JARRETT-ISOTECH
WATER TRIPLE POINT CELLS
User Maintenance Manual/Handbook

Isothermal Technology Limited, Pine Grove, Southport, PR9 9AG, England
Tel: +44 (0)1704 543830 Fax: +44 (0)1704 544799 Internet: www.isotech.co.uk E-mail: info@isotech.co.uk

The company is always willing to give technical advice and assistance where appropriate. Equally, because of the programme of continual development and improvement we reserve the right to amend or alter characteristics and design without prior notice. This publication is for information only

CONTENTS

ISOTECH

⚠ CAUTIONARY NOTE

ISOTECH PRODUCTS ARE INTENDED FOR USE BY TECHNICALLY TRAINED AND COMPETENT PERSONNEL FAMILIAR WITH GOOD MEASUREMENT PRACTICES.

IT IS EXPECTED THAT PERSONNEL USING THIS EQUIPMENT WILL BE COMPETENT WITH THE MANAGEMENT OF APPARATUS WHICH MAY BE POWERED OR UNDER EXTREMES OF TEMPERATURE, AND ARE ABLE TO APPRECIATE THE HAZARDS WHICH MAY BE ASSOCIATED WITH, AND THE PRECAUTIONS TO BE TAKEN WITH, SUCH EQUIPMENT.

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 vapour phases) are independent of ambient pressure and have zero degrees of thermodynamic freedom. The temperature of the Water Triple Point is a constant of nature.

The Triple Point of Water is the sole defining Fixed Point common to the Kelvin Thermodynamic Temperature Scale (KTTS) and the ITS-90. Its assigned value on these Scales is 273.16K (0.01°C).

The Triple Point of Water is one of the most accurately realizable of the defining Fixed Points.
The temperature of the Triple Point of Water is more accurate than any measurement of it can be made. Properly used, the Triple Point of Water temperature can be realized with an accuracy of $\pm 20\mu$K of ITS-90. (For comparison, it is difficult to prepare and use an ice bath with accuracy better than 0.002K)

The Triple Point of Water is the temperature to which the resistance-ratios $W = R(t_2)/R(t_1)$ given in Standard Platinum Resistance Thermometer calibrations are referred. On the ITS-90, t_1 is 0.01°C without uncertainty.

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, compared to the Water Triple Point resistance reported by the calibrating Laboratory, 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 transferred to a control chart each time the thermometer is measured at the Triple Point of Water. If the Triple Point resistance remains unchanged with use, no re-calibration of the thermometer is necessary.

1. Scope

1.1 This guide describes the nature of a Jarrett-Isotech Triple Point of Water Cell and provides a method for realizing the Triple Point of Water phase equilibrium for use in calibrating thermometers. Tests for verifying the integrity of the Cell are 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.

CAUTION: If an A11 type cell is being used, at no time should the McLoud Gauge (bent portion of glass) be used as a handle to hold or carry the cell. When handling all cells this should always be done by holding the main body of the cell. If this is not possible because the cell is in an ice/water bath then it should initially be picked up by the straight portion of the re entrant tube until enough of the main body is exposed after which the main body should be handled and supported.

NOTE: This Guide specifically disclaims any intent to describe health and safety consideration in its use.

It is assumed that the user of this Guide and the apparatus which it describes is knowledgeable in the handling of Laboratory glassware and of very cold materials (such as dry ice or liquid nitrogen) and has taken action to establish policies with regard to health and safety and to any legal or regulatory standards which are appropriate.

1.3 The reference temperature obtained is that of a fundamental state of pure water, the equilibrium between the solid, liquid and vapour phases in co-existence.

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 filled with water, purged of all air and permanently sealed. A coaxial re-entrant tube 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. It must have essentially the isotopic composition of naturally occurring ocean water.

2.3. A portion of the water is frozen so as to form a mantle of ice that surrounds the re entrant tube. An "inner melt" is created to provide a thin film of water between the ice mantle and the re entrant tube.

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 the maintenance bath water does not flow into the re-entrant tube. 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 weeks. With less equipment cost and considerably more effort, the equilibrium may be maintained for a few days in a water-and-ice-filled dewar flask where the ice depth is larger than the length of the cell.

3. Assurance of Integrity

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 vapour pressure. If the Water Triple Point conditions are satisfied, the temperature which the Cell defines is realized within some $\pm 20\mu$K of the ITS-90 value.

3.2. The accuracy depends upon the purity and composition of the water in the Cell and the continued physical integrity of the Cell to exclude environmental air.

3.3. Initial and continued physical condition of the Cell may be confirmed by the following procedures:

3.3.1. [Verifying the purity of the water in the Cell]:

This test for the purity of water in the Cell relies on the fact that impurities are soluble in the liquid phase of water and are insoluble in the solid phase, so that, as the ice mantle is frozen away from the re entrant tube, these impurities are rejected into the remaining liquid phase surrounding the ice mantle, enriching the liquid phase surrounding the ice mantle with impurities.

3.3.2. With the water in the Cell entirely liquid, prepare a fresh ice mantle using the procedure of section 4.1. Assure that the thickness of the ice mantle is about ½ the distance from the outer diameter of the re entrant tube to the inner wall of the outer glass shell. This must be estimated from experience, since the lenticular shape of the Cell distorts the image of the mantle, or by inverting the Cell to observe the mantle thickness.

NOTE: For the following test, do not invert the Cell during Steps 3.3.3 and 3.3.4. as this will invalidate the test, requiring that the ice in the Cell be completely melted and a fresh mantle formed.

3.3.3. Form an inner melt, following the procedure of Section 4.2. The water of the inner melt will be water which has been further purified by the freezing procedure described in 3.3.1.

3.3.4. Using the procedures described in Section 5, measure the temperature in the re entrant tube of the Cell (Note: the measurement must be capable of determining a difference of at most 0.000,01°C, 10μK).

3.3.5. Gently invert the Cell several times, so as to mix the pure water of the inner melt with the impurity-enriched liquid water surrounding the ice mantle. The mantle should be free to float, drawing in water from the space outside the mantle and rejecting it when the Cell is returned to the upright position.

3.3.6. Using the same procedure as 3.3.4, measure the temperature again. The temperature difference between 3.3.4 and 3.3.6 should be not more than $\Delta t = 0.00003°C$ (30μK).

3.3.7. [Verifying the integrity of the Cell]:

Remove all objects from the re entrant tube and use a cell which is fully liquid, i.e. with no ice inside.

3.3.8. With the Cell initially upright and the re entrant tube 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 un-cushioned by air, a sharp clicking sound should be heard. The click results from the collapse of vapour bubbles and is evidence that the gas in the Cell is water vapour and not excess air. The vapour pressure of water at the Triple Point is about 600 Pa (4.5 torr). The click is more audible when the Cell is at room temperature.

3.3.9. Continue to tilt the Cell until the vapour bubble is entirely captured in the McLeod pressure gauge (bent portion of an A11 type cell or extended fill tube of a B11 type cell). The vapour bubble should compress to a volume of approximately $0.3cm^3$ (4mm φ), 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 (See Fig. 2(a) and Fig. 2 (b).

3.3.10. Any Cell that has been qualified by comparison with Cells of known integrity as in (1.4) and which passes the tests of (3.3.6) and (3.3.9) is qualified as a Triple Point of Water Cell to realize the ITS-90.

3.3.11. Any Cell that fails to pass the tests of (3.3.6) and (3.3.9) is not qualified for use as a Triple Point of Water Cell.

NOTE: (There have been reports that Water Triple Point Cells may eventually lose accuracy after long storage (e.g. 10 to 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 a 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. Owners of Cells more than 10 years old may wish to consider the purchase of at least one new Jarrett-Isotech Cell (3 provide better statistics) to act as reference).

Isotech now offers cells made from quartz glass whose life is estimated at 100 years!

4. Realization of the Triple Point of Water

The ice mantle that is required to realize the Triple Point of Water can be established by the following procedure. A number of techniques have been published, some of which do not permit the test of 3.3.1 - 3.3.6. Isotech recommends the following:

4.1(a). Empty the re entrant tube and remove any solids or liquids.

4.1(b). Immerse the Cell completely in a bath of water and crushed ice to chill it to near 0°C.

4.1(c). Remove the Cell from the bath. Slowly invert the Cell to drain liquid from the re entrant tube.

4.1(d). Fill the re entrant tube with denatured alcohol to remove traces of water, and then drain it to empty the re entrant tube of alcohol.

4.1(e). Re fill the re-entrant tube with denatured alcohol to serve as a heat-transfer medium during the freezing of the ice mantle.

4.1(f). Place a solid stainless steel rod pre chilled in liquid nitrogen into the re entrant tube of the cell.

4.1(g). Observe the interface between the surface of the re entrant tube and the water that surrounds it. The ice mantle should slowly start to form around the re entrant tube.

4.1(h). After a few minutes remove the rod and replace with another, or alternatively at this stage use an Isotech Model 452 ice mantle maker that has been filled with liquid nitrogen. Continue to build the ice mantle until the desired thickness is achieved (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 alcohol from the re entrant tube.

CAUTION: (The mantle should never be allowed to grow so as to completely bridge the space between the re entrant tube 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 vapour space. If a bridge develops, melt the bridge by warming locally with the hand or use a ice bridge prevention collar).

4.2. Free the ice mantle from the outer surface of the re entrant tube by performing an "inner melt". To do this, briefly insert a rod of Aluminium or glass at room temperature into the re entrant tube. Remove the rod and tilt the cell gently from the vertical (only a slight tilt is required, too far will enable mixing of the outer impurity - rich water with the pure inner melt water) while observing the ice mantle.

If the mantle is properly free, it will spin freely about the re entrant tube. The existence of a liquid water film between the mantle and the re entrant tube is essential to the proper realization of the Triple Point and should be assured prior to calibrating thermometers.

NOTE: When the ice is first frozen it is under strain and the Cell temperature can be as much as 0.5mK below the Triple Point temperature. This strain will relieve in a few days. After seven days of relaxation, the Triple Point temperature may be realized accurately.

4.3 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.

5. Use of the Triple Point of Water Cell

5.1. Determine that the Triple Point of Water Cell meets the requirements of 3.3.4 and 3.3.9.

5.2. Assure that the ice mantle is well-formed, covers the bottom of the re entrant tube and also most of the vertical wall and spins freely about the re entrant tube after the formation of the "inner melt" by the procedure of 4.2.

5.3. Chill any thermometer or test object which is to be inserted into the re entrant tube by immersing it in water at a temperature near 0°C prior to placing it in the re entrant tube. This will prolong the duration of the Triple Point state.

5.4. Immerse the Cell in the Maintenance Bath to such a depth that bath water does not flow into the re entrant tube. Fill the re entrant tube with pre chilled water.

NOTE: If the Cell is maintained in a Dewar flask containing water and ice, avoid the presence in the re entrant tube of ice particles from the Dewar flask, which would cause unwanted depression of the cell temperature.

5.5. Immerse the chilled thermometer or test object into the re entrant tube and allow the system to equilibrate.

5.6. 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-vapour 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 -0.73mK per metre of water height above the thermal centre of the sensing element of the thermometer. For a thermometer inserted in a typical Cell to a depth of 300mm below the upper surface of the water, the depression is about -0.2mK.

CAUTION: [Care must be taken that the thermometer or test object does not conduct significant heat to or from the sensing element in the re entrant tube.

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 re entrant tube and to maintain the emergent portion outside the re entrant tube 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 an opaque black velvet cloth.

ISOTECH

KEY WORDS

Triple Point of Water, Jarrett-Isotech 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).

NOTES AND REFERENCES

Further information about the Water Triple Point may be found in the literature. We suggest the following references:

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

For additional information on the Water Triple Point and its realization, you may wish to consult the following:

The Measurement of Some Thermal Properties of Water, H. F. Stimson, Isotech Journal of Thermometry*, Vol. 5 No. 2 (1994)

Do you know where your Ice Point is tonight?, H. E. Sostmann, Isotech Journal of Thermometry, Vol. 5 No. 2 (1994)

Reproducibility of some Water Triple Point Cells, G. T. Furukawa, W. R. Bigge, Isotech Journal of Thermometry*, Vol. 6 No. 1 (1995)

Standard Guide for the Use of Water Triple Point Cells, ASTM E-1750-95, which can be purchased from American National Standards Institute (ANSI) and other National Standards Institutes.

*indicates a reprint from the original publication.

(Back issues of the Isotech Journal of Thermometry may be obtained from Isothermal Technology Ltd., Pine Grove, Southport, PR9 9AG, Merseyside, England. Telephone +44 1704 543830, Fax +44 1704 544799

To assure that you obtain the World's best Triple Point of Water Cell, use the trade mark name Jarrett-Isotech; Cells whose manufacture began in 1954 and were fully evaluated by Furukawa and Bigge in 1982 and BIPM CCT-K7 in 2006.

Figure 1: Triple Point of Water Cells with re entrant tubes for Platinum Resistance Thermometers. The cells contain pure air-free water

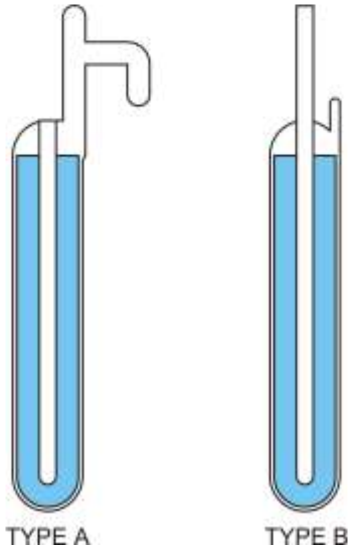

Figure 2: Procedure for entrapping gas bubbles in Triple Point of Water Cells

Type A: Position cell as in (a) gently tip bottom of cell upward as in (b) entrapping gas.
Type B: Position cell as in (c) gently tilt bottom of cell upward to position (d) any further tilting will cause the bubble to escape