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Original scientific paper

FREEZING POINTS OF PURE METALS AS DEFINING POINTS OF INTERNATIONAL TEMPERATURE SCALE ITS-90

Tomislav VELIKI

Abstract: Melting and freezing temperatures are one of the most important features of metals, both in production and application. For the extremely pure metals where purity higher than 99.9999% is reached, difference between the melting and the freezing temperature is less than 1 mK (1/1000 °C). This virtue has been used for establishment of the temperature fixed points, on which the Practical temperature scales were laid upon. Temperatures of the fixed points are determined on the basis of thermodynamics. The temperature fixed points are used for the calibration of thermometers, which are then in turn used for interpolation between the fixed points. Every realization of the Practical temperature scale is an independent experiment. In this sense, this paper describes mathematical modeling and equipment used for the realization of the temperature scale in the Republic of Croatia in the range from −0 °C to 660 °C, accompanied with the measurement uncertainties.

Keywords: international temperature scale; melting and freezing temperatures; pure petals

1 INTRODUCTION

To achieve the uniformity in measurement of temperature in a way that was achieved in length measurements with *Meter Convention* and the unique standard for length established in 1875, it was needed to invent the practical standard for temperature. The first International Temperature Scale was adopted in 1927 to overcome the practical difficulties of the direct realization of thermodynamic temperatures by gas thermometry and to unify existing temperature scales. It was introduced by the Seventh General Conference on Weights and Measures (CIPM) with the intention of producing a practical scale of temperature which would be easily and accurately reproducible and which would give the best approximation of thermodynamic temperatures. The Scale was revised in 1948, amended in 1960, and revised again in 1968 and 1990. The International Temperature Scale of 1990, known as ITS-90 [1], was adopted by the International Committee for Weights and Measures (BIPM) at its meeting in 1989. However, this scale prescribes numerical values of the temperature at the temperature fixed points, interpolation function and instrument between fixed points while the physical realization is left to the user of the scale. This paper will describe the independent realization of the ITS-90 as primary standard in the Republic of Croatia in the range where freezing points of the pure metal are used, accompanied with description of equipment and uncertainties achieved.

2 DEFINITION OF THE INTERNATIONAL TEMPERATURE SCALE ITS-90

International Temperature Scale ITS-90[1] extends upwards from 0.65 K to the highest temperature practicably measurable in terms of the Planck radiation law using monochromatic radiation. The ITS-90 comprises a number of ranges and sub-ranges throughout each of which temperatures T_{90} are defined. Definition prescribes thermometric fixed points which are based on melting, freezing or triple points of pure substances to which precise values of temperature were measured by thermodynamic thermometers. An excerpt from [1] is presented in Tab. 1.

Table 1 Defining temperature points of International Temperature Scale ITS-90 assigned to the specific phase transitions of pure substances, [1]

Equilibrium state	T_{90} /K	t_{90} /°C
Triple point of hydrogen	13.8033	−259.3467
Boiling point of hydrogen at a pressure of 33321.3 Pa	17.035	−256.115
Boiling point of hydrogen at a pressure of 101292 Pa	20.27	−252.88
Triple point of neon	24.5561	−248.5939
Triple point of oxygen	54.3584	−218.7916
Triple point of argon	83.8058	−189.3442
Triple point of mercury	234.3156	−38.8344
Triple point of water	273.16	0.01
Melting point of gallium	302.9146	29.7646
Freezing point of indium	429.7485	156.5985
Freezing point of tin	505.078	231.928
Freezing point of zinc	692.677	419.527
Freezing point of aluminum	933.473	660.323
Freezing point of silver	1234.93	961.78
Freezing point of gold	1337.33	1064.18
Freezing point of copper	1357.77	1084.62

The comparison of fixed-point temperatures and the interpolation of the scale between fixed points in the temperature range between about 0 °C and 962 °C is by definition of ITS-90 carried out by platinum resistance thermometry. In this range, defining temperatures are phase transitions of metallic fixed points materials (Ga, Sn, Zn, Al, Ag) having nominal purity in-between 99.9999 % and 99.99999%. Thermometers calibrated per ITS–90 use prescribed mathematical formulas to interpolate between its defined points. ITS–90 also draws a distinction between "freezing" and "melting" points. The distinction depends on whether heat is going into (melting) or out of (freezing) the sample when the measurement is made. Only gallium is measured while melting; all the other metals are measured while the samples are freezing.

Temperature T_{90} in this range is expressed through ratio of resistances of platinum resistance thermometer $R(T_{90})$ and the resistance of the same thermometer at temperature of triple point of water $R(273{,}16)$:

$$W(T_{90}) = R(T_{90}) / R(273{,}16) \tag{1}$$

Reference function at this range of ITS-90 is defined according to [1]:

$$W_r(T_{90}) = C_0 + \sum_{i=1}^{9} C_i \left[\frac{T_{90}/K - 754{,}15}{481} \right]^i \tag{2}$$

and numerical values of the coefficients c_0 to c_9 are available in [1] .

Deviation function of the thermometer which after calibration in defining fixed points is used for interpolation across the range has the following form:

$$\begin{aligned} &W(T_{90}) - W_r(T_{90}) = a\left[W(T_{90}) - 1\right] + \\ &+ b\left[W(T_{90}) - 1\right]^2 + c\left[W(T_{90}) - 1\right]^3 + \\ &+ d\left[W(T_{90}) - W(660{,}323°C)\right]^2 \end{aligned} \tag{3}$$

Thus, after measuring resistance of the thermometer in the temperature fixed points and immediate measuring of the resistance in the triple point of water during calibration, coefficients a to d from Eq. (3) can be calculated for specific thermometer. That thermometer is then used for the interpolation of the temperature according to ITS-90 with calculated measurement uncertainty.

3 DEVELOPMENT OF THE INDEPENDENT REALIZATION OF THE ITS-90

Realization of the International Temperature Scale ITS-90 was performed in the Laboratory for Process Measurement located at the Faculty of Mechanical Engineering and Naval Architecture, University of Zagreb, in the period from 2002 to 2011. As the definition of the ITS-90 described in the previous chapter does not stipulate technical details but offers general recommendations elaborated in [2] and [3], every national laboratory is obliged to design and purchase equipment and devise a method adequate for the experiment. For the establishment of the freezing point of tin, zinc and aluminum the open type of fixed point was chosen, with quartz envelope and pure graphite parts delivered by company Isotech. Materials required for filling the points were acquired by the producer Johnson Matthey. Dimensions and specifications are given in Tab. 2.

The main purpose of the open fixed-point cells is the ability to regulate pressure of argon gas during phase transition, thus lowering the uncertainties. The second benefit comes into play in the case of the rupture of the quartz envelope during melting and freezing of the fixed-point material, when overpressure of argon can prevent volatile oxidation of graphite container containing pure metal, as well as contamination of the pure metal with impurities from atmosphere.

Table 2 Specifications of the fixed points used for realization of the ITS-90

Type	ITL-M-17669	ITL-M-17671	ITL-M-17672
Material	Sn	Zn	Al
Producer	Johnson Matthey	Johnson Matthey	Johnson Matthey
Outer diameter	50 mm	50 mm	50 mm
Thermometer tube	8 mm	8 mm	8 mm
Height	520 mm	520 mm	610 mm
Height of molten material	200 mm	200 mm	200 mm
Nominal Purity	99.9999 %	99.9999 %	99.9999 %

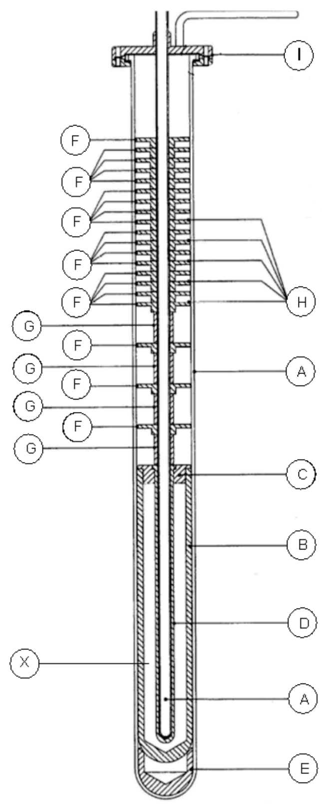

Figure 1 Cross section of the open temperature fixed point. Height of the cell is approximately 520 mm. Description of the labels on the figure are given in text.

Fig. 1 depicts cross section and main parts of the physical realization of the fixed point which is to be inserted into thermometric three zone controlled furnace. Quartz envelope (A) is used to separate the interior filled with argon from the surroundings, thus preventing oxidation, while allowing thermometer to be inserted into the middle of the material going through phase transition. A graphite container (B) is used to hold pure metal (X) both in molten and solidified state. It is sealed by the graphite top (C) and the graphite re-entrance tube for thermometer (D), and is positioned on the graphite cushioning insert (E). The graphite rings (E) with accompanying bushings (G) are used to decrease heat transfer toward the top of the fixed point. In the area where largest temperature gradients are expected, additional platinum foil plates are applied for lower radiation losses. The top of the fixed point is sealed with a flange connecting quartz tube for thermometer and quartz envelope, and contains connection for argon gas installation.

During a regular course of calibration, material would be left overnight on temperature 2÷5 °C over phase transition. Then temperature of the furnace would be set to approximately 2 °C under phase transition. When thermometer would reach that temperature, it would be removed and a pre-cooled quartz tube would be inserted to start crystallization since pure metals have pronounced supercooling effect, as described in [4]. Once the phase transition front would start from both outside and the thermometer entrance, thermometer would be reinserted into the fixed point and the measurement could commence after the stabilization phase, as described in [5] .

4 MATHEMATICAL MODEL OF MEASUREMENT

The values of the resistance of the thermometer $R(T_{90})$ during phase transition on defining temperature T_{90} and resistance $R(273,16)$ on temperature of the triple point of water are obtained from readings from resistance thermometry, X_t and $X_{273,16}$. The reading of the bridge X_t is the ratio of unknown resistance of the thermometer $R_t(T_{90})$ and resistance of known standard resistor, R_{s1}.

$$R(T_{90}) = X_t \cdot R_{S1} \tag{4}$$

Similarly, the reading of the bridge $X_{273,16}$ corresponds to the ratio of the resistance of the thermometer inserted into triple point of water and resistance of the standard resistor R_{s2}. The resistance of the thermometer at the triple point of water is determined from the following:

$$R(273{,}16) = X_{273,16} \cdot R_{s2} \tag{5}$$

At each temperature, the minimum of 32 readings from the bridge are taken at two different electrical excitation currents, usually 1 mA and √2 mA, to allow extrapolation to the ideal value of 0 mA, as elaborated in [6].

However, the reading of the bridge is influenced by the various phenomena whose effects are to be corrected and uncertainties of the corrections estimated. Firstly, the values of the standard resistor have drifted from the time of calibration by $C_{RS1/1}$ and $C_{RS2/1}$. Secondly, corrections have to be made due to deviation of the temperature of the oil bath in which standard resistors are kept $C_{RS1/2}$, $C_{RS2/2}$. Thirdly, temperatures of the phase transitions in fixed points are to be corrected due to dissolved impurities in the metals and the water used for the triple point, deviation of temperature due to hydrostatic head from free surface to thermometer, effect of self-heating of the thermometer due to passing current, stray heat fluxes, and effect of argon pressure during realization. Lastly, corrections in the measurement system such as nonlinearity of the resistance bridge, electromagnetic disturbances and loss of isolation in the thermometer are to be estimated. After taking into account all known corrections, the mathematical model of the measurement has a form:

$$W(T_{90}) = \frac{R_{0s1} + C_{RS1/1} + C_{RS1/2}}{R_{0s1} + C_{RS1/1} + C_{RS1/2}} \cdot \frac{X_t + \sum_{l=1}^{l} C_{xt/l}}{X_{273,16} + \sum_{k=1}^{k} C_{x273,16/k}} \tag{6}$$

where $\sum_{l=1}^{l} C_{xt/l}$ and $\sum_{k=1}^{k} C_{x273,16/k}$ are known corrections of the temperature of the phase transition in the fixed point and in the triple point of water.

The value of corrections described in Eq. (6) and their intrinsic uncertainties are the main challenge in realization of the International Temperature Scale. During the experiment, some of the corrections were estimated from the data available in available literature, others were measured experimentally, as described in [7]. For estimation of thermal stray fluxes numerical simulations were used, as described in [8]. The largest uncertainty contribution is the purity of the fixed-point material. In order to have confidence in its value, it is calculated, then measured experimentally, and then finally verified by the laboratory inter-comparisons with other National Laboratories [9, 10].

5 MEASUREMENT RESULTS

During the process of realization of the Temperature Scale, measurements are performed with twofold purpose: to characterize the experimental realization of the scale as standard, and to calibrate interpolating thermometers against standard.

The metals used for temperature fixed points are the purest commercially available (with nominal mass purity >99.9999 %), but the effects of dissolved impurities must not be taken for granted. All materials were purchased with chemical trace analysis conforming nominal purity. From this chemical analysis and using publicly available data such as [11], corrections of the temperature can be calculated. However, those corrections are to be checked experimentally since impurities stated in the analysis are on the edge of detection threshold and refer to the lot of the material and not to the purchased sample. The experimental verification of the impurities dissolved on the fixed point material is performed by continuous melting and freezing of pure metal and measurement of the duration and slope of temperature arrest during phase transition, [12].

For ideally pure metals melting and freezing temperature would be the same, while the presence of impurities changes the shape and lowers the values of the phase transition, as depicted in Fig. 2, where 5N material (mass purity 99.999 %) has substantially lower melting and freezing temperatures than 6N (mass purity 99.9999 %).

The temperatures of the phase transition and its slope are measured using the standard platinum thermometer.

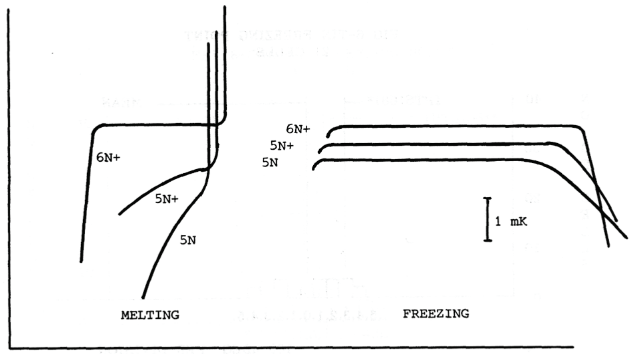

Figure 2 Typical melting and freezing behavior of a dilute binary alloy, [12]. Marks 6N and 5N stand for mass purity of 99.9999 % and 99.999 %.

As this correction accounts for the major attribution in the overall uncertainty, the measurements were performed for every fixed point used for realization of the ITS-90. To allow the analysis of measurement results, metrological furnace, in which fixed points were inserted, was controlled in such a way that melting and freezing would last for at least 3 hours.

The experimental results of the measurement of phase transitions in melting and freezing for fixed point filled with aluminum are shown in Fig. 3. The values measured during melting are shown in grey, while those measured during freezing are shown in black. For the ease of graphical explanation both processes are shifted to start at the same point.

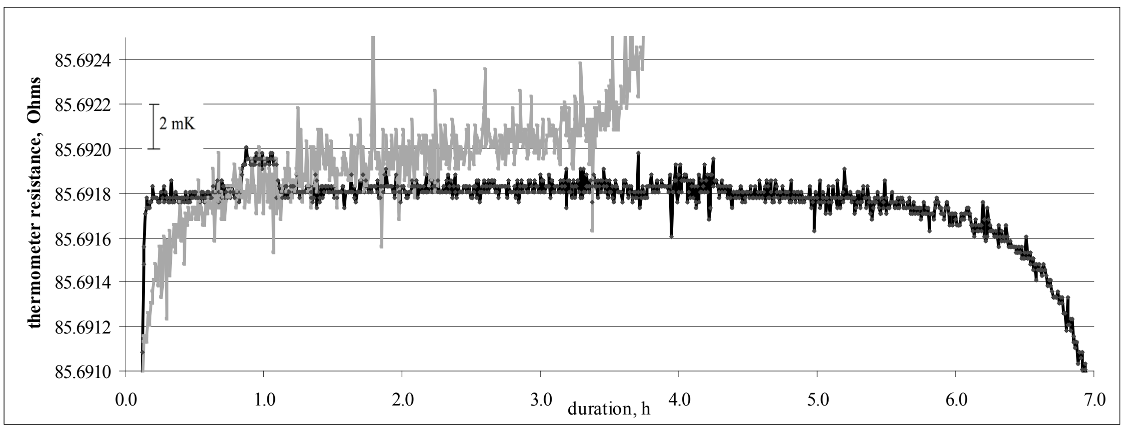

Figure 3 Measurement results showing resistance of the thermometer during melting and freezing for characterization of the aluminum fixed point. Melting process is shown in grey, while freezing is represented by black curve.

Table 3 Final values of the calculated temperature corrections due to impurities in the fixed point after laboratory inter-comparisons, and accompanying EURAMET projects from which they were calculated.

Fixed point	Correction, mK	Uncertainty, mK, k=2	Inter-laboratory comparison
Sn	0.0	0.5	EURAMET 1144, EURAMET 1167
Zn	−1.2	0.9	EURAMET 1144, EURAMET 1167
Al	−4.1	1.5	EURAMET 820 [9], LPM-PTB 2009

As the data obtained from the chemical analysis were inconclusive, for the realization of the ITS 90 corrections due to impurity are calculated based on measurements of melting and freezing behavior. In the first step, corrections are estimated to have value zero, with pertaining uncertainties being equal to the temperature span in which 80 % of the phase transition takes place. In the second step, the temperature during phase transition is compared using platinum resistance thermometer with realizations in different European National Institutes, enabling better calculation of the correction of temperature in every fixed point. For every fixed point several inter-comparison measurements were performed with other laboratories comprising European Association of National Metrology Institutes – EURAMET. Based on the analysis of those measurements, the final values of corrections due to impurities of the fixed points materials are calculated with their pertaining uncertainties as shown in Tab. 3.

The development of the independent experimental realization of the ITS-90 in the above-mentioned way has enabled calibration of the platinum resistance thermometers according to ITS-90. Those thermometers are then used as temperature standard in dissemination of the ITS-90 for all temperature measurements in scientific, industrial and legal metrology. However, when calibration of the platinum resistance thermometer is performed, new corrections are added upon those corrections due to impurities of the material in fixed points, and overall uncertainty is calculated. Tab. 4 shows overall uncertainties achieved with measurement setup for the calibration of the thermometers in fixed points.

Table 4 Overall calculated uncertainties for calibration of platinum resistance thermometers in the temperature fixed points

Fixed Point	Temperature, °C	Uncertainty of calibration, mK, k=2
Al FP	660.323	9.0
Zn FP	419.527	7.0
Sn FP	231.928	3.0
Ga MP	29.765	1.0

6 CONCLUSION

The freezing points of pure metals are the basis for realization of International Temperature Scale ITS-90 as standard for measurements in temperature. Limiting factors in achieving lower uncertainties in such experiments are impurities in the material of fixed point. In this paper, the method for estimation on the correction due to impurities is presented, with uncertainties achievable in the calibration of the platinum resistance thermometers, which are then used for dissemination of the ITS-90. Methods and values presented in the paper were not only achieved in laboratory environment, but were tested and verified by the German Accreditation Service DAkKS in 2009 and the Croatian Accreditation Agency HAA in 2013.

Note: This research was presented at the International Conference MATRIB 2017 (29 June - 2 July 2017, Vela Luka, Croatia).

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Author's contacts:

Tomislav VELIKI, Assistant Professor
University North
Ul. 104. brigade 3, 42000 Varaždin, Croatia
E-mail: tveliki@unin.hr