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THE CARE AND MAINTENANCE OF STANDARD PLATINUM RESISTANCE THERMOMETERS

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1 Introduction

Standard Platinum Resistance thermometers (SPRTs) are the workhorses of calibration laboratories throughout the world. SPRTs are delicate instruments and should be treated with great care. Handled properly and well maintained, these instruments will give many years of trouble free service. This document was written, as a tool in understand the importance of their care, use and maintenance. Control charts are discussed as a means of evaluating and diagnosing problems, including photographs of damaged sensors. Also discussed are the possible causes for the damage.

2 SPRT Construction

2.1 To understand why SPRTs need to be handled carefully, it helps to understand how these thermometers are manufactured. We begin with very high purity platinum wire. The diameter of wire will depend on whether it's a 100-ohm, 25 ohm, 2.5 ohm or a 0.25-ohm. Higher resistance thermometers require a smaller diameter wire for its sensor. Prior to making the sensor, the platinum wire is subjected to a very high temperature. This process is to burn off any remaining contaminants, which improves the already high purity. It also anneals the wire by removing any stress in the crystal lattice structure. Later for discussion, it is important to note that the annealing process also causes the wire to become very soft. The wire is then made into a coil and carefully wound onto a fused silica (quartz) cross frame to make it "strain-free". Lead wires and insulators are then added before it goes into either a clean Inconel or fused silica sheath. Some SPRT sensors, like the model 5699, are incased in a platinum capsule. This protects them from metal ion contamination at temperatures >500°C. The SPRT assembly is then purged with argon gas and evacuated at a high temperature many times. The assembly is then sealed containing a mixture of pure argon and oxygen. Some oxygen is required to protect the sensor from contaminants that are naturally found in the parts that make up the SPRT. After construction, the SPRT is annealed again to take out any stress during the manufacturing process. This annealing is done repeated until the resistance at the water triple point has stabilized. The SPRT is now ready for calibration.

Figure 1 Newly made sensor, note how the coils are very uniform and evenly spaced.

3 Mechanical Treatment

3.1 During the annealing process, the platinum wire becomes very soft. Because the platinum sensor is fragile, it is important to handle the SPRT carefully. The number one cause for

SPRT inaccuracies is due to improper handling. Just because an SPRT may have a metal sheath, it doesn't make it any less susceptible to mechanical shock. A metal-sheathed SPRT should be handled with the same care as one that has a fused silica sheath. These are delicate instruments and they should not be subject to any vibration, shock or form of acceleration.

Figure 2 This sensor was probably damaged by acceleration during handling or shipping.

Figure 3 This sensor was probably damaged due to excessive vibration.
Notice that many of the coils are shorted together.
(The lead pencil is for reference only.)

3.2 An accumulation of rough handling if left unchecked could cause the resistance at the water triple point (R_{tpw}) to increase dramatically. For a 25-ohm thermometer it only requires a change of 0.1 milliohms to cause a 1 mK in temperature.

3.3 Even with careful use, changes of 1 or 2 mK at the triple point water are typical. Thermal cycling, slight mechanical shock and or oxidation usually cause this change.

4 Thermal Treatment

4.1 Always clean an SPRT sheath with pure ethanol alcohol prior to using it above 100°C[4]. A fingerprint left on a fused silica sheath will cause devitrification in that area. Devitrification is visible milky white area and is irreversible. It causes the fused silica to revert back to its crystalline form. It's very brittle and is gas-permeable[4]. Given enough use and time, the sheath will eventually crumble apart.

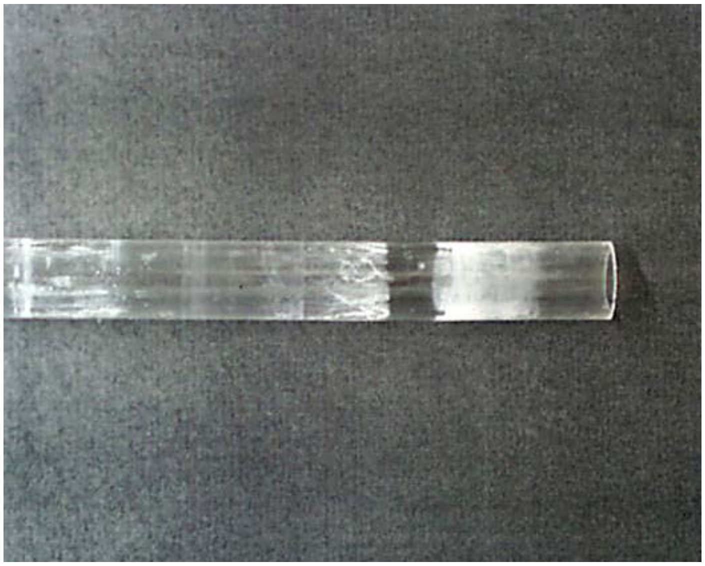

Figure 4 Devitrification of fused silica tube.

4.2 Metal sheathed SPRTs should be cleaned with ethanol alcohol if they are to be used in a metal freeze point cell, whose outer shell is made of fused silica. If this isn't done, this could cause devitrification of the metal freeze point cell.

4.3 Do not subject the SPRTs above their maximum temperatures; doing so may cause permanent damage.

Hart Model #	Maximum Temperature
5680	480°C
5681	670°C
5682	480°C
5683	480°C
5684	1070°C
5684	1070°C
5698	670°C
5699	670°C

Table 2

4.4 An SPRT can be removed from a heat source into room air safely at =< 450°C. At temperatures higher than 450°C, it is required that the SPRT be cooled slowly at a rate of 150°C per hour. Cooling it faster will cause some point defects in the platinum to be trapped, which will cause a slight increase in resistance[7].

4.5 If an SPRT is removed for a heat source at high temperature, it should be kept in a vertical position until it has time to cool. Suspended horizontally while hot, may introduce mechanical strains in the platinum wire.

4.6 Keep the SPRT handle cool; generally long stem SPRT handles should not be too hot to the touch. High temperatures may cause irreparable damage to the hermetic seal, painted handles, and cable insulation and soldered lead wires.

4.7 Never leave an SPRT exposed to temperatures other than room temperatures for long periods of time. Prolonged use at temperatures in the range of -40 to 300°C causes a surface film of oxide to form on the body of the wire. This can cause an increase in resistance up to 0.5 mK per hour. In the range of 300 to 500°C, the resistance can rise up to several mK per hour[5].

5 Maintenance

5.1 Generally changes of 1 or 2 mK at the triple point of water are typical, even with careful use. These changes can be attributed to thermal cycling, slight mechanical shock or oxidation.

5.2 The temperature at which the SPRT is annealed will depend on its maximum operating temperature. Caution: Never anneal or use a fused silica (quartz) sheathed thermometer in a metal dry block or furnace at temperatures => 500°C. This may cause metal ion contamination, which is permanent.

5.3 Recommended Annealing temperatures and times for Hart SPRTs.

Hart Model #	***Annealing Temp (°C)**	**Time (hrs)**
5680	480	2
5681	670	2
5682	480	2
5683	480	2
5684	700	2
5698	670	2
5699	670	2

Table 3

*The annealing temperature should be based on the highest temperature point used when the SPRT was calibrated. For example, if the SPRT was calibrated only to zinc, it should not be annealed higher than 480°C. This temperature is still high enough to burn off any oxidation but if it were annealed at a higher temperature, it would cause a shift in resistance. The SPRT then would have to be recalibrated.

5.4 A control chart or log should be maintained on each SPRT's R_{tpw}. This should be scheduled on a regular basis. The interval will be according to frequency of use and it's application. If used heavily or for doing critical work, check Rtpw at the end of each use. Also, it should be checked if there are any reasons to doubt its calibration integrity, which should be done immediately. Always use the most recent Rtpw value when measuring or calculating temperature to achieve the greatest accuracy. Generally the offset will be linear as long as the ratio between gallium and the water triple point is => 1.1187. But for evaluating an SPRT's stability or drift, use the original R_{tpw} as a baseline.

5.5 A scatter chart can be created from the recorded data. This is useful for trend analysis. Ideally, the SPRT data should appear random as in figure 6. As long as the data falls within the +/- 0.003°C window, the SPRT should not need annealing

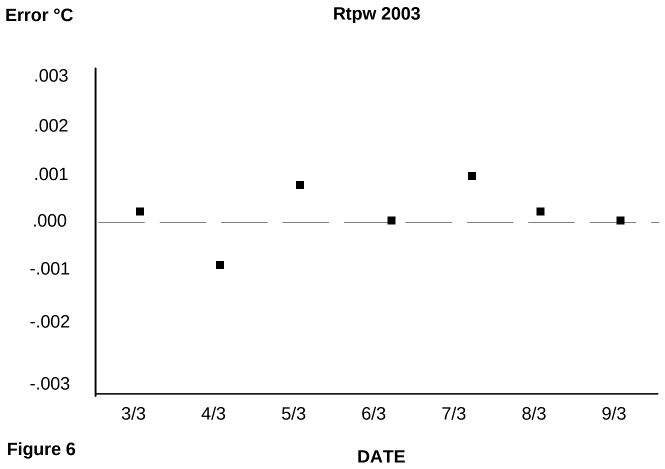

Figure 6

5.6 The R_{tpw} in Figure 7 shows a steady upward trend. This may be the result of metal ion contamination, severe mechanical shock or oxidation of the platinum.

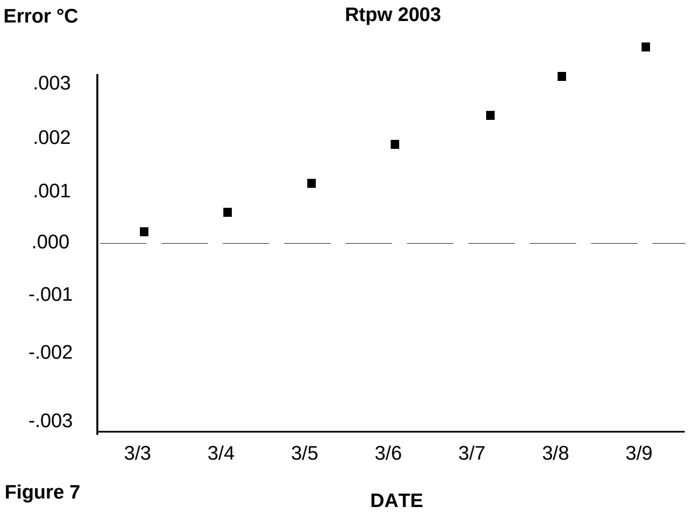

Figure 7

5.7 The R_{tpw} in Figure 8 shows a continuous downward drift. This problem can easily be seen while SPRT is trying to stabilize at the triple point of water. A faulty seal, allowing condensation to collect on the sensor and lead wires, can cause this. Since the moisture is conductive, this causes a decrease in the resistance.

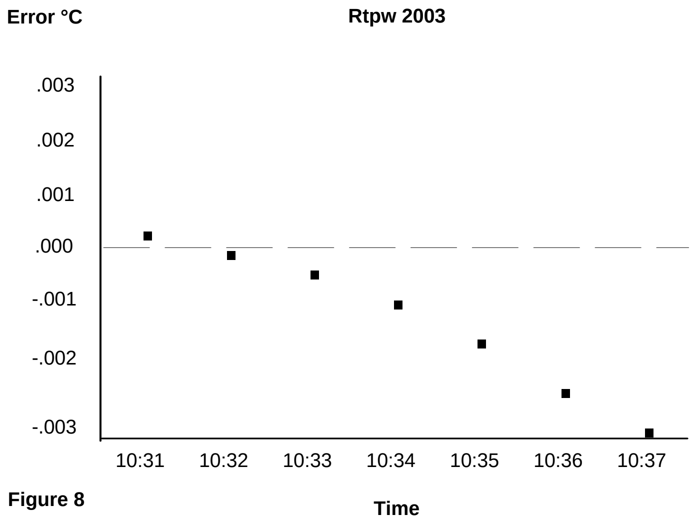

Figure 8

5.8 Figure 9 shows erratic R_{tpw} values. This problem is usually a result of coils that are touching, a broken wire, grain growth or poor cable connection. Generally if it is a problem with the SPRT sensor, lead wires or cable, a slight tap on the handle will generally cause the reading to jump.

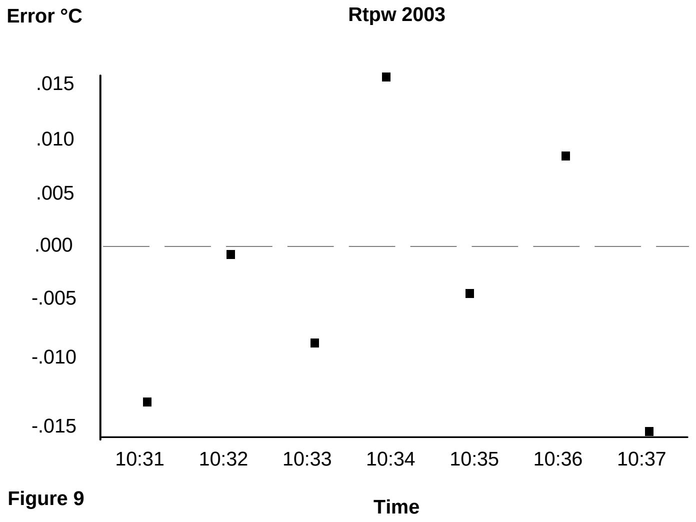

Figure 9

5.9 If the Rtpw is => than 3 mK, the SPRT should be annealed. The R_{tpw} should be taken before the annealing cycle. The annealing should be kept to a minimum to avoid grain growth. Normally the grain size is small. If the SPRT is annealed or used at high temperatures for long periods of time, the grain size will increase. A large grain size causes the SPRT to lose structural strength and become less stable. Over time, the weak areas may cause the wire to fracture.

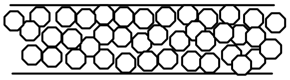

Figure 10 Normal Grain Structure

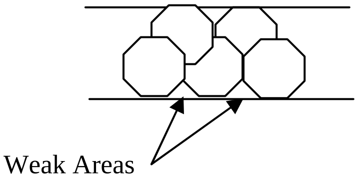

Figure 11 Increased Grain Size

5.10 If the SPRT was annealed but the error is still greater than 3 mK, anneal again for 2 hours then measure the R_{tpw}. If the resistance indicates a downward trend, repeat the annealing process until the readings are stable. If the readings are stable but still higher than 3 mK, the SPRT should be recalibrated.

5.11 ANNEALING FURNACE

Figure 13 Model 9117

Hart Scientific, Inc.The International Temperature Scale of 1990 (ITS-90) expanded the range of the Standard Platinum Resistance Thermometer (SPRT). This expansion presented new challenges to the thermometer industry. Among these challenges are the care and maintenance of the SPRT and the High Temperature Standard Platinum Resistance Thermometer (HTSPRT). With correct care and maintenance, an SPRT can provide years of accurate, stable measurements. Without proper care and maintenance, an SPRT can be damaged beyond repair or recalibration in a very short period of time. In fact, careless day-to-day handling of an SPRT over a one-year period has been observed to increase its resistance at the triple point of water (R_{TPW}) by an amount equivalent to 0.1 K. This could result in temperature errors as high as 10 mK without recalibration.[1]

In the past, many engineers have not understood the need for an annealing furnace. Today more people are coming to understand the importance of the annealing furnace in the care and maintenance of their SPRTs as they become more comfortable with the ITS-90. Most national laboratories have at least one annealing furnace and many have several. In the early 1980s, the Chinese developed HTSPRTs, which were recognized throughout the world for their excellent stability. A carefully designed, non-contaminating annealing furnace was an important factor contributing to the remarkable stability of these HTSPRTs. Today Hart has incorporated similar technology in our 9117 Annealing Furnace. (For the purpose of this paper, both SPRTs and HTSPRTs will be referred to as SPRTs.)

The first question that comes to mind is: "How does annealing aid in the care and maintenance of an SPRT?" Several answers can be provided for this question.

First, during the course of normal use, an SPRT is subjected to mechanical shock, which induces strain in the sensor wire resulting in a change in resistance. Mechanical shock can be incurred by the slightest tap to the SPRT sensor while inserting or removing it from an instrument. Vibration during transport can also be a cause of mechanical shock. The SPRT is an extremely delicate instrument. Even with great care, mechanical shock can be introduced causing a significant change in resistance. Annealing the SPRT at 660°C for one hour can eliminate most of the strains caused by minor shocks and restore the resistance close to its original value. Annealing is always advisable after any transport of an SPRT. [2]

Second, all solids inherently contain defects. A "crystalline defect" is defined as a lattice irregularity having one or more of it dimensions on the order of an Angstrom. Point defects, a type of crystalline defect, are associated with one or two atomic positions in the crystalline structure. The simplest and most common point defect is a vacancy or vacant lattice site, one normally occupied from which an atom is missing. Vacancies are formed during solidification and as a result of atomic vibrations. The concentration of the point defects is dependent upon the temperature. The equilibrium concentration of vacancies (N_v) in the pure platinum wire of an SPRT increases exponentially to an increase in temperature as shown by

$$N_v = N \exp\left(-\frac{Q_v}{kT}\right)$$

Where N is the total number of atomic sites, Q_v is the vibration energy required for the formation of a vacancy, T is the absolute temperature in Kelvins, and k is Boltzmann's constant.

For most metals, the fraction of vacancies (N_v/N) just below the melting point is on the order of 10^{-4} or one lattice site out of every 10,000.[3] Removing an SPRT from a high temperature and rapidly cooling it to room temperature traps this high concentration of point defects in the crystalline structure causing an increase in resistance. This increase can be as high as 30 mK. Annealing the SPRT at 700°C for two hours can significantly reduce the increase due to the trapped point defects. The SPRT should be cooled to at least 500°C at a rate of roughly 100°C per hour. Once the SPRT has reached 500°C, it may be removed immediately to room temperature without harm. Although the removal of the SPRT to room temperature from high temperatures should be avoided as much as possible, it is an inescapable part of fixed-point calibration.

During the calibration process at high temperatures, it is recommended that the SPRT be preheated and kept in an annealing furnace at a temperature close to the fixed point to be calibrated. Once the SPRT has been calibrated, it can be removed quickly from the fixed-point cell and returned to the annealing furnace. Annealing the SPRT for two hours after calibration and slowly lowering the temperature to 500°C prevents the quenching in of lattice defects found in the platinum wire.

Third, oxidation impacts the purity of the element and therefore, the accuracy of the temperature readings. A surface film of platinum oxide (PtO_2) forms in the range of –40 to 300°C. Initially; this can increase resistance at rates equivalent to 0.5 mK per hour. Oxidation forms in the body of the wire in the range of 300 to 500°C and can cause resistance to increase by a rate as high as several mK per hour.[4] The platinum oxides can be dissociated by annealing the SPRT at 660°C for 1–2 hours.[5]

Fourth, according to supplemental information for the ITS-90, "after using a high-temperature resistance thermometer at temperatures above about 700°C, the thermometer should be annealed before making measurements at lower temperatures, in particular before making the measurements at R_{TPW}."[6]

The National Institute of Standards and Technology (NIST) lists annealing as the first step in the calibration procedure for SPRTs. Experimentation specific to NIST's PRT laboratory conducted by B.W. Mangum, E.R. Pfeiffer, and G.F. Strouse provides the "optimum" time for annealing an SPRT before calibration (listed in Table 1).[7] Although Table 1 lists specific cool-down times for specific temperatures, Hart experts recommend the general 100°C-per-hour rule, which will satisfy the cool down requirements, equalize the point-defect concentration, and simplify the process.

Table 1: SPRT Annealing Procedure Based on NIST Research

Range of SPRT Use	**Procedure**	**Time**
Up to Zinc Point (419.527°C)	Hold at 450°C–480°C	4 hours
Up to Aluminum Point (660.323°C)	Thoroughly clean Heat from 500°C to 670°C Hold at 670°C Cool to 500°C Remove to room temperature	Over 1 hour 1.5 hours Over 3 hours
Up to Silver Point (961.78°C)	Measure R_{TPW} for baseline Thoroughly clean Heat to 970°C Hold at 970°C Cool to 500°C Remove to room temperature	Over 2 hours 1 hour Over 4 hours

The second question to be answered is: "What type of furnace is needed to anneal an SPRT?" At high temperatures, the lattice structure of most metals becomes quite loose. This allows some metal ions to come off the surface of any metal used in the furnace at high temperatures. This is analogous to steam rising from hot water. Since molecular activity increases with temperature, so does the amount of ion loss and the risk of contamination. Ion transfer occurs at different temperatures for different metals. Contamination has been attributed to copper, nickel, iron, and manganese. In addition, super-cooled quartz becomes transparent to these metal ions permitting their transfer to the pure platinum wire of the SPRT sensor. The new alloy formed by this process has a different alpha (a) curve than the pure platinum, which results in a loss of calibration.

Contamination from metal ions may come from a metal furnace block, heating elements, or any other source inside the furnace. Small amounts of metal used in the processing of ceramics may also cause contamination. Contamination is a significant problem encountered by many SPRT users. It is virtually impossible to recover a contaminated SPRT, therefore, contamination should be avoided if at all possible.
Consequently, it is extremely important that the annealing furnace be designed to eliminate any possibility of contamination to the SPRT. The Hart 9117 Annealing Furnace utilizes a specially designed quartz-encased graphite cell to prevent contamination to the thermometer. The block is assembled into a high-purity, specially cleaned quartz container, which is then evacuated and charged with argon to prevent oxidation. This specially designed quartz/graphite cell provides uniformity and stability while preventing contamination of the thermometer.

The annealing furnace must also provide good stability and uniformity. The Hart 9117 provides a stability of ±0.5°C with a uniformity of 1°C over the first three inches of the thermometer. Finally, the furnace should provide a means of setting a ramp rate for the heating and cooling of the SPRT. The Hart 9117 controller has fully programmable ramp and soak rates specifically designed for annealing. The furnace operates in a range of 300°C to 1100°C providing a full temperature range for the annealing of SPRTs.
The annealing furnace is not an option in the modern temperature laboratory but a necessity for the proper care and maintenance of SPRTs. Whether the laboratory calibrates its own SPRTs using fixed-point cells or ships the SPRT to a competent laboratory for calibration, an annealing furnace is an invaluable tool for maintaining the SPRT calibration—from annealing after shipment to assisting in the fixed-point calibration process[8].

All HTPRTs and SPRTs are subject to mechanical shock no matter how carefully you handle them. This shock changes the resistance characteristics of the platinum and shows up as temperature measurement errors. Annealing relieves the stress on the platinum sensor caused by mechanical shock and is recommended by NIST prior to any calibration of an SPRT.
In addition to removing mechanical strain, annealing also removes the oxidation from sensors that have been used for long periods at temperatures between 200°C and 450°C. Oxidation impacts the purity of the element and therefore the accuracy of temperature readings. Oxide is easily removed by annealing at 660°C for one or two hours.
During the annealing process, contamination must be controlled. At temperatures above 500°C, the lattice structure of a quartz sheath is transparent to metal ions. The thermometer must be cleaned and all contaminating material removed from its sheath. To avoid emitting metal ion contamination, annealing should only be done in a furnace that’s designed for this purpose. Hart solves this problem in its 9117 furnace by using a quartz-encased graphite block that is specially prepared to guard against contamination before assembly.
The furnace also has a programmable controller specifically designed for the annealing process.

5.12 The gallium cell is useful for testing the purity of the platinum wire. An SPRT is defined by the resistance ratio (W) between the gallium and triple point of water. This ratio should be => 1.11807. If the ratio is less than the required value, the problem could be from metal ion contamination or oxidation.

6 Transportation

6.1 If the SPRT is to be transported, it is advisable to hand carry it to maintain its calibration integrity. However, this may not be convenient or cost effective if the thermometer must be transported over long distances. In this case, the thermometer must be shipped in a suitable container. First place it in a rigid container, lined with a soft material to protect it from vibration and shock. The container should be large enough to provide sufficient space around the SPRT. This container should be placed in an even larger one, supported on either end with foam to attenuate any shock that may occur during transportation. It is recommended that it be shipped overnight or second day air.

Figure 10 SPRT placed in carrying case

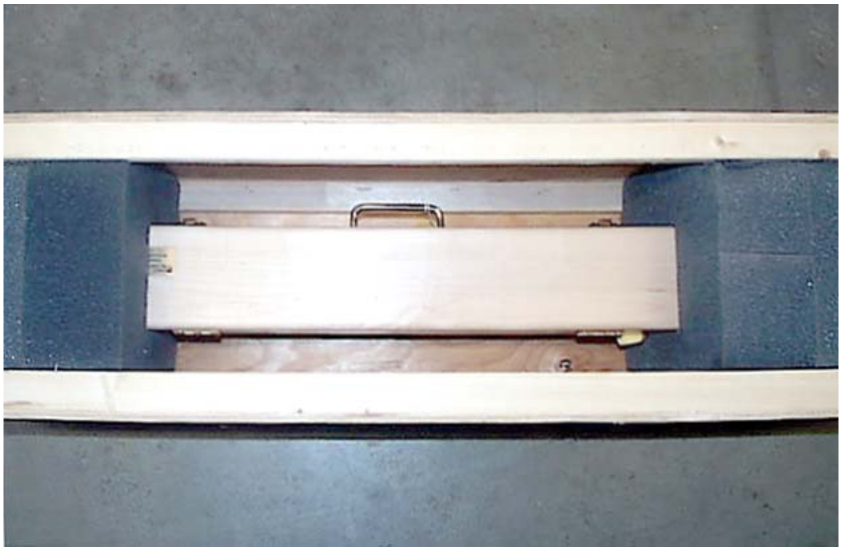

Figure 11 Carrying case is then placed into the shipping crate. Note the foam end pieces that attenuate vibration during shipping.

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Appendix

1 Formulas:

1.1 Calculating the ratio (W) from the resistance at gallium and the triple point of water (TPW).

$$W = \frac{R_{ga}}{R_{tpw}}$$

Where: R_{ga} is the SPRT resistance at the gallium point.

R_{tpw} is the SPRT resistance at the water triple point.

1.2 Interpolating temperature from a ratio table.

Generally a ratio table or in rare cases, a resistance table is provided when an SPRT is calibrated. These tables can be used to interpolate temperature based on the probes resistance.

6.1 Interpolating From a Ratio Table

T(°C)	**W(t)**	**Dt/dW(t)**	**T(°C)**	**W(t)**	**dt/W(t)**
0	0.9999601	250.8149	50	1.1978242	254.6804
1	1.0039471	250.8916	51	1.2017507	254.7584
2	1.0079329	250.9684	52	1.2056760	254.8364
3	1.0119175	251.0452	53	1.2096001	254.9145

1)	Measure reference probe resistance R(t)	30.6517
2)	Measure the resistance at the triple point of water	25.5120
3)	Calculate the resistance ratio $W(t)=R(t)/R_{tpw}$	1.20146
4)	Locate where W(t) falls on the table	Between 1.1978242 and 1.2017507
5)	Subtract lower table value from measured value	1.20146-1.1978242=0.0036358

6) Multiply by dt/dW(t) 254.6804 * 0.0036358 = 0.925967

7) Add Fractional Temperature to table value 50 + .925967 = 50.925967°C

1.3 Interpolating temperature from a resistance table.

$$\mathbf{Ta} = \mathbf{Th} - \left(\frac{\mathbf{Rh} - \mathbf{Ra}}{\mathbf{1} * \mathbf{d(R)}} \right) \mathbf{d(^\circ C)}$$

Where:

Ta = Actual Temperature
Th = High temperature from the table.
Rh = High resistance from the table.
Ra = Actual resistance as read from the meter.
d(°C) = High temperature – low temperature from the table.
d(R) = High resistance – low resistance from the table.