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FIXED POINT CALIBRATION FOR TYPE N THERMOCOUPLES IN THE 0°C TO 1000°C RANGE

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Abstract – Noble metal thermocouples are suitable for fixed point calibration method. Basic metal thermocouples, on the other hand, are usually calibrated by comparison. This happens because of their electromotive force (emf) instability in short time. In the range from 0 to 1084°C, according to the Monograph CCT/WG1 – BIPM [1] the typical uncertainty of type N thermocouple is about 0.2 °C (k=2) at the fixed points and 1.0 °C (k=2) in the interpolated values. This paper tries to enlighten this discussion presenting results which confirm that type N thermocouples have the best emf stability among base metal thermocouples up to 1000°C, when it is used by customers for calibrations by comparison, after have being calibrated at fixed points cells in primary laboratories. In this condition, it is possible to show that type N thermocouple permits to achieve results near to mentioned uncertainties. The calibration method, laboratory facilities, results and uncertainty budget are reported in this paper. A sheathed thermocouple having compacted mineral oxide insulation was calibrated by fixed points method at Inmetro and by comparison in Brazilian secondary laboratories along two years. This thermocouple has accumulated more than 200h at 1000°C .

Keywords: Thermocouple, Type N, Calibration

1. INTRODUCTION

Type N thermocouple emf is affected by wire contamination, mechanical strain (cold work) and inhomogeneities [2]. Even though the thermocouple assembly is annealed to stabilise the calibration, some procedures shall be adopted to keep the emf stability in the temperature range 0°C to 1000°C. After annealing at 962°C (silver point) for many hours, the emf can change at other fixed points due to those factors. Specially if the thermocouples are removed quickly from furnaces in 962°C or 1000°C.

Thermocouples will only present reproducibility and stability in their measurements if they are in a metallurgical stable condition, reached through annealing. The process seeks to the balance strain due to cold work, to remove contaminants, and to equilibrate point defects. Thus, it is recommendable a special procedure to reach the best emf stability and the minimum uncertainties in the range of 0°C to 1000°C.

This work presents the results of a type N thermocouple, calibrated by fixed points in the temperature range of 0°C to 1000°C , which are near from the best results achieved in [1]. It will be also discussed calibration by comparison in addition to fixed point calibration in order to achieve best results in interpolated emf values.

2. EQUIPMENT

Normally a typical thermocouple calibration in the range from 0°C to 1000°C is realised at four fixed points: Silver, Aluminium, Zinc, and Tin. Sometimes, Gallium and Indium fixed points are used to verify the calibration curve. All substances are kept in fixed point cells - graphite crucibles maintained in an inert atmosphere inside borosilicate or quartz containers. The substances in those cells have a very high purity (99,999%) which are used in sealed cells.

In order to realise those fixed points, the thermometry lab of Inmetro has two kind of furnaces: three heating zone furnaces, and Sodium or Potassium heat pipe furnaces. The former are used to realise fixed points up to 450°C, and the latter are used to realise both Aluminium (660.323°C) and Silver (961.78°C) freezing point.

The reference junctions of thermocouples were kept in dewar vases with ice produced from distilled water. Two types of voltmeters were used to measure thermocouple electromotive forces: Hewlett Packard DMM model 3457A and Keythley nanovoltmeter model 182. Both were automatically read by a personal computer which works with a Visual Basic data acquisition program developed at Inmetro.

3 CALIBRATION METHODOLOGY

3.1 FIXED POINT CALIBRATION

Thermocouple calibrations are realised in the following fixed points: Silver freezing point (961.78°C), Aluminium freezing point (660.323°C), Zinc freezing point (419.527°C), and Tin freezing point (231.928°C), in this order. This procedure is adopted for noble metal thermocouple calibrations, as described in [3]. Concerning to type N thermocouple calibrations, their electromotive forces can be measured either in melting or freezing points, because those alloys do not allow an accuracy whose reproducibility between melting and freezing would be noticed, this will be taken into account when we evaluate uncertainties.

Usually, one type N thermocouples is calibrated in a plateau, in order to verify when the melting or the freezing point starts and finishes. This methodology helps us to study the reproducibility and degradation of those thermocouples and their emf short time stability. So, at least one type N thermocouple shall be calibrated in Silver and Aluminium point to avoid thermal shock (quenching) if it was removed during these fixed point realisations.

Figure 1 shows a Aluminium freezing point curve performed with type N thermocouple INM 003 on 20th September 2002.

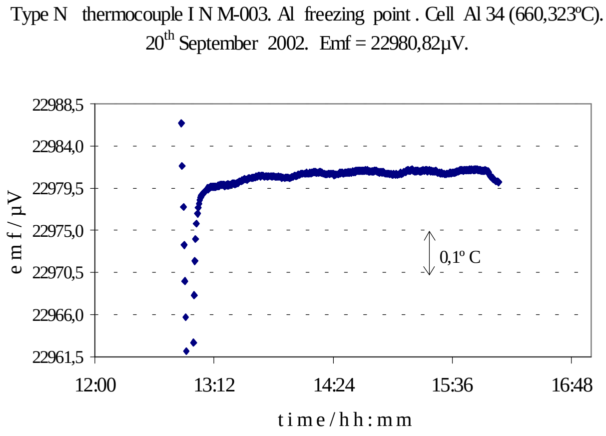

Figure 1 – Aluminium freezing point measured with type N thermocouple INM 003 in 20th September 2002. Emf mean value = 22980.8µV.

3.2 CALIBRATION BY COMPARISON

Thermocouple calibration by comparison can be performed together with fixed points calibration when the difference between measured emf and reference emf is not linear along the temperature range. Thus, it is necessary to have intermediate points to fit the calibration curve with lower fitting uncertainty.

The equipment used in thermocouple calibration by comparison basically comprises thermostatic baths and furnaces. Thermostatic baths use water, silicon oil or molten salt in the temperature range of 10°C to 550°C. The uniformity and stability temperature for these special baths are within few milikelvins. This equipment allows to check intermediate points between fixed points calibration with low type B uncertainty for temperature reference values.

3.3 INHOMOGENEITY EVALUATION

Inhomogeneity evaluation is performed through withdrawals with immersion depths commonly used during the calibrations [4]. For fixed point method, immersion depths in cells and furnaces are approximately between 300mm and 450mm. In calibrations by comparison, realised in thermostatic baths, immersion depths are approximately between 150mm and 450mm.

Graphs below show withdrawals realised with type N thermocouple INM 003 in Silver fixed point cell and in salt bath.

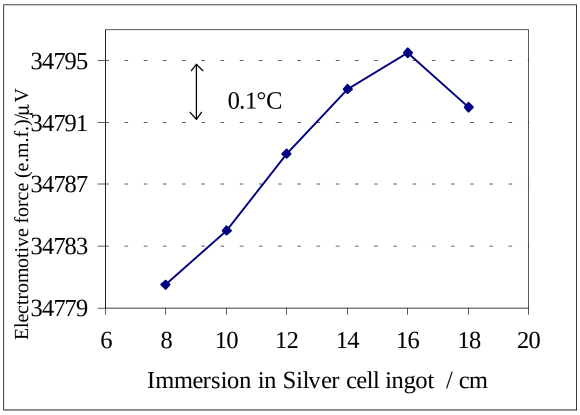

Figure 2 – Withdrawal realised with type N thermocouple INM 003 during a Silver freezing point (961.78°C) on 20th February 2002. When the thermocouple was at the bottom zone of thermometric well (18 cm), the emf mean value was 34792 µV. The furnace temperature was set approximately 1.2°C above the freezing point temperature (961.78°C). The freezing plateau lasted 6.5 hours. During the withdrawal it is possible to note the strange behaviour of the thermocouple INM 003: the electromotive force increased approximately by 3.5 µV (0.09°C) and after that the emf decreased with respect to the plateau value.

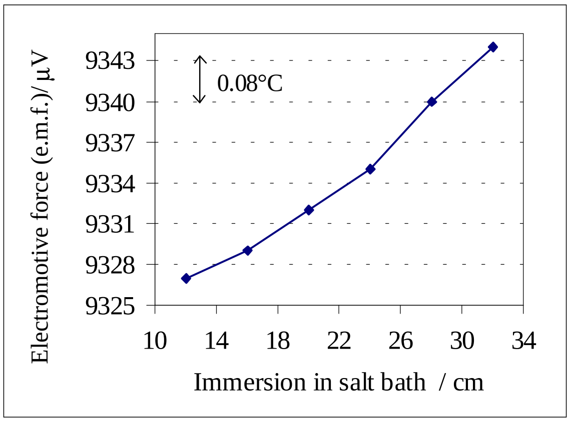

Figure 3 – Withdrawal realised with type thermocouple INM 003 in salt bath (300.1°C) on 09th January 2002

According to figures 2 and 3, type N INM 003 thermocouple presented emf changes during the withdrawal. Along 10cm in Silver cell ingot, the thermocouple emf changed approximately 15µV (0.39°C) and in salt bath at 300°C the thermocouple emf changed approximately 18µV (0.51°C) between 12cm and 32cm depth immersion. So, it is important to define the thermocouple immersion depth during the calibration.

Changes in the thermocouple electromotive force can occur due to the following factors:

- Contamination /oxidation of thermocouple wires;
- Migration of elements in thermocouple wires alloy;
- Cold work in thermocouple wires;
- Vaporisation of elements in thermocouple wires alloy.

Elements migration can occur during withdrawal in high temperatures (above 500°C), when the thermocouple is quenched. Different immersion depth at high temperatures can provide also emf changes along time during various calibrations.

4. CURVE FITTING PROCEDURE

After measuring the emf of the fixed points (Ag, Al, Zn, Sn), the difference between the measured and the reference emf values are calculated. Four relative values are presented in terms of temperature/°C versus ΔEmf /μV (deviation of the reference table or residue) [3,5]. Ice point (0°C) has an electromotive force of 0 μV. Then, there are five values suitable to fit a third degree equation (or a second degree equation). The curve of fitted electromotive force and measured electromotive force is given by the expression: measured electromotive force = ΔEmf + ITS-90 electromotive force reference table. As the ΔEmf function (deviation function) is of third degree, the fitted function for measured electromotive forces contains a polynomial of the same degree as the reference function in which the terms of first, second, and third degrees were changed by the sum with the same degree of the ΔEmf function. The fitting by the Least Squares method will be as efficient as the smaller ΔEmf is (if ΔEmf = 0, then, measured electromotive force = reference electromotive force). So, the uncertainty fitting is the root square of the sum of the square of residues (ΔEmf), divided by the number of degrees of freedom. This uncertainty can also be evaluated by means of the partial derivative procedure of the emf function [3].

5. RESULTS

The results of four fixed points calibrations in the temperature range of 0°C to 962°C are shown in the table 1:

Table 1 : Results of fixed points calibrations of the type N thermocouple INM 003 (Three calibrations).

Fixed Point	Sept. 2000 emf / μV	June 2001 emf / μV	Dec. 2001 emf / μV	Std dev. /°C
Ag	34773,27	34776,51	34778,49	0,07
Al	22969,89	22964,21	22975,55	0,14
Zn	13693,16	13696,97	13702,98	0,13
Sn	6981,51	6979,09	6985,82	0,10

Between December 2001 and September 2002 this type N thermocouple was calibrated by comparison in furnaces up to 1000°C. So, it was used at 1000°C approximately for 200 hours during two years.

Table 2 : Results of fixed points calibrations of the type N thermocouple INM 003 (Five calibrations).

Fixed Point	Sept. 2000 emf / μV	Jun. 2001 emf / μV	Dec. 2001 emf / μV	Mar. 2002 emf / μV	Sept. 2002 emf / μV	S. dev. /°C
Ag	34773,27	34776,51	34778,49	34791,79	34794,66	0,25
Al	22969,89	22964,21	22975,55	22977,51	22980,82	0,17
Zn	13693,16	13696,97	13702,98	13709,11	13695,18	0,17
Sn	6981,51	6979,09	6985,82	6987,27	6976,71	0,13

After Tin fixed point realisation in September 2002, it was performed the Indium freezing point and other points by comparison. The main reason for this was the signal changes of the deviation of the reference table in temperatures below Tin fixed point.

Table 3 shows temperature (°C) versus deviation of the reference table (ΔEmf/μV), where ΔEmf is positive to values below 231.928°C and above 660.323°C (Aluminium fixed-point).

Table 3: Results of INM 003 thermocouple fixed point calibration combined with some points realised by comparison (September 2002).

Temperature/°C	ΔEmf/μV
30.04	14.39
60.02	13.49
90.01	15.42
120.00	13.62
156.5985 (In)	3.15
200.00	1.26
231.928 (Sn)	-4.18
250.01	-2.12
350.00	-5.44
419.527 (Zn)	-6.07
660.323 (Al)	10.34
961.78 (Ag)	19.53

Other points were realised to find ΔEmf function and to reduce the fitted curve uncertainty (see item 3.2 CALIBRATION BY COMPARISON).

This was possible because that calibration by comparison was performed with low type B uncertainties in thermostatic baths.

Graph 4 shows a fifth degree curve fitting to 12 points listed in table 3 plus 0°C:

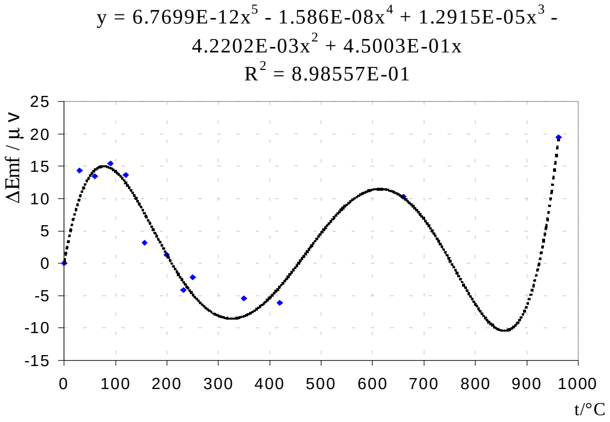

Figure 4. Fitted curve of fifth degree for 12 measured points in the temperature range of 0°C to 1000°C (Thermocouple INM 003).

For the fitted curve above, the calculated uncertainty was 0.09°C (k=1). If it was used a third degree curve, the uncertainty would be 0.33°C (k=1).

5. UNCERTAINTY BUDGET

5. 1 UNCERTAINTY BUDGET AT 961.78°C

Table 4 : Contributions to uncertainty of measurement

Uncertainty Component	Standard Uncert./ ±mK
Fixed Point Cell	7.0
Calibration Reproducibility	250.0
Reference Junction	2.9
Voltmeter Calibration	1.3
Voltmeter Resolution	0.7
Reading Dispersion	0.4
Combined Uncertainty	250.0

The expanded uncertainty U (k=2) is therefore 0.5°C.

5.2 TABLE UNCERTAINTY IN THE TEMPERATURE RANGE OF 0°C TO 1000°C

Table 5 : Temperature range versus expanded uncertainty (k =2)

Temperature Range/°C	Expanded uncertainty/±°C
0 to 100	0.2
>100 to 500	0.3
>500 to 800	0.4
>800 to 900	0.5
>900 to 1000	0.6

6. CONCLUSIONS

Concerning the thermocouple emf stability, it is the main component to determine the expanded uncertainty for fixed point calibration method. Tables 1 and 2 show that the emf standard deviations in the fixed points measurements represent the calibration reproducibility. This component represents also the emf stability along time.

After 40 hours at 962°C, the maximum standard deviation was at Aluminium fixed point (0.14°C). It means that, after three fixed point calibrations, the maximum expanded uncertainty at fixed points was 0.28°C (k=2) — a calculated value near to increasing reference[1] (0.2°C).

Aiming to test the type N thermocouple INM003 in comparisons with secondary laboratories, it was calibrated by comparison up to 1000°C, and after that it was calibrated at fixed points. It was observed a increase of the emf at Aluminium and Silver fixed points (see table 2), however interpolated uncertainties in the range 0°C to 1000°C were calculated between 0.2°C to 0.6°C (k=2) — calculated values better than reference[1] (1.0°C).

This was possible because other auxiliary points were measured by comparison in thermostatic baths with low type B uncertainties in the range 0°C to 350°C.

So, it is important to evaluate the deviation of the reference table (ΔEmf) versus temperature to determine other points to the calibration. It will modify also the degree of the fitting curve degree to calculate interpolated values.

Finally, it is also important to determine the immersion depth during the calibrations. Thus, it will decrease the inhomogeneity influence in emfs measured.

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