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GOLD/PLATINUM THERMOCOUPLE AND THE DC MEASUREMENT REQUIREMENTS

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NOVEMBER 2000

INTRODUCTION

Thermocouples are nasty complicated ill understood things that measure temperature differences badly and should be avoided at all cost.

Calibration of thermocouples - if possible at all - is a topic fraught with measurement problems. This author has avoided them as far as possible for the past 30 years and refuses to calibrate most types of thermocouple in Isotech's UKAS Laboratory.

A great friend of mine once said of a fellow scientist "what a pity that such a great man should have devoted so much of his life to such an inferior thing."

ITS-90 removed them in favour of the Standard Platinum Resistance Thermometer.

The limiting factor with all normal thermocouples is that one or both of the thermo-elements is an alloy and an alloy can not be produced that is homogeneous. This means that, because the Emf of a thermocouple is generated along the wire where there exists a thermal gradient, if the thermal gradient is moved along the thermocouple the Emf will change.

This limits the best thermocouple accuracy to about ±0.3°C, 2 sigma.

If both thermo-elements were of pure metal, then this limitation would not exist, giving the possibility of more accurate thermocouple measurement.

For good stability noble metals are preferable to base metals and in particular Gold/Platinum and Platinum/Palladium have been investigated.

The first published tables for Au/Pt and Pt/Pd thermocouples dates to 1941 (Roesner & Wensel), however it was not until the 1980's with better purity metals available that the Au/Pt thermocouple was reconsidered.

In Canada the research was carried out by McLaren & Murdoch[2] who solved one of the problems with the thermocouple that of expansion mis-match. By adding a fine spring of Platinum to the junction between the Gold and Platinum the Gold could expand freely without straining the Platinum thermo-element.

McLaren & Murdoch considered all aspects of construction and performance publishing a lengthy 2 part article in 1987 which is still the standard work and essential reading to all who are interested in Gold/Platinum thermocouples.

To summarize and simplify their work they found that this thermocouple if made according to their prescription was capable of accuracies of ±0.02°C from 0°C to 962°C.

It’s output increases from some 6µV/°C at 0°C to about 25µV°C at 962°C.

During the 1990's Burns et al of NIST have confirmed and extended their work. A reference list is attached at the end of this article [1].

During the 1990's, reluctantly at first, this author has been looking at the Gold/Platinum thermocouple to see from a Laboratory and Industrial point of view its advantages and limitations.

To construct such a thermocouple is a sophisticated project in itself.

Following the prescription of McLaren & Murdoch, wires of 99.999% purity are required and a long complex process of annealing taking many days.

However, making the thermocouple is only a small part of the project.

As the introduction mentions thermocouples measure temperature difference and so both the temperature at the reference and measuring ends must be considered.

Before selecting equipment to turn the thermocouple into a measurement system it is necessary to consider some electrical quantities.

At the Silver point the Au/Pt thermocouple generates 25µV/°C and may be capable of accuracies approaching ±0.01°C. To match this, the total measuring system should have, in terms of voltage an uncertainty of ±0.25µV or in terms of temperature ±0.01°C.

Considering the temperature constraints, and firstly focussing on the reference junction, a good quality Stirred Ice Bath made using distilled water would have an uncertainty of ±0.005°C, or half the total uncertainties. If a Water Triple Point Cell is utilized this reduces to ±0005°C and so a Water Triple Point must be used.

Next, considering the upper calibration temperature, a pure (99.9999%) Silver Cell in a heat pipe apparatus can realize a temperature of 961.78°C within 1 to 4mK. This is adequate.

The third component of the measuring system is the voltage measuring device. After research, the Wavetek 1281 7½ digit voltmeter was chosen, however the best UKAS uncertainty that could be issued with the meter was ±0.5µV 2 sigma, which is equivalent to ±0.02°C.

Combining these uncertainties it is possible to calculate the overall uncertainties at each calibration Fixed Point - 4 are used: Water Triple Point, Zinc, Aluminium and Silver.

PHYSICAL CONSTRAINTS

The length of the thermocouple produced was two metres from measuring to reference junction and 3 metres from reference junction to digital voltmeter. This means that the reference junction and digital voltmeter must be mobile as the thermocouple measuring junction is calibrated. A mobile computer trolley was found to be ideal.

PLATINUM/GOLD THERMOCOUPLE - CALIBRATION AT FIXED POINTS

METHOD:

The thermocouple is made according to the descriptions in the literature.

Both the reference end and the measuring end are placed in Water Triple Point Cells and the digital voltmeter reading noted with connections made, and then reversed.

The thermocouple reference junction is then raised 1,2 and 3cm to check immersion characteristics.

Next the measuring junction is placed after pre-warming in a freezing Silver Point Cell and after 20 minutes the Emf is noted over 10 minutes, connections are reversed and the readings repeated.

The measuring junction is withdrawn 2 and 4cm to measure homogeneity then moved to the Al and Zn Points in turn then the Ag process is repeated.

The complete calibration is repeated to check reproducibility.

RESULTS:

See Attachment.

RESULTS

A number of Gold/Platinum Thermocouples have been produced and calibrated. The Emf's at Silver, Aluminium and Zinc of some of them are tabulated in table 1 below.

TABLE 1
GOLD/PLATINUM THERMOCOUPLES VOLTAGE AT THE FIXED POINTS

µV	Burns	001	002	009	010	012	013	015
Ag	16,120.5	16,116	16,115.0	16,117.3	16,115.6	16,116.9	16,117.6	16,116.2
Al	9,320.44	9,316.3	9,316.3	9,318	9,316.8	9,317.65	9,317.8	9,317.3
Zn	4,945.6	4,943.7	4,943.7	4,944	4,934.1	4,943.65	4,943.7	4,943.6

Even at 5N purity the composition of the 10ppm impurities will influence the output Emf of the thermocouple. McLaren suggests a value of 20µV at the Silver point as a typical spread of 5N Material and all the results are well within this expectation.

To establish International credence for the results, 3 thermocouples were sent to IMGC for Intercomparison with the Italian laboratory's fixed point and standard volt.

The results are presented in Table 2.

TABLE 2

	009 µV	010 µV	012 µV	K=2 U/C µV
Ag	16,116.9	15,115.3	16,116.9	±0.9
Al	9,317.9	9,317.1	9,318.1	±0.7
Zn	4,944.3	4,943.7	4,944.4	±0.6
Sn	2,235.4	2,235.2	2,235.6	±0.6
O				

And lastly. One year after the first calibration G.012 was recalibrated at NTPL - see Table 3.

TABLE 3

G012	µK
Ag	16,117.6
Al	9,318.2
Zn	4,943.8
TPW	-0.1

SENSITIVITIES

The Gold/Platinum Thermocouple has the following sensitivities to temperature.

TABLE 4

°C	µV/°C
0	6.1
100	9.35
200	11.89
300	14
400	15.8
500	17.5
600	19.16
700	20.78
800	22.38
900	23.97
962	24.94

In graphs 1,2 and 3 the results of the calibrations at NTPL are compared with those at IMGC at the Silver Point, the Aluminium Point and the Zinc Point.

All show agreement well within the combined uncertainties of the two laboratories. In fact agreement is in the majority of cases within the uncertainties of IMGC alone.

UNCERTAINTIES

Based on the above, a submission was made to UKAS for the calibration of Gold/Platinum Thermocouples.

6 sources of uncertainties were identified as listed below.

A- Reproducibility of Fixed Points	0.003°C
B- Reproducibility of Thermocouple	0.012°C
C- Reference Junction Temperature Uncertainty	0.001°C
D- Voltage Uncertainty (worst case)	0.016°C
E- Polynominal interpolation	0.03°C
F- Stray Thermal Emfs and effects of small changes in immersion	0.03°C

Combined Uncertainty	0.047°C
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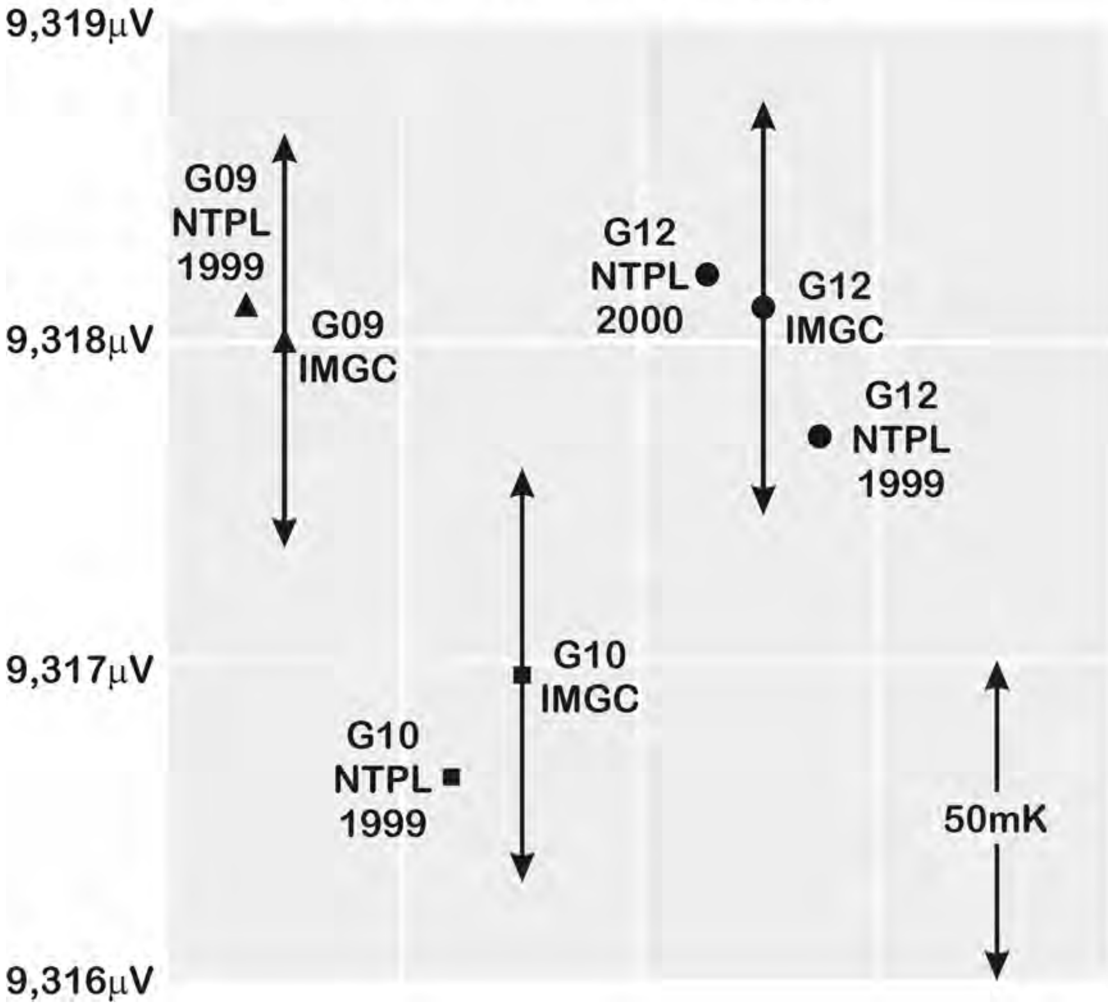
2 Sigma Uncertainty	0.094°C

Or ±0.1°C to nearest whole number

NTPL is now the first laboratory with accreditation for the calibration of Gold/Platinum Thermocouples.

Gold / Platinum Thermocouple Intercomparison NTPL vs. IMGC

Aluminium Point



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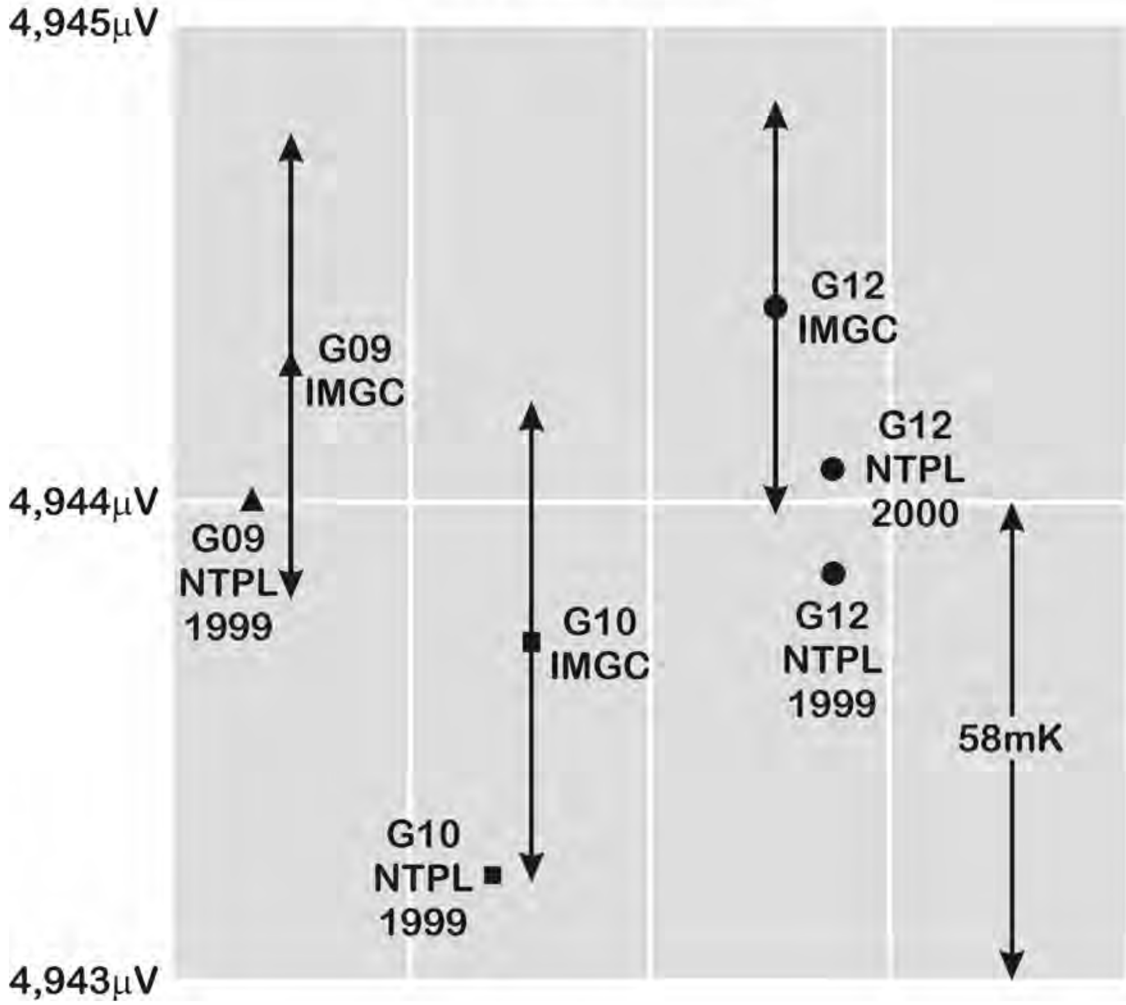
Gold / Platinum Thermocouple Intercomparison NTPL vs. IMGC

Zinc Point



DISCUSSION

With considerable care in construction and annealing, with patience and skill in calibration, the limiting factor in the use of the Gold/Platinum thermocouple is the accuracy of the digital voltmeter. This and the allowance for uncertainties in the polynomial make practical uncertainties about 0.1°C 2 sigma. This is some 3 x better than any other thermocouple.

CONCLUSION

The Gold/Platinum thermocouple is worthwhile considering for accurate temperature measurement over the range 0 to 962°C where uncertainties of ±0.05°C are required. However, close attention needs to be given to the cold or reference junction and to the accuracy of the voltage measuring device.

The Gold/Platinum thermocouple has the potential to reproduce the Silver Point ±0.01°C from day to day and so the if the voltmeter is sufficiently accurate and the uncertainties associated with the polynomial can be reduced this thermocouple has the potential to have smaller uncertainties than are currently claimed.

NOTE

All work so far has been done with Platinum and Gold of 99.999% purity.

The 10ppm impurities vary from lot to lot and account for variations in the Emf vs. Temperature, being about 20µV or 0.8°C at the Silver Point.

One route towards a more reproducible thermocouple would be to use 99.9999% pure wires.
These can be purchased. However it is no exaggeration to say that wire of this purity is so weak mechanically that it becomes impractical to produce a robust thermocouple.

So here is the ultimate limitation to the thermocouple.

SUGGESTED READING

[1] G.W.Burns, G.F.Strouse, B.M.Lui, and B.W.Mangum
Gold versus Platinum Thermocouples:
Performance Data and an ITS-90 based
Reference Function
National Institute of Standards and Technology, Gaithersburg, Maryland 20899 copyright American Institute of Physics.

[2] E.H.McLaren and E.G.Murdoch
The Pt/Au Thermocouple
Part I: Essential Performance
Part II: Preparatory Heat Treatment, Wire
Comparisons and Provisional Scale.
Ottawa, Canada, K1A 0S1