AN APPARATUS FOR THE APPROXIMATION OF THE TRIPLE POINT OF ARGON

Thomas Wiandt

Hart Scientific, American Fork, Utah, USA

ABSTRACT

SPRT calibration over the ITS-90 sub-range of 83.8058 K to 273.16 K requires measurement at three defining fixed points—the triple points of water, mercury, and argon. Cells and apparatus are commercially available for the realization of these defining fixed points. Several factors have resulted in the widespread implementation of only two of these defining fixed points—the triple points of water and mercury. Comparison calibration in a simple liquid nitrogen comparison apparatus is typically substituted for the triple point of argon. For this substitution to be useful, the measurement uncertainty achievable in the comparison system must approach that achievable in the argon system. Several challenges arise. At one standard atmosphere, the normal boiling point of liquid nitrogen is approximately 77.36 K, about 6.4 K below the lower limit of the sub-range, resulting in extrapolation of the reference thermometer. Additionally, the design of the comparison apparatus affects the uncertainties attainable. Finally, boiling points are highly influenced by environmental conditions, further complicating the measurements. Metrologists at Hart Scientific have developed and built an apparatus intended to attain sub-millikelvin uncertainties using comparison techniques in liquid nitrogen. The apparatus was designed to reduce effects from conduction and is capable of self-pressurization to increase the boiling point to a value closer to the argon triple point. This paper will discuss the apparatus, techniques, and results of this effort.

1. INTRODUCTION

The triple point of argon is one of the defining points of the ITS-90 and is used along with the triple points of mercury and water to calibrate SPRTs over the sub-range 83.8058 K to 273.16 K [1]. Cells and apparatus for realization are available commercially and are in use throughout the world. Many laboratories substitute comparison calibration for one or more of these fixed points. Conventional refrigerated calibration baths can be used to reach temperatures approximating the triple points of mercury and water, but not the triple point of argon. Typically, a dewar flask that is open to atmosphere along with a low oxygen or oxygen free copper block submerged in liquid nitrogen or argon is used as the comparison device. Some designs incorporate a manifold with tubes for protection of the SPRTs while others allow the SPRTS to come into direct contact with the cryogen and copper block. Such devices utilize the boiling point of the cryogen and can be very stable when used carefully. Unfortunately, the temperatures realized using such a device cannot be adjusted and vary with atmospheric pressure and elevation. Furthermore, the boiling points of nitrogen and argon miss the triple point of argon by several kelvins at minimum. We decided to construct a device that will allow the boiling point temperature to be adjusted through adjustment of the pressure of the system. Similar apparatus has been used for realization of cryogenic triple points [2]. Our investigation focused primarily on the feasibility of the device for comparison measurements and the benefits, if any, of performing the comparison at a temperature closer to the triple point of argon.

2. THEORY

The normal boiling point of liquid nitrogen is approximately 77.35 K at a pressure of 101.325 kPa [3]. Our laboratory is located in Utah, USA at approximately 1350 meters elevation [4]. At this elevation, atmospheric pressure drops to approximately 87.0 kPa and the predicted value for the boiling point of nitrogen is approximately 76.12 K [5]. During routine operations, we observe temperatures in the

range of 76.0 K to 76.5 K. The increase in pressure required to reach the triple point of argon is relatively modest and is easily attained by utilizing the gas released during boiling. However, for sub-millikelvin comparisons to be successful, the pressure must be held quite stable during the measurements. Specialized apparatus and techniques will be required to achieve this goal. In order to gain a more complete understanding regarding the capability of the apparatus and comparison technique, we decided to perform measurements at the temperatures shown in Table 1 [5].

Table 1: Comparison Temperatures

Target	T_{90} (K)	Pressure Required (kPa)
NBP of nitrogen at 1350 meters elevation	76.12	87.0 (open)
NBP of nitrogen at 0 meters elevation	77.35	101.3
Argon triple point	83.8058	204.20
NBP of argon at 0 meters elevation	87.29	281.52

3. CRYOSTAT DESCRIPTION

The special cryostat was designed and constructed in our laboratory. It consists of a gold-plated, low-oxygen copper block suspended in a super-insulated dewar flask. The dewar flask is sealed using silicone o-rings with fill and purge valves. The pressure of the vessel is regulated with a precision backpressure regulator. A heat exchanger is placed between the vessel and the regulator to prevent regulator freezing. A Hart Scientific Model 5686 capsule SPRT inserted into the bottom of the copper block is used as the reference thermometer. The electrical leads are thermally anchored at several points. Long stem SPRTs enter the vessel through a manifold with six re-entrant tubes. The manifold is connected to a rough vacuum pump and a helium supply. The level of cryogen is monitored by temperature sensing diodes placed at several depths. Absolute pressure transducers are used to monitor the pressure of both the manifold and vessel. The transducers are interfaced with amplifiers and digital displays calibrated in kPa. Additionally, the vessel transducer is connected to an RS-232 interface for ease of vessel pressure data collection. Refer to Figure 1.

4. CRYOSTAT OPERATION

The cryostat is operated by first removing ambient air from the manifold through repeated evacuation and refilling with He gas. A slight positive pressure of He gas is maintained during use. Second, the fill and purge valves are opened and the vessel is filled with LN_2. Initially, the filling is done slowly to avoid thermally shocking the reference SPRT. After the SPRT is submerged the filling rate is increased. The diodes are switched on in turn to indicate the depth of LN_2. The voltage drop across the diode will change from approximately 0.9 V at ambient conditions to 1.2 V when fully submerged. When energized, the diodes are forward biased with approximately 75mA of current. The high current causes significant self-heating resulting in an immediate decrease in voltage when the LN_2 falls below the diode and the diode becomes exposed. This technique provides a resolution of about 2 mm at the location of a diode. If the LN_2 level drops below the uppermost diode before the temperature has stabilized, the vessel is topped off before proceeding. The power to the diodes is switched off when the uppermost diode indicates that the vessel is full. Next, using the backpressure regulator, the pressure is set to the value corresponding to the temperature desired. The gas released during boiling of the LN_2 produces the pressure; consequently, pressure stabilization takes a few minutes. Because the system is well insulated, the temperature increases very slowly after pressure stabilization has been achieved. To accelerate the increase in temperature, two 25 watt heaters are introduced into re-entrant wells for approximately 20 minutes. When the temperature is approximately 0.25 K above the target as

indicated by the reference SPRT, the heaters are removed. After 45 to 60 minutes, the temperature is sufficiently stable to start the measurements. Although 1 ½ to 2 hours time has elapsed since the vessel was filled, very little LN_2 has been lost. Typically, the level remains at or above the uppermost diode.

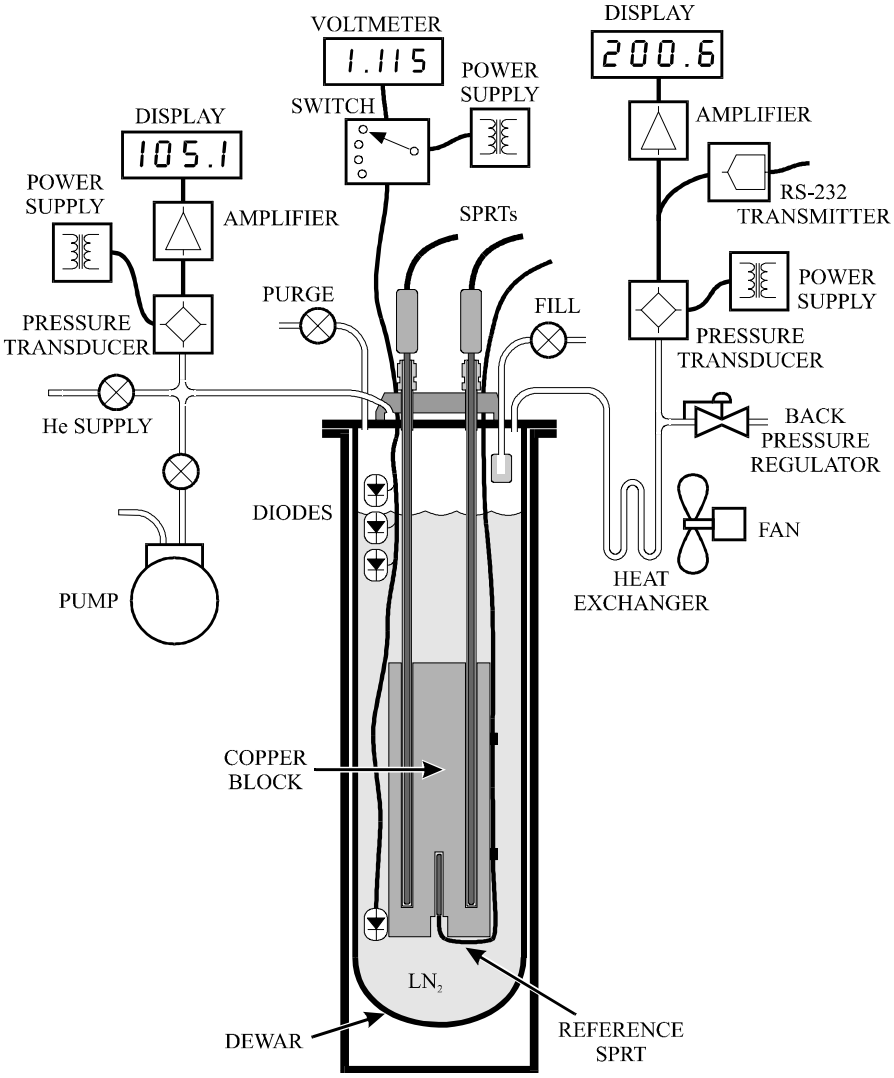

Figure 1: Schematic diagram of the cryostat

5. MEASUREMENT TECHNIQUE AND CALIBRATION PROCEDURE

The measurements were performed using a Measurements International Model 6010B direct current comparator resistance bridge equipped with a Model 4220A 20-channel matrix scanner. Resistance bridges of this type do not measure resistance directly; rather, they measure the ratio of the resistance of the unknown to the resistance of the reference. The resistance of the unknown is then computed by multiplication of the reference resistance and the indicated ratio (R_X/R_S).

$$\textit{measured resistance} = R_X / R_S \times \textit{reference resistance} \qquad (1)$$

Direct comparison of the resistance ratio of the unknown SPRT to the reference SPRT can be accomplished by performing a measurement with the unknown SPRT connected to the R_X terminals

and the reference SPRT connected to the R_S terminals. The resistance of the unknown SPRT at the temperature of the comparison can then be computed as shown.

$$R(T90)_{unknown\ SPRT} = measured\ resistance\ ratio \times R(tpw)_{reference\ SPRT} \times W(T90)_{reference\ SPRT} \qquad (2)$$

This technique has two significant benefits. First, the effects of drifting temperature are minimized by a direct measurement rather than a sequential measurement. Both SPRTs are inserted into the copper block and will be subjected to similar rates of drift. The actual resistance will be changing slightly, but the ratio between the two SPRTs will remain quite stable. Second, because of the high degree of linearity of SPRTs over small intervals, only the approximate temperature of the comparison needs to be known. The resistance can be computed at a (desired) temperature close to the actual temperature of comparison with negligible error having been introduced. The presumed large temperature allowance reduces the precision required of the backpressure regulator. For our experiments, care was taken to set the cryostat to a temperature within 0.25 K of the target temperature and the temperature of the system was recorded before the actual comparisons were initiated. The computations were then performed at the target temperature. Because the link to resistance is determined by the R_{TPW} of the reference SPRT, the accuracy of this measurement is critical. We have been using this technique in an open system for quite some time in our laboratory with excellent results.

The calibration procedure was carried out in the conventional manner. Three unknown SPRTs were calibrated at the triple points of water and mercury and then by comparison in the cryostat. The calibrations were conducted at two levels of current and zero power values were computed. The measurement sequence was R_{1mA}, $R_{1.414mA}$, R_{1mA}. For each value a total of 80 individual measurements were taken over a period of eight minutes. The first 40 measurements provide for SPRT self-heating and the final 40 measurements are averaged for each result. The difference between the first and second 1 mA measurements is used as an indication of the thermodynamic stability of the system. Insufficient stability typically indicates that the calibration was initiated before equilibrium was achieved. If needed, the measurement sequence is repeated. The measurements on all three SPRTs were performed serially and then repeated to simulate a total of six SPRTs. A forth, previously calibrated SPRT was used as the control standard and to monitor the temperature during the run. The measurement sequence required approximately three hours to complete, during which time the apparatus remained unattended. After completion of the measurements, the cryostat was refilled, the pressure was adjusted, and the process was repeated at the next temperature. Eventually, completing measurements at the four temperatures listed in Table 1. The pressure and temperature were recorded during each calibration run.

6. RESULTS

The backpressure regulator was unable to hold the pressure perfectly stable during the calibration process. Drift was observed from 0.54 kPa at best (the vessel vented to ambient) to 1.8 kPa at worst (NBP LN_2 at 101.325 kPa). The temperature drift corresponded at 0.04 K to 0.19 K. With the exception of the data at the NBP of argon (more on this later), the noise of the measurements (represented by σ the of the data) ranged from 0.3 ppm to 0.7 ppm ($\approx$ 15 μK to 35 μK). The precision of the measurements does not appear to be correlated to the pressure drift. Additionally, the σ values were in the range of values that we routinely observe with our open LN_2 comparator. As expected, the slow drift in pressure does not seem to adversely affect the calibration.

The data was fitted in two ways. First, the direct comparison values obtained at all four temperatures were used to compute W_{TPAr} using the linear relationship of the SPRTs. This represents an extrapolation of several kelvins and the method was expected to introduce a significant error. The purpose was to quantify the magnitude of the error. Second, the values were used to represent W_{T90} at

the nominal temperatures of each comparison and the ITS-90 coefficients were then computed using the respective temperatures. In both cases, the values obtained at the triple point of argon comparison were taken as the baseline. Finally, the W_{T90} differences were translated into temperature and evaluated. The results of the calibrations are shown in Figures 2 and 3. The measurements at the NBP of argon indicated an error in excess of 30 mK with a σ of from 3 ppm to 5 ppm (≈ 0.15 mK to 0.25 mK) for all three SPRTs and the results have been omitted from the graphs. Further investigation will be required to determine the cause.

As expected, the data fitted by extrapolation indicates differences of up to 5 mK. This method is not recommended for high-accuracy calibrations. The results obtained using the second method indicate differences of less than 0.5 mK. The results do not suggest a clear relationship between the magnitude of the difference and the relative distance from the triple point of argon.

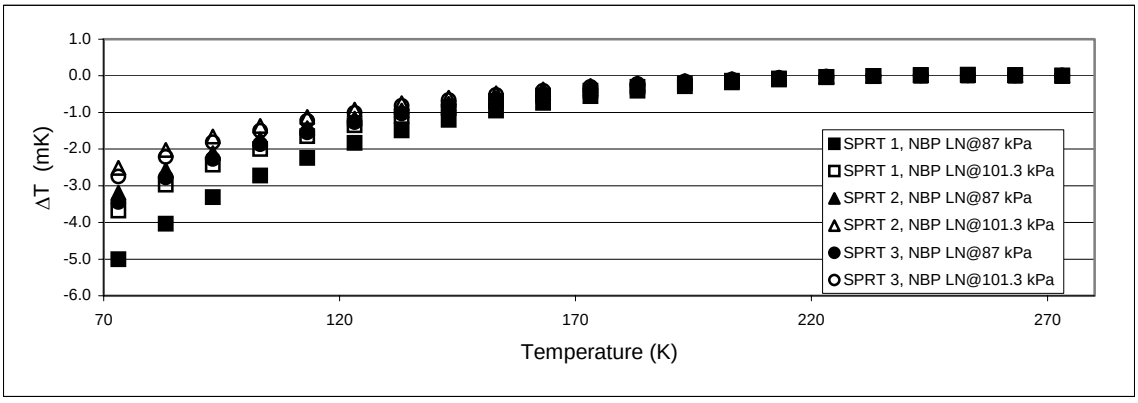

Figure 2: Deviations of SPRT Calibrations at LN_2 Boiling Point From Calibration at TPAr Approximation Using Extrapolation of Measured Data For Calculations

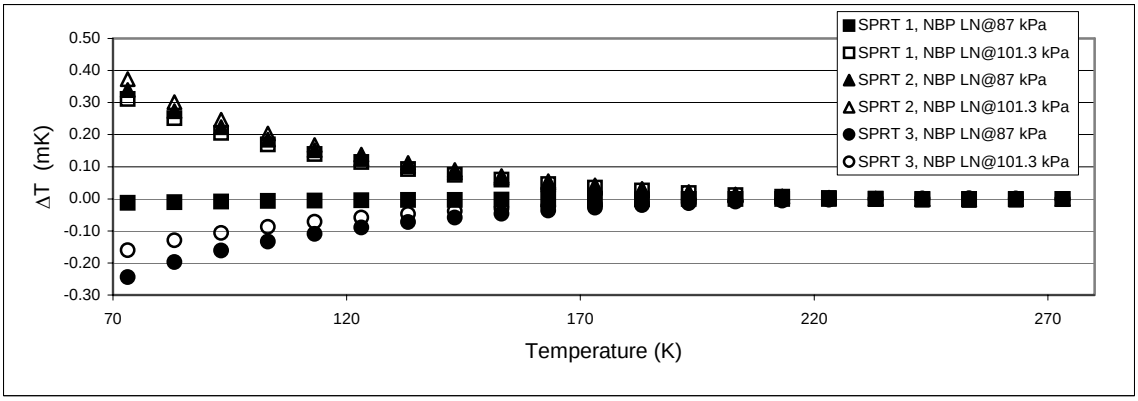

Figure 3: Deviations of SPRT Calibrations at LN_2 Boiling Point From Calibration at TPAr Approximation Using Target Temperatures For Calculations

7. UNCERTAINTY ANALYSIS

The expanded uncertainty is the combined uncertainty from all known components.. Equation (3) is used to compute the uncertainty where k is the coverage factor and s_i and u_i are the Type A and Type B standard uncertainties, respectively [6].

$$U = k\sqrt{\sum s_i^2 + \sum u_i^2} \tag{3}$$

Table 2: Measurement Uncertainty

Item	Type	Uncertainty (mK) (k = 1)
Repeatability & Uniformity (check standard, n = 84)	A	0.15
Reference SPRT Stability (R_{TPW} repeatability)	A	0.08
Precision of Comparison Measurements	A	0.03
Vertical non-uniformity of the copper block	B	0.12
Reference SPRT Calibration Uncertainty (from NIST Report)	B	0.06
Reference SPRT R_{TPW} Propagation	B	0.02
Stability of Reference Resistor	B	0.03
SPRT Self Heating	B	0.02
Bridge Linearity	B	0.01
Combined and Expanded (k = 2)		**0.45**

8. CONCLUSIONS

The results reported herein indicate that sub-mK uncertainties are attainable at a temperature approximating the triple point of argon using a fairly simple LN_2 cooled cryostat. A specialized technique was described that allows a number of SPRTs to be calibrated unattended while simultaneously reducing the effects of slowly drifting pressure and temperature experienced during the calibration. One goal of the project was to determine the additional uncertainty introduced by performing the comparison at a temperature several kelvins away from the ITS-90 temperature assigned to the triple point of argon. The data suggests that a small error may be introduced by this practice; however, the results were not definitive. More work will be required on this aspect. Additionally, the data suggests that the spatial uniformity is far more critical to the uncertainty realized than the temporal stability during the calibration sequence.

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Address of the Author:

Thomas Wiandt, Hart Scientific, 799 E. Utah Valley Dr., American Fork, UT 84003, USA, Tel: 801-763-1600, E-mail: tom_wiandt@hartscientific.com, Internet: www.hartscientific.com