XVII IMEKO World Congress
Metrology in the 3rd Millennium
June 22–27, 2003, Dubrovnik, Croatia

STABILITY EVALUATION OF A GOLD-PLATINUM THERMOCOUPLE AS AN INTERPOLATING INSTRUMENT IN THE TEMPERATURE SCALE

Marcelo dos Santos Monteiro, INMETRO, Rio de Janeiro, BRAZIL
Alcir de Faro Orlando, PUC-Rio, Rio de Janeiro, BRAZIL

Abstract − The 1990 International Temperature Scale (ITS-90) substituted the platinum-platinum-10% rhodium thermocouple by the high temperature standard platinum resistance thermometer (HTSPRT) and the radiation thermometer, as an interpolating instrument in the 630 °C to 1064 °C range, due to the lower stability of the thermocouple. Although the uncertainty of reproducing the temperature scale became much lower, the cost of the required measuring equipments was raised. Aiming to offer the Brazilian Calibration Network accredited laboratories a lower cost temperature scale traceability alternative, at a smaller uncertainty than the standard type S thermocouple can provide, a 99,999% purity gold-platinum (AuPt) thermoucouple was exposed systematically to a high temperature environment (close to 1000 °C) for more than 1500 hours, with its stability and homogeneity being evaluated with the aid of a silver fixed point cell. It was shown that a ± 25 mK (k=2) uncertainty can be achieved. This works details the methodology and the cares that have to be taken in order assure the reliability of the results.

Keywords: Thermometry, Gold-Platinum Thermocouple, Interpolating Instruments.

1. INTRODUCTION

The Temperature Laboratory (LATER) of the National Institute of Metrology and Industrial Quality of Brazil (INMETRO) is responsible for :

- Having the guard, maintaining, preserving and reproducing the national temperature standards, besides disseminating and standardizing temperature measurement in Brazil;
- Maintaining the traceability of its standards through comparison with international laboratories;
- Calibrating temperature measurement instruments for clients, if the accredited laboratories in the National Calibration Network (RBC) cannot provide the service;
- Developing and disseminating the knowledge of temperature measurement techniques for Brazilian institutions, like industries, and supporting the accredited laboratories in their calibration methodology.

All the accredited laboratories in the National Calibration Network (RBC) are frequently evaluated according to ISO/IEC 17025 Standards. INMETRO follows ISO/IEC Guide 58 to assure their acceptance by international organizations.

In the ITS-90 (1990 International Temperature Scale), the high temperature standard platinum resistance thermometer (HTSPRT), with a typical uncertainty of ± 10 mK at the silver point, k=2, substituted the former standard platinum-platinum-10% rhodium thermocouple, with an uncertainty of at least ± 200 mK at the silver point, k=2, because of its higher stability, repeatibility and reproducibility. The uncertainty of reproducing the temperature scale became one order of magnitude better than the one achieved by the thermocouple. However, the required setup for measuring the resistance became much more expensive than that required for the thermocouple. Furthermore, some extra care is required to handle the HTSPRT, so that to avoid the influence of vibration and mechanical shock on the response of the thermometer, which tend to modify its resistance. As a result, several countries in the world have been making studies on new measurement instruments to be used as a standard interpolating device in the high temperature range, below the silver point. The gold-platinum (AuPt) thermocouple has been given a special attention and it is the focus of this study.

When calibrating the AuPt thermocouple of this research by the fixed point method, the following fixed points of the ITS-90 scale were used by INMETRO in the 0 – 1000 °C range :

- Water triple point, 0,01 °C ± 0,1 mK (k=2)
- Tin, 231,928 °C ± 1,2 mK (k=2)
- Zinc, 419,527 °C ± 2,2 mK (k=2)
- Aluminum, 660,323 °C ± 4,8 mK (k=2)
- Silver, 961,78 °C ± 14 mK (k=2)

The AuPt thermocouple, manufactured by HART Scientific, Inc, with a 99,999% purity, was calibrated by its own laboratory with an uncertainty (k=2) of ± 20 mK, before being delivered to INMETRO. The measuring region of the thermocouple is composed of 0,5 mm diameter gold and platinum wires, 630 mm long, running inside a two hole compacted ceramic insulating tube (aluminum oxide), held within a 7 mm diameter protection quartz tube. It is then connected to a 64 mm long head, and then to a two wire reference junction (ice point), inside a 5 mm diameter, 230 mm long, stainless steel protection tube. The total length of the gold and platinum wires is 1200 mm. Two 1060 mm long copper wires connect the reference junction to a calibrated measuring 7½ digit HP 3457A voltmeter, with a measuring uncertainty (k=2) of ± 0,001% at the silver fixed point, ± 0,002% at the aluminum fixed point, ± 0,005% at the zinc fixed point, and ± 0,01% at the tin fixed point.

Following [1], before mounting the thermocouple, the gold wire was annealed at 1000 ^oC for 10 hours. The platinum wire was annealed at 1300 ^oC for 10 hours.

Because of the fact that a large difference in expansion coefficient between two wires, like gold and platinum, can result in stress and cold work, a 0,2 mm platinum wire was used to build a small 1 mm diameter spring, placed between the two wires in the measuring junction, so that the thermal stability of the thermocouple could be increased.

2. METHODOLOGY

The objective of the study is to get performance data for different operating conditions, so that both calibration stability and thermoelectric homogeneity can be determined. Stability is defined as the ability of the thermocouple to keep its metrological characteristics along the time, between two successive calibrations. The thermocouple is defined as homogeneous when the Seebeck coefficient is the same along its length.

2.1. Cares for assuring reliability of results

In the used experimental procedure, the following cares were taken to assure the reliability of the results, according to [1].

- The same voltmeter was used for all e.m.f. measurements, so that to reduce systematic errors.
- The reference junction protection metallic tube was covered by a silicon rubber layer and placed completely inside the ice bath, so that to minimize conduction heat transfer to environment.
- When finishing a set of measurement data, the thermocouple was kept at 450 ^oC for about 12 hours, in order to relieve mechanical stresses. When the allowed maximum temperature excursion of thermocouple was exceeded, the annealing time was doubled.
- The thermocouple inside the annealing furnace was placed in a quartz-platinum-quartz sandwich protection tube to prevent metallic ions to attack the thermocouple wires, and thus changing the thermocouple homogeneity.
- A complete melting and freezing plateau were used in the measurement, so that any e.m.f. difference could be detected, due to mechanical stresses. In this case, the thermocouple was submitted to a thermal treatment again.

2.2. Reference function for the AuPt thermocouple

ASTM E-1751[2] standard presents the reference function of the AuPt thermocouple, that is, a ninth degree polynomial for its e.m.f. as a function of temperature (^oC), as indicated by "(1)" and Table 1. HART Scientific, Inc, [4] present a table for these values.

$$E_R = \sum_0^9 c_i T^i \tag{1}$$

where,

E_R, e.m.f. reference function, μV

T, temperature, ^oC

2.3. Calibration of the AuPt thermocouple

When calibrating the AuPt thermocouple by the fixed point method, its corresponding e.m.f. reference function value at each fixed point temperature ($E_{R,i}$) must be subtracted from the measured e.m.f. output (E_i), resulting in an error function ΔE_i at each fixed point. Then, a second degree polynomial is fitted to the data points by the least square method, determining a_1 and a_2 :

$$\Delta E_i = E_i - E_{R,i} \tag{2}$$

$$\Delta E = a_1 T + a_2 T^2 \tag{3}$$

Therefore, the actual calibration curve of the thermocouple becomes :

$$E = \sum_0^9 (c_i + a_i) T^i \tag{4}$$

where $a_i = 0$ for i not equal to 1 or 2.

Table 1. Initial and Final Calibration Coefficients

Symbol	Initial Calibration	Final Calibration
c_0	0,00000000E+00	0,00000000E+00
$c_1 + a_1$	6,03619861E+00	6,03450989E+00
$c_2 + a_2$	1,93672974E-02	1,93688460E-02
c_3	-2,22998614E-05	-2,22998614E-05
c_4	3,28711859E-08	3,28711859E-08
c_5	-4,24206193E-11	-4,24206193E-11
c_6	4,56927038E-14	4,56927038E-14
c_7	-3,39430259E-17	-3,39430259E-17
c_8	1,42981590E-20	1,42981590E-20
c_9	-2,51672787E-24	-2,51672787E-24

Table 2. Standard uncertainty components

Uncertainty Component	Symbol	Unit	U/u
Fixed Point Cell	u_{cel}	mK	2
Calibration Repeatibility	u_{rep}	mK	2
Reference Junction	u_{jre}	mK	$3^{1/2}$
Voltmeter Calibration	u_{cmu}	μV	2
Voltmeter Resolution	u_{rmu}	μV	$2.3^{1/2}$
Reading Dispersion	u_{dep}	μV	2
Calibration Fitting	u_{aju}	mK	2

2.4. Uncertainty analysis

The uncertainty analysis was carried out using the procedures as described by [6]. The uncertainty components in Table 2 were used to calculate the combined uncertainty of temperature measurement with the AuPt thermocouple.

The combined standard uncertainty can be calculated as the square root of the sum of squares of the standard uncertainty components. The combined uncertainty can be calculate with a coverage factor of 2, at 95,45% confidence level.

2.5. Experimental procedure

An experimental procedure was developed to carefully determine the performance of the AuPt thermocouple, as far as calibration stability and thermoelectric homogeneity are concerned. Three steps were followed :

2.5.1 Initial performance

The objective of this experimental phase was to determine the initial characteristics of the thermocouple, to be used as a reference in this study. The following tests were conducted :

- Calibration of the thermocouple by the fixed point method, using ice point [5], tin, zinc and silver fixed points.
- Comparison with the original manufacturer calibration.
- Determination of the thermoelectric homogeneity by varying its immersion depth in a isothermal environment from 0 to 18 cm, and measuring its output.
- Determination of the short term repeatibility by measuring its output under successive daily immersions into the silver fixed point well, alternately melting and freezing, totalling ten days.

2.5.2. Long term repeatibility (1500 h)

The objective of this experimental phase is to determine the long term repeatibility of the thermocouple as a function of use and time, for over more than 1500 hours. Its output was measured under successive daily immersions into the silver fixed point, totalling 27 days. After an initial 200 h period, in which alternately melting and freezing points were measured in successive days, the thermocouple was annealed at about 1000 ^{o}C for 200 h. Then, melting and freezing points were measured in successive days. This procedure was repeated until reaching 1500 h of tests.

2.5.3. Final performance

The objective of this experimental phase was to determine the final characteristics of the thermocouple, so that significative differences in output could be detected as a function of long term use and time. The same tests, as for the initial performance of the thermocouple, were conducted, with exception of short term repeatibility tests.

3. RESULTS

3.1. Initial Performance

- Firstly, the thermocouple was calibrated by the fixed point method (Table 1), and the values were compared to the original curve as supplied by the manufacturer HART, which is traceable to NIST (USA). Silver, aluminum, zinc and tin points were chosen. A maximum 8,1 mK difference was found between HART and INMETRO calibrations, according to Table 3.

Table 3. Initial Calibration. Comparison with HART calibration.

Temp.	e.m.f. (µV)			Diff.
^{o}C	Reference	HART	INMETRO	mK
0,000	0,000	0,000	0,000	0,0
231,928	2236,184	2236,123	2236,164	-3,3
419,527	4945,627	4945,534	4945,567	-2,0
660,323	9320,441	9320,328	9320,296	1,6
961,780	16120,495	16120,392	16120,190	8,1

- Then, by varying the thermocouple immersion in the fixed point well, the homogeneity was determined. The temperature was found to be the same, to within less than 8 mK, between 0 and 8 cm from the bottom of the well (Table 4).

Table 4. Thermoelectric Homogeneity at silver freezing point (output – initial value at bottom of well)

Distance from Bottom		Temperature Increase	
Value	Unit	Value	Unit
0	cm	+1	mK
2	cm	+8	mK
4	cm	+6	mK
6	cm	+3	mK
8	cm	-6	mK
10	cm	-44	mK
12	cm	-202	mK
14	cm	-414	mK
16	cm	-585	mK
18	cm	-706	mK

Table 5. Short term repeatibility at silver fixed point

Date	Condition	Deviation
		mK
12/13/01	Melting	-0,8
12/14/01	Freezing	0,2
12/26/01	Melting	4,5
12/27/01	Freezing	-2,0
01/07/02	Melting	1,1
01/08/02	Freezing	-4,4
01/09/02	Melting	-0,4
10/01/02	Freezing	-0,8
02/06/02	Melting	2,2
02/07/02	Freezing	0,2

- The short term repeatibility was determined by making successive measurements in the silver point well. For the melting point, an average standard deviation of 2,8 mK was found. For freezing, 2,2 mK, which is more repeatable than melting. The data in Table 5 were considered as the baseline for this study, showing deviation from average value.

3.2. Long term repeatibility (1500 h)

Following the initial evaluation, the thermocouple was exposed, in a furnace, to a temperature in the neighbourhood of 1000 ^{o}C, for about 200 hours. Then its output was measured at the silver point, both in melting and freezing conditions. This procedure was repeated regularly every 200 hours, until a total period of about 1500 hours was reached. The average standard deviation with respect to the initial calibration was about 2,6 mK for melting and 1,7 mK for freezing. Table 6 shows the temperature deviation from the average value during the tests, as a function of time.

Table 6. Long term repeatability at silver point (1500 h)

Date	Time	Condition	Deviation
	h:mm		mK
12/12/01	1:50	Freezing	-1,0
12/13/01	7:55	Melting	-0,2
12/14/01	11:30	Freezing	0,8
12/26/01	16:30	Melting	5,0
12/27/01	32:30	Freezing	-1,5
01/07/02	38:00	Melting	1,6
01/08/02	57:00	Freezing	-3,9
01/09/02	63:15	Melting	0,1
01/10/02	69:15	Freezing	-0,3
02/06/02	163:00	Melting	2,8
02/07/02	182:15	Freezing	0,8
04/15/02	401:50	Melting	-3,5
04/16/02	424:40	Freezing	-4,2
04/16/02	434:45	Melting	-0,6
04/17/02	447:20	Freezing	-2,0
06/06/02	633:25	Melting	6,0
06/04//02	645:30	Freezing	1,5
06/05/02	670:45	Melting	-0,4
06/06/02	694:30	Freezing	-2,5
06/18/02	885:25	Melting	1,6
06/19/02	906:30	Freezing	-1,9
06/27/02	1044:20	Melting	2,8
06/28/02	1067:15	Freezing	-2,2
07/11/02	1245:45	Melting	0,8
07/12/02	1270:15	Freezing	-2,9
07/24/02	1471:50	Melting	4,3
0813/02	1508:05	Freezing	-0,8

3.3. Final Performance

- Finally, a calibration procedure at the silver, aluminum, zinc and tin fixed points was conducted and the results compared to the initial calibration. Table 7 presents the results. The calibration difference is defined as the thermocouple indicated e.m.f. after the tests minus the thermocouple indicated e.m.f. before the tests, divided by the Seebeck coefficient. It can be seen that a maximum temperature difference of –23,3 mK was found.
- Then, by varying the thermocouple immersion in the fix point well, the homogeneity was determined. The temperature was found to be the same, to within less than 10 mK, between 0 and 8 cm from the bottom of the well (Table 8).

Table 7 : Comparison between calibrations (before and after tests)

Temp.	e.m.f. (µV)			Diff.
^{o}C	Reference	Initial	Final	mK
0,000	0,000	0,000	0,000	0,0
231,928	2236,184	2236,164	2235,875	-22,9
419,527	4945,627	4945,567	4945,191	-23,3
660,323	9320,441	9320,296	9320,001	-14,6
961,780	16120,495	16120,190	16120,303	4,5

Table 8. Thermoelectric Homogeneity at silver freezing point (output - initial value at bottom of well)

Distance from Bottom		Temperature Increase	
Value	Unit	Value	Unit
0	cm	+3	mK
2	cm	+7	mK
4	cm	+10	mK
6	cm	+10	mK
8	cm	-7	mK
10	cm	-63	mK
12	cm	-170	mK
14	cm	-425	mK
16	cm	-651	mK
18	cm	-1116	mK

3.4. Uncertainty analysis

The temperature measurement uncertainty with the gold-platinum thermocouple was estimated following [6]. Table 9 presents the standard uncertainty (u) for each component that contributes to the total uncertainty, and expressed in mK.

Table 9 : Contributions to uncertainty of measurement

Uncertainty Component	Standard
	Uncertainty (mK)
Fixed Point Cell	± 7,0
Calibration Repeatibility	± 2,7
Reference Junction	± 2,9
Voltmeter Calibration	± 8,9
Voltmeter Resolution	± 0,2
Reading Dispersion	± 0,8
Calibration Fitting	± 3,5
Combined Uncertainty	± 12,5

The expanded uncertainty U (k=2) for the final calibration is therefore ± 25 mK.

A similar analysis was carried out for the initial calibration, resulting in ± 36 mK (k=2) for the expanded uncertainty.

The declared uncertainty of measurement by the manufacturer HART is ± 20 mK (k=2).

The compatibility between the calibrations can thus be analysed.

3.5. Compatibility between calibrations

A comparison between the initial and final calibrations by INMETRO, and HART calibration can be done by using the normalized error (E_n) method , as expressed by “(5)”. If the calibrations are compatible, the normalyzed error must be less than 1.

$$E_n = \frac{|V_1 - V_2|}{[U_1^2 + U_2^2]^{1/2}} \quad (5)$$

where,

V_1 and V_2 are measured values in calibrations 1 and 2

U_1 and U_2 are uncertainties of calibrations 1 and 2.

The analysis was done considering pairs of calibrations and calculating the maximum deviation in the whole range, using the calibration curves. Table 10 shows that all the calibrations are compatible.

Table 10.Compatibility between calibrations

Calibrations comparison	Maximum deviation mK	Normalized Error
Final/Initial	24,1	0,56
Final/HART	21,4	0,67
Initial/HART	9,0	0,22

3.6. Standard Type S thermocouple homogeneity

Table 11. Thermoelectric Homogeneity at silver freezing point (output - initial value at bottom of well) ,Type S thermocouple

Distance from Bottom		Temperature Increase	
Value	Unit	Value	Unit
0	cm	-19	mK
2	cm	-58	mK
4	cm	-63	mK
6	cm	-32	mK
8	cm	+17	mK
10	cm	+82	mK
12	cm	+55	mK
14	cm	-107	mK
16	cm	-383	mK
18	cm	-686	mK

The thermoelectric homogeneity of a standard type S thermocouple, used in INMETRO, was measured, being higher than it is for the AuPt thermocouple, as in Table 11.

4. CONCLUSIONS

The tests conducted with the gold-platinum (AuPt) thermocouple in the 0 °C to 1000 °C range show that the uncertainty of measurement (k=2) remains approximately the same (± 25 mK), after about 1500 hours, which is much less than what can be achieved by the platinum-platinum-10% rhodium standard thermocouple (± 200 mK), and slightly higher than what can be achieved by the high temperature standard platinum resistance thermometer (HTSPRT) (± 10 mK). The thermoelectric homogeneity of the AuPt thermocouple is much better than for the Standard type S thermocouple. Due to the fact that the cost of the equipments required for reading the AuPt thermocouple output is much less than for the HTSPRT, it can be considered a very good alternative for secondary laboratories around the world, and at the same time preserving an uncertainty level compatible to what is required for industrial instrument calibrations.

REFERENCES

[1] McLaren,E.H. & Murdock,E.G., “The Pt/Au Thermocouple, Part I: Essential Performance, Part II: Preparatory Heat Treatment, Wire Comparisons and Provisional Scale, National Research Council of Canada, Publication NRC/27703, Ottawa, Canada,1987.

[2] ASTM E-1751-00, “Standard Guide for Temperature Electromotive Force (e.m.f.) Tables for Non-Letter Designated Thermocouple Combination”, 2000.

[3] ASTM E-230-98,”Standard Specification and Temperature-Electromotive Force (e.m.f.) Tables for Standardized Thermocouples”, 1998.

[4] HART Scientific,Inc,”5629 AuPt Thermocouple, User Manual”, 1997.

[5] ASTM E-563-97, “Standard Practice for Preparation and Use of an Ice-Point Bath as a Reference Temperature”, 1997.

[6] ISO, “Guide to the Expression of Uncertainty of Measurement”, International Organization of Standardization, 1995.

Authors :

Marcelo dos Santos Monteiro, INMETRO, Temperature Division, msmonteiro@inmetro.gov.br, Rio de Janeiro, Brazil, 55.21.26799027

Alcir de Faro Orlando, PUC-Rio, Mechanical Engineering Department, afo@mec.puc-rio.br, Rio de Janeiro, Brazil, 55.21.31151176, Fax : 55.21.31141165