Characteristics of Rhodium-Iron Resistance Thermometers and Interpolation Properties from 0.65 K To 24.5561 K

R. L. Rusby¹ and W. L. Tew²

¹National Physical Laboratory, Teddington TW11 0LW, UK ²National Institute of Standards and Technology, Gaithersburg MD 20899, USA

Abstract. Resistance thermometers using wires of rhodium with 0.5 mol % of iron (Rh-Fe thermometers or RIRTs) were first made by H Tinsley & Co in 1969 for applications at low temperatures, below the range where standard platinum resistance thermometers can be used, and down to 0.5 K or lower. They were investigated at NPL and found to have good sensitivity and excellent stability. Subsequently RIRTs have been used as the standard thermometers which record and compare the results of experiments in thermometry particularly below 24.5561 K, the triple-point of neon. From 1969 until the early 2000s, when Tinsley ceased to manufacture them, several hundred RIRTs were made and many were calibrated at NPL, NIST and elsewhere. In order to document the resistance-temperature characteristics of the production, and indicate the variability from batch to batch, the present paper analyses representative data for the resistance at the triple-point of water and the low-temperature calibrations of a number of thermometers produced at various times. The opportunity has been taken to include data for three RIRTs which were made independently, two in Russia and one in China.

Keywords: Rhodium-iron, RIRT, resistance thermometer, low temperature.

INTRODUCTION

The addition of a small concentration (up to ~1 mol %) of iron to rhodium was found in 1964 to give rise to an anomalous low-temperature resistivity with a significant positive temperature coefficient [1]. This is associated with the fluctuation of the localised magnetic moments on the iron atoms, which is slow compared with other scattering mechanisms at high temperatures but relatively fast at low temperatures. As a result the iron effectively loses its moment and the impurity resistivity gradually falls as the temperature passes through a characteristic spin fluctuation temperature of ~15 K [2].

Figure 1 shows that the resistivity, $\rho(T)$, of Rh-0.5 % Fe is dominated by the impurity effect at low temperatures, but that the resistivity of the host rhodium increasingly dominates above ~ 30 K. The cross-over point is marked by a minimum in the slope, below which the sensitivity, $d\rho(T)/dT$, increases to much larger values than are found in pure rhodium (or platinum) at these temperatures.

In the original publication Coles suggested that 'these materials could form very useful resistance thermometers down to very low temperatures'. To follow this up, wires of various iron concentrations were made by Engelhard Industries (UK) Ltd[†], by depositing iron on rhodium powder, sintering, then hot-swaging and hot-drawing to the final diameter. The wires were then strand-annealed in hydrogen at >1100 °C to recrystallise the material without oxidising the iron. They were tested at NPL and a concentration of 0.5 mol % Fe was adopted for use in the thermometers, as a compromise between achieving a large enough resistivity and sensitivity, while avoiding excessive interaction between Fe atoms which tends to stabilise the moments and stifle the effect. Engelhard designated the product 'Alloy 1200'.



FIGURE 1. Resistivity of rhodium -0.5 % iron [3], top, and rhodium [4], bottom, and the difference, being mainly due to the dissolved iron (dashed).

[†] The identification of commercial products is not intended to imply recommendation or endorsement by the NIST or NPL, nor is it intended to imply that the products identified are necessarily the best available for the purpose.

The first prototype thermometers were made by H. Tinsley and Co, in 1969, following their design of capsule-type Standard Platinum Resistance Thermometers (SPRTs). Before sealing in helium at ~ 30 kPa, the coil assembly was given a stress-relieving anneal at ~ 700 °C. Since the wires are not as soft as platinum wires used in SPRTs they are self-supporting in straight vertical tubes without any helical twist. As a result four tubes could be included in the capsule, rather than two as for SPRTs, and a shorter capsule was used which could more easily be accommodated in the confined space of a cryostat. The first results of measurements with these prototypes were presented at the 5th International Temperature Symposium in 1971 [5]. Later a thermometer of higher resistance was wanted for gas thermometry experiments [6], and fullsized capsules were used. This is the origin of the two types, designated by Tinsley 5187U and 5187W.

The main criteria for suitability of the wire are that the iron should be unoxidised and fully dissolved in the rhodium host, and that the annealing should lead to a resistance ratio $R_{4.2 \text{ K}} / R_{273 \text{ K}}$ in the region of 0.07. However, good thermometers can be made with a wide range of characteristics and there was no requirement to match a particular reference specification or tolerance. The basic data for the Type 5187U and Type 5187W RIRTs are given in Table 1, with data for Type 5187L SPRTs for comparison.

TABLE 1. Parameters and approximate values forTinsley RIRTs and SPRTs

Parameter	RIRT	RIRT	SPRT
	5187U	5187W	5187L
Capsule dia., mm	5	5	5
Capsule length, mm	30	50	50
Overall length, mm	50	70	70
Wire diameter, mm	0.05	0.05	0.076
Wire length, m	2 - 2.5	4	1.2
R_{273K} , Ω	50 - 65	100	25
$R_{24.5 K}, \Omega$	6 - 8	12	0.21
$R_{4.2 K}, \Omega$	3.5 - 4.5	7	0.012
$(dR/dT)_{24.5 \text{ K}}, \Omega \cdot \text{K}^{-1}$	0.08 - 0.10	0.15	0.03
$(dR/dT)_{4.2 \text{ K}}, \Omega \cdot \text{K}^{-1}$	0.25 - 0.35	0.5	0.0004
$(d \ln R/dT)_{4.2 \text{ K}}, \text{ K}^{-1}$	0.07	0.07	0.034

RIRTs can be measured using similar techniques and equipment as are commonly used for SPRTs, and precisions of 0.1 mK or better can be achieved throughout their range. Their first serious uses were in the gas thermometry of Berry in 1973-5 from 2.6 K to 27.1 K [6] and the helium vapour-pressure determinations of Rusby and Swenson, 1975-8, down to 0.5 K [7]. The long-term repeatability has been excellent [8], and they became the preferred sensor for working standards calibrated according to the ITS-90 (and the EPT-76 before it) from 0.65 K to 24.5561 K. Over the years since 1970 several hundred Type U and W RIRTs were made but ultimately, as a result of saturation of the market and falling demand, making another new batch of wire could not be justified commercially and the production stopped. The purpose of this paper is to examine and document the characteristics of the thermometers which were made in that time and measured at NPL or NIST. It has not been practicable to include all the RIRTs, but over 40 examples have been taken covering almost the whole period of manufacture, with no other selection criteria and without discarding any cases examined. Some basic data for these RIRTs are given in Appendix 1.

Data for three thermometers sent to NPL from other sources have been included for comparison. One was from NIM, Beijing, made in China and received in 1978, and two were made at VNIIFTRI in Russia and submitted to the key comparison CCT-K1 [9] in 1989.

RESISTANCE CHARACTERISTICS

To compare characteristics of RIRTs with widely varying resistances it is necessary to normalise the data. Figure 2 shows W(T) = R(T)/R(273.16 K), for the 14 RIRTs which took part in CCT-K1, including the two from VNIIFTRI, plus three others from NIST and one from NIM. As expected the ratios are similar, and mainly differ in vertical displacement. Above the main group are the three 1973 RIRTs and, at the top, an outlier from the early 1980s. The thermometer from NIM has a lower sensitivity, presumably because of a lower concentration of dissolved iron (nearer 0.4 % than 0.5 %), and as a result, W(T) cuts across from the main group at 25 K to the 1973 group at 0.65 K.

The vertical shifts between W(T) for different RIRTs strongly suggest that the concentration of dissolved iron was quite well controlled, but that the annealing treatments, which are intended to reduce the temperature-independent resistivity due to crystal defects, etc, were not. This has been tested by plotting dW/dT and the relative sensitivity, $d\ln W/dT$, versus W, all at 4.22 K. If the concentration varied, dW/dT would scale with W, but their ratio $d\ln W/dT$ should be constant. However, if the annealing were inadequate, W would be increased while dW/dT would be unchanged, so $d\ln W/dT$ would be decreased.

Figure 3 shows the correlations and confirms, on the above reasoning, that the annealing is the main cause of the variability in characteristic, though the scatter about the lines suggests that it is not the only factor. The NIM RIRT lies off the Tinsley lines, as a result of the lower concentration of dissolved iron. All but two of the Tinsley RIRTs made since 1974 are toward the left side of the figure, with W(4.2 K) <0.075. It seems likely that the final stress anneal of the two exceptional thermometers was insufficient.



FIGURE 2. The normalized resistance W(T) versus T for 16 RIRTs

Z-FUNCTION INTERPOLATION

The variations in W(T) are too large to allow a successful reference function to be produced. Normalisation to a low temperature reference point, such as the triple point of neon, brings the characteristics together at the top end of the range, but the values at 0.65 K still differ by as much as 10 %. In these circumstances it is necessary to normalise the characteristic at two points using a *Z*-function [10],

$$Z(T) = \frac{R(T) - R(T_{1})}{R(T_{2}) - R(T_{1})}$$

which scales the resistance from 0 at $T_1 = 4.2221$ K to 1 at $T_2 = 24.5561$ K. The characteristics are now close enough that they are superimposed on each other in a graph of Z(T) versus T. We can therefore plot the deviations ΔZ between RIRTs and consider the scope for defining a calibration using a reference Z-function.

An example is shown in Figure 4, where the reference is NIST RIRT 233180, and the deviations for 17 other RIRTs are converted to the temperature equivalents by dividing by dZ/dT. Except at the lowest temperatures twelve of the thermometers are grouped within 10 mK of the axis. Below them are the VNIIFTRI thermometers, and above them are the 1973 thermometers, and two later outliers at the top. These extrapolate to ~-70 mK at 0.65 K. The NIM thermometer oscillates centrally about the axis and extrapolates to +38 mK at 0.65 K.

The dispersion at low temperatures can be reduced by using a lower normalisation temperature. For example if the lambda temperature (2.1768 K) is used the maximum dispersion is reduced to 43 mK at 0.65 K, though the maximum deviations around 15 K are mostly about 50 % higher.



FIGURE 3. Relative sensitivity $d\ln W/dT$ (upper data) and $10 \cdot dW/dT$ (lower data) versus *W*, all at 4.22 K, for Tinsley RIRTs. Data are for 29 RIRTs from NPL (triangles), and 13 from NIST (diamonds). Data are also shown for the VNIIFTRI (X) and NIM (+) RIRTs.

Several RIRTs, notably the NIM thermometer, but also the VNIIFTRI and to a lesser extent some Tinsley thermometers, show two or three inversions in ΔZ with respect to the baseline RIRT, and it seems likely that this behaviour is related to concentration differences. In any case there is enough structure to suggest that several additional points would be needed to achieve a satisfactory interpolation over the range, say within 1 mK, even for the later (1974-) Tinsley RIRTs. Conversely, much tighter control of the thermometer production would be needed if interpolation based on

measurements at a few fixed-points, as has been proposed by Lin Peng [11], is to be reliable.



FIGURE 4. Deviations ΔZ from a reference Z-function, expressed in mK equivalents.

Finally, it should be noted that while Figure 4 relates to a small sample of RIRTs, those which happened to be compared together in CCT-K1 plus four others, they were not specially selected for their characteristics. In fact the 1973 RIRTs and two later outliers have been deliberately included, and the Tinsley production in general may bunch more closely as in the main group of 10. Moreover, they all function equally well as thermometers. It should also be clear that the ΔZ derived from resistance comparisons in CCT-K1 at a series of ~40 temperatures, make no reference to a particular temperature scale or realisation: ΔZ could just as well have been plotted against Z.

SUMMARY

RIRTs have been found to be reliable secondary standards for thermometry at low temperatures, especially below the triple point of neon. They provide good sensitivity coupled with excellent stability and repeatability. The calibrations are generally obtained by comparison with standard thermometers at many points using a least-squares curve-fit for interpolation. Typically more than 30 points were used at NPL to achieve standard deviations < 0.2 mK over the range 0.65 K to 24.5561 K, though this could probably be achieved with 15-20 if the points are carefully spaced. Other possible economies have been considered in [8]. It must be expected that a reference function interpolation, as used for platinum thermometers in the ITS-90, would work less well for an alloy system such as this. The available fixed points may not be sufficient or suitably spaced, and making measurements at them is likely to prove more timeconsuming and therefore more expensive than a comparison against standard RIRTs.

In contrast, reference functions have been successfully used for representing calibrations of the small rugged 'industrial' RIRT which has been made in large numbers (many 1000s) for general purposes, and with larger uncertainties, up to 300 K and even beyond [12].

REFERENCES

- 1. Coles B. R., Phys. Letters 8, 243-244 (1964).
- 2. Rivier N. and Zlatic V., *J Phys F: Metal Physics* **2**, L87-92 and L99-104, (1972).
- 3. Rusby R. L., *J Phys F: Metal Physics* **4**, 1265-1274 (1974).
- White G. K. and Woods S. B., *Phil. Trans. Roy. Soc.* A251, 273-302 (1959).
- Rusby R. L., *Temperature, its measurement and Control* in Science and Industry, Vol. 4, edited by H. H. Plumb, Instrument Society of America, Pittsburgh, USA, 1972, pp 865-869.
- 6. Berry K. H., Metrologia 15, 89-115 (1979).

- 7. Rusby R. L. and Swenson C. A., *Metrologia* **16**, 73-87 (1980).
- Rusby R. L., *Temperature, its measurement and Control* in Science and Industry, Vol. 5, edited by J. F. Schooley, American Institute of Physics, New York, 1982, pp 829-833.
- 9. Rusby R. L. et al., Metrologia 43, Tech. Suppl. 03002 (2006).
- 10. Cragoe C. S., *Proces verbaux du CIPM* 1948 **21** T84-86. See also Chapter 8 of *Techniques for Approximating the ITS-90*, BIPM, 1997.
- 11. Lin Peng, *Acta Metrologica Sinica* **29**, No 5A, 171-178 (2008).
- 12. Ricketson B. W. A. and Watkins R. E. J., *Cryogenics* 49, 320-325 (2009).

APPENDIX 1. Basic data for RIRTs plotted in Figure 3. Uncertainties, including small scale differences, are generally 0.5 mK equivalent or less.

	Serial number	Date made	Calibration date	$R_{273.16 \text{ K}}$ Ω	$egin{array}{c} R_{4,2221 \mathrm{K}} \ \Omega \end{array}$	W _{4.2221 К}	d <i>R/</i> d <i>T</i> Ω / K	dW/dT K ⁻¹	dlnW/dT K ⁻¹
NPL									
5187U	193880	1970	1977	40.96511	3.55594	0.086804	0.2037	0.00497	0.0573
	19387	1970	1977	40.04728	3.46452	0.086511	0.1970	0.00492	0.0569
	229822	1976	1976	63.61126	4.53995	0.071370	0.3102	0.00488	0.0683
	231966	1978	1978	58.37667	4.05072	0.069389	0.2807	0.00481	0.0693
	231969	1978	1978	56.28621	3.87396	0.068826	0.2705	0.00481	0.0698
	A15	1980	1980	56.56185	3.77044	0.066660	0.2719	0.00481	0.0721
	A22	1981	1981	52.39506	3.92199	0.074854	0.2508	0.00479	0.0639
	A77	1986	1986	55.04115	3.60771	0.065546	0.2526	0.00459	0.0700
	A88	1986	1986	55.39979	3.66519	0.066159	0.2469	0.00446	0.0674
	A140	~1990	1998	67.92071	4.81642	0.070912	0.3372	0.00496	0.0700
5187W	221481	1973	1974-76	102.9759	8.24444	0.080062	0.5236	0.00508	0.0635
	221484	1973	1974-76	93.71739	8.10550	0.086489	0.4769	0.00509	0.0588
	221485	1973	1974-76	90.18323	7.26337	0.080540	0.4625	0.00513	0.0637
	226242	1975	1977	99.20147	6.32886	0.063798	0.4545	0.00458	0.0718
	226950	1975	1977	105.516	7.55155	0.071568	0.5086	0.00482	0.0674
	229074	1976	1977	101.8174	6.90730	0.067840	0.4888	0.00480	0.0708
	229832	1977	1977	101.6394	7.03841	0.069249	0.4946	0.00487	0.0703
	232296	1978	1980	101.1755	7.18694	0.071034	0.4870	0.00481	0.0678
	234726	1981	1981	98.83987	6.71401	0.067928	0.4729	0.00478	0.0704
	B34	1981	1981	98.40426	7.95684	0.080859	0.4707	0.00478	0.0592
	B178	~1987	1990	94.87914	6.30722	0.066476	0.4484	0.00473	0.0711
	B183	~1987	2000	91.48168	6.16820	0.067425	0.4399	0.00481	0.0713
	B187	~1987	1990	93.79837	6.31742	0.067351	0.4525	0.00482	0.0716
	B271	~1995	1998	100.4481	7.20369	0.071716	0.4977	0.00495	0.0691
	B310	~1995	1998	99.392	7.04703	0.070901	0.4911	0.00494	0.0697
	B366	1999	2000	98.00733	7.30898	0.074576	0.4900	0.00500	0.0670
	B372	1999	2000	102.5726	7.56694	0.073772	0.5149	0.00502	0.0680
NIST									
5187U	233180	~1979	2007	48.19572	3.39332	0.070407	0.2316	0.004806	0.0683
	A38	~1983	2000	42.98	3.05084	0.07099	0.2076	0.004831	0.0681
	A48	~1983	2001	58.05	4.24702	0.07316	0.2803	0.004827	0.0660
	A128	~1989	1997	65.45653	4.43684	0.067783	0.3150	0.004812	0.0710
	A129	~1989	1997	61.27166	4.19405	0.06845	0.2956	0.004824	0.0705
5187W	229078	1976	2004	103.7902	6.90581	0.066536	0.4973	0.004791	0.0720
	229079	1976	2004	101.7166	6.73158	0.06618	0.4880	0.004798	0.0725
	229092	1976	2007	100.222	7.08499	0.070693	0.4820	0.004809	0.0680
	B115	~1985	2007	99.71032	8.86793	0.088937	0.4871	0.004885	0.0549
	B155	~1986	1992	97.49925	6.86914	0.070453	0.4753	0.004875	0.0692
	B168	~1987	1997	102.347	7.20304	0.070379	0.4978	0.004864	0.0691
	B174	~1988	1997	99.00589	7.01833	0.070888	0.4842	0.004891	0.0690
	B211	~1989	1997	100.6794	7.23116	0.071824	0.4918	0.004885	0.0680
NIM	77111	unknown	1978	48.79969	3.72135	0.076258	0.2123	0.004350	0.0570
VNIIFTRI	T79	unknown	2000	102.54041	7.68821	0.074977	0.4992	0.004869	0.0649
	T89	unknown	2000	99.23446	7.44836	0.075058	0.4839	0.004876	0.0650