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CALIBRATION OF SPRTs IN THE SUB-RANGE BETWEEN THE TRIPLE POINT OF Hg AND THE MELTING POINT OF Ga

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ABSTRACT

It has been observed that several standard platinum resistance thermometers show resistance leakage due to humidity inside their sheath. This insulation leakage depends on the frequency of the resistance bridge that is used for the measurement of the platinum resistance thermometers, because of the polarisation of the water molecules in the thermometer.

Therefore, a set of standard platinum resistance thermometers has been calibrated between the triple point of mercury and the melting point of gallium with d.c. and a.c. bridges at different frequencies, in order to investigate the polarisation effect due to humidity. At the triple point of water, a larger polarisation effect was observed than at the melting point of gallium, while no such effect was observed at the triple point of mercury. This is due to the different values of the water vapour pressure at the temperatures of the calibration fixed points.

The calibration results so obtained are compared and analysed, and information on the reproducibility and accuracy of the ITS-90 realisation in this range is presented.

INTRODUCTION

The range between the triple point of mercury and the melting point of gallium is the most accurate range provided by the International Temperature Scale of 1990 (ITS-90). It is based on three very reproducible and accurate fixed points: the triple points of mercury and water and the melting point of gallium. In this range, very stable platinum resistance thermometers can be calibrated with an accuracy better than ±0.2 mK.

In the past, results were published on standard platinum resistance thermometers (SPRTs) showing resistance leakage due to humidity inside their sheath [1]. This humidity was detected by measuring with an a.c. bridge the difference in thermometer resistance at the triple point of water (TPW), with or without a nitrogen trap around their sheath.

Now, since a new d.c. bridge is available, the resistance leakage for humidity previously measured is compared with the difference between a.c. and d.c. measurements. Indeed, the polarisation of the water molecule depends on the frequency of the thermometer current. In the past, Berry had detected such a polarisation effect in mica thermometers, calling it "wet kick" because of the observed galvanometer deflection [2].

This effect has been compared at the TPW, where the humidity effect is largest, with the effect at the melting point of gallium, where the expected humidity effect is lower because of a lower water vapour pressure, and with the effect at the triple point of mercury, where no humidity can be observed since all the water in the thermometers is frozen.

RESISTANCE LEAKAGE FOR HUMIDITY AT THE TRIPLE POINT OF WATER

Initially it was found that platinum resistance thermometers at the TPW showed a very long settling time because of humidity inside their sheath [1]. After this first observation, the presence of humidity in thermometers was detected by recording their resistance for about two hours after their introduction in the TPW cell, whether in normal conditions or with a cold trap. This trap, cooled with liquid nitrogen or dry ice, was placed around their sheath at about 5 cm from the head in order to freeze out all humidity in the filling gas. The resistance leakage due to humidity was determined by the difference between the resistance values measured with or without the trap.

The test was carried out on a set of SPRTs, some of IMGC and some of third parties, having either mica or silica insulation. The results of these two experiments are compared in Table 1. The values in column 3 are expressed in terms of insulation leakage, column 4, and as temperature error, column 5. A very good correlation appears to exist between the two phenomena, showing that both are due to the presence of humidity in the thermometer sheath [1].

A first important result is that humidity was observed in SPRTs with both mica insulation and silica insulation.

Table 1: Results of humidity tests at the TPW of some SPRTs.

25-Ω SPRT (m = mica ins. s = silica ins.)	Time required to reach equilibrium at the TPW to within 0.05 mK [min]	Difference between TPW measurements with and without cold trap on the sheath [μΩ]	Insulation leakage at TPW [MΩ]	Error for humidity at TPW [mK]
LN 8167-01 /m	70	45	15	0.45
LN 8167-02 /m	30	31	21	0.31
LN 8167-42 /m	10	15	43	0.15
LN 8167-GTI /m	10	33	20	0.33
LN 8167-OCE /m	50	164	4	1.64
Chino RS 5YA -2 /s	15	17	40	0.17
ZSI 91001 /s	50	52	12	0.52
ZSI 91010 /s	15	34	19	0.34
Tinsley 253090 /s	80	116	6	1.16

Since the resistance leakage observed at the TPW is due to the condensation of the humidity in the thermometer stem introduced in the TPW cell, a dependence of the leakage on the amount of the thermometer immersion can be supposed. Some experiments on thermometer LN 8167-OCE had shown a systematic resistance change, corresponding to about 0.05 mK, when the water level in the thermometer well of the TPW cell was decreased by about 10 cm. No changes had been detected when the water level in the thermometer well was increased. Therefore, it can be supposed that humidity transport to the coldest part of the thermometer takes place only in the vapour phase and not after condensation. By pre-cooling only the bottom part of the thermometer, this result was confirmed at different immersion depths in the cell. A resistance decrease corresponding to about 0.1 mK was measured by changing the pre-cooling immersion of the thermometer in the water at 0 °C from 39 cm to 19 cm.

CALIBRATION WITH A.C. AND D.C. BRIDGES IN THE Hg - Ga TEMPERATURE RANGE

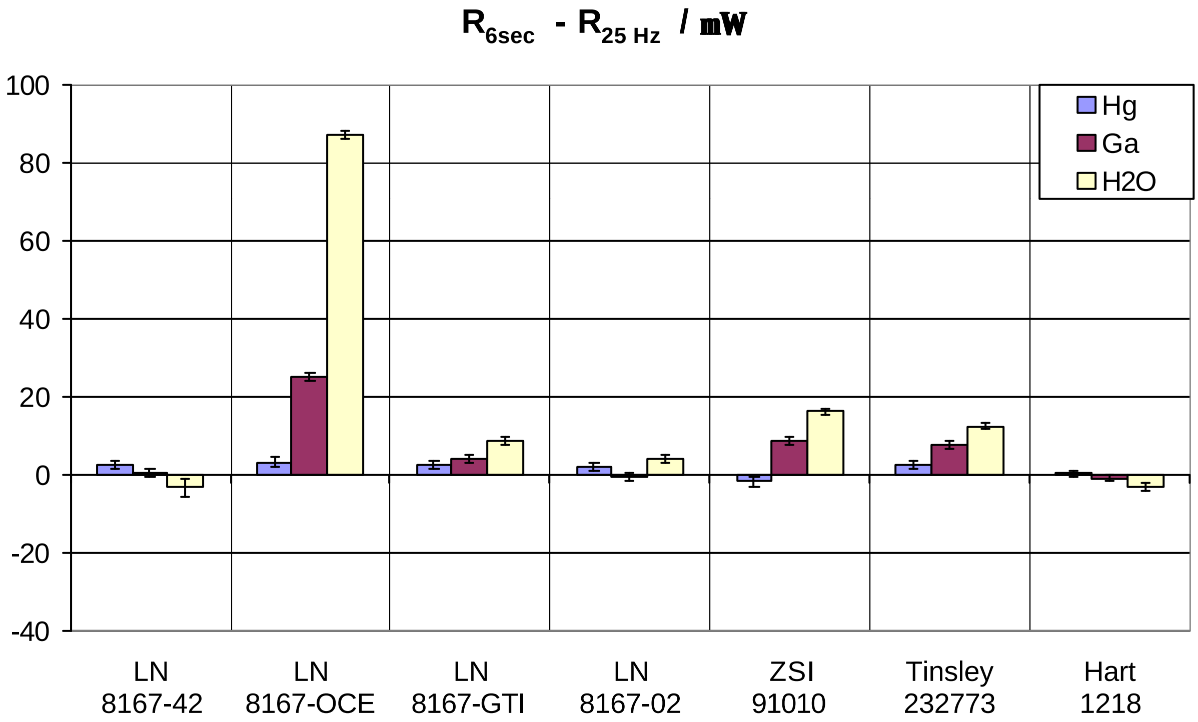
Most of the SPRTs previously tested for resistance leakage at the TPW have now been measured with an a.c. F18 bridge, from ASL, at both 25 Hz and 75 Hz, and with a d.c. 6010B bridge, from MI, at two current reversal times, 6 s and 12 s. Some thermometers used in the previous test are, unfortunately, not available anymore. The measurements have been carried out at the triple point of mercury, at the triple point of water and at the melting point of gallium as maintained at IMGC [3]. This is the most accurate range provided by the ITS-90. The reproducibility of these fixed points are well within ±0.1 mK for the triple point of mercury and the melting point of gallium, and within ±0.05 mK for the triple point of water. Therefore, a stable standard platinum resistance thermometer can be calibrated in this range with an accuracy better than ±0.2 mK. All uncertainties stated are to be intended at the 1 σ level.

The results of the measurements with the F18 bridge do not show any significant difference between the measurements at 25 Hz and at 75 Hz, the agreement being always within ±2 μΩ, the reproducibility of the IMGC bridge with a 25-Ω thermometer.

Also the results of the measurements with the MI bridge at 6s and 12 s settling time do not show any significant differences, being always within ±2 μΩ, the reproducibility of the IMGC d.c. bridge.

On the contrary, systematic differences have been detected between the measurements carried out with the a.c. and the d.c. bridges, beyond the accuracy previously verified by calibration. These differences are shown in Fig. 1.

Fig. 1: Differences between the measurements carried out with the d.c. and a.c. bridges.



These results show that thermometer LN 8167-OCE presents the largest difference between a.c. and d.c. measurements, confirming the previous tests showing the largest amount of humidity in that thermometer with respect to the others.

Three additional thermometers show systematic differences between a.c. and d.c. measurements, be it much smaller. Two of them, thermometers LN 8167-GTI and ZSI 91010, have shown previously appreciable leakage at the TPW, but less than thermometer LN 8167-OCE. The Tinsley thermometer is a new one and was introduced in this experiment because the previous one of this brand is no more available.

All these four thermometers show d.c. values higher than the a.c. values. Each measurement has been repeated several times. The systematic differences are largest at the TPW, as expected because of the largest water vapour pressure at that temperature. No differences have been detected at the triple point of mercury, confirming that all humidity is frozen. Intermediate systematic differences have been measured at the melting point of gallium. These results confirm the dependence of the difference between d.c. and a.c. measurements on the presence of humidity in the thermometers sheath, because of the polarisation of the water molecule.

In the past, Berry had described a “wet kick” effect due to the polarisation of the water molecule due to the presence of humidity in the sheath of SPRTs [2]. This “wet kick” effect is due to the deflection of the galvanometer from balance during current reversal. Since then, automatic a.c. bridges became more commonly used, but resistance leakage for humidity was not detectable anymore. Berry stated that the effect occurred only in thermometers having mica insulation, because mica releases humidity on exposure at temperatures above 600 °C.

In the previous tests, described before, the presence of humidity was detected also in thermometers having silica insulators. The new experiment confirms this. Both the ZSI and Tinsley thermometers show systematic differences. The ZSI thermometer was also used in the previous test, while the Tinsley thermometer is a new one. Since also the other Tinsley thermometer used in the previous test showed leakage for humidity, it is suspected that it is very difficult to dry the thermometer after construction because of the design.

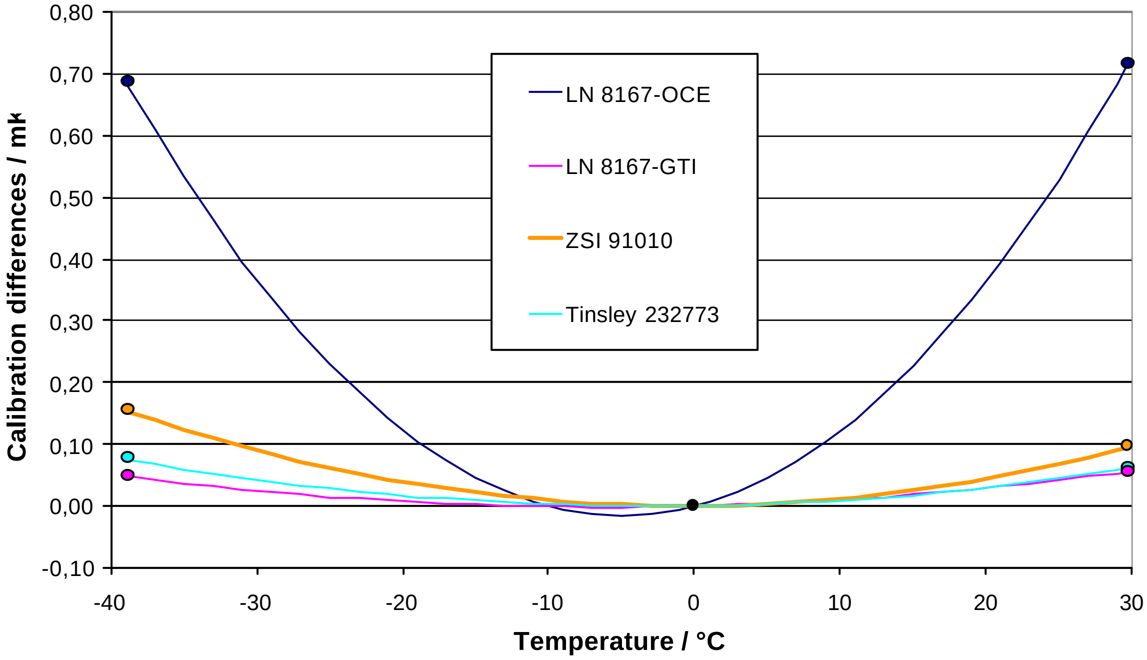
The presence of humidity in the thermometers having silica insulators are due to the hygroscopic property of silica. It happens that silica contains a certain amount of water and silica surfaces in contact with water vapour firmly retain a layer of water of variable thickness [4]. This water layer can reach a thickness sufficient to cause electric leakage or polarisation effects.

The electric leakage measured in the previous experiment, in Table 1, gives rise to errors due to humidity larger than the errors shown in Fig. 1. It may be that this leakage is more influenced by the thickness of the water layer on silica than by the polarisation effect.

CALIBRATION DIFFERENCES IN THE Hg – Ga RANGE

Based on the data represented in Fig. 1, two calibrations have been obtained for each platinum resistance thermometer, one based on the a.c. bridge and the other on the d.c. bridge. The difference between these calibrations is shown in Fig. 2.

Fig. 2: Difference between a.c. and d.c. calibrations.



The main conclusion that can be drawn from this is that the average user risks errors of this size because he is unaware whether or not the bridge used during calibration is the same as his own, where measurements with an a.c. bridge are in error by the above amounts.

Further, the measurement with an a.c. bridge of a platinum resistance thermometer having a large insulation leakage error due to humidity, gives rise to a discontinuity in the resistance-temperature relationship at the freezing temperature of water vapour.

Lastly, the W values at the triple point of mercury and the melting point of gallium may be off considerably with important consequences for those thermometers with values close to the limits allowed by the ITS-90. Not only, but the equivalence of the mercury and gallium points may be compromised.

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