FUNDAMENTALS OF THERMOMETRY
PART III

THE STANDARD PLATINUM RESISTANCE THERMOMETER

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ABSTRACT

The Standard Platinum Resistance Thermometer, acronym SPRT, is the stipulated interpolation instrument for realizing the International Temperature Scale of 1990 between the defining fixed points, over the range from 13.8 K (the triple point of eka-hydrogen) to 961.78 °C, the freezing point of silver. However it must be said immediately that no single thermometer or design of thermometer can be expected to cover this entire 1221 K span, but that it can be covered by three designs of thermometer, with substantial overlap of range. The three designs are the long-stem SPRT, the cryogenic or capsule SPRT and the high-temperature SPRT or HTSPRT.

1: THE LONG-STEM SPRT AND ITS USEFUL RANGE

The long-stem SPRT is the most commonly encountered of the types, and is the accepted interpolating standard over that portion of the temperature range from -189.352 °C (the triple point of argon) to the freezing point of zinc (+419.527).

The principle reason for limiting the range at the cold end is that the thermometer tube, which extends from the thermal environment into ambient, can conduct unwanted heat into a cryogenic situation. There is usually no difficulty about using this thermometer down to -200 °C.

The upper limit of +420 °C is a convention only. Certain such thermometers (those with quartz sheaths and high-temperature mica insulation) can be used, with proper precautions, to 630 °C; others (with Pyrex sheaths) can be used safely below 500 °C. 630.74 °C, the freezing point of antimony, was a secondary fixed point of the International Practical Temperature Scale of 1968, which the ITS-90 replaces, and was considered to be the upper end of the platinum thermometer range on that Scale. The antimony point, which was not very satisfactory to realize, has been replaced by the freezing point of aluminum, 660.323 °C, and this must be considered beyond the safe upper limit for any mica-insulated SPRT.

On IPTS-68, it was customary to issue a calibration table for SPRTs with an upper limit of either 500 °C or 630 °C, as the construction of the thermometer permitted and the customer requested. The calibration points were the water triple point and the freezing points of tin and zinc, and the propagation of a 1 mK error at tin and zinc could produce an uncertainty of about 8 mK at 630 °C.

On ITS-90, there are a number of specified ranges above 0 °C. These include the range 0.01° to 419.527 °C (the freezing point of zinc) and 0.01° to 660.323 °C (the freezing point of aluminum). Current NIST policy on calibration ranges is as follows:

> "If a customer requests that his SPRT be calibrated through the zinc point and that we provide tables with extrapolation to 500 °C, we will honor that request, with a warning that the uncertainty is unknown above 420 °C. We will not extrapolate to 630 °C.
>
> If we get a request to calibrate an 8163 or 8167 type SPRT to the aluminum point, we call the customer and advise him that the SPRT should not be calibrated at that temperature, and that if it is, it may be destroyed in calibration. If he, nevertheless, insists upon such a calibration, we will provide it, reluctantly."[1]

The platinum resistance thermometer has a long and honorable history. It was proposed first by Siemens in a Bakerian Lecture in 1871. Siemens' thermometer consisted of a fine platinum wire wound on a fire-clay cylinder, which was then enclosed in a protective iron tube. The thermometer gained rapid acceptance, due principally to the reputation of its creator, and was abandoned almost as quickly when it was discovered to be unstable (due most likely to contamination).[2] Also, at the cost (then) of refined platinum and good porcelain, it was too expensive for industrial use.

Callender, less than twenty years later, revived the platinum thermometer for laboratory work. Instead of a mandrel of fire clay or porcelain, he wound the platinum element on mica. He realized also that any necessary joints must be autogenously welded, since the migration of components of solders would contaminate the pure platinum. The first documented statement of an interpolation algorithm for platinum, the Callender equation (later modified by van Dusen to include temperatures below 0 °C) is given in the epochal Callender paper, "On the practical measurement of temperature" read to the Royal Society in 1886.[3] The elements of today's thermometer are all here, waiting only refinement and reduction to practice. Among the numerous refiners, Griffiths, Holborn and Wien, Barber, one

worker whose name stands out is C. H. Meyers, and a seminal paper of his is reproduced elsewhere in this issue of the Isotech Journal.[4]

2: THE 25 OHM LONG-STEM THERMOMETER FOR -200 ° TO ABOUT 600 °C

CONSTRUCTION OF THE THERMOMETER ELEMENT

I have elected to begin discussion of construction with this type, because it includes the basic principles, and the other two are variants on it.

The thermometer element is considered to be that length of platinum wire which is active in the measuring circuit and the structure which supports it. In standards use, the element is always connected as a 4-wire resistor, so that the long lead wires which extend up the thermometer tube, and the cable from the thermometer head to the resistance-measuring instrument, do not enter into the resistance determination.

In the traditional constructions, the former or mandrel upon which the platinum wire is wound is a cross made of thin sheet mica. The four edges of the mica are cut with fine teeth or grooves to contain the wire, which is on the order of 0.1 mm (.004 inch) in diameter. The grooves form a double helix, so that one half of the platinum wire is wound toward the outboard end of the element, leaving each intermediate groove empty, and the remaining wire is wound back into these grooves. The result is a bifilar winding which is approximately non-inductive (but which may have capacitive reactance). Fig. 1 shows, sketchily, such an element. The resistance is commonly about 25.5 Ω at 0 °C. (This seemingly odd value was chosen to allow crude estimation; for a 25.5 Ω thermometer, at moderate temperatures, 0.1 Ω represents approximately 1.0 °C.)
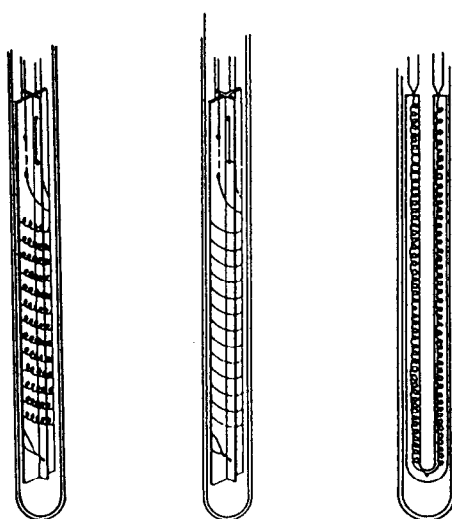

FIG 1   FIG 2   FIG 3

The mica former limits the upper temperature at which the thermometer may be used. Mica is a natural material; any of several silicates, including muscovite (ruby mica) and phlogopite (amber mica). Both forms are bound with water, and will deteriorate and flake at temperatures which drive off the water. Phlogopitic mica is used in the later quartz-tubed designs, and is limited to below 600 °C for frequent use . The older designs using Pyrex tubes and ruby mica are limited to 500 °C.

The wire is the purest platinum obtainable. It is referred to as "reference grade", taking the name from its acceptability as the reference leg of a standard platinum-platinum/rhodium thermocouple. Refiners of platinum, of whom only one or two produce thermometer-grade metal, occasionally make a bar of platinum which is recognized as superior, and thermometer makers reserve long-term supplies from that specific bar.

3: OTHER DETAILS OF CONSTRUCTION

The four lead wires which proceed up the thermometer stem (tube, sheath) and into the head, or handle, are generally 0.4 mm (.015 in) diameter. They are ordered, spaced and kept from touching each other by some sort of insulating device; a common plan is to use a number of four-hole mica washers, often separated by spacers of quartz tubing. Early thermometers were made with gold leads, perhaps as a matter of cost of material (or see the Meyers paper in this issue of the Journal). This had the disadvantage of placing the platinum-to-gold junctions at the hot end of the thermometer, where thermoelectric effects could occur. Most thermometers are now made with lead wires of commercial grade (or better) platinum extending into the cool thermometer head, where they are attached to the copper leads of the external cable, with great attention paid to isothermality by appropriate heat-sinking.

At the cool end of the thermometer tube (which in today's thermometers is always quartz) the lead wires are hermetically sealed into the tube. In early thermometers this was done by sealing the platinum directly through the glass, or by Housekeeper seals. Both such seals effectively prevent repairs of broken tubes except by the most heroic means. For a number of years, it has been customary to close the cool end of the tube with a glass-to-metal header including four Kovar tubes, into which the lead wires are sealed by hydrogen brazing. The glass seal includes a fifth tube which is used to evacuate the tube assembly, perform occasionally arcane and sometimes mystical cleaning processes, to finally fill the tube with a gas, and to seal off. The gas in a long-stem thermometer of this range is commonly 90% dry argon, 10% oxygen, at a pressure which will be equivalent to 1 atmosphere at the hot end of the thermometer's range.

The quartz tubes of most thermometers are clear at the hot end for the length of the element, and for the rest of their length are roughened by sand-blasting, or coated with a black material such as Aquadag. Quartz has marvellous optical properties, and it is necessary to avoid piping heat out of (or into) the the sensitive element by breaking up internal reflections of radiant energy within the walls of the quartz tube. (For fun, try pointing one end of a quartz tube at a wall while heating the other end luminously hot. The circle of light projected onto the wall drives the lesson home).

The four wires in the external cable are required to (a) be flexible and (b) represent constant resistances under such conditions as flexing. While the lead wires and the cable are not measured during a four-wire measurement, any wire not constant in resistance might change and cause errors during a measurement, say with a Mueller bridge, which requires several steps; or with a modern automatic bridge could be a source of noise. Requirement (a) could be met with stranded wire, but the strands of a stranded cable touch each other in random and inconstant parallel connections, which contradicts requirement (b). The wire commonly used is Litz wire (Litzendraht), in which the individual strands are enamel-insulated from each other except at the ends where they are soldered to the platinum lead wires or to terminal lugs. The solders used should be thermal-free. The four Litz wires are made into a cable by some sort of woven serving. Terminal lugs are advisedly gold-plated copper, appropriately labeled as current or potential leads.

4: VARIATIONS ON THE ABOVE

Virtually all thermometer designs agree with the description given above, but there are a number of different ways of arranging the platinum wire relative to its supporting structure.

It is essential that the wire, whose resistance versus temperature characteristic is the essence of the measurement, be and be maintained in a fully annealed and strain-free condition. Strained or work-hardened platinum can will be higher in resistance and lower in sensitivity than it is in the fully annealed condition. Meyer's mica cross attempted to speak to this by providing essentially point contacts between platinum and the supporting structure, and leaving it freely suspended elsewhere. Fig. 1 shows a design in which the platinum is first coiled into a helix (with a pitch diameter of about 0.4 mm (.0125 in) and then wound on the mica. There are about 30 turns; thus there are about 120 places at which platinum touches mica. Fig. 2 shows a later Meyers design in which the platinum is not coiled, but is wound straight on the cross, for about 120 turns, or about 480 points of contact.

The first Meyers design coils the wire to allow more ohms in the linear length. The second design is an attempt to place more of the wire nearer the inside diameter of the quartz, to reduce thermal losses and thermal lag, and to improve dissipation of I^2R heat. Whether one prefers Fig. 1 or Fig. 2 is a highly personal matter. My preference is for the coiled-coil design of Fig. 1. I have never found the self-heat or lag to be a nuisance, and I feel that Fig. 1, in which the platinum enjoys an additional degree of freedom, is marginally more stable.

Fig. 3 is a design by Barber, of NPL, in which the coil of platinum wire is allowed to hang freely in a U-shaped quartz capillary inside the main thermometer tube. Other designs, such as that of Curtis at Rosemount Engineering, dispose a coil of platinum inside a number of axial holes in ceramic, or on two sides of a helically-twisted ribbon of quartz which serves to separate the two coils. My experience suggests that all of these designs are marginally inferior to Meyers', in the amount of space which is left between the quartz tube and the sensing wire, and the consequent thermal loss and response lag; and the larger distance from the platinum to the quartz makes self-heating effects worse to much worse.

5: THE CRYOGENIC, OR CAPSULE, THERMOMETER

The cryogenic, or capsule thermometer, is short (usually less than 50 mm (2 in) long. The point is that does not have a stem which must emerge from the thermal zone into ambient, and does not serve as a conductor of unwanted heat into a zone one is trying to keep very cold. It is often built into equipment in a semi-permanent fashion. Its lead wires are also short, and usually are welded to thin copper or Constantan extensions, which are carefully thermally tied to cold parts of the apparatus. The element designs are similar to those for long-stem thermometers. The tube or sheath is usually not quartz but commercial grade platinum. The gas used to fill is usually helium with a fraction of oxygen, to facilitate thermal transfer at temperatures where the conductance of helium is superior to that of any other gas.

While intended for use at low temperatures, the capsule thermometer range extends from 13.8 K to as high as 250 °C, and it is used not only in cryogenics but also in equipment, such as calorimeters, where it is desirable to build in a short sensor semi-permanently.

6: THE HIGH-TEMPERATURE PLATINUM RESISTANCE THERMOMETER

The extension, in ITS-90, of the platinum range to the freezing point of silver (961.93 °C) has required the development of a new platinum resistance thermometer; acronym HTSPRT.

The first problem of extending the range is insulation. Mica cannot tolerate the temperatures. It has been necessary to make the former on which the platinum is wound of high-purity quartz. Even quartz does not provide absolute isolation at the high temperature end of the range (I have tried monocrystalline sapphire, at much greater cost than quartz, and it is about twice as good, which is not good enough). The former, or mandrel, is thus a shunt resistance across the platinum winding, and because of the uncertainty of the contacts between platinum and quartz, it is uncertain and unstable in magnitude. The practicable solution is to reduce the element resistance so that the shunt resistance produces a smaller network effect. For example, for a 25.5 Ω thermometer, suppose that the shunt resistance were 20 MΩ. Then the network resistance is 25.499967 Ω. But we require measurement assurance of better than 1 part per million, so this won't do, even if the shunt were a constant (calibratable) value, which it is not. For a 0.25 Ω thermometer, a 20 MΩ shunt gives a network resistance of 0.24999997 Ω, which is tolerable. The cost, and there is a cost, is increased difficulty on the electrical measurement side, particularly in the face of noise, which is present at high temperatures.

Another benefit accrues from a lower resistance. Platinum wire tends to show crystal growth above approximately °C. The inevitable result is a crystallization so profound that, in fine wire, fractures at the grain boundaries develop. The 0.25 Ω choice allows the use of much heavier platinum wire for the element, which prolongs life and minimizes drift. Indeed, Evans developed a 0.25 Ω high temperature thermometer, called the "birdcage", which employed platinum rods instead of wire and which was produced commercially, but years ahead of a scale to use it. In more conventional designs, the heavy wire allows the support to be a blade rather than a cross, reducing the number of quartz-to-platinum contacts by 1/2. Tavener has described such a thermometer in an earlier issue of this Journal[5] and the detail of its element and lead arrangement is shown in Fig. 4. It is in current production, and has been shown by calibrations in several National Laboratories to be extremely stable.
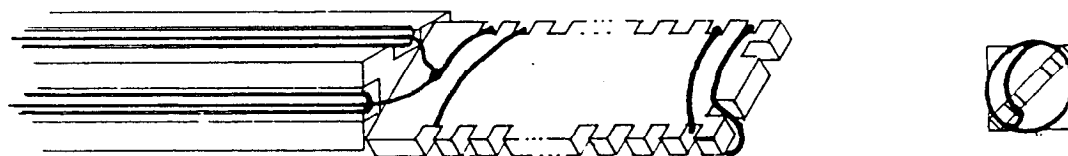
CONTINOUS CAPILLARIES
CONTAINING LEAD WIRES   SPADE AND 0.25Ω WINDING

FIG 4

(Isotech and I are studying the design of a thermometer, the top of whose range will be the aluminum point, the former of quartz, and the 0 °C value 10 Ω. For the user who does not require temperatures higher than 660 °C, the higher resistance will be attractive).

Another problem which can occur at the higher temperatures, and which is subtle, is the migration of metal ions from the immediate environment, through the quartz (which is transparent to such ions as copper, iron, nickel and chromium at these temperatures) into the platinum, resulting in degradation of its purity and large consequent calibration shifts. The Inconel liner of a furnace will cause such an effect, if the thermometer is not isolated from it by, say, a thin sleeve of graphite. (The graphite crucible and sleeve of the Isotech fixed-point cells are sufficient protection). Isotech also furnishes a patented, battery-powered field generator which, when used with its Model 962 thermometers, will shield the thermometer against contaminating metal ions.

7: USING SPRTs: MECHANICAL

It has been said that, if one puts an SPRT down onto a workbench hard enough to hear it touch, it will probably be strained. Mechanical strain of the wires, due to shock or acceleration between their points of support, will shift a thermometer throughout its range, increasing W values below 0 °C and decreasing them above 0 °C, because the 0 °C value which is the W divisor has increased. The same effect can be caused by using the thermometer in an environment which imparts continuing vibration to it. Attention must be given to such factors during storage, as well.

When a thermometer is sent elsewhere for calibration, it has been my preference to carry it by hand, and to retrieve it the same way. If a thermometer must be shipped, it should be packed adequately in a rigid box, in turn contained in a box full of resilient material, and the box closed by some means which is not in itself shocking; e.g., a wooden crate closed by woodscrews, not by nails.

8: USING SPRTs: QUALITY ASSURANCE

Any thermometry laboratory should be prepared to realize the triple point of water, for at least the following reasons:

a) The ratio W of the resistance at temperature to the resistance at the triple point of water:

$$W = R_{(t)} / R_{(tp)}$$

is more stable and repeatable than the resistance. The calibration received from a calibration laboratory is given in terms of W vs. t, not R vs. t. To realize a temperature measurement accurately, the measurement of resistance at temperature must be followed by a measurement of resistance at the water triple point, and the W value calculated, so that the tables may be used.

Furthermore, Berry has shown that as platinum is heated, several surface oxidation states are produced sequentially, which alter the resistance. However a measurement at a temperature and a measurement immediately following, at the water triple point, report the platinum in the same state. (The original state may be restored by an anneal, as described in c) below).

(NOTE: In previous scales, the denominator for W was the resistance at 0 °C. In the ITS-90, it is the resistance at 0.01 °C)

b) The resistance at the water triple point is a good indication of the state of the thermometer with respect to change. Quality control requires that, each time the thermometer is used, the resistance at the water triple point be placed on a control chart. The history thus developed aids confidence immeasurably. I am not a believer in fixed calibration intervals for SPRTs. I am a believer in following the control chart, which will tell me whether and when the thermometer has shifted too much. Against risks in transportation, and compared to the present cost of a National Laboratory calibration, a water triple point system may pay for itself in one interval.

c) When the thermometer is returned after calibration, a check at the water triple point will indicate whether or not there has been a subsequent shift due to transportation, and whether one may use the calibration with confidence.

For those laboratories which are equipped to do their fixed-point calibrations in house (a rapidly increasing number) it is wise, before calibrating, to perform a measurement at the water triple point, then anneal for 4 hours at 450 °C, and measure at the water triple point again. Any measurable change will indicate that the thermometer is either unstable or not fully annealed. In the latter case, repeating the process until a constant value is obtained can save much calibration time and expense. (Recommendations for handling HTSPRTs during and after exposure to high temperatures, and annealing such thermometers, should be sought from the manufacturer).

9: USING SPRTs: SELF-HEATING EFFECTS

A resistance is passive; to measure it requires that a current be passed through it, and the inevitable effect is I^2R heating. It is typical practice in calibration laboratories to calibrate a 25.5 Ω thermometer with 1 mA applied, and a 0.25 Ω thermometer with 10 mA. (It is never wise to apply more than 5 times these current levels, even momentarily). These calibration currents will result in a slightly elevated temperature. It is the First Law of Thermometry that a thermometer measures no temperature other than its own. In the designs of Fig. 1 and Fig. 2, the elevation, at the water triple point temperature, may be as much as 0.5 mK; with designs of less favorable heat transfer it may be substantially higher.

More accuracy may be achieved, at more effort, by reducing the reading to the resistance which would be obtained if there were no source of power. This can be done by measuring the resistance at two currents, for example x 1 and x $\sqrt{2}$ the accustomed level, in the identical environment. Converted to terms of power, the zero power resistance can be extrapolated.

The heat generated by the thermometer is, of course, transferred to the medium in which it is immersed. The self-heat so dissipated in a large volume of flowing liquid is then less than that in a suffocating environment. In most circumstances, the heat generated will not be such as to consequentially raise the temperature of the environment.

10: USING SPRTs: INTERPOLATION CALCULATIONS

The mathematics of the ITS-90 has been treated elsewhere, and need not be repeated. References 6, 7, 8, 9, 10 and 11 contain complete details. Reference 9 provides valuable advice for those who specify and order calibration services. For laboratories equipped to calibrate at fixed points, Isotech has available Daedalus 1.1, an MS-DOS interpolation program covering the full SPRT ranges. For information, consult Isothermal Technology Ltd., Pine Grove, Southport, England, or Isothermal (USA) Ltd, 250 West 57 Street, New York N.Y. 10107.

11: USING HIGH TEMPERATURE SPRTs

Quartz, as used in high-temperature thermometer sheaths, is a non-crystalline form of a material which may lapse into the crystalline form at temperatures within the upper range of HTSPRTs. This will occur inevitably if the thermometer sheath is exposed without being scrupulously cleaned of any contaminants; dust, oil, fingerprints. Manufacturers will advise methods of cleaning. The effect of devitrification is to make the quartz leaky to

gasses, including its own internal gas, and ultimately to destroy its mechanical strength and integrity.

For the calibration points below aluminum, HTSPRTs may be handled in the same way as the 25.5 Ω conventional thermometers. That is, the thermometers are preheated to avoid sudden cooling of the fixed-point cell when they are inserted, and to prevent excess shock to the thermometer.

At the higher calibration points (aluminum and silver), and in measurement situations at higher temperatures, special precautions are necessary, in inserting and also in removing the thermometer, to prevent excessive shifts. When used above 500 °C, it is advisable to raise the temperature of the environment containing the thermometer at a rate which achieves the desired temperature in 2 hours or more. This can be accomplished in either of two ways; at the beginning of the cycle, by placing the thermometer in a furnace which is below 500 °C and ramping the temperature gradually, or by preheating the thermometer in a second furnace on a similar time program. After the measurements are made, the thermometer should be allowed to cool in the furnace at a rate not exceeding a drop to 480 °C in 2 hours. At 480 °C the thermometer may be withdrawn safely.

It is usually necessary, during calibration, to withdraw the thermometer from the cell, so that the inner mantle can be formed in the cell using quartz rods. This is best done by raising the thermometer so that its tip is located a few centimeters above the graphite lid of the cell, waiting 5 minutes or so, raising the thermometer another 5 cm, waiting another 5 minutes, etc., until the thermometer is free from the cell guide tube. The thermometer may be transferred to another furnace at the appropriate temperature. When the thermometer is re-inserted into the cell, the procedure is followed in reverse, until the thermometer is bottomed in the cell.

The shifts which may be observed when a thermometer is cooled too rapidly are due to quenched-in crystal lattice vacancies. These can usually be removed, and the thermometer restored, by heating the thermometer, with the rise time precautions given above, to 960°C, and holding it there for 30 to 60 minutes; then gradually cooling to below 500°C before withdrawing the thermometer. A check at the water triple point will indicate whether the treatment has been adequate, or whether it needs to be repeated.

In Part IV of this ongoing series, we will consider resistance-measuring equipment for standard platinum resistance thermometry, and industrial platinum sensors.

FOOTNOTES AND REFERENCES

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