MSL Technical Guide 21

Using SPRT Calibration Certificates

Introduction

In the temperature range between 24 K (–250 °C) and 960 °C, the International Temperature Scale of 1990 (ITS-90) defines temperature in terms of the resistance of a standard platinum resistance thermometer (SPRT). Calibration of an SPRT involves the measurement and reporting of the SPRT resistance at a number of melting, freezing, and triple points specified by ITS-90. SPRT calibration certificates typically report these measurements as resistance ratios with respect to the SPRT resistance at the triple point of water and give the uncertainties in these measured resistance ratios.

This guide explains how to use the certificate with the SPRT to measure temperature, and how to calculate the uncertainty in the measured temperature caused by the calibration uncertainties. For simplicity, the guide covers only the temperature ranges from 84 K to 660 °C, but the principles are the same for other temperature ranges. Further detail can be found in the references.

ITS-90

Temperatures on ITS-90 are referred to by the symbol T_{90}, and the resistance of an SPRT at temperature T_{90} by $R(T_{90})$. To convert the resistance to temperature, ITS-90 makes three calculations. The first calculation gives the resistance ratio:

$$W(T_{90}) = \frac{R(T_{90})}{R(273.16\ \mathrm{K})}\ , \qquad (1)$$

where R(273.16 K) is the resistance of the SPRT at the triple point of water. Because SPRTs are all made from very pure platinum wire, values of $W(T_{90})$ are almost identical for every SPRT.

To compensate for the very slight differences in the $W(T_{90})$ values for each SPRT, ITS-90 applies a small correction to the $W(T_{90})$ values to obtain a reference resistance ratio, $W_r(T_{90})$. All of the correction equations have the form

$$W_r(T_{90}) = W(T_{90}) - \Delta W(T_{90})\ , \qquad (2)$$

where $\Delta W(T_{90})$, called the deviation function for the SPRT, is determined during calibration.

Once the value of $W_r(T_{90})$ has been determined, the temperature can be calculated using a reference function defined by ITS-90. As a rough guide, with care, temperatures can be measured to a best expanded uncertainty (k = 2) of about 2 mK (0.002 °C) over most of the SPRT sub-ranges of ITS-90.

The Reference Function

The reference function has two parts. For the range 13.8033 K to 273.16 K, the function is

$$W_r(T_{90}) = \exp\left\{A_0 + \sum_{i=1}^{12} A_i \left[\frac{\ln(T_{90}/273.16\ \mathrm{K}) + 1.5}{1.5}\right]^i\right\}. \qquad (3)$$

This equation is inconvenient to solve, so an inverse function (accurate to 0.13 mK), is defined as

$$T_{90}(W_r) = 273.16\ \mathrm{K}\left\{B_0 + \sum_{i=1}^{15} B_i \left[\frac{W_r(T_{90})^{1/6} - 0.65}{0.35}\right]^i\right\}. \qquad (4)$$

In the higher temperature range, from 0.01 °C to 961.78 °C, the reference function is

$$W_r(T_{90}) = C_0 + \sum_{i=1}^{9} C_i \left[\frac{T_{90}/K - 754.15}{481}\right]^i , \qquad (5)$$

and the inverse function (accurate to 0.1 mK) is

$$T_{90}(W_r) = 273.15 + D_0 + \sum_{i=1}^{9} D_i \left[\frac{W_r(T_{90}) - 2.64}{1.64}\right]^i . \qquad (6)$$

The A_i, B_i, C_i, and D_i coefficients are in Table 1.

Table 1: The A_i, B_i, C_i, and D_i coefficients of the reference and inverse functions of equations (3) to (6).

i	A_i	B_i	C_i	D_i
0	–2.135 347 29	0.183 324 722	2.781 572 54	439.932 854
1	3.183 247 20	0.240 975 303	1.646 509 16	472.418 020
2	–1.801 435 97	0.209 108 771	–0.137 143 90	37.684 494
3	0.717 272 04	0.190 439 972	–0.006 497 67	7.472 018
4	0.503 440 27	0.142 648 498	–0.002 344 44	2.920 828
5	–0.618 993 95	0.077 993 465	0.005 118 68	0.005 184
6	–0.053 323 22	0.012 475 611	0.001 879 82	–0.963 864
7	0.280 213 62	–0.032 267 127	–0.002 044 72	–0.188 732
8	0.107 152 24	–0.075 291 522	–0.000 461 22	0.191 203
9	–0.293 028 65	–0.056 470 670	0.000 457 24	0.049 025
10	0.044 598 72	0.076 201 285		
11	0.118 686 32	0.123 893 204		
12	–0.052 481 34	–0.029 201 193		
13		–0.091 173 542		
14		0.001 317 696		
15		0.026 025 526		

Table 2: The sub-ranges, deviation functions in terms of adjustable parameters *a*, *b*, and *c*, and calibration points for platinum resistance thermometers used to realise ITS-90.

Temperature sub-range	Deviation function	Fixed points
83.8058 K to 0.01 °C	$a(W-1)+b(W-1)\ln(W)$	Ar, Hg
–38.8344 °C to 29.7646 °C	$a(W-1)+b(W-1)^2$	Hg, Ga
0.01 °C to 29.7646 °C	$a(W-1)$	Ga
0.01 °C to 156.5985 °C	$a(W-1)$	In
0.01 °C to 231.928 °C	$a(W-1)+b(W-1)^2$	In, Sn
0.01 °C to 419.527 °C	$a(W-1)+b(W-1)^2$	Sn, Zn
0.01 °C to 660.323 °C	$a(W-1)+b(W-1)^2+c(W-1)^3$	Sn, Zn, Al

The Deviation Functions

The deviations functions, $\Delta W(T_{90})$, depend on the temperature range. Table 2 lists the deviation functions for the temperature sub-ranges between 84 K and 660 °C. Each deviation function has adjustable parameters *a*, *b*, and *c*, which are the calibration constants for the SPRT. The number of constants equals the number of fixed points (excluding the water triple point, which is required to calculate the resistance ratio).

The values for the SPRT calibration constants are found by solving simultaneous equations, of the form of equation (2), for each fixed point. For example, for the water–zinc sub-range (0.01 °C to 419.527 °C), the two constants *a* and *b* are found by solving the two equations

$$W_{r,Sn} = W_{Sn} - a(W_{Sn}-1) - b(W_{Sn}-1)^2, \quad (7a)$$

$$W_{r,Zn} = W_{Zn} - a(W_{Zn}-1) - b(W_{Zn}-1)^2, \quad (7b)$$

where W_{Sn} and W_{Zn} are the measured resistance ratios for the SPRT at the freezing points of tin and zinc, respectively, and $W_{r,Sn}$ and $W_{r,Zn}$ are the values of the reference function at the tin and zinc points. The reference resistance ratios for the various fixed points are given in Table 3.

Your SPRT calibration certificate should have the measured resistance ratios for each fixed point (e.g., the values for W_{Sn} and W_{Zn}). In some cases, the calculated *a*, *b*, and *c* values for each temperature sub-range may also be given.

Table 3: Defined temperatures and reference resistance ratios for the ITS-90 fixed points.

Fixed Point	t_{90} (°C)	T_{90} (K)	$W_r(T_{90})$
Ar	–189.3442	83.8058	0.215 859 75
Hg	–38.8344	234.3156	0.844 142 11
H_2O	0.01	273.16	1.000 000 00
Ga	29.7646	302.9146	1.118 138 89
In	156.5985	429.7485	1.609 801 85
Sn	231.928	505.078	1.892 797 68
Zn	419.527	692.677	2.568 917 30
Al	660.323	933.473	3.376 008 60

Although it is not obvious, equation (2) describes an interpolation. Interpolation is the process of finding a value between two or more defined points. This is shown in Figure 1 for the water–zinc sub-range. The three points in the figure are the calibration points for the SPRT, and the line is given by equation (2). Any other measured resistance ratio $W(T_{90})$ is related to the $W_r(T_{90})$ value via the line, as symbolised by the arrows in Figure 1.

The interpolation becomes more obvious if we take the values of *a* and *b* calculated from the simultaneous equations (7a) and (7b) and insert them into equation (2). In this case, equation (2) becomes:

$$W_r = \frac{(W-W_{Sn})(W-W_{Zn})}{(1-W_{Sn})(1-W_{Zn})} + W_{r,Sn}\frac{(W-1)(W-W_{Zn})}{(W_{Sn}-1)(W_{Sn}-W_{Zn})} + W_{r,Zn}\frac{(W-1)(W-W_{Sn})}{(W_{Zn}-1)(W_{Zn}-W_{Sn})}. \quad (8)$$

Equation (8) is actually the full calibration equation for the SPRT. In this version of the equation, the calibration constants are the resistance ratios measured at the fixed points, W_{Sn} and W_{Zn}. The equation looks a lot more complicated than equation (2), but it has some nice features that we require for the uncertainty analysis (see below).

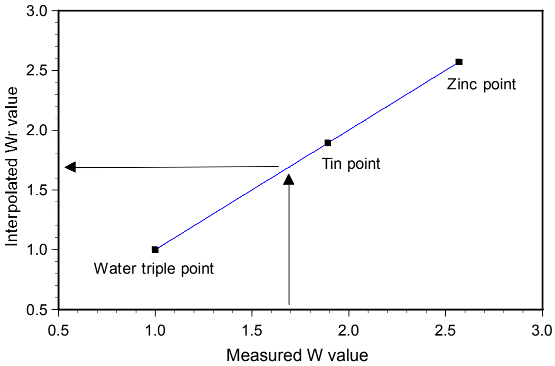

Figure 1. The deviation functions interpolate between the measured $W(T_{90})$ values to find the $W_r(T_{90})$ values.

All of the ITS-90 equations can be written in a form similar to equation (8):

$$W_r = f_{H_2O} + W_{r,Sn} f_{Sn} + W_{r,Zn} f_{Zn} \,. \qquad (9)$$

Each term of equation (9) is an interpolating function, *f,* named after one of the SPRT calibration points, multiplied by the reference resistance ratio for the calibration point (the reference resistance ratio for the water triple point is 1.0). Table 4 lists all of these equations and the interpolating functions for the ITS-90 equations covered by this guide.

Calculating Unknown Temperatures

To calculate temperature there are three mathematical steps.

Step 1: Use equation (1) to calculate the resistance ratio, W, for the unknown temperature. The two resistance measurements used to calculate W should be made using the same resistance bridge. This practice eliminates a couple of potentially large systematic errors, but means that you will need your own resistance bridge and triple-point-of-water cell.

Step 2: Use equation (2) (or the appropriate equation from Table 4) to calculate the W_r value. For this step you will need the values of a, b, and c, or the values of W_{Sn}, W_{Zn}, etc, from the SPRT calibration certificate.

Step 3: Use the inverse function (4) or (6) to calculate T_{90}.

For the best reliability and accuracy, the equations should be set up in software, such as a spreadsheet application. The calculations for the reference functions and the interpolating equations can be tested using the values given in Table 3.

Propagation of Uncertainty

A full and detailed uncertainty analysis for a temperature measurement with an SPRT is complicated; however, for most measurements we can make a simple approximation. The equation for the total uncertainty is

$$u_{total}^2 \approx u^2(W) + \sum_{i=2}^{N} f_i^2 u^2(W_i) \,, \qquad (10)$$

where $u(x)$ indicates the uncertainty in x, and the index i corresponds to the various fixed points used to calibrate the SPRT (Hg, Ga, Sn, …). Note that i = 1 corresponds to the triple point of water.

The first term of equation (10) is the uncertainty in the W value for the unknown temperature that is being measured – more detail on that shortly. The remaining terms of equation (10) are due to the uncertainties in the measured resistance ratios at the calibration points – these numbers should be given on the SPRT certificate. Note that each uncertainty is multiplied by the corresponding interpolating function from Table 4, and there is no term due to the uncertainty in the triple point of water (this is already included in the other uncertainties).

The uncertainty in the measured W value can be broken down into several other terms:

$$u^2(W) = \frac{1}{R_{H_2O}^2}\left(u^2(R) + W^2 u^2(R_{H_2O})\right) + \left(\frac{dW_r}{dT_{90}}\right)^2 \left(u^2(T) + W^2 u^2(T_{H_2O})\right) \qquad (11)$$

The first line includes the uncertainties in the two resistance measurements. If a high-quality resistance bridge is used, and the same bridge is used for both measurements, these two terms should be very small, and can often be neglected.

The second line of equation (11) includes the uncertainties in the measured temperatures. The uncertainty $u(T)$ looks like the uncertainty you are trying to measure, but this term includes effects that cause the SPRT to be at the incorrect temperature or cause it to give an incorrect resistance reading. This includes things like self-heating of the SPRT due to the sensing current, immersion effects, background heat fluxes, and oxidation of the platinum in the SPRT. The term $u(T_{H_2O})$ is the uncertainty in your measurement of the triple point of water. This includes effects that cause the SPRT to be at the incorrect temperature when immersed in the triple-point cell, such as self-heating, the hydrostatic effect, and isotopic effects.

An Example

Suppose we are measuring a temperature near 320 °C using an SPRT with the calibration constants and uncertainties shown in Table 5. Your certificate should have a very similar table. Suppose the measured SPRT resistances at the unknown temperature and at the triple point of water are:

$R\,(T_{90})$ = 56.53462 Ω,

R (273.16 K) = 25.47864 Ω.

Finally, suppose that the uncertainties in the various measurements are:

$u(R)$ = 0.00001 Ω

$u(R_{H_2O})$ = 0.00001 Ω

$u(T)$ = 0.006 °C

$u(T_{H2O})$ = 0.001 °C

Table 5. Calibration constants and uncertainties for an SPRT.

Fixed point	W_i value	$u(W_i)$
Mercury (Hg)	0.844 193 8	0.000 004 0
Gallium (Ga)	1.118 138 9	0.000 004 0
Indium (In)	1.609 568 8	0.000 005 7
Tin (Sn)	1.892 465 8	0.000 007 4
Zinc (Zn)	2.568 917 3	0.000 012

Table 4. The sub-ranges, reference functions, and interpolating functions in terms of measured resistance ratios, for platinum resistance thermometers used to realise ITS-90. In these equations:

- W is the resistance ratio at the unknown temperature, calculated using equation (1).
- W_{Hg}, W_{Ga}, W_{In}, W_{Sn}, W_{Zn}, and W_{Al} are the resistance ratios of the SPRT at the calibration points. These values should be reported on the SPRT certificate.
- $W_{r,Hg}$, $W_{r,Ga}$, $W_{r,In}$, $W_{r,Sn}$, $W_{r,Zn}$, and $W_{r,Al}$ are the reference resistance ratios defined by ITS-90 at the calibration points (see Table 3).

Temperature sub-range	Reference function, W_r, and interpolating functions
83.8058 K to 0.01 °C	$W_r = f_{H_2O} + W_{r,Hg} f_{Hg} + W_{r,Ar} f_{Ar}$ $f_{H_2O} = 1 - f_{Hg} - f_{Ar}$, $f_{Hg} = \frac{(W-1)(\ln W - \ln W_{Ar})}{(W_{Hg}-1)(\ln W_{Hg} - \ln W_{Ar})}$, $f_{Ar} = \frac{(W-1)(\ln W - \ln W_{Hg})}{(W_{Ar}-1)(\ln W_{Ar} - \ln W_{Hg})}$
–38.8344 °C to 29.7646 °C	$W_r = f_{Hg} W_{r,Hg} + f_{H_2O} + f_{Ga} W_{r,Ga}$ $f_{Hg} = \frac{(W-1)(W-W_{Ga})}{(W_{Hg}-1)(W_{Hg}-W_{Ga})}$, $f_{H_2O} = \frac{(W-W_{Hg})(W-W_{Ga})}{(1-W_{Hg})(1-W_{Ga})}$, $f_{Ga} = \frac{(W-W_{Hg})(W-1)}{(W_{Ga}-W_{Hg})(W_{Ga}-1)}$
0.01 °C to 29.7646 °C	$W_r = f_{H_2O} + f_{Ga} W_{r,Ga}$ $f_{H_2O} = \frac{(W-W_{Ga})}{(1-W_{Ga})}$, $f_{Ga} = \frac{(W-1)}{(W_{Ga}-1)}$
0.01 °C to 156.5985 °C	$W_r = f_{H_2O} + f_{In} W_{r,In}$ $f_{H_2O} = \frac{(W-W_{In})}{(1-W_{In})}$, $f_{In} = \frac{(W-1)}{(W_{In}-1)}$
0.01 °C to 231.928 °C	$W_r = f_{H_2O} + f_{In} W_{r,In} + f_{Sn} W_{r,Sn}$ $f_{H_2O} = \frac{(W-W_{In})(W-W_{Sn})}{(1-W_{In})(1-W_{Sn})}$, $f_{In} = \frac{(W-1)(W-W_{Sn})}{(W_{In}-1)(W_{In}-W_{Sn})}$, $f_{Sn} = \frac{(W-1)(W-W_{In})}{(W_{Sn}-1)(W_{Sn}-W_{In})}$
0.01 °C to 419.527 °C	$W_r = f_{H_2O} + f_{Sn} W_{r,Sn} + f_{Zn} W_{r,Zn}$ $f_{H_2O} = \frac{(W-W_{Sn})(W-W_{Zn})}{(1-W_{Sn})(1-W_{Zn})}$, $f_{Sn} = \frac{(W-1)(W-W_{Zn})}{(W_{Sn}-1)(W_{Sn}-W_{Zn})}$, $f_{Zn} = \frac{(W-1)(W-W_{Sn})}{(W_{Zn}-1)(W_{Zn}-W_{Sn})}$
0.01 °C to 660.323 °C	$W_r = f_{H_2O} + f_{Sn} W_{r,Sn} + f_{Zn} W_{r,Zn} + f_{Al} W_{r,Al}$ $f_{H_2O} = \frac{(W-W_{Sn})(W-W_{Zn})(W-W_{Al})}{(1-W_{Sn})(1-W_{Zn})(1-W_{Al})}$, $f_{Sn} = \frac{(W-1)(W-W_{Zn})(W-W_{Al})}{(W_{Sn}-1)(W_{Sn}-W_{Zn})(W_{Sn}-W_{Al})}$, $f_{Zn} = \frac{(W-1)(W-W_{Sn})(W-W_{Al})}{(W_{Zn}-1)(W_{Zn}-W_{Sn})(W_{Zn}-W_{Al})}$, $f_{Al} = \frac{(W-1)(W-W_{Sn})(W-W_{Zn})}{(W_{Al}-1)(W_{Al}-W_{Sn})(W_{Al}-W_{Zn})}$

The calculation for the temperature uses the calibration values and equations for the water–zinc sub-range, and proceeds as follows:

Step 1: From equation (1), $W(T_{90})$ = 2.2189026.
Step 2: From equation (8), $W_r(T_{90})$ = 2.21913711.
Step 3: From equation (6), T_{90} = 321.067 °C.

The uncertainty in the calculated temperature proceeds as follows:

Step 1: The contribution of the calibration uncertainty is calculated using the summation term of equation (10). For the example here, the two relevant calibration points are the tin point and zinc point, so that calibration uncertainty is

$$\sqrt{f_{\mathrm{Sn}}^2 u^2(W_{\mathrm{Sn}}) + f_{\mathrm{Zn}}^2 u^2(W_{\mathrm{Zn}})}\ , \qquad (12)$$

where the numerical values of the two uncertainties are in column 3 of Table 5. The calculated value is 0.000 006 9. This is the uncertainty in the calculated W_r value due to the uncertainty in the SPRT calibration, and is equivalent to about 1.8 mK.

Step 2: The contribution of the resistance measurements is calculated as the square root of the first line of equation (11). The calculated value is 0.000 000 96 (equivalent to about 0.25 mK).

Step 3: The contribution of the uncertainty in the temperature measurements is given by the square root of the second line of equation (11). The value is 0.000 024 (about 6.5 mK). To do this calculation you will require a value for dW_r/dT_{90}; a good approximation is 1/260.

Step 4: Sum in quadrature all of the uncertainty terms from above (i.e. sum the squares of each term, then take the square root). The result is the total $u(W_r)$ = 0.000 025. This is then multiplied by dT_{90}/dW_r to give an equivalent temperature uncertainty of 6.7 mK. It is usual for the uncertainty associated with the measurement at the unknown temperature to dominate (in this case 6.7 mK is not much greater than 6 mK).

Further Reading

This guide is a very short summary of the process for calculating temperatures and their uncertainties for measurements made using an SPRT. The uncertainty equations are approximations that will generally be satisfactory for uncertainties about a factor of 3 larger than the calibration uncertainties.

For the approximations in the uncertainty equations to be valid, it is necessary that:

- the two measurements required for calculation of a single resistance ratio, *W*, should be made using the same resistance bridge;
- the uncertainties in the resistance measurements are negligible; and
- the uncertainties due to the triple-point-of-water measurements are negligible for both the calibration laboratory and the user of the SPRT.

Additionally, we have only made brief mention of some of the sources of uncertainty in the SPRT measurements. For further information you should contact your national measurement laboratory (MSL in New Zealand). They have access to more accurate expressions for the uncertainty and information and advice on using SPRTs at the lowest uncertainties. Information on the ITS-90, including the definition of ITS-90, the *mise en pratique for the kelvin*, and *Supplementary Information for ITS-90*, and a number of other useful thermometry publications are available under *publications* in the thermometry section of the BIPM website:

http://www.bipm.org/en/committees/cc/cct/.

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