A TECHNICAL GUIDE AND STANDARD FOR THE QUALIFICATION AND USE OF WATER TRIPLE POINT CELLS

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RATIONALE

A number of guides exist or have been proposed for describing, qualifying and using cells which realize the triple point of water for the calibration of thermometers. To our view, some of these are philosophically elegant but lack details about practice, while others dwell heavily on practice but neglect important arguments. We offer the following, which we hope manages balance.

ABSTRACT AND INTRODUCTION

The triple point of water is the most important defining thermometric fixed point used in the calibration of thermometers to the International Temperature Scale of 1990 (ITS-90) for practical and theoretical reasons [1]

Triple points of various materials (3-phase equilibria between solid, liquid and vapor phases) are independent of ambient pressure.

The triple point of water is the sole realizable defining fixed point common to the Kelvin Thermodynamic Temperature Scale (KTTS) and the ITS-90. Its assigned value on these Scales is 273.16 K (0.01 C).

The triple point of water is one of the most accurately realizable of the defining fixed points. Properly used, the triple point of water temperature can be realized with an accuracy of +0.0 C, -0.00015 C. (For comparison, it is difficult to prepare and use an ice bath with accuracy better than 0.002 K.)

The triple point of water is the temperature to which the resistance-ratios ($W = R(t2)/R(t1)$) given in Standard Platinum Resistance Thermometer calibrations are referred. In the ITS- 90, t1 is 0.01 C.

The triple point of water provides a useful check point in verifying the condition of thermometers. A measurement at the triple point of water made immediately upon the thermometer's return from calibration will reveal a shift which has occurred in transportation. Valuable history of the thermometer's stability is obtained if a record of the measurement results is placed on a control chart each time the thermometer is measured at the triple point of water.

1. Scope

1.1 This guide describes the nature of a representative commercial triple point of water cell and provides a method for realizing the triple point of water phase equilibrium preparatory for the cell's use in calibrating thermometers. A test for insuring the integrity of the cell is given. Precautions for handling the cell to avoid breakage are included.

1.2 This Guide presents a procedure for placing the triple point of water cell into service and using it as a thermometer calibration standard.

1.3 The reference temperature obtained is that of a fundamental state of pure water, the equilibrium between the solid, liquid and vapor phases in co-existence. The cell is not subject to calibration.

1.4 The cell may be qualified as capable of representing the three-phase equilibrium state of pure water by comparison with a bank of similar cells of known history, and is usually so qualified by its manufacturer. (ISOTECH cells are so qualified and certified). Continued accuracy depends upon physical integrity, which may be verified easily by techniques given in (3) below.

2. Apparatus

2.1 The essential features of a triple point of water cell are shown in Fig. 1. A glass flask is nearly filled with water and permanently sealed. A coaxial re-entrant well is provided to receive the device that is to be exposed to the reference temperature.

2.2 The water used as the reference medium must be very pure, condensed directly into the cell. It should have essentially the isotopic composition of naturally occurring water. (Extreme variations in isotopic composition of naturally occurring water can affect the realized temperature by as much as 0.05 mK.)

2.3 A portion of the water is frozen so as to form a mantle of ice that surrounds the well.

2.4 The temperature of the triple point of water realized in the cell is independent of the external environment; however to keep the ice mantle from melting quickly, it is necessary to minimize heat flow to the cell. This may be done by immersing the cell in an ice-and-water bath that maintains the full length of the cell at or near the freezing point of water, to a depth that will assure that bath water flows into the well. Commercially-available automatic-maintenance baths (ISOTECH Model 18233 Water Triple Point Maintenance Bath) use thermoelectric modules for convenient cooling. In these baths the triple point equilibrium, once established, can be maintained for many months.

3. Assurance of integrity

3.1 The temperature realized within the triple point of water cell is an intrinsic property of the solid and liquid phases of water under its own vapor pressure. If the water triple point conditions are satisfied, the temperature which the cell defines is realized with higher accuracy than any measurement which can be made of it.

3.2 The accuracy depends upon continued physical integrity of the seal and the walls of the cell to exclude environmental air.

3.3 Initial and continued physical integrity is confirmed by the following procedures:

3.3.1 Remove all objects from the thermometer well.

3.3.2 With the cell initially upright and the well opening upward, slowly invert the cell. As the cylindrical axis passes through horizontal, and the water within the cell strikes the end of the cell uncushioned by air, a sharp clicking sound should be heard. The click results from the collapse of vapor bubbles, and is evidence that the gas in the cell is water vapor and not excess air. The vapor pressure of water at the triple point is about 600 Pa (4.5 torr). The click is more audible when the cell is cold.

3.3.3 Continue to tilt the cell until the vapor bubble is entirely captured in the handle. The vapor bubble should compress to a volume no larger than about 0.3 cm3 (4 mm dia), or even vanish, as it is compressed by the weight of the water column. The bubble test is more sensitive when the cell is at room temperature.

3.3.4 Any cell which has been qualified by comparison with cells of known integrity as in (1.4) and which passes the tests of (3.3.2) and (3.3.3) is qualified as a triple point of water cell to realize the ITS-90. No calibration is required or indeed possible, although certification of a cell qualified according to (1.4) is possible.

(There have been reports that water triple point cells may eventually lose accuracy after long storage (e.g., 20 years) as the water leaches ions from the wall of the borosilicate glass. This effect is said to be slowed by a factor of at least 2 if the cells are stored, when not in use, in the vicinity of 0 C rather than at room temperature. This may be done in a suitable bath such as ISOTECH'S Model 18233.)

3.3.5 Any cell which fails to pass the tests of (3.3.2) and (3.3.3) is not qualified for use as a triple point of water cell.

5. Realization of the triple point of water

The ice mantle that is required to realize the triple point of water can be established in several ways, to produce the same result. A common procedure is as follows:

5.1 Empty the thermometer well and remove any stopper, solids or liquids.

5.2 Immerse the cell completely in a bath of water and crushed ice to chill it to near 0 C.

5.3 Remove the cell from the bath. Slowly invert the cell to drain liquid from the well.

5.4 Fill the well with denatured alcohol to remove traces of water, then drain it to empty the well of alcohol.

5.5 Place about 1 cm3 of denatured alcohol in the well to serve as a heat-transfer medium during the freezing of the ice mantle.

5.6 Fill the well with crushed dry ice obtained from a block or by expansion from a syphon-tube tank of liquid CO_2 into a collecting bag (do not vent the syphon tube directly into the cell).

5.7 Observe the interface between the surface of the well and the water that surrounds it. The well should suddenly be coated with fine needles of ice frozen from the supercooled water.

5.8 Replenish the Dry Ice as it sublimes, maintaining the well essentially full, until a continuous ice mantle is formed on the surface of the well as thick as desired (usually 4 to 10 mm). The mantle may appear thicker than its actual thickness because of the lenticular shape of the cell and the refractive index of water. The actual thickness may be estimated by viewing the cell from the bottom or inverted. When the mantle attains the desired thickness, remove any remnant of Dry Ice and/or alcohol from the well.

Caution: the mantle should never be allowed to grow so as to completely bridge the space between the well and the inner wall of the cell, since the expansion of the ice may break the cell. In particular, note whether there is bridging at the surface of the water under the vapor space. If a bridge develops, melt the bridge by warming locally with the hand.

5.9 Free the ice mantle from the outer surface of the well by performing an "inner melt". To do this, briefly insert a rod of aluminum or glass at room temperature into the well. Remove the rod and give the cell a quick but gentle axial twist, while observing the ice mantle. If the mantle is properly free, it will spin freely about the well. The existence of a liquid water film between the mantle and the well is essential to the proper realization of the triple point, and should be assured prior to calibrating thermometers.

5.10: A method alternative to 5.2 through 5.9 (commonly called the "mush" method) may be used to realize the water triple point without the use of dry ice [2]. This method forms a sheath of ice on the outer wall of the cell. It requires a bath which fits the cell and is capable of control at -7 C and at 0 C, such as the ISOTECH Oceanus block bath).

> 5.10(a) Place the water triple point cell in the bath with the controller set at -7 C. Allow the cell to cool thoroughly to this temperature (~2 hours). Assure that the bath and cell are not shaken or vibrated during this period.
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> 5.10(b) Remove the cell from the bath and, holding it vertically (with the thermometer well upward) shake it gently. If the cell is cool enough, and if the shake is sufficient, a "mush" of ice will be seen to form throughout the contained water.
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> 5.10(c) Return the cell to the bath at -7 C, and immediately set the bath controller to 0 C. Check in half an hour to see if a suitable ice mantle has formed on the inside surface of the outer wall of the cell. If not, return the cell to the bath for an additional period of time. It is not necessary to free the ice mantle as in (5.9) since there already exists a layer of liquid water between the ice and the thermometer well.
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> 5.10(d) Proceed to 5.11. Observe the CAUTION of 5.8

5.11 When the ice is first frozen, it is under strain and the cell temperature can be as much as 0.5 mK below the triple point temperature. This strain will relieve in a few hours. After a full day of relaxation, the triple point temperature may be realized accurately.

5.12 Examine the cell at intervals of a few days to assure that the mantle does not continue to grow and that ice bridges do not form.

6. Use of the Triple Point of Water Cell

6.1 Determine that the triple point of water cell meets the requirements of (3.3.4).

6.2 Assure that the ice mantle is well-formed, covers the bottom of the well and also most of the vertical wall, and spins freely about the well (except in the "mush" method).

6.3 Chill any thermometer or test object which is to be inserted into the well by immersing it in water at a temperature near 0 C prior to placing it in the well. This will prolong the duration of the triple point state.

6.4 Immerse the cell in the maintenance bath to such a depth that bath water flows into the well. Avoid the presence in the well of ice particles from the maintenance bath, which would cause unwanted depression of the well temperature.

6.5 Immerse the chilled thermometer or test object into the well, and allow the system to equilibrate.

6.6 With the triple point established, the temperature within the cell is independent of atmospheric pressure. However the true triple-point temperature is realized only at the solid-liquid-vapor interface. At the location of the sensing element of the thermometer, the temperature is influenced by the hydrostatic head pressure of the internal water column. For the most accurate measurements a correction must be made of -0.73 mK per meter of water height above the thermal center of the sensing element of the thermometer. For a thermometer inserted in a typical cell to a depth of 300 mm below the upper surface of the water, the correction is about -0.2 mK.

Caution: care must be taken that the thermometer or test object does not conduct significant heat to or from the sensing element in the well.

Test objects of high thermal conductivity, such as some metal-sheathed industrial thermometers, may conduct ambient heat to the sensing element along their sheaths. For these it is advisable to insert them fully into the well and to maintain the emergent portion outside the well as close to 0 C as possible.

Transparent test objects, such as quartz-sheathed thermometers, may transmit radiant energy to the sensor from radiation sources, such as fluorescent lights, in the laboratory environment. For these, it is advisable to cover the emergent portion of the thermometer with an opaque cover such as a black velvet cloth.

7. Key words

Triple point of water, water triple point cell, calibration, qualification, fixed point, defining fixed point, intrinsic property, International Temperature Scale of 1990 (ITS-90), Kelvin Thermodynamic Temperature Scale (KTTS), Standard Platinum Resistance Thermometer (SPRT)

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[1] H. Preston -Thomas, The International Temperature Scale of 1990 (ITS-90) *Metrologia* 27, 3-10 (1990)

[2] This method is due to the National Physical Laboratory (England) and is described on page 272 of *Temperature, Its measurement and control in science and industry*, Vol 5, ed Schooley, American Institute of Physics (1982).

About the Author

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