Original Research Article

Reliability of argon triple point cells materializing the ITS-90 temperature fixed point

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ABSTRACT

The triple point of argon is one of the defining fixed-points of the International Temperature Scale of 1990, ITS-90. Its value was assigned to be 83.8058 K by ITS-90. The thermal metrology laboratory of the National Institute for Standards, NIS has chosen, several years ago, to realize this fixed point through batch of thermometric cells. In the present work, three cells of different designs, composing the batch of reference, are inter-compared. The results of these inter-comparisons, over a period of time that reaches 17 years, showed the excellent reliability of these cells. No malfunction has arisen for the oldest cell "Ar-INM-42-NIS" over this period, it has 0.24 mK as the maximum variation among the other cells. For the other cells variations were found to be 0.17 and 0.18 mK for "Ar-NIS-QA" and "Ar-LNE-NIS-MC" respectively. The recent estimations of uncertainties for the batch of cells that include all the factors affecting the measurements showed values of 0.52, 0.33 and 0.31 mK for "Ar-INM-42-NIS", "Ar-NIS-QA" and "Ar-LNE-NIS-MC" respectively, and that cell "Ar-INM-42-NIS" has the maximum expanded uncertainty of 0.52 mK.

Keywords: Argon triple point; ITS-90; Thermometric cell; Inter-comparison; Uncertainty.

1. INTRODUCTION

The International Temperature Scale of 1990 (ITS-90) [1] defines all the necessary parameters to approximate as close as possible the thermodynamic temperature. ITS-90 offers defined calibration points ranging from 0.65 K to approximately 1358 K (-272.5 ℃ to 1085 ℃) and is subdivided into multiple temperature ranges which overlap in some instances. ITS-90 uses numerous defined points, all of which are based on various thermodynamic equilibrium states of fourteen pure chemical elements. Most of the defined points are based on a phase transition; specifically the melting/freezing point of a pure chemical element. However, the deepest cryogenic points are based exclusively on the vapor pressure/temperature relationship of helium and its isotopes whereas the remainder of its cold points (those less than room temperature) are based on triple points. Examples of other defining points are the triple point of argon (83.8058 K) and the freezing point of aluminum (660.323 ℃).

National Metrological Institutes allover the world are charged to realize these fixed points based on "Supplementary Information for the International Temperature Scale of 1990" [2], accompanying document to the ITS-90. These realizations require the use of Standard Platinum Resistance thermometers (SPRTs) and thermometric cells [3-6].

The laboratory can either realize the fixed point on a single cell or a batch of cells. The second solution is more expensive but it guarantees the continuity of the realization of the fixed point. In any case a complete uncertainty budget needs to be established for the realization.

Thermometric cells can be purchased from an industrial company or could be fabricated in the laboratory.

For the argon triple point, 83.8058 K, NIS has chosen, several years ago, to base their reference on batch of thermometric cells. All the cells are compared with each other periodically. The frequency of this activity is maximum four years and may be reduced if the experimental results suggest a possible degradation of a cell.
The reference to a domestic fixed point is defined as the average temperature materialized by all cells belonging to the reference lot as described also in [7, 8]. The temperature of the fixed point as given in the ITS-90 is assigned to this average:

$$T_{average} = \frac{\sum_{i=1}^{N} T_{celli}}{N} = T_{ITS-90} \qquad (1)$$

A correction is applied to the temperature achieved by each cell as:

$$C_{cellX} = T_{average} - T_{cellX} \qquad (2)$$

This reference batch is regularly enriched by new cells in order to highlight a possible drift of the whole batch. Thermometric cells constituting this lot have been realized in the laboratory and some of them are manufactured by the "Institut Nationale de Métrologie" (LNE-Cnam, France).

2. EXPERIMENTAL DETAILS

2.1 Thermometric cells

Figure 1 shows three cells; constituting the lot. The first of them were imported on 1997 from LNE-Cnam, France encoded "Ar-INM-42-NIS". The second cell "Ar-NIS-QA" has been developed and characterized in the frame of a PhD thesis [9, 10]. The third cell "Ar-LNE-NIS-MC" has been developed and characterized through an international scientific-cooperation project "IMHOTEP" between LNE-Cnam and NIS [11].

The first cell "Ar-INM-42-NIS" is used in most national metrological institutes (NMIs) [3, 12, 13] having 350 mm height and a volume of 1 cubic decimeter. It was filled at room temperature with 60 bar of argon with purity of 99.9999%. It could accommodate both long-stem and capsule SPRTs.

The second cell "Ar-NIS-QA" was constructed to be suitable for calibration of also long-stem and capsule SPRTs. It has a length of 370 mm and a total volume of about 180 cm3. It was filled at room temperature with 50 bar of argon with purity of 99.9999%.

The third cell "Ar-LNE-NIS-MC" is of a compact size having dimensions of 55 mm outer-diameter and 15 mm height. It was filled with pure argon gas, 99.9999%, at room temperature under a pressure of nearly 60 bar. This type of cell is similar to those of the EU project "MULTICELLS" [14] and it was made to be suitable for calibration of only capsule thermometers.

Table 1 shows the details of the three cells.

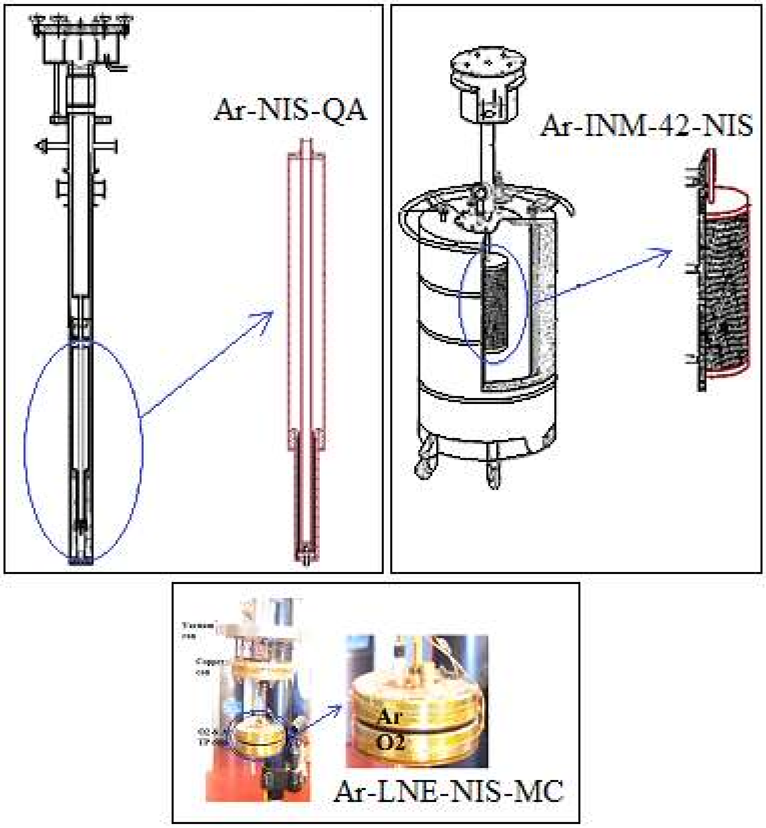

Fig. 1. Batch of argon triple-point cells

Table 1. Description of argon triple point cells

Specifications	Cells		
	Ar-INM-42-NIS	**Ar-NIS-QA**	**Ar-LNE-NIS-MC**
Origin	France	France-Egypt	France-Egypt
Purity	99.9999%	99.9999%	99.9999%
Fabrication	LNE-Cnam	LNE-Cnam, NIS	LNE-Cnam, NIS
Year of fabrication	1997	2003	2008

2.2 Equipment and measuring techniques

For the present work, two capsule thermometers CSPRTs (25.5 Ω Tinsley type 5187L) SN. B300 and SN. B304 calibrated, according to ITS-90 in the temperature range from 13.8 K to 303 K, were used in the measurements. These thermometers were chosen after showing a good stability of less than 0.1 mK over several years at the triple point of water.

All resistance measurements of both of CSPRTs were performed with an automatic ASL F18, alternating current resistance bridge, having accuracy better than 0.1 PPM (25 µK) and resolution of 0.003 PPM (0.75 µK), in combination with Tinsley 100 Ω standard resistor. This resistor was placed in a thermostatic controlled oil bath at 20 ^{o}C.

The measurements were performed with currents of 1 mA and √2 mA for the determination of the self-heating correction. The hydrostatic head corrections were made in accordance with the dimensions of the cells.

SPRTs data are collected from the bridge via an IEEE interface to the PC running under LABVIEW environment

According to the types and design of the cells, each one was measured with different realization technique.

For the first cell "Ar-INM-42-NIS", only one CSPRT could be accommodated. The argon cell is totally and directly immersed in the liquid nitrogen bath. This bath behaves as a temperature regulated enclosure. The cell body is separated from the liquid nitrogen bath by several layers of thin stainless steel grid. Helium gas was admitted through the thermometer well, at a slight excess pressure to prevent condensation of moisture around the thermometer sheath and to enhance thermal conduction between the thermometer and the tube. After argon liquefaction and solidification, the temperature of the liquid nitrogen bath is increased by pressurizing the main bath. The argon triple point is then realized by adjusting the pressure in such a way the bath temperature is just above the argon transition temperature. Full details and description of this system can be found elsewhere [2, 12].

The second cell "Ar-NIS-QA" accommodates only one CSPRT and it was realized using a quasi-adiabatic cryostat where the cell was surrounded by a radiation shield in contact with the liquid nitrogen bath, which is the bath used for the first cell, at the level of the bottom of the cryostat outer-tube. The cryostat was operated by: a regulation block consisting of a Pt-100 sensor and of an electrical heater to fix the temperature at the top of the thermometric cell. The realization was started by allowing helium exchange gas to fill the space around the cell. After total freezing of the argon, the helium exchange gas was removed using a pumping system with pressure of 10-4 mbar to ensure good thermal insulation. The frozen cell was kept for 30 min to attain temperature stability, and then the small electric heater wrapped around the bottom part of the cell was fed with electric current to start the melting plateau. More details and description of this system can be found in [13].

The third cell "Ar-LNE-NIS-MC" is capable of accommodating both of the two CSPRTs simultaneously. The cell was realized using an adiabatic calorimeter different from the one that is used for realizing the second cell "Ar-NIS-QA". This calorimeter was built in order to realize both of argon and oxygen triple points. For the present work, the cell was mounted in the cryostat. It was surrounded by an adiabatic shield (copper can), whose temperature was always controlled in order to suppress the spurious heat flux. Another vacuum can accommodated the adiabatic shield was mounted in the cryostat. The realization was started by allowing helium exchange gas to fill the space around the cell. The cryostat was immersed in liquid nitrogen dewar of special design having a super-insulated walls. Normally the cryostat was built to go down to a temperature of about 50 K and this was performed by evacuation above the liquid nitrogen surface. This technique was used to mainly realize the oxygen triple-point followed by realization of the argon triple-point. Thus, upon reaching a temperature value of 2 K less than the plateau value, the helium exchange gas was removed using another pumping system that could go less than 10-4 mbar to ensure good thermal insulation. The frozen cell was kept for 30 min to attain temperature stability. Temperature control of the copper can was started at a temperature close to the triple point of argon. This control was performed automatically using a self-developed PID software working under LabView environment. Normally intermittent heat technique was adopted to melt the argon but in the present work a constant flux technique was used. More details regarding the operation of this system is described in [15].

3. RESULTS AND DISCUSSION

In the present work, CSPRT B300 was first inserted in the first cell "Ar-INM-42-NIS" followed with CSPRT B304. The melting plateau of argon was repeated five times thus having five plateaus for each thermometer.

The system was then dismounted and the second cell "Ar-NIS-QA" with its cryostat were inserted in the liquid nitrogen dewar of the first cell. The two CSPRTs were inserted in the cell one by one to have five completed plateaus for each thermometer. Upon completion of the measurements, the CSPRTs were removed from the cell and they were prepared for the third step of measurements on the third cell "Ar-LNE-NIS-MC". The thermometers were inserted together in the cell using vacuum grease and the cryostat was mounted into its dewar. Measurements were obtained through five completed plateau.

All the obtained plateaus from all of the three cells were performed using a constant heat flux technique.

Each cell has been realized five times in order to study the phase transition repeatability. Figure 2 and table 2 show realizations performed for all of the batch of cells in terms of W(ArTP); where W(ArTP) = R(ArTP)/ R(WTP). R(ArTP) and R(WTP) are the measured resistances taken as the average of resistances measured by both of CSPRT B300 and CSPRT B304 at argon and water triple points respectively.

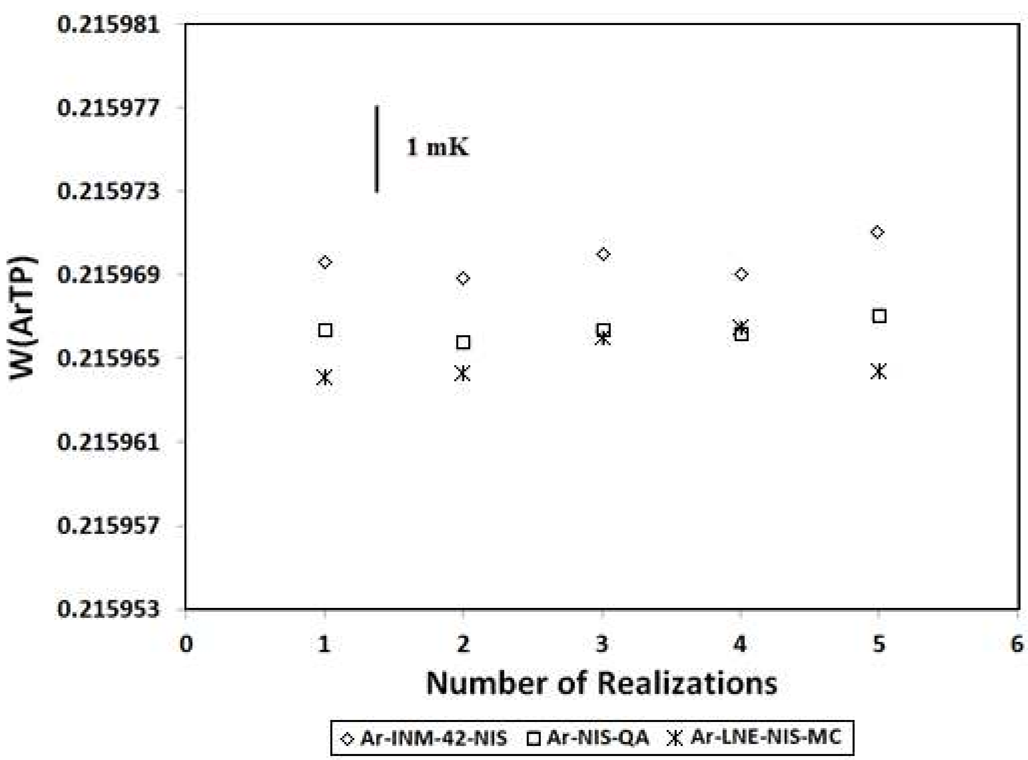

Fig. 2. Repeatability achieved by the batch of cells using CSPRTs B300 & B304

Table 2. Measured resistance ratios W(ArTP) of the batch cells using CSPRT B300 & B304

Run	Cells		
	Ar-INM-42-NIS	**Ar-NIS-QA**	**Ar-LNE-NIS-MC**
1	0.2159696	0.2159664	0.2159641
2	0.2159689	0.2159658	0.2159643
3	0.2159700	0.2159664	0.2159660
4	0.2159690	0.2159662	0.2159665
5	0.2159710	0.2159671	0.2159644
Average	0.2159697	0.2159664	0.2159651
Standard Deviation	0.0000009	0.0000005	0.0000011

These recent measurements were compared to the past measurements taken, for example for cell "Ar-INM-42-NIS", over the period of 17 years. Figure 3 shows a summary of these results.

As shown in the figure, there is a good reproducibility of temperatures delivered by the cells. The maximum variation is observed for cell "Ar-INM-42-NIS" with a value of 0.24 mK. For the other cells variations were found to be 0.17 and 0.18 mK for "Ar-NIS-QA" and "Ar-LNE-NIS-MC" respectively.

These values reflect good performance of the cells having accepted differences that arose from one CSPRT to the other. These differences are systematic and they may arise from the thermometers inconsistencies [2]. In accounting for the cells, it should be recalled that the hydrostatic pressure correction for a centimeter of argon is 0.33 µK [1]. Since the height of the column of liquid argon above the sensor varied less than a centimeter, both as a result of the volume change on freezing and from cell to cell, the largest possible effect on the equilibrium temperature is of order 0.01 mK.

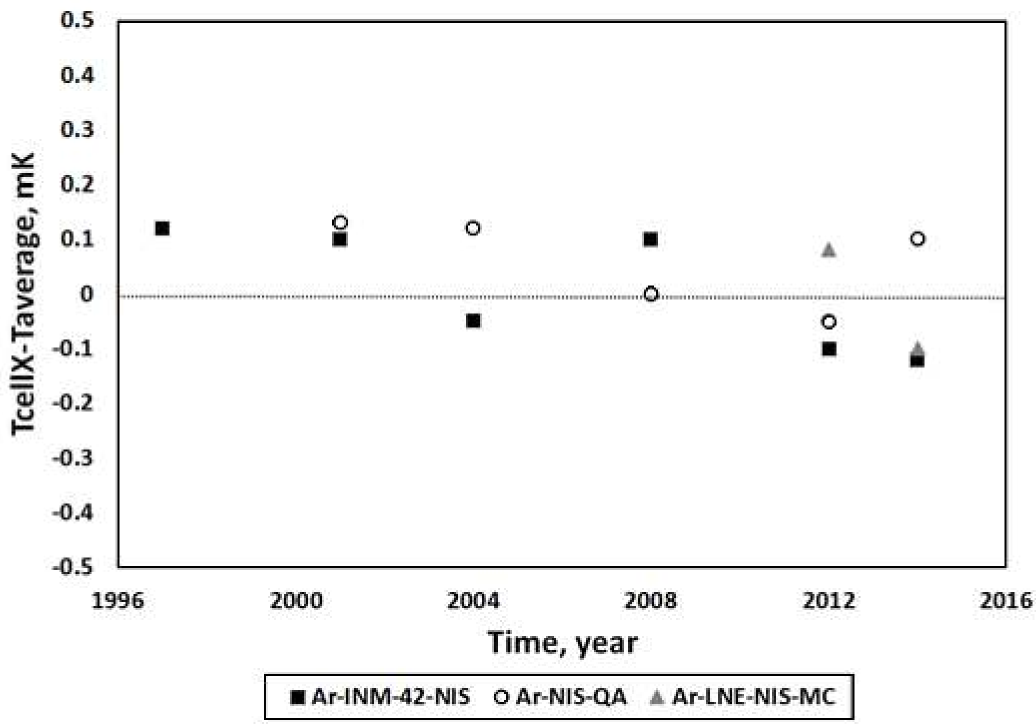

Fig. 3. Intercomparison of argon triple-point cells from average value given by equation (1) and (2)

For the uncertainty estimations, the budget related to the comparison is shown in Table 3. It comprises estimates of the components such as, determination of the plateau value, plateau repeatability, chemical impurities, hydrostatic pressure correction, self-heating correction and spurious heat fluxes. Since the same SPRTs, bridge and water triple point cell were used during the comparison, the contributions arising from these items were excluded. The estimations of uncertainties for the batch of cells were 0.52, 0.33 and 0.31 mK for "Ar-INM-42-NIS", "Ar-NIS-QA" and "Ar-LNE-NIS-MC" respectively.

Table 3. Uncertainty budget for the batch of cells of argon triple point

Uncertainty component	**Value (mK)**		
	Ar-INM-42-NIS	**Ar-NIS-QA**	**Ar-LNE-NIS-MC**
Determination of plateau value	0.10	0.05	0.10
Plateau repeatability	0.10	0.10	0.08
Chemical impurities	0.15	0.05	0.05
Hydrostatic pressure correction	0.03	0.03	0.03
Self-heating correction	0.04	0.03	0.02
Spurious heat fluxes	0.15	0.10	0.06
Combined standard uncertainty	0.26	0.16	0.15
Expanded uncertainty (*k* = 2)	0.52	0.33	0.31

4. CONCLUSION

Comparisons of argon triple-point cells composing the thermometric reference batch helped to highlight the long-term reliability of the thermometric cells. In the present work each cell has been realized five times. These recent measurements were compared to the past measurements taken. It was found that there is a good reproducibility of temperatures delivered by the cells. The maximum variation is observed for cell "Ar-INM-42-NIS" with a value of 0.24 mK. For the other cells variations were found to be 0.17 and 0.18 mK for "Ar-NIS-QA" and "Ar-LNE-NIS-MC" respectively.

Thus, over a period of 17 years no malfunction has arisen for the oldest cell "Ar-INM-42-NIS", it has 0.24 mK as the maximum variation among the other cells. The recent estimations of uncertainties for the batch of cells showed that cell "Ar-INM-42-NIS" has the maximum expanded uncertainty of 0.52 mK. This is due to the contributions arisen from the impurities and spurious heat fluxes affecting the triple point realizations. For the other cells "Ar-NIS-QA" and "Ar-LNE-NIS-MC" it was found to be 0.33 and 0.31 mK respectively.

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