

A Study on the Stability of Standard Platinum Resistance Thermometer in the Temperature Range from 0°C through 720°C

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Abstract

Stabilities of standard platinum resistance thermometers (SPRTs) were tested in the temperature range from 250°C to 720°C. The reason the SPRT stability should be tested not only at the maximum temperature but also at a few other temperatures is explained. Five specially made SPRTs with different filling gases were tested for this purpose. These SPRTs were annealed at four different temperatures (720°C, 675°C, 450°C, and 250°C) for up to 2000 hours. Two SPRTs with higher partial oxygen pressure showed excellent stabilities in the temperature range from 675°C to 720°C, and the total changes in their R_{tp} during annealing at 675°C for 200 hours were equivalent to less than 0.8 mK. But they were unstable at 250°C and 450°C with drift rates as high as 43 mK per 100 hours at 450°C. SPRTs with lower partial oxygen pressure showed very good stability in the temperature range from 250°C to 450°C, but the one with the lowest partial oxygen pressure showed upward drift in its R_{tp} in the temperature range from 675°C to 720°C. The factors which caused SPRT drifts were investigated and are discussed.

1. Introduction

Frequently, stabilities of many thermometer sensors are tested at temperatures near their upper limit [1- 4] because people think the maximum temperature might be the most severe condition under which to test thermometer stability. In recent years, we found a few 25.5-ohm standard platinum resistance thermometers (SPRTs) with excellent stability when heated at 675°C but which showed some drift in the lower temperature range. So we started an investigation on into the stability of 25.5-ohm SPRTs over the range from room temperature to 720°C.

The drifts in the lower temperature range are mainly caused by oxidation of platinum according to a broad investigation made by Berry [5-6]. Until 1975, there was little knowledge that platinum would oxidize significantly in air or mixed gases containing oxygen at the pressures and temperatures encountered in SPRTs. Indeed, it was the fact that platinum was considered to be such a stable material with no serious oxidation problems that helped lead to its adoption as a standard thermometric material about a hundred years ago. A platinum oxide film does grow on the surface of platinum wire in the presence of as little as 2 kPa of oxygen at room temperature when heated in the range of 0°C to 500°C. The resistance of an SPRT with such oxide film on

the surface of its sensor platinum wire will rise as a result of the reduction of the platinum wire's cross-section area[not sure I understand what you mean by section area]. The drift rate in resistance, or the growth rate of oxide film, depends on the temperature it is heated to and the oxygen partial pressure within the SPRT.

2. SPRTs Investigated

A large number of specially made 25.5-ohm SPRTs with different oxygen partial pressures were investigated in the work. The manufacturing processes of these SPRTs were almost the same as we described previously [3] except for the filling gas content. The pressures, oxygen partial pressures, and some other thermometer characteristics of five of them are listed in Table 1. All of the five SPRTs were sealed at a temperature of 280°C and at a pressure of 66 kPa. The filling gases were mixtures of argon and oxygen for three of them (#S1, #S2 and #1211) with oxygen contents indicated in Table 1. #S3 and #S4 were filled with dry air, but the filling gases for #S4 contained higher oxygen content than normal air. The pressure in an SPRT sheath will change with temperature and temperature distribution along the entire sheath. The sealing pressure (66 kPa at 280°C) was selected so that the pressure in the sheath at the maximum temperature (675°C) would be close to the room pressure (the average local pressure at our annealing furnaces' location is 86 kPa). If the temperatures in the sheath are uniform, the pressure can be calculated according to the perfect gas law:

$$PV = nRT \quad (1)$$

where P is the pressure, V the volume, n the quantity of gas present expressed in moles, T the temperature expressed in Kelvin, and R the universal gas constant. Consider two states: one is at P_1 , V_1 , and T_1 ; and the second at P_2 , V_2 , and T_2 . The equation (1) becomes the following:

$$P_1 V_1 / T_1 = P_2 V_2 / T_2 \quad (2)$$

If we suppose $V_1 = V_2$, then we get $P_1 / T_1 = P_2 / T_2$, or $P_2 = P_1 T_2 / T_1$. Actually, the temperatures along the sheath are not uniform at all. We can divide the whole thermometer sheath into many incremental volumes, each at a different temperature. The pressure in a sheath will vary slightly with vertical position along the sheath because of gravity, but the differences in pressure are so small (less than 0.01%) that we can assume the pressure is constant. Then we can obtain the following equation:

$$P_1 \int \frac{A(x)}{T_1(x)} dx = P_2 \int \frac{A(x)}{T_2(x)} dx \quad (3)$$

where P_1 and P_2 are the pressures at the first state and the second state respectively; $T_1(x)$ and $T_2(x)$ the temperatures at position x at the first state and second state respectively; and $A(x)$ the cross-sectional area at position x .

For many applications, we can use the following approximate equation instead of Equation (3):

$$P_1 \sum_{i=1}^{i=n} \Delta V_{1,i} / T_{1,i} = P_2 \sum_{i=1}^{i=n} \Delta V_{2,i} / T_{2,i} \quad (4)$$

Equation (3) and Equation (4) are a more universal versions compared to Equation (2). If $n = 1$ in Equation (4), Equation (4) becomes Equation (2). So Equation (2) can be considered as a special situation of Equation (4). Equation (4) is a very useful tool for calculating the pressure in an SPRT sheath in various situations. Of course, one should know the temperature distribution along the sheath first, and then one can calculate the pressure of one state from the pressure of another state. To determine the temperature distribution of the SPRT, we measured the temperature profile in the oven in which the SPRTs were sealed, and the temperature profiles in the annealing furnace at a few different temperatures. The total pressures and the oxygen partial pressures in the thermometer sheaths of the five SPRTs mentioned above are calculated using Equation (4) and listed in Table 1.

Table 1. Filling gas compositions, pressures, and other thermometer characteristics

S/N	R _{tp} (ohms)	W(Ga)	Filling gases	Total pressure (kPa) at			Oxygen partial pressure at 23°C (kPa)
				23°C	280°C	675°C	
S01	25.497	1.11812	O ₂ 1% + Ar 99%	40.2	66	86.1	0.40
S02	25.521	1.11813	O ₂ 2.5% + Ar 97.5%	40.2	66	86.1	1.00
1211	25.595	1.11814	O ₂ 5% + Ar 95 %	40.2	66	86.1	2.00
S03	25.333	1.11813	Dry air (O ₂ 21%)	40.2	66	86.1	8.44
S04	25.619	1.11813	Dry air (O ₂ 40%)	40.2	66	86.1	16.1

3. Stability Test

The electrical resistance of the SPRTs was measured on a Model 6675A DC automatic bridge. The bridge compared the resistance R_{tp} of an SPRT against a 10-ohm reference resistance, R_s. The bridge linearity is better than 0.2 ppm. The stability of the 10-ohm reference resistance is better than 1 ppm annually. Resistance measurements were made at two currents, 1 mA and 1.414 mA, so that the results could be extrapolated to zero current. A few triple point of water cells and a maintenance bath were used throughout the tests. A melting point of gallium cell, with its maintenance bath, was used occasionally in the tests. The expanded uncertainties ($k=2$) of both fixed points are better than 0.1 mK.

3.1 Stability Tests in the Range from 675°C to 720°C

The five SPRTs were heated at 720°C for 250 hours, and then at 675°C for 250 hours. The resistances at the triple point of water, R_{tp}, were measured after each 50-hour annealing at both temperatures. The changes in R_{tp} of the five SPRTs are shown in Fig. 1 during the last 200-hours at 675°C (total annealing time from 300 hours to 500 hours). The maximum changes in R_{tp} during the entire 200-hour annealing at 675°C for four of five SPRTs were within 0.0001 ohms (equivalent to 1 mK). There were no significant differences of stabilities among the four SPRTs. We think the stabilities of these four SPRTs at 675°C are satisfactory. The R_{tp} of the fifth SPRT (#S01) rose by 0.00025 ohms (equivalent to 2.5 mK). The platinum sensor of #S01 was thought

to be contaminated lightly during annealing at 720°C and 675°C, since the R_{tp} rises when the platinum sensor is contaminated. The oxygen partial pressure of #S01 is the lowest (0.40 kPa at 23°C) of the five SPRTs. The oxygen in the SPRT filling gases is important in order to prevent contamination of the platinum sensor by metallic impurities reduced from their oxides at high temperatures. It may be that there was not enough oxygen in the #S01 filling gas to protect its platinum sensor from contamination. The changes in R_{tp} of #S01 during the entire annealing at 720°C and 675°C for 500 hours are shown in Fig. 2. The R_{tp} of #S01 rose by 0.0018 ohms (18 mK) during the 500-hour annealing. On the other hand, the $W(Ga)$ of #S01 decreased by about 0.00001 during the same period. This is another indication that the platinum sensor was contaminated, since the purer the platinum, the higher the $W(Ga)$ value.

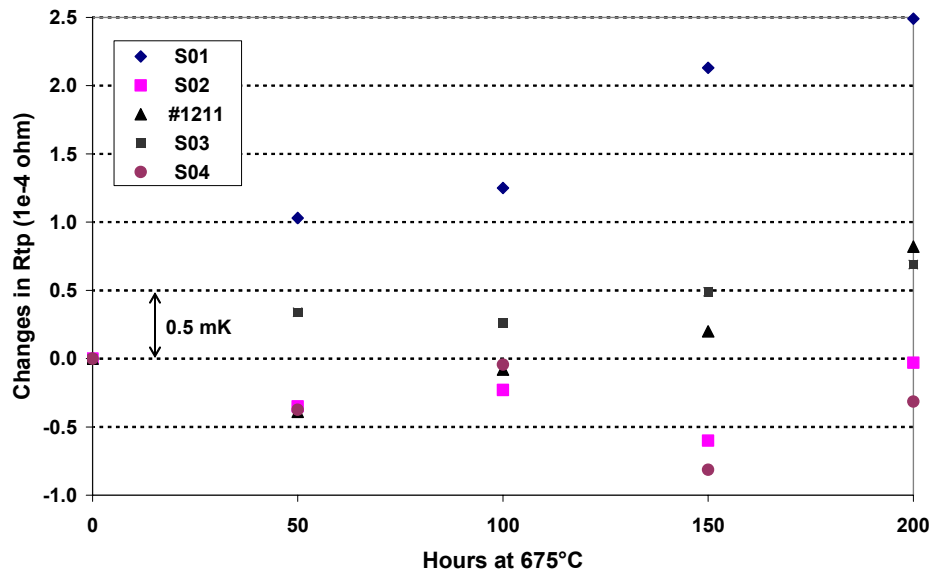


Fig. 1 The changes in R_{tp} of five SPRTs during the last 200-hour annealing at 675 °C

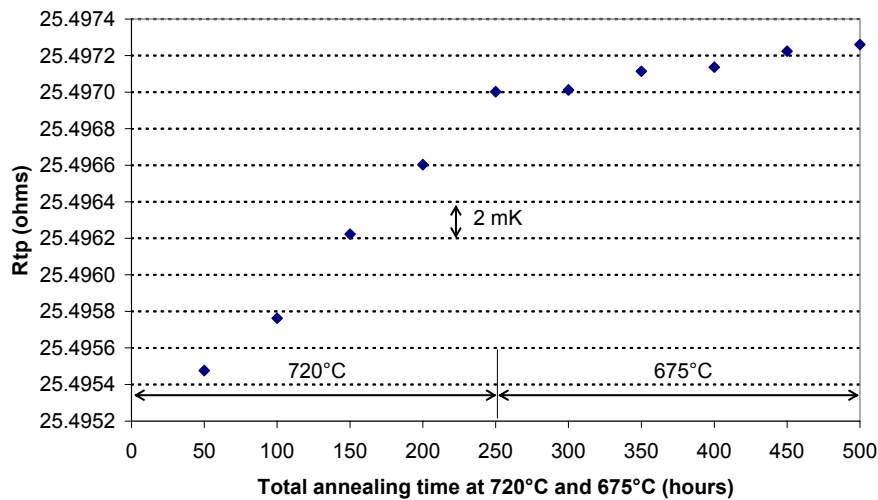


Fig. 2 R_{tp} of #S01 during annealing at 720°C and 675°C

3.2 Stability Tests at 250 °C

The five SPRTs were annealed at 250°C for 250 hours following the annealing at 720°C and 675°C mentioned above. The changes in R_{tp} during the 250-hour period are shown in Fig. 3. In contrast to the situation at 720°C and 675°C, the #S01 was the most stable SPRT at 250°C among the five thermometers tested here. The maximum change in R_{tp} was less than 0.00002 ohms (0.2 mK) for #S01, and less than 0.00003 ohms (0.3 mK) for #S02 during the entire 250-hour period. The stabilities of these two SPRTs were excellent at 250°C. The other three SPRTs showed a rising trend in R_{tp} during annealing at 250°C. The average drift rate was +0.000013 ohms per 100 hours (0.13 mK) for #1211, +0.000036 ohms per 100 hours for #S03 and +0.000044 ohms per 100 hours for #S04. The maximum change in R_{tp} was 0.000032 ohms (0.32 mK) for #1211, 0.00009 ohms (0.9 mK) for #S03, and 0.00011 ohms (1.1 mK) for #S04. The drift rate of #1211 might be acceptable, but the drift rates of #S03 and #S04 were too high for high-accuracy applications. The upward drifts were caused by the so-called 2-dimensional platinum oxidation effect [6]. The drift rates strongly depend on the partial oxygen pressures, as is seen in Fig. 4. But we think more tests are required to determine the relationship between the drift rates and partial oxygen pressures, and Fig. 4 only provides preliminary data about this relationship.

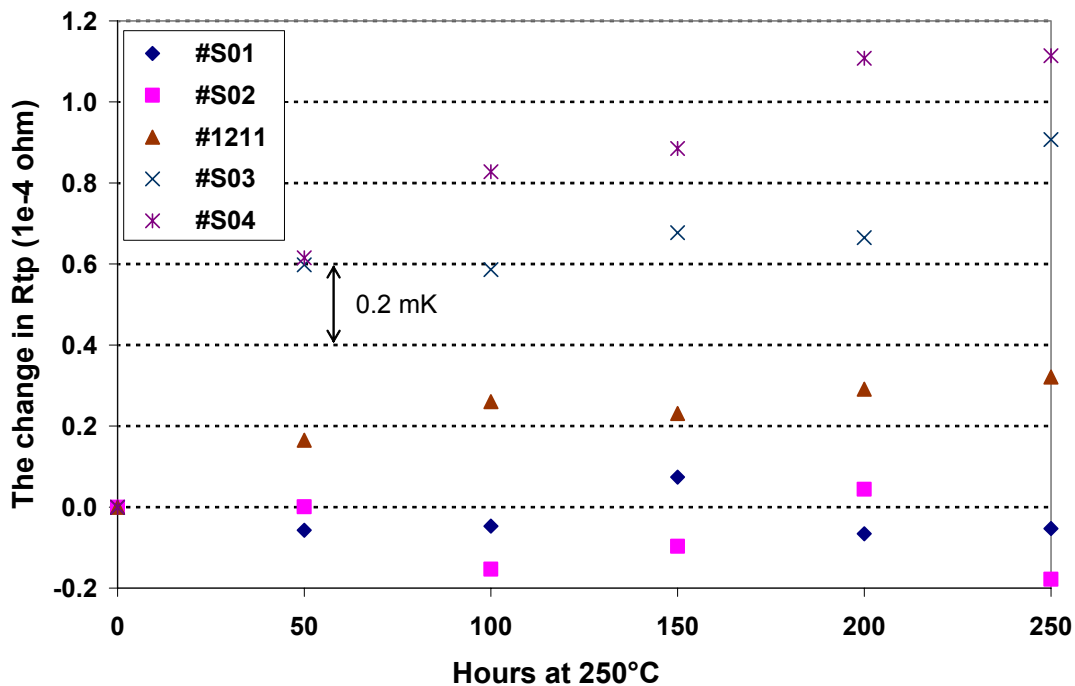


Fig. 3 The changes in R_{tp} of five SPRTs during annealing at 250 °C

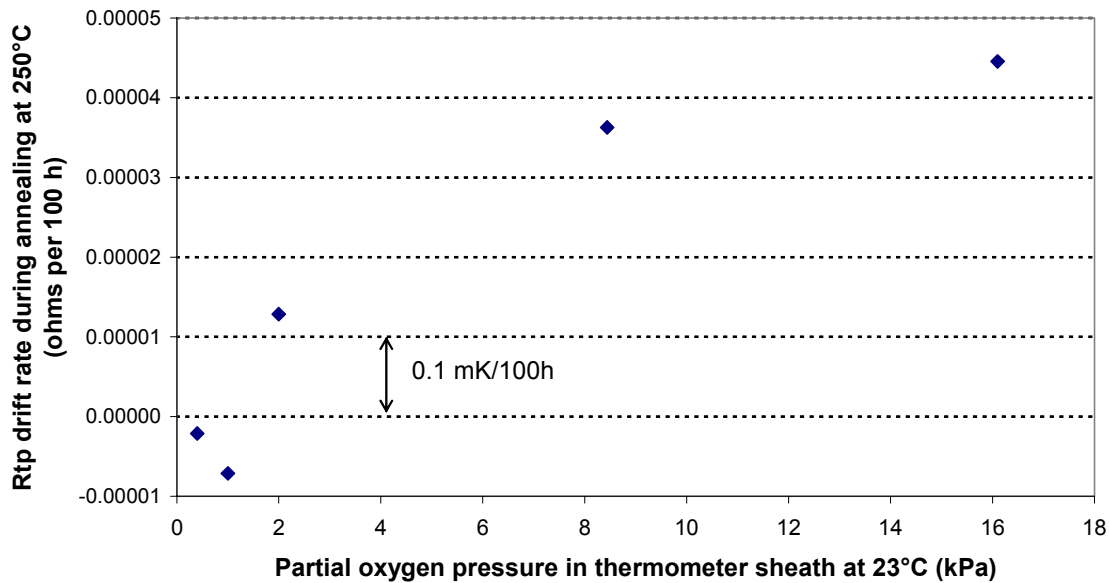


Fig 4. Relationship between drift rate at 250°C and partial oxygen pressure, according to tests of five SPRTs

3.4 Stability Tests at 450°C

The five SPRTs were annealed at 450°C for 250 hours after annealing at 250°C. The changes in R_{tp} during the 250-hour period are shown in Fig. 5. The R_{tp} of #S03 and #S04 rose sharply during annealing at 450°C. The maximum change in R_{tp} was 0.00432 ohms (43.2 mK) with a drift rate of 0.00173 ohms per 100 hours (17.3 mK) for #S03; and 0.01091 ohms (109.1 mK) with a drift rate of 0.00436 ohms per 100 hours (43.6 mK) for #S04 during a period of 250 hours at 450°C. The drifts at 450°C were much higher than at 250°C. These two SPRTs have excellent stabilities at 720°C and 675°C, but they are unstable at 450°C. The high drift rates at 450°C were caused by the so-called 3-dimensional oxidation of platinum [6]. The stabilities of the other three SPRTs can be seen in Fig. 6. Once again, #S01 is the best among the five SPRTs. The maximum change in R_{tp} during the 250-hour annealing was within 0.00002 ohms (0.2 mK) for #S01, and within 0.00004 ohms (0.4 mK) for #S02. The R_{tp} of #1211 dropped by 0.000097 ohms (0.97 mK) during the first 50-hour annealing at 450°C. But after that, the maximum change in R_{tp} was within 0.00003 ohms (0.3 mK). The drop in R_{tp} in the first 50-hour annealing at 450°C was explained by the dissociation of 2-dimensional platinum oxide at 450°C. Such a drop in R_{tp} can also be seen for #S2, but the amount of the drop was only one third of that for #1211. From Fig. 6 we can see that there was no drop in R_{tp} for #S01. That means no significant platinum oxidation occurred in the #S01 platinum sensor.

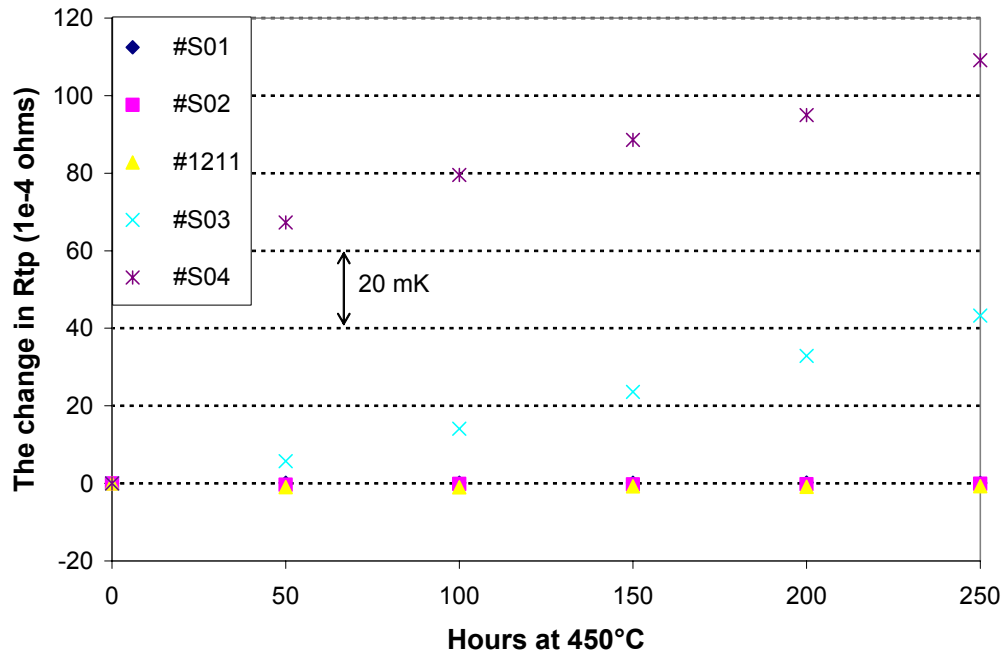


Fig. 5 The changes in R_{tp} of five SPRTs during annealing at 450 °C

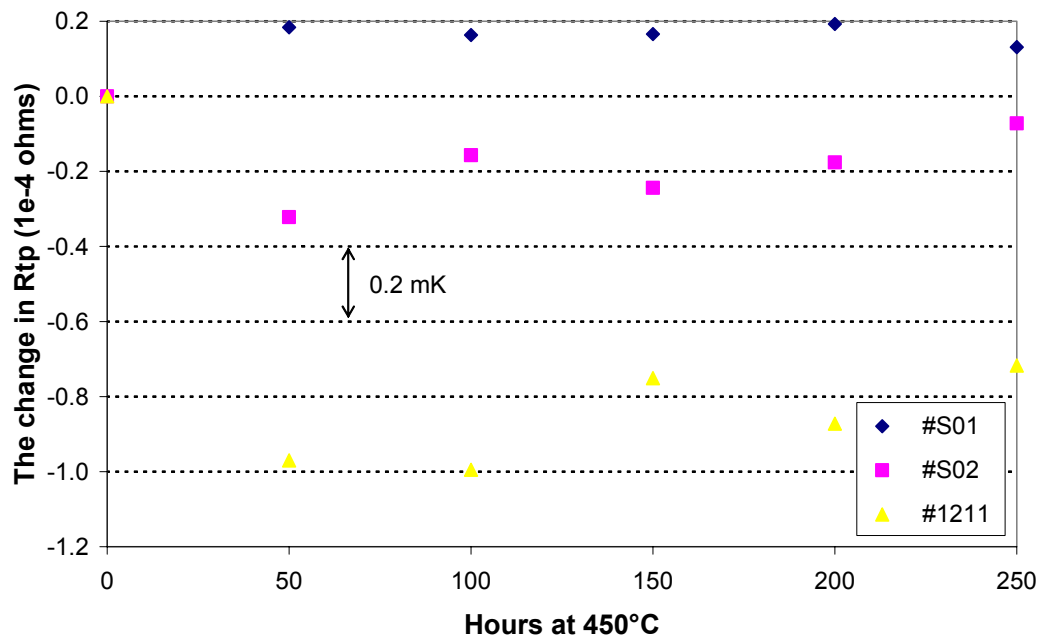


Fig. 6 The changes in R_{tp} of three SPRTs during annealing at 450 °C

4. Discussion

The following points are clear from our investigations reported in this paper:

1. SPRT stability should be tested not only at the maximum temperature but also at a few other temperatures.
2. Contamination of platinum is the main contributor to the instability of SPRTs in the range around 675°C. It is important to include a certain amount of oxygen in the SPRT filling gas to avoid such contamination. Partial oxygen pressure of 1 kPa is enough to protect the platinum from contamination. There were no significant differences in stabilities of SPRTs at 675°C with partial oxygen pressure from 1 kPa to 16.1 kPa (at 23°C).
3. Oxidation of platinum is the main contributor to the instability of SPRTs in the range from about 250°C to 450°C. The drift rate caused by platinum oxidation strongly depends on the partial oxygen pressure. Higher partial oxygen pressure causes instability of the SPRT in the range from about 250°C to 450°C. An SPRT with partial oxygen pressure of 0.4 kPa showed no platinum oxidation at all.

Acknowledgments

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