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High-temperature platinum resistance thermometry: the problem with silver and the case for gold

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Abstract

The diffusion of silver through quartz at high temperatures leads to contamination of the platinum sensing element of high temperature platinum resistance thermometers. While some protection of the PRT element may be afforded by the application of appropriate electric fields, the contamination of the quartz elements of silver fixed points causes their premature failure. Contamination is evidenced by the yellowish colour imparted to the glass by the silver particles growing within the quartz glass matrix. The presence of silver as the contaminating element has been confirmed unambiguously through energy dispersive x-ray analysis and secondary ion mass spectrometry. To mitigate the risk of silver contamination, the gold point is proposed as an alternative calibration point. PRT resistance ratios measured at the freezing points of silver and gold in different laboratories at different times are highly correlated. This suggests that the ITS-90 reference function might be extrapolated to 1064.18 °C (the gold fixed point). However, it remains unclear from the gold and silver PRT resistance ratios from the literature whether extrapolation of the reference function leads to the correct value at the gold point. A direct comparison of gold fixed points may be required to resolve the inconsistencies. Additional PRT data may help resolve the discrepancy.

Keywords : platinum resistance thermometer; silver fixed point; gold fixed point; contamination.

1. Introduction

When the International Temperature Scale of 1990 (ITS-90) [1] was introduced, it extended the upper temperature limit of the platinum resistance thermometer (PRT) by nearly 300°C beyond that of its predecessor, the International Practical Temperature Scale of 1968 [2]. Although increasing the upper temperature limit of the PRT range of the ITS from 630.74°C to 961.78°C has improved the accuracy of the temperature scale in this range by replacing the Pt-Pt10%Rh thermocouple with a PRT, the most recent revision of the ITS – now 25 years old – has created new challenges that are yet to be fully understood and overcome. The contamination of PRTs by silver is one of the “new” problems identified [3] shortly following the promulgation of ITS-90. Realization of the ITS-90 within the temperature range 660.323 °C to 961.78 °C requires that a PRT be calibrated at the freezing points of tin, zinc, aluminium and silver, so the risk of silver contamination seems unavoidable.

The challenges presented by high-temperature platinum resistance thermometry are such that some have questioned whether it might be better to limit the PRT range of the ITS to 660.323 °C. A gold-platinum thermocouple is considerably more robust than a PRT, and a possible contender to replace the PRT as a designated interpolating thermometer from the aluminium point (660.323 °C) to the silver point (961.78 °C) in a future revision of the ITS, if the reliability of its interpolating equation can be assured with acceptable uncertainty. This strategy of avoidance can also be exploited by increasing the upper limit of the PRT range to the gold point (1064.18 °C), a proposal that will be expanded upon later.

Alternatively, we can accept that the PRT remains the preferred interpolation thermometer and the freezing point of silver the upper limit of its range. The focus then must turn to preventing silver from contaminating the platinum sensing element of the PRT. One approach is to interpose an impermeable barrier between the silver and the PRT. At NRC, attempts to contain the silver within a glassy carbon crucible assembly, and protect the PRT within a 0.1 mm thick platinum sheath, proved unsuccessful [4]. Other laboratories have reported success with the platinum sheath, so it is possible that variations in implementation determine success or failure. A sapphire thermowell was also tested as a barrier, but proved ineffective in preventing contamination – perhaps due to the cracking that resulted from the repeated thermal shocks associated with periodically removing and reinserting the PRT in order to monitor changes in its electrical resistance at the triple point of water.

As an alternative to the electrically passive barrier presented by a platinum sheath or sapphire thermowell, an electric field of an appropriate magnitude and polarity was demonstrated to be capable of preventing contamination of a PRT in the freezing point of silver for an extended period, and such an approach appears to reverse the effects of prior contamination [5]. Here, a variation of the electric field approach is presented with hitherto unreported test results for long-term exposure of a PRT to a silver fixed point furnace. To better understand the process by which silver passes from the fixed point to the PRT, various supplementary data are presented.

2. Silver and quartz

2.1. Optical absorption

Our earlier publications [3–5] mentioned the characteristic yellowish tint imparted to quartz glass following sufficient exposure to the silver fixed-point environment. To better characterise the discolouration, the NRC Photometry and Radiometry Group was requested to measure the absorption spectrum of a section of silver-contaminated quartz thermowell that had been part of the silver-fixed point assembly. The vertical axis of figure 1 represents the ratio of the absorption spectrum of the silver-contaminated thermowell relative to that of an uncontaminated quartz sample. The absorption band peaks near 418 nm and the full width at half height of the band is broad – approximately 121 nm. The characteristic yellow colour of the silver-contaminated quartz results from absorption of the blue part of the spectrum by silver particles within the glass. For comparison, Doremus [6] incorporated silver into a glass melt which was then cooled rapidly to room temperature to prevent precipitation of the silver. He used ultraviolet light to nucleate the silver particles followed by heat treatment at 580 °C to grow the particles. This resulted in a relatively narrow (20 nm full width at half height) absorption band peaking near 406 nm. Compared to figure 1, the peak of the absorption band that Doremus obtained occurs at a similar wavelength but the bandwidth of the spectral feature is substantially narrower. He states that the absorption band would shift to longer wavelengths if the particles were non-spherical or above a certain particle size, that the bandwidth depends on the particle size, and that a broader distribution of particle sizes would lead to a broader absorption band.

Kreibig and Fragstein [7] followed a similar approach to that of Doremus by producing glass melts containing silver oxide among their components. Nucleation of the silver particles was carried out using either ultraviolet light or x-rays. Annealing at 550 °C provided the mobility needed to grow the silver particles. The absorption spectrum exhibited a peak near 405 nm. Smaller particle sizes were associated with broader half-widths due to the limited electron mean-free path imposed by the particle boundary with the glass in which it is imbedded.

More recently, Tanashi *et al.* [8] used sputtering techniques to produce composite Ag/SiO₂ thin films on SiO₂ and GaAs substrates. The particles were grown by heating the films for 1 hour at various temperatures up to 800 °C. Particle growth was observed for annealing temperatures of 600 °C and above. The measured optical absorption spectra exhibit peak wavelengths ranging from approximately 410 nm to 430 nm and bandwidths from approximately 180 nm to 83 nm, with

decreases in peak wavelength and bandwidth correlated with increasing heat-treatment temperature as the mean particle size increased from 5 nm to 19 nm.

The consistency of figure 1 with the results of other investigators establishes the characteristic colouration of the quartz as attributable to the presence of silver particles within the glass matrix.

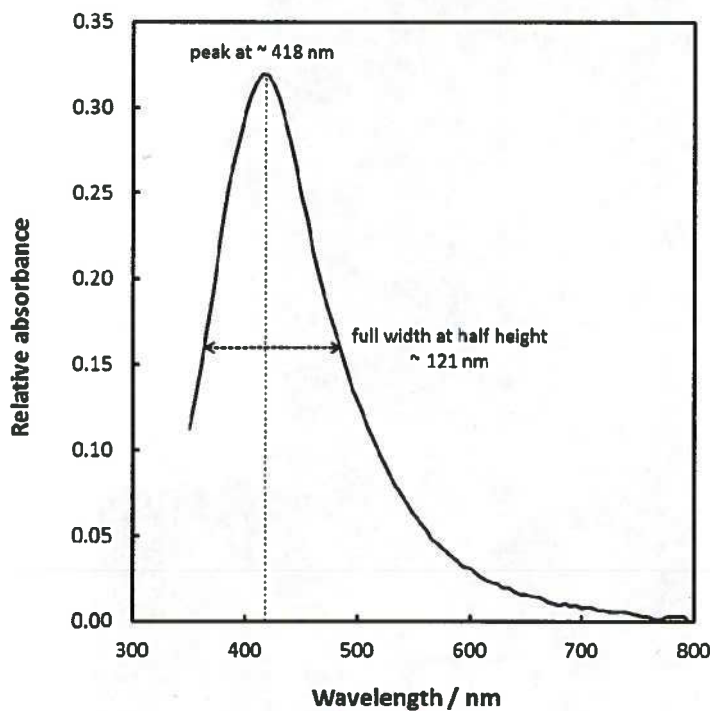


Figure 1. The absorption spectrum of a quartz thermowell contaminated by silver. The vertical axis represents the optical transmission relative to that of an uncontaminated quartz sample.

2.2. Electron microscopy of silver-contaminated quartz

Transmission electron microscope (TEM) images obtained at NRC of a fragment of silver-contaminated quartz from a silver fixed-point assembly are presented in figure 2. One of the silver particles at the edge of the fractured quartz sample was imaged at high resolution (764,000x magnification) to provide some crystallographic detail (i.e. the twinning plane running through the middle of the image) and this appears as the bottom image of figure 2. The dark spots are silver particles that have agglomerated within the quartz, as confirmed by energy dispersive x-ray analysis (EDX). The principle behind EDX is that each element exhibits unique peaks in its X-ray emission spectrum, thereby allowing unambiguous element identification. In the present case, an electron beam stimulates the emission of X-rays from the sample. Within other parts of the imaged area, the EDX signal shows only silicon from the quartz matrix.

Doremus and Turkalo [9] published TEM images of gold and silver particles nucleated and grown from glass melts (with a strong emphasis on the gold results), so our images are by no means the first to be published. However, the process by which the silver particles grew within our quartz samples is very different from that of other investigators. In the present case, the presence of silver is an undesirable occurrence and the goal in applying the various analytical techniques is the unambiguous identification of the contaminating species. The EDX signal confirms the presence of silver particles within the quartz matrix.

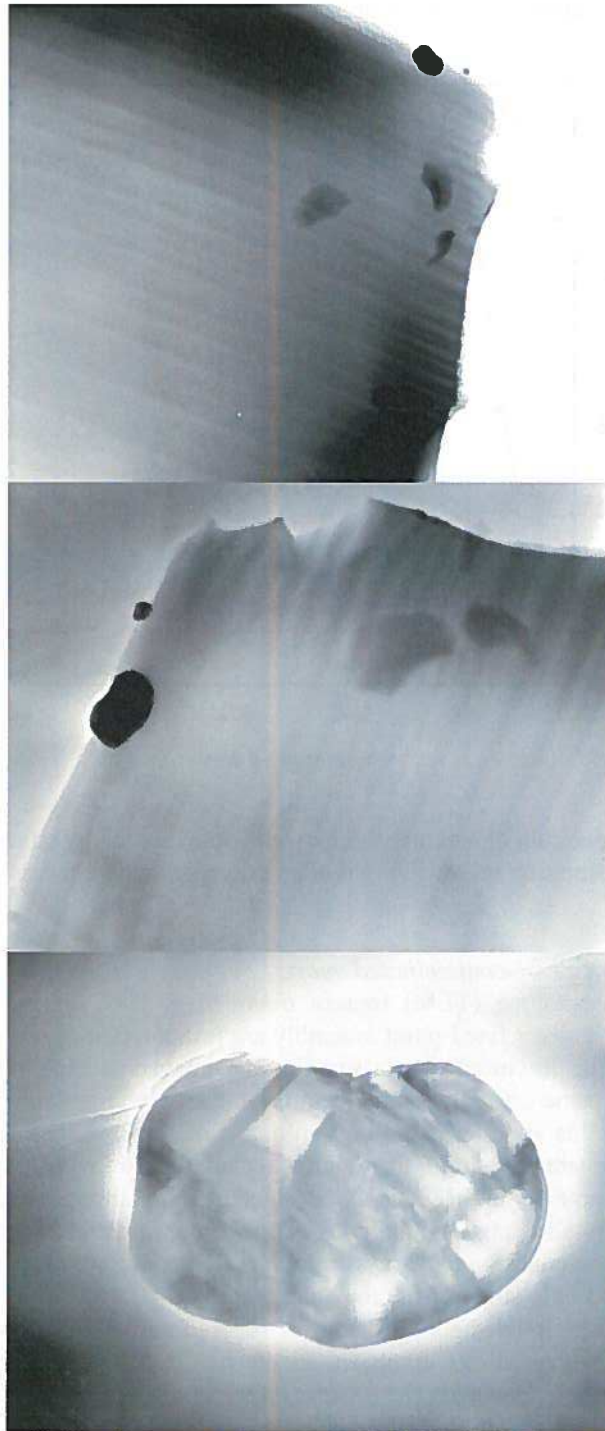


Figure 2. A fragment of silver-contaminated quartz as imaged by a transmission electron microscope. Top image –62,000x magnification, middle image –154,000x magnification, bottom image –764,000x magnification.

2.3. Secondary ion mass spectrometry

With EDX confirming silver as the elemental species contaminating the quartz, we decided to quantify the relative concentrations of silver and silicon within a contaminated quartz sample using secondary ion mass spectrometry (SIMS). SIMS is a technique used to analyse the composition of solids by sputtering the surface with a focused ion beam and collecting and analysing the ejected secondary ions with a mass spectrometer to determine the elemental composition. Figure 3 shows the ion counts of silicon and silver for a quartz thermowell exposed to the silver fixed point for 150 hours. The ion counts are accumulated as a function of sputtering time. The depth indicated on the horizontal axis of figure 3 is assumed to evolve linearly as material is sputtered away by the ion beam. The depth of the pit sputtered into the sample was determined by a stylus profilometer (after the sputtering was complete). The silicon signal remains relatively constant throughout the profile whereas the silver concentration exhibits a nearly linear (on a semi-log plot) decrease in concentration with increasing depth. Importantly, the contaminating species is unambiguously identified by the mass spectrometer as silver.

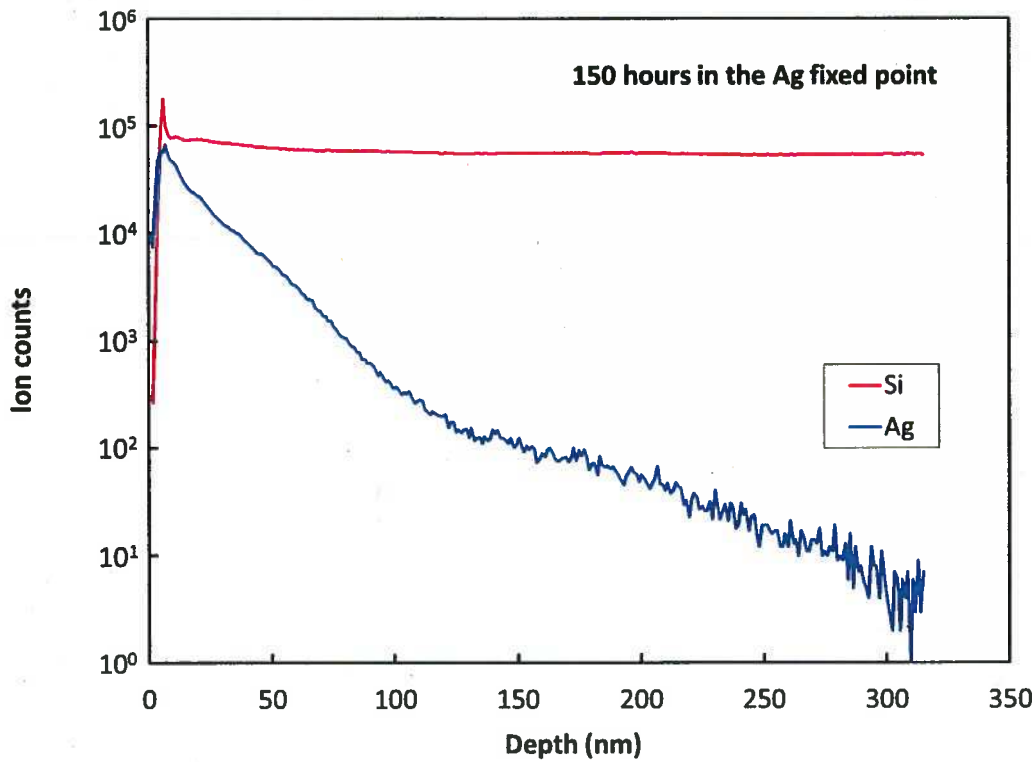


Figure 3. The SIMS ion counts as a function of depth for a quartz thermowell exposed to the silver fixed point for 150 hours.

2.4. Diffusion of silver in quartz

McBrayer *et al.* [10, 11] investigated the diffusion of metals in silicon dioxide by fabricating metal-oxide semiconductor structures grown on n-type silicon. Their observations indicated that copper and silver diffused readily through silicon dioxide while the diffusion of gold and palladium were undetectable. Their data predict diffusion coefficients of $3.6 \times 10^{-6} \text{ cm}^2/\text{s}$ and $4.4 \times 10^{-7} \text{ cm}^2/\text{s}$ for copper and silver, respectively, at 1000 °C. The time constant for the diffusion of atoms through the typical 1 mm sheath of a PRT is approximately given by

$$\tau_d = 4w^2 / \pi^2 D \quad (1)$$

where w is the thickness of the quartz and D is the diffusion coefficient. For the values above, the corresponding time constants for copper and silver are 1126 and 9211 seconds (19 minutes for Cu and 2.5 hours for Ag). Importantly, their electric field-aided diffusion experiments indicated that silver diffused through SiO_2 as a positively-charged ion. This observation is of paramount importance when considering protection mechanisms for platinum resistance thermometry.

In an effort to further study the diffusion process, a thin film of silver 150 nm thick was evaporated onto a quartz substrate approximately 0.85 mm thick. The round substrate was cut into quadrants and two of the nominally identical samples were heat treated at 953 °C for periods of 2 hours and 48 hours, respectively. The relative concentrations of silver and silicon ions as a function of depth were determined by SIMS, with the resulting data presented in figure 4. The profile of the “as deposited” sample appears at the top of the figure. The Ag film is clearly dominant in the ion counts initially, with the concentrations declining as the Si counts increase. After 2 hours of heat treatment at 953 °C (middle pane of figure 4), the SIMS profile shows a nearly constant Si count while the Ag count shows that diffusion into the quartz has begun. It is important to note that the diffusion here is entirely thermal in nature, and not aided by electric fields as utilised by McBrayer *et al.* [10,11]. The bottom pane of figure 4 shows the SIMS profile after 48 hours of heat treatment at 953 °C. The Si counts are nearly constant whereas the Ag counts show a concentration distributed over a larger extent. Overall, the SIMS data shows the expected qualitative behaviour. However, a quantitative estimate of the diffusion coefficient has not been attempted.

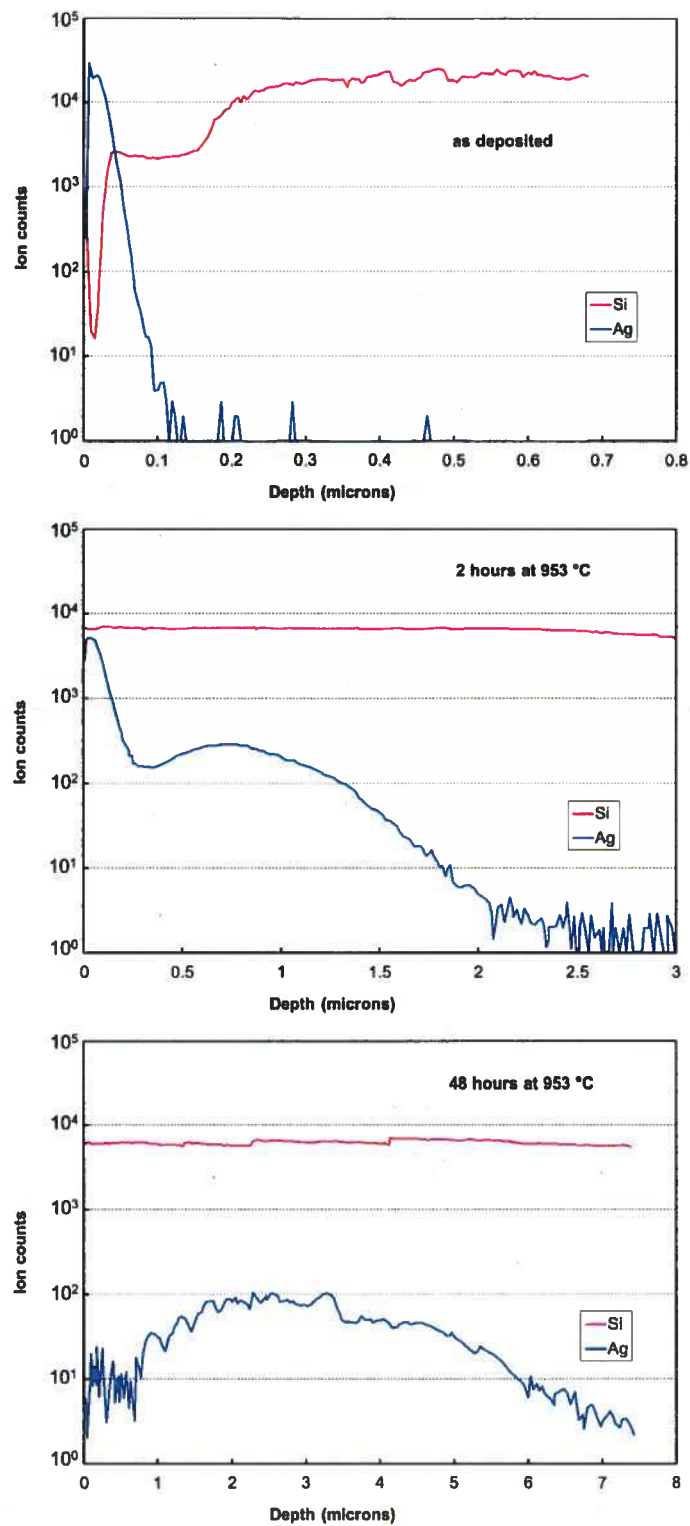


Figure 4. The SIMS ion counts as a function of depth for a 150 nm silver thin film deposited on a quartz substrate. From top to bottom: a) as deposited, b) heat treated for 2 hours at 953 °C and c) heat treated for 48 hours at 953 °C.

2.5. *Protecting PRTs from silver contamination*

Our attempts to utilize passive barriers (glassy carbon crucible, sapphire thermowell, Pt sheath) and dc electric fields to protect PRTs from silver are published [4, 5] and the details of those investigations will not be reproduced here. The electric fields were generated by applying a bias voltage to a platinum sheath surrounding the PRT or biasing a dc resistance bridge to operate at a potential different from ground.

Subsequent to those investigations, we investigated whether connecting the positive terminal of the dc power supply powering the furnace heater to ground (rather than the conventional configuration where the negative terminal is grounded) might result in an electric field of sufficient magnitude and orientation that a separate bias supply would not be needed. A PRT (S/N 267) fabricated in Russia with a triple point of water resistance of approximately 0.6 ohms was used for the test. A dc resistance bridge operated with a measuring current of 10 mA and a 1 ohm standard resistor was used to determine the resistance of the PRT. Except for the times when the PRT resistance was being determined at the triple point of water, the PRT remained in the silver fixed point throughout the 150 days of the experiment. From figure 5, the trend is a decreasing resistance at the triple point of water accompanied by an increase in the silver point resistance ratio with time in the silver fixed point. This behaviour (of the electrical resistance) suggests that connecting the positive terminal of the dc power supply to ground is an effective method to prevent the contamination of PRTs by silver. To confirm the hypothesis, the platinum sensing element of PRT S/N 267 was removed and analysed using glow discharge mass spectrometry (GDMS). The results appear in Table 1. A silver mass fraction of 260×10^{-9} should not be considered indicative of contamination, confirming the effectiveness of the electrical field in protecting the sensing element of the PRT. The electrical environment of the silver fixed point is clearly an important factor in determining whether or not silver contamination of a PRT is likely to occur.

Table 1. Glow discharge mass spectrometry (GDMS) analysis of the platinum sensing element of PRT S/N 267.

| Element | $10^9 \times$ mass fraction | Element | $10^9 \times$ mass fraction | Element | $10^9 \times$ mass fraction |
|---------|-----------------------------|---------|-----------------------------|---------|-----------------------------|
| Li | <5 | Fe | 1200 | Sn | 16 |
| Be | <0.8 | Co | 5 | Sb | <6 |
| B | <2 | Ni | 74 | Te | <12 |
| C | 22 | Cu | 520 | I | <2 |
| N | 6 | Zn | 100 | Cs | <0.7 |
| O | 430 | Ga | <7 | Ba | <0.8 |
| H | | Ge | <20 | La | <0.4 |
| F | <9 | As | <4 | Ce | <0.4 |
| Na | 32 | Se | <50 | Hf | <1 |
| Mg | 260 | Br | <20 | Ta | <1400 |
| Al | 74 | Rb | <1 | W | <2 |
| Si | 84 | Sr | <6 | Re | <4 |
| P | <4 | Y | <0.7 | Os | <50 |
| S | 53 | Zr | <1 | Ir | <730 |
| Cl | <8 | Nb | <0.4 | Pt | Matrix |
| K | <7 | Mo | <6 | Au | 2900 |
| Ca | 9300 | Ru | 220 | Hg | <200 |
| Sc | <0.8 | Rh | 570 | Tl | <7 |
| Ti | 14 | Pd | 1400 | Pb | <4 |
| V | <0.5 | Ag | 260 | Bi | <3 |
| Cr | 120 | Cd | <11 | Th | <16 |
| Mn | 20 | In | <2 | U | <160 |

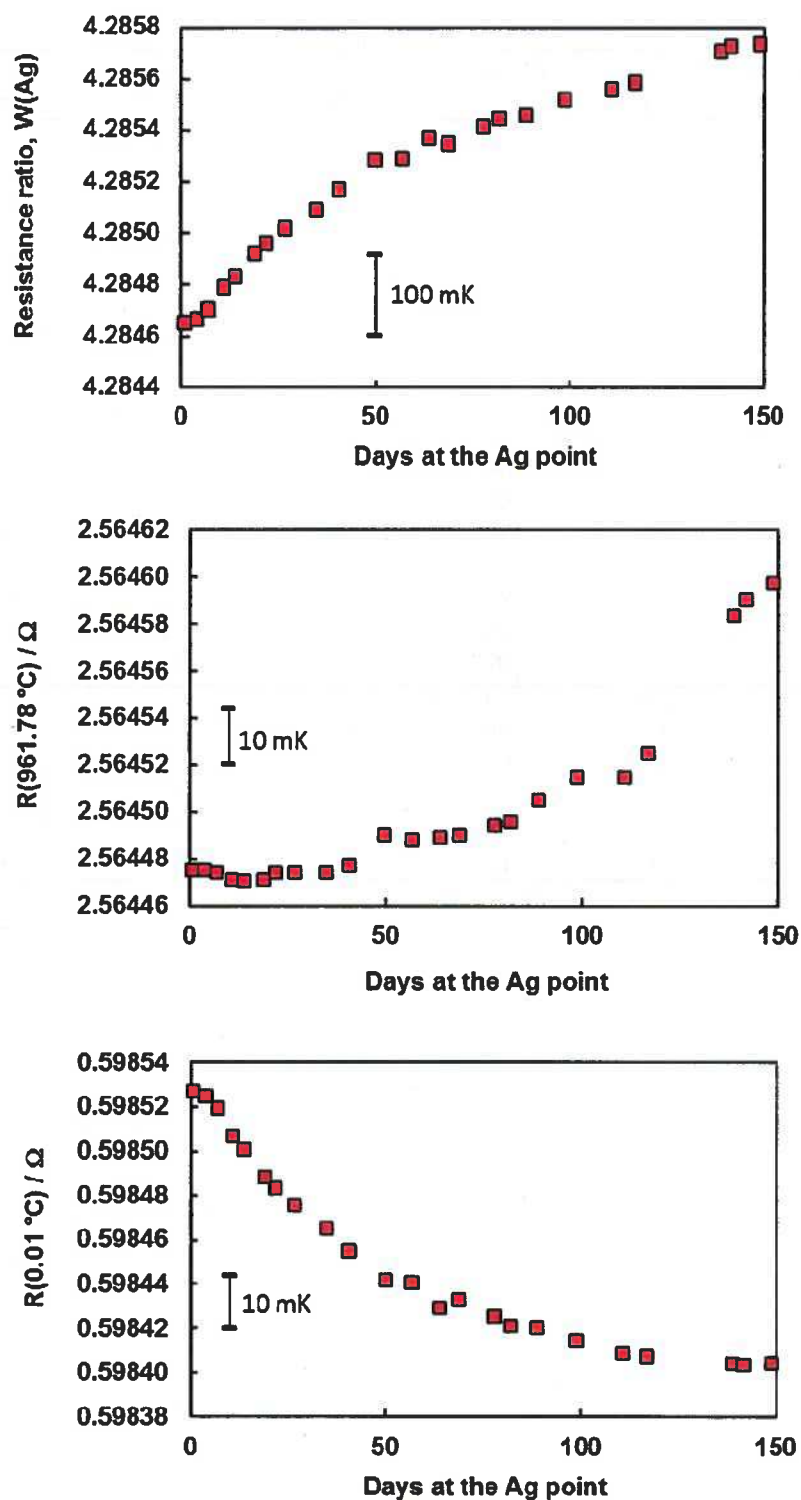


Figure 5. The changes in the resistance of PRT 267 were recorded over a period of 150 days in the silver fixed point with the positive terminal of the furnace power supply connected to ground.

3. The case for gold

The diffusion of gold through silicon dioxide has been investigated by several authors [12-14]. Their experiments lead to values for the diffusion coefficients of gold through silicon dioxide at 1000 °C of 5×10^{-15} , 5×10^{-16} , and 1.9×10^{-11} cm²/s with corresponding time constants of 8×10^{11} , 8×10^{12} , and 2×10^8 s (25,000 years, 250,000 years and 6 years) to permeate a 1 mm thickness of quartz. While the diffusion coefficients for gold span several orders of magnitude, it appears that the diffusion of gold through quartz may be considered irrelevant for thermometry applications. Thus, the contamination of PRTs by silver could be avoided if the silver point were replaced by the gold point when calibrating a PRT.

If the freezing point of gold were to be introduced into a future version of the ITS, then one way to do so would be to extrapolate the ITS-90 PRT reference function to the gold point and combine this with the deviation function currently in use for the range ending at the silver point. By extrapolating the ITS-90 reference function to the gold freezing point (1064.18 °C), we obtain the value $W_r(\text{Au}) = 4.57154847$ (for comparison, $W_r(\text{Ag}) = 4.28642053$). We can compare the resistance ratios generated by the ITS-90 reference function with experimental $W(\text{Ag})$ and $W(\text{Au})$ values from the literature.

Figure 6 illustrates the correlation of silver and gold fixed-point resistance ratios reported by three laboratories, the National Institute of Standards and Technology (NIST, formerly NBS, USA), the National Physical Laboratory (NPL, UK) and the D.I. Mendeleyev Institute for Metrology (VNIIM, Russia), and spanning a period of more than 30 years. In 1971, Evans and Wood reported [15] data for nine PRTs of “birdcage” design obtained from commercial sources whose resistances at the triple point of water ranged from approximately 0.19 ohms to 0.27 ohms. Three runs were carried out with resistances reported at each fixed point and a corresponding triple point of water resistance for each run, so the resistance ratio can be readily computed from the tabulated data. The values plotted in figure 6 were obtained by averaging the data from the three runs for each PRT. In 1972, Chattle presented [16] resistance ratios for five PRTs expressed with respect to the ice point – the convention used for IPTS-68. To ensure a common basis for comparison, the values were modified to represent ratios with respect to the triple point of water. In 1984, Evans presented measurements carried out at NBS using four PRTs constructed by the National Institute of Metrology (NIM, China) and three constructed at NBS. The NIM PRTs were of a bifilar helix construction while those from NBS were described as “toroidal”, with corresponding resistances near the triple point of water of approximately 0.25 ohms and 0.37 ohms, respectively. The resistance ratios were reported with respect to the ice point, so they were scaled to the ITS-90 convention. In 1992, Strouse *et al.* [18] presented resistance ratios for eighteen PRTs constructed at VNIIM. Two of the PRTs were measured at NIST and the remaining sixteen were measured at VNIIM. The NIST data includes four measurements for the first thermometer and three measurements for the second thermometer. For the VNIIM data, one value is reported for each PRT. In 2003, Moiseeva and Pokhodun reported [19] the average resistance ratios over three calibration cycles for thirteen PRTs with a resistance of approximately 0.6 ohms at the triple point of water.

From figure 6, it is obvious that the silver and gold PRT resistance ratios are highly correlated. The solid lines represent linear regressions to each data set (see Table 2). While the NPL data appears to be in reasonably good agreement with the various NIST/NBS data sets, the VNIIM data appear offset by the equivalent of approximately 0.1 °C (i.e. the difference between the regression lines suggests that the temperature interval between the freezing points of silver and gold is 0.1 °C larger for the NIST fixed points than for the VNIIM fixed points) despite their very good internal consistency over the 11 years between data sets. The ITS-90 values, indicated by the solid circle representing resistance ratios obtained from the ITS-90 high temperature reference function (extrapolated to the gold point), appear consistent with the VNIIM data. It is unlikely that the apparent temperature difference can be resolved from the PRT data alone. Nonetheless, the strong

correlation between the $W(\text{Ag})$ and $W(\text{Au})$ values suggests that there is an experimental basis to extend platinum resistance thermometry to the gold point.

According to the results of CCT-K4, the silver fixed point of VNIIM is $3.32 \text{ mK} \pm 2.69 \text{ mK}$ ($k=2$) colder than that of NIST while that of NPL is $5.05 \text{ mK} \pm 2.43 \text{ mK}$ ($k=2$) colder than that of NIST. It therefore appears unlikely that the temperature differences suggested by figure 6 are attributable to the silver fixed points. I am unaware of any equivalent direct comparisons of gold fixed points. If the gold points are found to be compatible, then the differences must lie in the nuances of platinum resistance thermometry – and such differences cannot be ruled out based on the data in hand.

There remains an additional test that can be applied to the PRT data. The S -parameter of White and Strouse [20] can be plotted as in figure 7; in this case the S -parameters at the tin, zinc, aluminium and silver fixed points [17] are generally consistent (or at least collinear) whereas the values calculated for the gold point differ markedly. This suggests that the W_r value calculated by extrapolating the ITS-90 reference function to $1064.18 \text{ }^\circ\text{C}$ is inconsistent with the measured W values. In the case of the Evans data [17] chosen here as a representative example, a gold-point temperature of $1064.23 \text{ }^\circ\text{C}$ would be consistent with the measured data. Either the temperature assigned to the gold point or the reference function for W_r (or both) may need to be altered to achieve the desired consistency. However, a necessary first step is to consider whether there is sufficient data on which to base a modified reference function, if that is the suggested course to be followed. There remains an alternative to consider. When the S -parameter is calculated for the VNIIM data, no such adjustment to the gold-point temperature seems necessary – not surprising given the fact that we have already remarked on the apparent consistency of the VNIIM regression line in figure 6 with the silver- and gold-point W_r values calculated from the ITS-90 reference function.

Table 2. Coefficients of the linear regressions to the data sets of figure 6.

| Laboratory | Year | Slope | Intercept | Reference |
|----------------|------|---------------|----------------|-----------|
| NBS | 1971 | 1.0860 | -0.0834 | 15 |
| NPL | 1972 | 1.0879 | -0.0913 | 16 |
| NBS | 1984 | 1.1617 | -0.4076 | 17 |
| NIST | 1992 | 1.0872 | -0.0884 | 18 |
| VNIIM | 1992 | 1.0646 | 0.0082 | 18 |
| VNIIM | 2003 | 1.0727 | -0.0264 | 19 |
| <i>average</i> | | <i>1.0934</i> | <i>-0.1148</i> | |

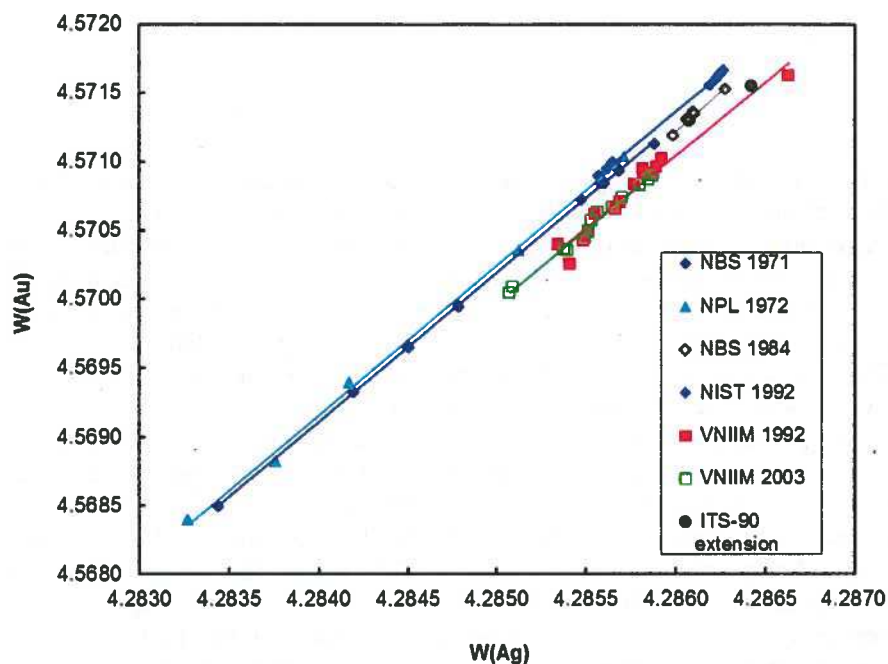


Figure 6. The PRT resistance ratios measured at the freezing points of silver and gold at the laboratories of NIST, NPL and VNIIM is plotted above. The gold value at the single point designated “ITS-90 extension” is the result of extrapolating the ITS-90 reference function to the temperature assigned to the gold freezing point, 1064.18 °C. As such, the value has no authority within the current ITS and is included solely to indicate consistency with the measured values. The solid lines represent linear regressions to the individual data sets.

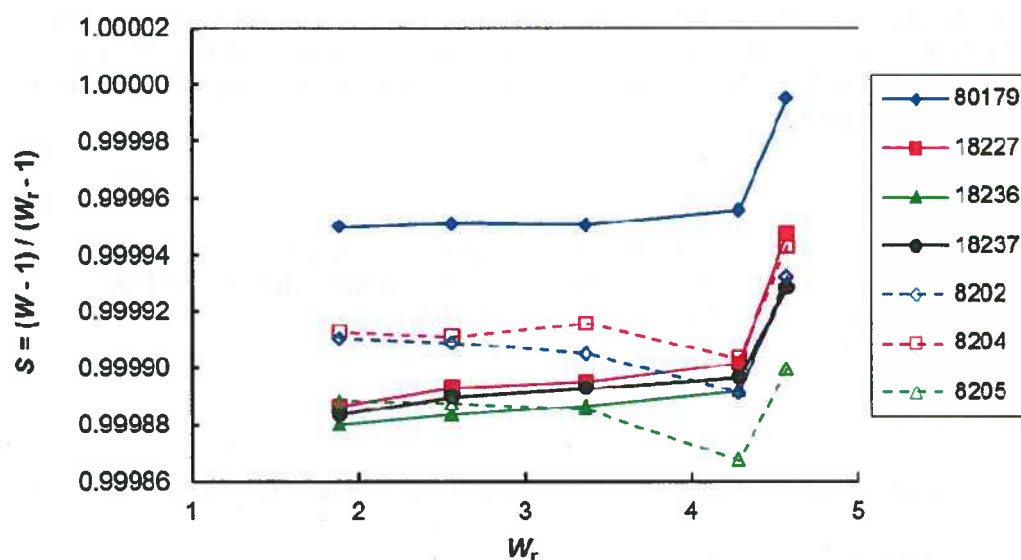


Figure 7. The S-parameter of White and Strouse [20] calculated for the PRT resistance ratios reported by Evans [17]. The legend identifies the PRTs by their serial number.

4. Discussion

The diffusion of silver through quartz at high temperatures results in contamination of the platinum sensing element of high-temperature platinum resistance thermometers. While the application of appropriate electric fields appears to offer some measure of protection to the PRT element, the contamination of the quartz elements of the silver fixed points leads to their premature failure. Contamination is evidenced by the yellowish colour imparted to the glass by the absorption band near 400 nm wavelength that is intrinsic to the silver particles within the quartz glass matrix. The presence of silver within the quartz has been confirmed unambiguously through energy dispersive x-ray analysis and secondary ion mass spectrometry.

As a means of avoiding altogether the risk of silver contamination of PRTs, the gold point has been proposed as an alternative calibration point. PRT resistance ratios measured at the freezing points of silver and gold in different laboratories at different times are highly correlated and in reasonable agreement. This suggests that the ITS-90 reference function could be extrapolated to 1064.18 °C. Within the optical pyrometry range of the ITS-90, any one of the freezing points of silver, gold, or copper are permitted as equivalent calibration points (though with different assigned temperatures, of course). The upper temperature limit of the PRT range might be similarly revised to permit calibration at either the silver or gold freezing point. For those laboratories that have a gold point, not only would this extend the accuracy of platinum resistance thermometry to higher temperatures, but it would also mitigate the degradation of the PRT by the diffusion of silver atoms through the quartz thermometer sheath.

Considering the discrepancies of the various gold and silver PRT resistance ratios reported in the literature, it remains unclear whether extrapolation of the ITS-90 high temperature reference function leads to the correct value at the gold point. A direct comparison of gold fixed points among national metrology institutes (NMIs) capable of contributing data to the discussion may be required to resolve the inconsistencies among the laboratories. NMIs able to determine both silver and gold point PRT resistance ratios are encouraged to help resolve the apparent discrepancy.

If the silver fixed point must be used, the simplest and most effective means to prevent the contamination of the PRT sensing element is to ground the positive output of the dc supply powering the furnace heater. This ensures that the furnace operates at a negative bias with respect to the PRT, which is normally near ground potential when connected to the typical instrumentation used to measure its resistance.

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