17}O = (1 + \delta^{18}O) 0.528$ . Therefore, the temperature correction can be predicted from measurements of  $\delta D$  only according to:

$$(T_{\text{meas}} - T_{V-SMOW}) \mu\text{K} = 712 \times \delta D - 0.8$$

A great effort has been made at Hart to reduce the uncertainty of TPW due to variations in the isotopic composition of water. We try to make the final isotopic composition of water in a Hart TPW as close to V-SMOW as possible. Because the isotopic composition of water will change during each operation of the manufacturing process (distill and degas), we should pay attention not only to the isotopic composition of the original water, but also to the manufacturing technique. Now we are glad to announce that the isotopic composition of water in Hart TPW cells is nearly identical to V-SMOW. The actual isotope ratios of water in a Hart TPW cell are as the follows:

$$\delta D = 0 \pm 0.010 \text{ (10‰)}$$

$$\delta^{18}O = 0 \pm 0.001 \text{ (1.0‰)}$$

The uncertainty from the isotopic deviation and variation of water in Hart TPW cells is estimated to be less than  $7 \mu\text{K}$  ( $< 0.007 \text{mK}$ ). An isotopic composition analysis report (sampling analysis) is attached in the TPW certificate. The water sample used for the analysis was directly taken from the final TPW cell after

degas and sealing process. As a matter of course, the water used in TPW cell manufacturing process is analyzed every month.

In order to reduce the uncertainty further, an individual isotopic composition analysis for a TPW cell is available. Hart provides two options:

- 1) When you order a TPW cell, you can order a water sample (about 10 ml in an ampoule) at the same time. The water sample was directly taken from the final TPW cell after the degas and sealing process. So the isotopic composition of the water sample is exactly the same as the one in the TPW cell. You can send the water sample to the laboratory of your choice to get an isotopic analysis. The actual isotopic composition of the water in the TPW cell will be known more accurately. A mini correction for the isotopic composition can be made if necessary. In this way the uncertainty component from the isotopic composition might be reduced to about 3  $\mu$ K (Model No. 5901-SMPL).
- 2) You can order an analysis report with a TPW cell. Hart will send a water sample (water is taken same as option 1) to a laboratory of our choice for the isotopic analysis the report will be delivered along with the cell (Model No. 5901-ITST).

## 8 Care of Your TPW Cell

The TPW cell is an extremely delicate device. Great care must be taken in handling, using, and transporting the cell. The glass outer shell is easily broken. It is suggested that the TPW cell be kept in the vertical position during transportation. Avoid violent vibration and jarring during transportation because TPW cells can be broken by the shock of the water hammering against the cell walls. The lack of cushioning air in the cell allows the water vapor to convert instantly to liquid water such that the glass receives the full impact of the liquid mass in motion. This explains the typical clicking sound of an airless cell as the water in the cell is gently rocked back and forth. If the cell does not produce a water hammer, the cell may have a leak. The surrounding temperature during transportation and storage should be above 0°C. It is very hazardous to the TPW cell to be exposed to an area where the temperatures are or can be below 0°C. Rapid freezing of the water in a TPW cell will break the cell.

Never allow an ice bridge (ice freezes completely across the top surface in the cell) to form across the top surface of water in the cell. If an ice bridge forms on the top in a TPW cell, it should be melted immediately; otherwise the pressure built from water freezing below the top will break the cell. Check the TPW cell regularly during maintenance in a bath or Dewar. If a TPW cell is preserved in very cold environment, the ice mantle will grow. As soon as the ice mantle touches the outer shell, the cell will rupture in a short period of time.

## 9 REFERENCES

1. 10th General Conference on Weights and Measures (10th CGPM, 1954)
2. 3th General Conference on Weights and Measures (13th CGPM, 1967-1968), Resolutions 3 and 4, p. 104
3. Preston-Thomas, H. "The International Temperature Scale of 1990 (ITS-90)", *Metrologia*, Vol. 27, p. 3–10 (1990); *ibid.* p. 107
4. BIPM, "Supplementary Information for the International Temperature Scale of 1990", 1990
5. Mangum, B.W., Furukawa, G.T., Guidelines for Realizing the International Temperature Scale of 1990 (ITS-90), NIST Technical Note 1265, U.S. Government Printing Office, Washington, D.C. 20402, Aug. 1990
6. Schooley, James F., *Thermometry*, CRC Press, Boca Raton, Florida 33431, Chap. 3, p.40 (1986)
7. Riddle, J.L. Furukawa, G. T. and Plumb, H. H., *Platinum Resistance Thermometry*, NBS Monograph 126, U.S. Government Printing Office, Washington, D.C. 20402, (Apr. 1972).
8. McLaren, E. H., "The Freezing Points of High Purity Metals as Precision Temperature Standards, I. Precision Measurements with Standard Resistance Thermometers", *Can. J. Phys.* Vol. 35, 78 (1957).
9. Berry, R. J., "The Temperature-Time Dependence of the Triple Point of Water", *Can. J. Phys.* Vol. 37 (1959).
10. Furukawa, G. T. and Bigge, W. R., "Reproducibility of Some Triple Point of Water Cells", *the American Institute of Physics*, Vol. 5. Part 1 , p. 291 (1982).
11. Stimson, H. F., *Precision Resistance Thermometry and Fixed Points, Temperature, Its Measurement and Control in Sci. and Ind.*, Reinhold Pub. Corp., New York, NY, Vol. 2, Chap. 9, p. 141 (1955).
12. White, D. R., Dransfield, T. D., Strouse, G. F., Tew, W. L., Rusby, R. L., and Gray, J. "Effects of Heavy Hydrogen and Oxygen on the Triple-Point Temperature of Water", *Temperature, Its Measurement and Control in Science and Industry, Volume 7*, edited by Dean C. Ripple, American Institute of Physics, p. 221-226 (2002).
13. Hill, K. D., "Is there a long-term drift in triple point of waters?" *Metrologia* 38, 79-82, (2001).