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### COMPARISON BETWEEN SIMPLE POLYNOMIALS AND AN ITS-90 BASED REFERENCE FUNCTIONS OF EMF VS. TEMPERATURE RELATION FOR HIGH PURITY NOBLE METAL THERMOCOUPLES

Emf versus temperature reference polynomial functions covering the temperature range from 100° C up to 960° C have been developed for three types of noble metal thermocouples, which are Pt-10%Rh/Pt, Au/Pt and Pt/Pd. Our functions are compared to the reference functions available in the literature. The thermocouples were fabricated and annealed for stabilization at 962° C for 300 hours before calibrations. After stabilization they were calibrated by comparison with Standard Platinum Resistance Thermometer (SPRT) in the temperature range from 100° C to 450° C and by comparison with a High temperature Standard Platinum Resistance Thermometer (HSPRT) in the temperature range from 450° C up to 950° C. The error of fit was evaluated and discussed.

Keywords: noble metal thermocouples, reference function, comparison calibration

#### 1. INTRODUCTION

Thermocouples constructed from Platinum - Rhodium alloys and pure Platinum were currently the predominant choice for use as a secondary reference standard prior to 1990. Type S (Pt 10%Rh vs. Pt) thermocouples served as interpolation instruments on the IPTS-1968 [1]. Pt 10%Rh vs. Pt thermocouples cover the temperature range from 0° C to approximately 1400° C. However, the smallest expanded uncertainty ( $k=2$ ) obtainable with any of the Platinum-Rhodium alloy thermocouples is 0.2° C at 1000° C, as consequences of preferential oxidation of Rhodium within the temperature range from 550° C to 900° C. As the Rhodium Oxide forms, a thermoelement formed from Platinum - Rhodium alloy will become depleted in Rhodium, and a change in the thermoelement will result in changes of the emf vs. temperature relationship and in thermoelectric inhomogeneity of the thermoelement. Thermocouples made from pure elements such as Gold versus Platinum (Au/Pt) or Platinum versus Palladium (Pt/Pd) do not exhibit the oxidation effects that limit the performance of Platinum alloy thermocouples.

Mclaren and Murdock [2] suggested that an Au/Pt thermocouple could achieve an accuracy comparable with the Platinum resistance thermometers above 630° C. Since then the Au/Pt thermocouple has been examined further [2, 3] and other combinations have been considered such as Pt/Pd [4] as practical sensors for precision thermometry above 600° C. Thermocouples constructed from pure elements don't suffer from preferential oxidation problems, pure elemental thermocouples are inherently more thermoelectrically homogeneous and their thermoelectric stability is not limited by shifts in alloy composition caused by preferential oxidation [5].

Because pure element thermocouples do not require adjustments of alloy composition to match a reference function, the interchangeability of thermocouples manufactured from sufficiently pure elements is excellent and the deviations of actual thermocouples from the

appropriate reference function are small.

A reference function for Au/Pt thermocouples on the International Temperature Scale of 1990 (ITS-90) has been given over the range 0° C to 1000° C. For Pt/Pd several studies on the emf temperature relationship have been published [6]. A reference function for Pt/Pd thermocouples extending up to 1500° C has been determined in a project [7] between NIST and IMGC. For Pt-10%Rh/Pt a reference function had been given in the literature [8].

Pure elemental thermocouples do have some limitations: special construction techniques are necessary to minimize the mechanical strain caused by the different thermal expansion coefficient of the pure element thermoelements. Because the pure elements used have lower melting points than Platinum- Rhodium alloys, the upper limit of use of Au/Pt and Pt/Pd thermocouples is 1000° C and 1500° C respectively.

## 2. FABRICATION

The Pt10%Rh/Pt, Au/Pt and Pt/Pd used in this study were prepared from reference grade Pt, Pt10%Rh, Au and Pd wires, all wires with 0.5 mm in diameter and 120 cm length purchased from Johnson Matthey.

The gold wire had a purity of 99.995 %, the platinum wire of 99.999 % purity and palladium wire of 99.997 % purity. The Pt, Pt-10%Rh and Pd wires were annealed electrically at 1300° C for approximately 10 hours, cooled rapidly to room temperature and then annealed for 1 hour at about 450° C to reduce the lattice vacancies that may be quenched into the wires during cooling from the high temperature anneal. The gold wires 1.5 m in length were installed in a high purity Al<sub>2</sub>O<sub>3</sub> tube and heated for 10 hours at 980° C (?) in a 90 cm long conventional tube furnace which had a 70 cm effective working length over which the temperature uniformity was within 3° C. After the heat treatment of the first 70 cm length, the gold wire was then shifted by 70 cm and heated in the same way. Thus the overall length of the gold wire was heat treated. After heat treatment the wire was cooled in the furnace, and then vacancy annealed overnight at 450° C.

The annealed wires were assembled by threading thermoelements into the 1.5 mm bores of a twin bore high purity alumina tube with overall diameter 4.5 mm and length 60 cm. Before use all alumina tubes were heated for 50 h at 1200° C.

For each of Au/Pt and Pt/Pd thermocouples, a five turn coil of 1 mm diameter constructed from 0.2 mm diameter Platinum wires was used to connect the thermoelements at the measuring junction, and a pair of insulated copper wires was soldered to the other ends of the thermoelements to form the reference junction.

## 3. CALIBRATION PROCEDURE

The Au/Pt, Pt/Pd and Pt10%Rh/Pt thermocouples were stabilized by annealing at the temperature of the freezing point of Ag (961.78° C) for a period of 300 hours. After stabilization they were calibrated by comparison with SPRT in the range from room temperature up to 450° C and by comparison with a HTSPRT in the range from 600° C to 960° C. Calibration to determine the emf versus temperature relation of thermocouples in the temperature range from 100° C up to 450° C was carried out in stirred liquid and salt baths. The temperature of the bath was determined with a 25Ω SPRT calibrated according to ITS-90. An oil bath was used from 100° C

to 200° C, and a salt bath from 220° C to 450° C. Hart Scientific manufactured all baths used in this calibration. The horizontal and vertical temperature stability of the baths is  $\pm 0.015^\circ\text{C}$ .

During measurements in each bath, the thermocouples were contained in a borosilicate glass tube (7 mm outer diameter and 5 mm inner diameter), 500 mm long, closed at the bottom. The thermocouples were positioned such that the measuring junctions were at the same immersion as the mid point of the sensing element of the SPRT. The depth of immersion was 30 cm below the liquid surface in the bath. In all baths the temperature difference between the sensing element of the SPRT and that of the measuring junction of the thermocouple differed by not more than  $0.01^\circ\text{C}$ , based on previous measurements of the temperature uniformity of each bath used.

A heat pipe furnace was used to compare the thermocouples with the HTSPRT at temperatures in the range from 600° C to 1000° C. The thermocouples and the HTSPRT were placed inside a comparator cell placed inside the heat pipe furnace; such a device realizes an isothermal enclosure with a high temperature homogeneity, suitable for accurate temperature measurements in the temperature range from the freezing point of Al 660.323° C to the freezing point of Ag 961.78° C. The temperature gradient detected over a zone of 10 cm from the bottom, was about  $0.05^\circ\text{C}$ . The comparison between the three thermocouples and the calibrated HTSPRT was performed following a sequence with the measuring temperature always increasing. Following this sequence the instability and hysteresis effects of the thermocouples during their measurements at high temperature were considerably reduced.

The reference ends of the thermocouples were maintained at the ice point and attached with pure copper wires leading to a digital nanovoltmeter and a selector switch. The ice point reference temperature was monitored during the experiment.

The emf readings of the thermocouples were measured with a digital nanovoltmeter type Keithley - 182 and were recorded within  $0.1\mu\text{V}$ . At the same time the resistance of the HTSPRT or SPRT were measured with an automatic bridge type F18 (Automatic System Laboratories, England). The resolution of the bridge was  $0.1\mu\Omega$ .

The data acquisition program was developed in this laboratory and a program for the computer to control the bridge and record measurements data.

#### 4. RESULTS AND DISCUSSIONS

Tables 1 and 2 present the measured emf data for Au/Pt, Pt/Pd and Pt10%Rh/Pt thermocouples both in liquid baths and heat pipe furnace by comparison with SPRT and HTSPRT.

Table 1. The measured emf data for Au/Pt, Pt/Pd and Pt10%Rh/Pt thermocouples in oil and salt baths and heat pipe furnace by comparison with SPRT.

$t_{90}$ measured by SPRT °C	Au/Pt $\mu\text{V}$	Pt/Pd $\mu\text{V}$	Type-S $\mu\text{V}$
<b><u>In oil bath</u></b>			
100.0803	777.13	570.52	646.14
200.1531	1843.94	1208.25	1441.75
<b><u>In salt bath</u></b>			
299.8291	3134.91	1931.86	2321.53
399.6667	4622.84	2777.31	3256.7
<b><u>In heat pipe furnace</u></b>			
449.5707	5386.57	3256.59	3741.05
497.2997	6246.16	3756.94	4209.06

545.6597	7110.39	4303.14	4691.24
596.6283	8062.08	4928.40	5208.47

Table 2. The measured emf data for Au/Pt, Pt/Pd and Pt10%Rh/Pt thermocouples in heat pipe furnace by comparison with HTSPRT

$t_{90}$ measured by HTSPRT °C	emf measured for thermocouple μV		$t_{90}$ measured by HTSPRT °C	emf measured for type-S thermocouple μV
	Au/Pt	Pt/Pd		
648.644	9077.3	517.28	646.869	5725.42
695.883	10037.1	6288.32	697.131	6250.48
748.686	11153.0	7087.22	746.482	6775.16
797.399	12221.6	7870.67	796.618	7313.98
848.201	13377.0	8730.62	845.754	7853.88
896.932	14523.8	9596.97	886.528	8308.03
946.185	15721.1	10511.75	943.130	8946.71
			958.686	9123.61

To obtain a mathematical calibration function for Au/Pt, Pt/Pd and Pt 10%Rh/Pt thermocouples, we have used two methods. In the first method, two polynomial functions were chosen to describe temperature vs. emf relations for the different thermocouples in the temperature range from 0° C to 1000° C. In this method the temperature range was bisected at 660° C and for higher and lower temperature ranges, data from the comparison of the three thermocouples with either HTSPRT or the SPRT were fitted to each of the fourth-degree polynomials in the following form

$$E = \sum_{i=0}^4 a_i (t_{90})^i \quad (1)$$

where  $E$  denotes emf in  $\mu V$  and  $t_{90}$  is the temperature in ° C. Except in case of Pt/Pd thermocouple in the range from 100° C to 600° C it was found that a 6th-order polynomial is required for best fit with experiment data.

Coefficients  $a_i$  of the two polynomial functions are tabulated in Table 3.

By using the experimental data given in Table 1 and 2 the coefficients of the 4<sup>th</sup> degree polynomial function (1) were calculated by the method of least squares for the three types of thermocouples under study.

Table 3. Coefficients of the polynomial function for the thermocouples Au/Pt, Pt/Pd and Pt-10%Rh/Pt thermocouples.

	Au/Pt Thermocouple	Pt/Pd Thermocouple	Pt-10%Rh/Pt Thermocouple
	From 100° C to 600° C	From 100° C to 600° C	From 100° C to 600° C
$a_0$	-13.90563	-114.47784	-14.02426
$a_1$	6.33794	8.1734	5.73017
$a_2$	0.01669	-0.02221	0.00972
$a_3$	$-1.09513 \times 10^{-5}$	$1.11922 \times 10^{-4}$	$-1.12867 \times 10^{-5}$
$a_4$	$5.36681 \times 10^{-9}$	$-2.56419 \times 10^{-7}$	$5.83585 \times 10^{-9}$
$a_5$		$3.12937 \times 10^{-10}$	

$a_6$		$-1.52192 \times 10^{-13}$	
	<b>From 600° C to 1000° C</b>	<b>From 600° C to 1000° C</b>	<b>From 600° C to 1000° C</b>
$a_0$	$-4.805487 \times 10^{-2}$	$1.5375744 \times 10^{-3}$	$-3.2823928 \times 10^{-3}$
$a_1$	9.63701	-2.36319	23.61114
$a_2$	0.00759	0.01534	-0.02774
$a_3$	$5.8859 \times 10^{-7}$	$-3.30289 \times 10^{-6}$	$2.47361 \times 10^{-5}$
$a_4$	$-2.58843 \times 10^{-10}$	$3.46494 \times 10^{-10}$	$-7.72959 \times 10^{-9}$

In the second method, to obtain a mathematical calibration function of each thermocouple, emf values computed from the following reference functions, which are:

for Au/Pt thermocouple [3] 
$$E_R = \sum_{i=1}^{i=9} a_i (t_{90})^i, \quad (2)$$

for Pt/Pd thermocouple [7] 
$$E_R = a_0 + \sum_{i=1}^{i=n} a_i (t_{90})^i, \quad (3)$$

for Pt-10%Rh/Pt thermocouple [9] 
$$E_R = \sum_{i=1}^{i=8} a_i (t_{90})^i, \quad (4)$$

were subtracted from the emf values measured at each temperature given in Tables 1 and 2 for each thermocouple. The resulting emf deviations were then modeled by a quadratic function of temperature. Coefficients of the quadratic function were determined by the method of least squares, and addition of these coefficients to those of the reference function for each thermocouple gave the calibration function for the thermocouples under test, as given in Table 4.

Table 4. Coefficients of the calibration functions (Eq. 2, 3 and 4) for the investigated thermocouples.

	<b>Au/Pt Thermocouple</b>	<b>Pt/Pd Thermocouple</b>	<b>Pt-10%Rh/Pt Thermocouple</b>
	<b>From 100° C to 960° C</b>	<b>From 100° C to 600° C</b>	<b>From 100° C to 960° C</b>
$a_0$	-----	5.3125506,	-----
$a_1$	6.02425610,	0.0045123,	5.3967443,
$a_2$	0.01934950,	$-9.4768134 \times 10^{-6}$ ,	0.0126205,
$a_3$	$-2.22837510 \times 10^{-5}$ ,	$2.9922430 \times 10^{-8}$ ,	$-2.3257212 \times 10^{-5}$ ,
$a_4$	$3.28711859 \times 10^{-8}$ ,	$-2.0125230 \times 10^{-11}$ ,	$3.2202882 \times 10^{-8}$ ,
$a_5$	$-4.24206190 \times 10^{-11}$ ,	$-1.268540 \times 10^{-14}$ ,	$-3.3146520 \times 10^{-11}$ ,
$a_6$	$4.56927038 \times 10^{-14}$ ,	$2.257823 \times 10^{-17}$ ,	$2.5574425 \times 10^{-14}$ ,
$a_7$	$-3.39430260 \times 10^{-17}$ ,	$-8.510068 \times 10^{-21}$ ,	$-1.2506887 \times 10^{-17}$ ,
$a_8$	$1.42981590 \times 10^{-20}$ ,		$2.7144318 \times 10^{-21}$ ,
$a_9$	$-2.51672787 \times 10^{-24}$		
		<b>From 600° C to 960° C</b>	
$a_0$		$-4.977140 \times 10^2$	
$a_1$		$1.019410 \times 10^1$ ,	
$a_2$		$-1.583520 \times 10^{-2}$ ,	
$a_3$		$3.636170 \times 10^{-5}$ ,	
$a_4$		$-2.690151 \times 10^{-8}$ ,	
$a_5$		$9.562737 \times 10^{-12}$ ,	
$a_6$		$-1.357074 \times 10^{-15}$ ,	

In the following discussion to differentiate between the two methods, we shall call the first

method the 4<sup>th</sup> degree polynomial and the second method the calibration function.

The coefficients of the calibration functions (Eqs. (2), (3) (4)), obtained by adding the coefficients of the deviation functions derived by the method of least squares, using the experimental data given in Tables 1 and 2 to those of the reference functions, for the three types of thermocouples under test, are given in Table 4.

Table 5. The values of  $(V_{exp}-V_{cal})$  in  $\mu V$  calculated by the two functions for Au/Pt thermocouple and the temperature equivalents of those differences in the range from 100° C to 960° C.

$T_{90}$ ° C	$V_{exp}$ $\mu V$	$V_{cal}$ By Eq. (1)			$V_{cal}$ By Eq. (2)			de/dt $\mu V/^\circ C$
		$V_{cal}$ $\mu V$	$(V_{exp}-V_{cal})$ $\mu V$	$(V_{exp}-V_{cal})$ $m^\circ C$	$V_{cal}$ $\mu V$	$(V_{exp}-V_{cal})$ $\mu V$	$(V_{exp}-V_{cal})$ $m^\circ C$	
<b><u>By SPRT</u></b>								
100.0803	777.1	777.1	0.0	0.0	776.0	1.2	126	9.4
200.1531	1843.9	1844.1	-0.1	-11	1842.3	1.7	139	11.9
299.8291	3134.9	3135.0	-0.1	-5	3133.5	1.4	100	14.0
399.6667	4622.8	4622.9	-0.1	-5	4621.3	1.5	97	15.8
446.8136	5386.6	5387.0	-0.5	-28	5385.5	1.1	67	16.6
497.2997	6246.2	6246.9	-0.7	-42	6245.4	0.8	46	17.4
545.6597	7110.4	7110.4	0.0	2	7108.9	1.5	84	18.3
596.6283	8062.1	8062.8	-0.7	-36	8060.6	1.5	80	19.1
<b><u>By HTSPRT</u></b>								
648.644	9077.3	9078.6	-1.3	-65	9075.5	1.8	90	20.0
695.883	10037.1	10038.8	-1.7	-84	10035.3	1.7	84	20.7
748.686	11153.0	11154.7	-1.6	-76	11151.0	2.1	96	21.6
797.399	12221.6	12223.9	-2.3	-102	12220.1	1.5	68	22.3
848.201	13377.0	13379.4	-2.4	-103	13375.5	1.5	64	23.2
896.932	14523.8	14526.5	-2.7	-112	14522.4	1.4	58	24.0
946.185	15721.1	15724.1	-3.0	-121	15719.8	1.3	51	24.7

Table 6. The values of  $(V_{exp} - V_{cal})$  in  $\mu V$  calculated by the two functions for Pt/Pd thermocouple and the temperature equivalents of these differences in the range from 100° C to 960° C.

$T_{90}$ ° C	$V_{exp}$ $\mu V$	$V_{cal}$ Using eq (1)			$V_{cal}$ Using eq (2)			de/dt $\mu V/^\circ C$
		$V_{cal1}$ $\mu V$	$(V_{exp}-V_{cal})$ $\mu V$	$(V_{exp}-V_{cal})$ $m^\circ C$	$V_{cal}$ $\mu V$	$(V_{exp}-V_{cal})$ $\mu V$	$(V_{exp}-V_{cal})$ $m^\circ C$	
<b><u>By SPRT</u></b>								
100.080	570.5	570.5	0.0	0.0	570.2	0.4	56	6.2
200.153	1208.3	1208.3	-0.1	-11	1209.1	-0.9	-132	6.7
299.829	1931.9	1931.7	0.2	22	1931.3	0.5	68	7.8
399.667	2777.3	2778.0	-0.7	-75	2776.9	0.4	45	9.2
449.571	3256.6	3256.6	-0.1	-5	3257.0	-0.4	-40	10.0
497.300	3756.9	3755.6	1.4	126	3756.1	0.9	79	10.8
545.660	4303.1	4304.9	-1.8	-148	4303.5	-0.3	-29	11.8
596.628	4928.4	4928.0	0.4	30	4928.0	0.4	30	12.6
<b><u>By HTSPRT</u></b>								
648.64	5617.3	5618.8	-1.4	-105	5616.9	0.4	32	13.3
695.88	6288.3	6289.8	-1.5	-103	6286.7	1.7	117	14.6
748.69	7087.2	7089.6	-2.4	-156	7085.2	2.0	133	15.3
797.40	7870.7	7872.5	-1.8	-111	7867.1	3.5	215	16.4
848.20	8730.6	8733.2	-2.6	-148	8727.8	2.8	100	17.4
896.93	9597.0	9599.8	-2.8	-154	9594.5	2.4	134	18.2
946.19	10511.8	10514.8	-3.1	-162	10509.7	2.1	108	19.0

The error of fit which is the difference between the experimental values  $V_{exp}$  and those

calculated by the 4<sup>th</sup> degree polynomial suggested by us and by the calibration functions (Eqs. (2), (3) (4))  $V_{calc}$  in microvolt is given in Tables 4, 5 and 6 together with the temperature equivalents of these differences ( $V_{exp} - V_{cal}$ ) for the three types of thermocouples. The tables also give the Seebeck coefficients for the three types of thermocouples at different temperatures.

Table 7. The values of ( $V_{exp} - V_{cal}$ ) in  $\mu\text{V}$  calculated by the two function for Pt-10%Rh/Pt thermocouple and the temperature equivalents of these differences in the range from 100° C to 960° C.

$T_{90}^{\circ}\text{C}$	$V_{exp}$ $\mu\text{V}$	$V_{cal}$ By Eq. (1)			$V_{cal}$ By Eq. (2)			de/dt $\mu\text{V}/^{\circ}\text{C}$
		$V_{cal}$ $\mu\text{V}$	$(V_{exp}-V_{cal})$ $\mu\text{V}$	$(V_{exp}-V_{cal})$ $\text{m}^{\circ}\text{C}$	$V_{cal}$ $\mu\text{V}$	$(V_{exp}-V_{cal})$ $\mu\text{V}$	$(V_{exp}-V_{cal})$ $\text{m}^{\circ}\text{C}$	
<b><u>By SPRT</u></b>								
100.0803	646.1	646.1	0.1	8	646.1	0.0	27	7.4
200.1531	1441.8	1441.2	0.6	70	1441.8	-0.1	-7	8.5
299.8291	2321.5	2320.8	0.7	81	2321.8	-0.2	24	9.1
399.6667	3256.7	3257.1	-0.4	-41	3257.3	-0.6	66	9.6
449.5707	3741.1	3739.5	1.6	161	3739.8	1.3	134	9.7
497.2997	4209.1	4208.2	0.8	83	4208.9	0.1	13	9.9
545.6597	4691.2	4690.4	0.8	82	4691.6	-0.4	-37	10.0
596.6283	5208.5	5207.2	1.3	129	5208.1	0.4	34	10.2
<b><u>By HTSPRT</u></b>								
646.869	5725.4	5725.5	-0.1	-7	5725.6	0.1	-13	10.4
697.131	6250.5	6251.2	-0.7	-69	6250.4	0.1	9	10.5
746.482	6775.2	6774.4	0.7	67	6774.3	0.9	79	10.7
796.618	7314.0	7314.9	-1.0	-89	7315.3	-1.3	-117	10.9
845.754	7853.9	7854.1	-1.1	-96	7853.9	-0.1	-5	11.1
886.528	8308.0	8308.2	-0.2	-16	8307.4	0.7	58	11.2
943.130	8946.7	8947.1	-0.4	-34	8946.5	0.2	20	11.4
958.686	9123.6	9124.0	-0.4	-31	9124.0	-0.4	-36	11.4

Table 8. The combined uncertainty  $U_c$  expressed in the form of 95% confidence level for the calibration of Pt/Pd, Au/Pt and type S thermocouples by comparison in the temperature range from 100° C to 960° C with SPRT and HTSPRT are estimated as given in the following table.

<b>Expected Components of Uncertainty</b>	<b>Au/Pt mK</b>	<b>Pt/Pd mK</b>	<b>Type S mK</b>
Standard Deviation (Type A)	27.8	39.6	114.8
Uncertainty due to inhomogeneity of thermocouples	5.8	15	50.5
Uncertainty due to interpolation formula	40.0	40.0	40.0
Comparator cell stability	30.0	30.0	30.0
Uncertainty of Voltmeter	20.0	26.0	43.0
Uncertainty of Ice Point	5.0	5.0	5.0
HTSPRT calibration	10.0	10.0	10.0
Combined Standard Uncertainty $U_c$	61.9	71.4	142.1
Expanded uncertainty U, k=2	123.8	142.7	284.3

Table 8 gives a summary of the uncertainty budget of the measurements by comparison. The components of the uncertainty are expressed as equivalent mK of the Au/Pt, Pt/Pd and Pt10%Rh/Pt thermocouples. The differences ( $V_{exp} - V_{cal}$ ) given in Tables 5, 6 and 7 are plotted in Fig. 1, 2 and 3 for Au/Pt, Pt/Pd and Pt-10%Rh/Pt respectively.

From figures it is clear that the error of fit in ( $V_{exp} - V_{calc}$ ) obtained by using the 4<sup>th</sup> degree polynomial for Au/Pt ranges from -0.7  $\mu\text{V}$  in the temperature range from 100° C to 600° C to -3.0  $\mu\text{V}$  in the range from 600° C to 950° C and by using the calibration function (2, 3 and 4) for

Au/Pt ranges from 1.7  $\mu\text{V}$  in the temperature range from 100° C to 600° C to 2.1  $\mu\text{V}$  in the range from 600° C to 950° C.

For type S thermocouple the error of fit ( $V_{exp} - V_{cal}$ ) obtained by using the polynomial function and calibration function is small and is about 1.6  $\mu\text{V}$  by using the polynomial function in the temperature range from 100° C to 960° C and it is about 1.3  $\mu\text{V}$  by using the calibration function in the temperature range from 100° C to 960° C.

For Pt/Pd thermocouple the difference between the two functions is very small up to 600° C and starts to increase to become -3.1  $\mu\text{V}$  at 950° C by using polynomial function and is 2.1  $\mu\text{V}$  at 950° C by calibration function.

## 5. CONCLUSION

In the present study on Pt-10%Rh/Pt, Au/Pt and Pt/Pd thermocouples after stabilization by annealing at 1000° C for 300 hours, an emf - temperature reference function is generated for the range from 100° C to 950° C with the technique of calibration by comparison with a Platinum resistance thermometer. The temperature equivalent of deviations of the suggested 4<sup>th</sup> degree polynomial from experimental values ranges from 0.0° C to 0.12° C for Au/Pt thermocouple, from 0.0° C to 0.16° C for Pt/Pd and from -0.01° C to 0.16° C for Pt10%Rh/Pt which are in the range of the expanded uncertainty of these thermocouples.

The deviations of the experimental values from the calculated values by using the functions derived from the reference functions given in the literature [2, 3, 4] range from 0.05° C to 0.14° C for Au/Pt thermocouple, from 0.03° C to 0.21° C for Pt/Pd thermocouple and from 0.0° C to 0.13° C for Pt 10%Rh/Pt thermocouple.

From these results we can conclude that the 4<sup>th</sup> degree polynomial can be an acceptable alternative to the reference function available in the literature for the three types of thermocouples.

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## PORÓWNANIE MIĘDZY PROSTYMI WIELOMIANAMI I OPARTĄ O ITS-90 FUNKCJĄ ODNIESIENIA DLA ZALEŻNOŚCI MIĘDZY SEM A TEMPERATURĄ W TERMOELEMENTACH Z METALI SZLACHETNYCH O DUŻEJ CZYSTOŚCI

### Streszczenie

Opracowano wielomianowe funkcje odniesienia opisujące zależność między siłą elektromotoryczną i temperaturą, obejmujące zakres temperatury od 100° C do 960° C, dla trzech typów termoelementów wykonanych z metali szlachetnych: Pt10%Rh/Pt, Au/Pt oraz Pt/Pd. Funkcje zostały porównane z funkcjami odniesienia dostępnymi w literaturze. Termoelementy zostały wykowane i przed kalibracją poddane procesowi wyżarzania w celu stabilizacji przez 300 godzin w temperaturze 962° C. Kalibrację przeprowadzono z wykorzystaniem standardowego oporowego termometru platynowego (SPRT) w zakresie temperatury od 100° C do 450° C oraz wysokotemperaturowego oporowego termometru platynowego (HTSPRT) w zakresie temperatury od 450° C do 950° C. Oszacowano i omówiono błąd dopasowania.

Funkcja odniesienia opisująca zależność między siłą elektromotoryczną i temperaturą określana jest dla zakresu od 100° C do 960° C z wykorzystaniem metody kalibracji polegającej na porównaniu wskazań z oporowym termometrem platynowym. Równoważnik temperaturowy odchyłek proponowanego wielomianu 4-tego stopnia od wartości doświadczalnych wynosi od 0,0° C do 0,12° C dla termoelementu Au/Pt, od 0,0° C do 0,16° C dla Pt/Pd i od -0,01° C do 0,16° C dla Pt10%Rh/Pt, co mieści się w zakresie rozszerzonej niepewności dla tych termoelementów.

Odchyłki między wartościami doświadczalnymi a wartościami obliczonymi z wykorzystaniem funkcji wyprowadzonych na podstawie funkcji odniesienia podanych w literaturze [2], [3], [4] mieszczą się w zakresie od 0,05° C do 0,14° C dla termoelementu Au/Pt, od 0,03° C do 0,21° C dla termometru Pt/Pd oraz od 0,0° C do 0,13° C dla termoelementu Pt10%Rh/Pt.

Na podstawie wyników można wyciągnąć wniosek, że wielomian 4-tego stopnia może stanowić akceptowalną alternatywę w stosunku do funkcji odniesienia dostępnej w literaturze dla wymienionych trzech rodzajów termoelementów.