

CONSIDERATIONS ON INTERNATIONAL KELVIN TEMPERATURE REALIZATION USING THE ROMANIAN TEMPERATURE NATIONAL MEASUREMENT STANDARD

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The paper presents the realization of International Kelvin Temperature T_{90} using the Romanian Temperature National Measurement Standard and the practical results obtained. Relevant metrological concepts were used such as “calibration” and “measurement result” and their evolved significance in addition to the International Temperature Scale (ITS-90) describing document. A tool was created that allows a better way of reporting the calibration results; after a calibration of a Standard Platinum Resistance Thermometer (SPRT) intended to realize T_{90} , for all the values of the interpolation variable W within the considered temperature subinterval.

Keywords: temperature, measurement, calibration, measurement uncertainty.

1. Introduction

The Romanian Temperature National Measurement Standard (next referred as *national standard*) materializes, at Romanian Bureau of Legal Metrology – National Institute of Metrology (BRML-INM), the International Temperature Scale of 1990 (ITS-90) and covers the temperature interval from 83.8058 K (the triple point of argon) up to 933.473 K (the freezing point of aluminium). ITS-90 is described in [1] and the main means of realizing this practical scale is described in [2].

The practical reproductions of ITS-90 needs the realization of the defining fixed points and the use of the interpolation means. In the temperature interval mentioned above the interpolation means are SPRT-s and interpolation relations.

2. The realization of the International Kelvin Temperature T_{90} between 83.8 K and 933 K

2.1 General

Within the interval from 83.8058 K up to 933.473 K, the defining fixed points are presented in table 1.

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Table 1

The ITS-90 defining fixed points and the Calibration and Measurement Capabilities (CMC) of BRML-INM

Num ber	Temperature		Sub stan ce ¹⁾	Equilib rium state ²⁾	BRML-INM capabilities	
	T_{90} / K	$t_{90} / ^\circ\text{C}$			U_{W_i} / mK	$U_{R_{\text{H}_2\text{O}}} / \text{mK}$
	$t_{90} / ^\circ\text{C} = T_{90} / \text{K} - 273.15$				(k=2)	(k=2)
1	83.8058	-189.3442	Ar	TP	0.80	-
2	234.3156	-38.8344	Hg	TP	0.80	-
3	273.16	0.01	H ₂ O	TP	-	0.30
4	302.9146	29.7646	Ga	MP	0.44	-
5	429.7485	156.5985	In	FP	5.0	-
6	505.078	231.928	Sn	FP	2.8	-
7	692.677	419.527	Zn	FP	3.6	-
8	933.473	660.323	Al	FP	6.0	-

Note: 1) All substances are of natural isotopic composition
 2) TR = triple point, FP = freezing point, MP = melting point

The national standard is characterized from metrological point of view and allows the traceability assurance to SI (The International System of Units) in a reliable way, using the frame created by CIPM-MRA [4]. The metrological characterization was mainly made for the ITS-90 defining fixed points specific temperature values [5] for which were carried out the main interlaboratory comparisons where BRML-INM participated [6;7]. Furthermore, the document [5] states that a possible use for the national standard is the calibration of SPRT-s, other than the ones from the national standard, at the ITS-90 defining fixed points belonging to the national standard.

The practical realization of ITS-90 implies the *calibration* of the interpolation instrument (SPRT) at the defining fixed points. According to [1], the result of the calibration is finding a customized relationship for the calibrated SPRT which can be considered a *calibration curve* ([8], 4.31).

However, according to the evolution in the last years of the metrological concepts agreed by the metrologists international community [8], the *calibration* should have as result, more than the result mentioned in the paragraph before, a relation that allows the determination of a *measurement result* starting from a indication of the calibrated SPRT and not only the determination of a singular value. It is known that a *measurement result* ([8], 2.9) is built from a set of quantity values assigned to the measurand (the temperature of a thermodynamic system intended to be measured) which is generally expressed, through a *measured quantity value* and a *measurement uncertainty*.

This second step of calibration ([8], 2.39) whose result is mentioned in the previous paragraph represents the main topic of the present paper.

2.2 Relations for the realization of the T_{90}

The relations for the realization of the T_{90} are relations that allow the determination of a *measurement result* starting from an *indication* of the interpolation instrument (SPRT) calibrated at the ITS-90 defining fixed points. In correlation to the meaning assigned to the concept *measurement result* from [8], 2 categories of relations for the realization of the T_{90} are distinguished.

2.2.1 Relations that allow the determination of a singular value starting from an indication

(a) The measured ratio W_I , the value of quantity W provided by SPRT, is determined:

$$W = R(T_{90}) / R(273.16K) \quad (1)$$

where $R(T_{90})$ and $R(273.16K)$ are the electric resistance at T_{90} and at 273.16 K respectively.

The indication and the corresponding measured value, $T_{90,m}$, of the measured quantity T_{90} , are not values of quantities of the same kind. As a result, at the moment of the indication determination, the measured value of T_{90} is not yet known. The means for the calculation of a measured value from the indication will be described. The way to reach the measured value starting from the indication is described in following (b), (c) and (d).

(b) The error $E_{W,I}$ is determined with the corresponding relation from table 2, column 5, where we use the value W_I for the quantity W and the values of the constants a, b determined at the calibration of the respective SPRT specimen at the ITS-90 defining fixed points realized with the national standard.

(c) W_I is compared with the reference value $W_{r,I}$ which is determined using the relationship:

$$W_r(T_{90}) = W(T_{90}) - E_W(T_{90}) \quad (2)$$

and the values W_I and $E_{W,I}$ of the quantities $W(T_{90})$, and $E_W(T_{90})$ respectively determined at points (a) and (b).

(d) The measured value, $T_{90,m}$, of the *international Kelvin temperature*, T_{90} , measured with the respective SPRT, is determined using the relation (7) from [1] and the values $W_{r,I}$ determined at point (c).

The relations from (a) ... (d) [1] represent the main form of the *measurement function* ([8], 2.49) expressed through the general relation:

$$T_{90} = f_{T_{90}}(W) \quad (3)$$

Table 2

The 7 ITS-90 subintervals between 83.8058 K and 933.473 K

Sub interval	Subinterval's limits	Defining fixed points			The error, $E_w(T_{90})$, is obtained with the relation:
		$i = 2$	$i = 3$	$i = 4$	
0	1	2	3	4	5
1	83.8058 K ÷ 273.16 K	TP Ar	TP Hg	-	$a \cdot (W - 1) + b \cdot (W - 1) \cdot \ln W$
2	-38.8344 °C ÷ 29.7646 °C	TP Hg	MP Ga	-	$a \cdot (W - 1) + b \cdot (W - 1)^2$
3	0 °C ÷ 29.7646 °C	MP Ga	-	-	$a \cdot (W - 1)$
4	0 °C ÷ 156.5985 °C	FP In	-	-	
5	0 °C ÷ 231.928 °C	FP In	FP Sn	-	$a \cdot (W - 1) + b \cdot (W - 1)^2$
6	0 °C ÷ 419.527 °C	FP Sn	FP Zn	-	
7	0 °C ÷ 660.323 °C	FP Sn	FP Zn	FP Al	$a \cdot (W - 1) + b \cdot (W - 1)^2 + c \cdot (W - 1)^3$

Note: The numerical index i refers to the fixed points used for the SPRT calibration;
 $i = 1$ for the water triple point.

2.2.2 Relations for the measurement uncertainty

The relations for the *measurement uncertainty* ([8] 2.26), parameter that expresses the values dispersion from the quantity set of values that form the measuring result and that can be found around the measured value are presented and discussed in chapters 3 and 4.

3. The propagation of the measurement uncertainties obtained at the calibration at fixed points

As stated in [1], in the interval between 83.8058 K and 933.473 K, the interpolation relation is based on relation (2) which can be written in the general form $W_r = W_r(W)$. The input variable for interpolation W is under measurement when the SPRT is used for the measurement of an unknown temperature. This relation allows the determination of the interpolated values and of the uncertainty propagation u_w to the uncertainty u_{W_r} .

The study of the obtained uncertainty propagation from the calibration at fixed points is realized by writing the interpolation relation in the form:

$$W_r = W_r(W, W_i, W_{r,i}) \quad (4)$$

where the number of input variables is $2 \cdot N + 1$;

N : is the number of ITS-90 fixed points, including the triple point of water, where the SPRT calibration is carried out;

W_i : the N results of the calibration at fixed points;

$W_{r,i}$: the N reference values at fixed points given by [1];

i : numerical index defined in table 2;

It is known that, in the general case of a measuring function $Q = f(Z_1, Z_2, \dots, Z_M)$ where the random variables estimations are according to the relation $q = f(z_1, z_2, \dots, z_M)$, the propagation relation of the standard uncertainties associated to the input quantities values to the combined standard uncertainty u_Q associated to a value q of a input quantity Q is:

$$u_Q^2 = \sum_{k=1}^M \left(\frac{\partial f}{\partial z_k} \right)^2 u_{z_k}^2 + 2 \sum_{k=1}^{M-1} \sum_{l=k+1}^M \frac{\partial f}{\partial z_k} \frac{\partial f}{\partial z_l} u_{z_k} u_{z_l} r_{z_k, z_l} \quad (5)$$

where $\frac{\partial f}{\partial z_k} = \frac{\partial f}{\partial Z_k} \Big|_{z_k}$.

Knowing that only the input quantity W is a interpolation variable, we may write $W_r = W_r(W)$ although W_i are inputs for the measurement function as well, becoming uncertainty sources at calibration. If the following substitutions are made : $M \rightarrow 2N+1$, $Z_1 \rightarrow W$, $(Z_2, \dots, Z_{N+1}) \rightarrow (W_i)$, $(Z_{N+2}, \dots, Z_{2N+1}) \rightarrow (W_{r,i})$, $Q \rightarrow W_r$ and $f \rightarrow$ the function from the right hand side of the relation (2) and considering only W and W_i affected by uncertainty ($u_{W_{r,i}} \cong 0$, because the values $W_{r,i}$ are defined in ITS-90), relation (4) becomes $W_r = W_r(W, W_i)$ and relation (5) becomes:

$$u_{W_r(W)}^2 = \left(\frac{\partial W_r}{\partial W} \right)^2 u_W^2 + \sum_{i=1}^N \left(\frac{\partial W_r}{\partial W_i} \right)^2 u_{W_i}^2 + 2 \left(\sum_{i=1}^N \frac{\partial W_r}{\partial W} \frac{\partial W_r}{\partial W_i} u_W u_{W_i} r_{W, W_i} \right) + 2 \sum_{i=1}^{N-1} \sum_{j=i+1}^N \frac{\partial W_r}{\partial W_i} \frac{\partial W_r}{\partial W_j} u_{W_i} u_{W_j} r_{W_i, W_j} \quad (6)$$

Relation (6) expresses the standard uncertainty propagation of the $N+1$ input quantities to the combined standard uncertainty of the output quantity estimation W_r . The first 2 terms from the right hand side of the relation are specific to the null correlation in any input quantity pair. The third term expresses the correlation between W and W_i , the correlation u-c (use-calibration) in the N (W, W_i) pairs through the correlation coefficient r_{W, W_i} . The fourth term expresses the correlation c-c (calibration-calibration) between the pairs $(W_i, W_j) | i=1 \dots N; j=1 \dots N, j \neq i$ through the correlation coefficient r_{W_i, W_j} .

The interpolation equations (2) can be expressed this way [9,10]:

$$W_r(W) = \sum_{i=1}^N W_{r,i} L_i(W) \quad (7)$$

The interpolation polynomial has the order $N-1$. There are N interpolation functions, $L_i(W)$ that satisfy the relation $\sum_{i=1}^N L_i(W) = 1$. The interpolation functions sets $L_i(W)$, specific for each of the 7 subintervals in table 2 are provided in annex D in [9]. These functions can be built for a specific calibrated SPRT specimen because $L_i = L_i(W, W_i)$ | i is a numerical index defined in table 2 and W_i are specific for the given specimen.

The relations $\frac{\partial W_r(W)}{\partial W_i} = -L_i(W) \left[\frac{\partial W_r(W)}{\partial W} \right]_{W=W_i}$, $dW_{H_2O} = 0$ and $u_{W_{H_2O}} = 0$ (because $W_{W_{H_2O}} = 1$) and the approximation $dW_r / dW \approx 1$ are confirmed in [9,10]. Relation (6) becomes:

$$\begin{aligned} u_{W_r(W)}^2 = & u_W^2 + \sum_{i=2}^N L_i^2(W) u_{W_i}^2 + 2 \left(\sum_{i=2}^N (-L_i(W)) u_W u_{W_i} r_{W,W_i} \right) \\ & + 2 \sum_{i=2}^{N-1} \sum_{j=i+1}^N (-L_i(W)) (-L_j(W)) u_{W_i} u_{W_j} r_{W_i,W_j} \end{aligned} \quad (8)$$

With relation (8) the uncertainty $u_{W_r(W)}$ can be calculated in the interpolated value as effect of standard uncertainty propagation u_W and u_{W_i} from the input quantities W and W_i for different values of the correlation coefficients r_{W,W_i} and r_{W_i,W_j} . In order to emphasize the propagation of uncertainties u_R and $u_{R_{H_2O}}$ from the input quantities in the measurement function of the ratio W , relation (9) is used [11,12]:

$$u_W^2 = \frac{1}{R_{H_2O}^2} \left[u_R^2 + W^2 u_{R_{H_2O}}^2 - 2W u_R u_{R_{H_2O}} r_{R,R_{H_2O}} \right] \quad (9)$$

Relation (9) expresses the standard uncertainty propagation of the inputs R și R_{H_2O} to the combined standard uncertainty of the output quantity estimation W . The third term in the brackets expresses the correlation between R and R_{H_2O} , the correlation u-u (use-use), through the correlation coefficient $r_{R,R_{H_2O}}$. For non-correlated inputs, relation (3) becomes:

$$u_W^2 = \frac{1}{R_{H_2O}^2} \left[u_R^2 + W^2 u_{R_{H_2O}}^2 \right] \quad (10)$$

4. Non-uniqueness uncertainty and total uncertainty

The non-uniqueness [13,9,1] is manifested through differences between measured temperature values when for the same ITS-90 subinterval more different interpolation relations are used (non-uniqueness type 1, NU1) or more interpolation instrument types are used (non-uniqueness type 2, NU2) or more interpolation means specimens of the same type are used (non-uniqueness type 3, NU3). In the present paper's case non-uniqueness type 1 and 3 are applicable. The measuring function for this approach is obtained from (3):

$$T_{90} = f_{T_{90}}(W) + C_{\text{NU}} \quad (11)$$

where the non-uniqueness correction estimation C_{NU} is considered to be null.

Considering the inputs in (11) non-correlated, the standard uncertainty given by the relation (12) associated with the T_{90} values obtained through measurement with the respective SPRT calibrated at the ITS-90 defining fixed points materialized at BRML-INM, which takes into consideration the sources from the calibration (the propagation from the fixed points and the non-uniqueness) and the sources that come from use as well.

$$u_{T_{90}, \text{E+U}}^2 = \left(\frac{dT_{90}}{dW_r} \right)^2 u_{W_r}^2 + u_{T_{90}, \text{NU}}^2 \quad (12)$$

where $u_{W_r}^2$ comes from (8). $u_{T_{90}, \text{NU}}^2$ associated to the correction C_{NU} is:

$$u_{T_{90}, \text{NU}}^2 = u_{T_{90}, \text{NU1}}^2 + u_{T_{90}, \text{NU3}}^2 \quad (13)$$

where $u_{T_{90}, \text{NU1}}$ and $u_{T_{90}, \text{NU3}}$ are obtained according to [9,13,14].

For the calculation of the type 1 non-uniqueness standard uncertainty between 83.8058 K and 234.315 6 K and between 234.3156 and 273.16 K relation (14) was used. Between 0.01 °C and 419.527 °C relation (15) was used [13,14]. Between 419.527 °C and 660.323 °C non-uniqueness type 1, NU1, is not present because there is only one interpolation relation.

$$u_{T_{90}, \text{NU1}} = 10^{-3} \times \sum_{j=1}^5 A_{4j} (T_{90} - T_0)^j \quad (14)$$

where the coefficients A_{4j} and the limit T_0 are given in [9,13].

$$u_{W, \text{NU1}} \approx 8,0 \times 10^{-6} |(W-1)(W-W_{\text{Sn}})(W-W_{\text{Zn}})| \quad (15)$$

5. Practical results

The measurement uncertainty associated to the T_{90} temperature values for the 7 sub intervals covered by the *national standard* were calculated using the relations presented in chapter 3 and 4 and using a computer program developed

for the propose of this paper. In figures 1 and 2 the standard and expanded uncertainties are shown. It can be seen that:

- (i) The calibration at fixed points mostly influences, through the BRML-INM's CMCs, the interpolated uncertainties: in subintervals 2 and 7 (the same in 3, 4 and 6), these usually remain inferior to the CMCs in the proximity of the respective fixed points;
- (ii) In subintervals 1 and 5, the interpolated uncertainties are mostly influenced by the interpolation relation as well and they are 101 % and 17 % higher than the fixed point uncertainties;
- (iii) The measurement uncertainty effect of the electric resistance R_{H_2O} at the SPRT's use increases with the increase of temperature and decreases in the other case;
- (iv) The non-uniqueness uncertainty effect or the triple point of water calibration uncertainty effect becomes insignificant when the fixed point uncertainties (e.g. U_{W_i} in fixed point at In, Sn, Zn, Al) are relatively high;

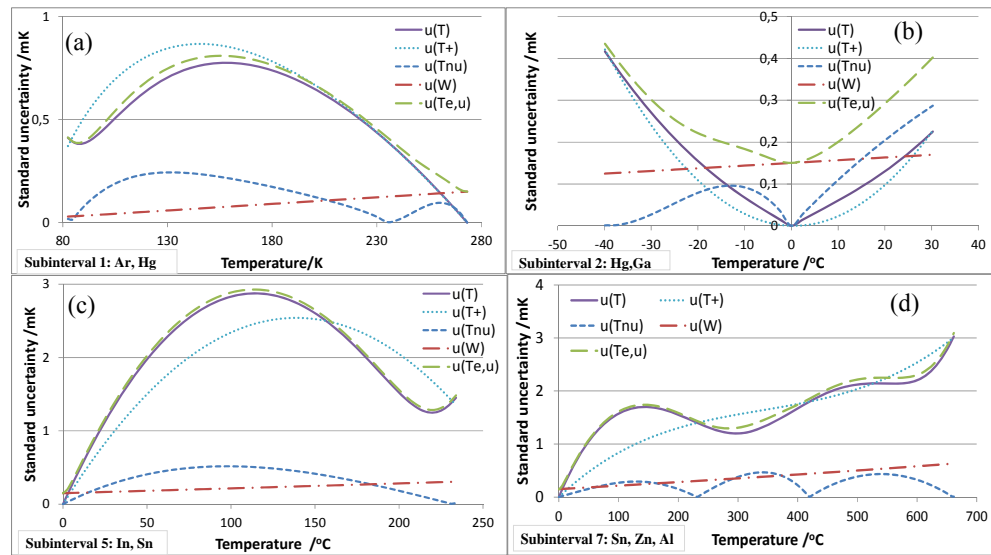


Fig. 1. The graphical representation of the standard uncertainties: (a)-subinterval 1; (b)-subinterval 2; (c)-subinterval 5; (d)-subinterval 7.

- (i) The correlation effect, at positive Celsius temperatures, reduces the uncertainty or reduces the uncertainty in the regions close to the intermediary maximum points (figure 1) and for negative Celsius

temperatures it increases the uncertainty towards the minimum limit of 83 K.

- (ii) In order to avoid the high uncertainties generated by the calibration at the freezing point of In, subinterval 6 can be used

The description of the curves from figure 1:

- „u(Tnu)”: The non-uniqueness uncertainty NU1 and NU3 (cumulated), obtained from the variance given in relation (13); comes from the second step of the SPRT calibration mentioned at section 2.1;
- „u(W)”: Standard uncertainty associated to the values of the ratio W (interpolation input variable defined in relation (1)) obtained with relation (9) where $R_{H_2O} \cong 25,5 \, \Omega$, $u_{R_{H_2O}}$ is according to table 1, $u_R \cong 0 \, \Omega$; comes from SPRT use;
- „u(T)”: Uncertainty associated to the T_{90} temperature values, obtained with relation (8) where $u_W \cong 0$, and the correlations between the input quantities are null. The used u_{W_i} values are according to the ones in table 1 and the W_i used values are the ones determined at BRML-INM at fixed point calibration of two SPRTs belonging to the *national standard* [5]. This uncertainty comes from calibration (propagation of the uncertainties at fixed points);
- „u(T+)”: Uncertainty associated to the T_{90} temperature values, obtained with relation (8) where $u_W \cong 0$, $r_{W_i, W_j} \cong +1$ (limit situation of strong positive correlation between the calibration results at fixed points); comes from calibration (propagation of the uncertainties at fixed points);
- „u(Te,u)”: Uncertainty associated to the T_{90} temperature values, obtained with relation (12) with null correlations between the input quantities; comes from calibration (propagation effect of the uncertainties at fixed points and non-uniqueness effect) and from use as well. Practically, this curve cumulates the curves „u(T)”, „u(Tnu)” and „u(W)”.

In fig. 2, the notations „s1” ... „s7” and „max” from the curve’s names signifies the subinterval mentioned in table 2 which the uncertainty and curve’s maximum refers to. The description of the curves from figure 2:

- „U(Te)”: Uncertainty associated to the T_{90} temperature values, obtained with relation (12) where u_W is considered null; comes from calibration (propagation effect of the uncertainties at fixed points and non-uniqueness effect). Practically, this curve cumulates the curves „u(T)” and „u(Tnu)” extends them through multiplication with 2;

- „U(W)”: This curve extends the curve “u(W)” through multiplication with 2.

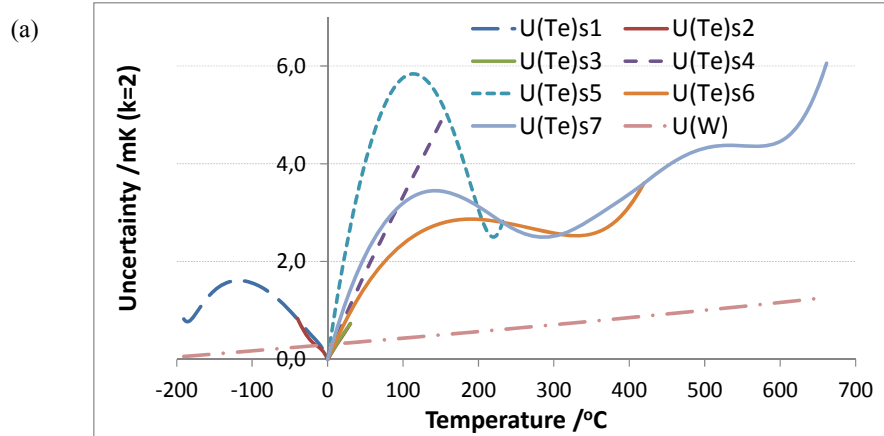


Fig. 2a. The graphical representation of the expanded uncertainties ($k=2$) for the 7 subintervals: uncertainties determined with the relations from section 3 and 4

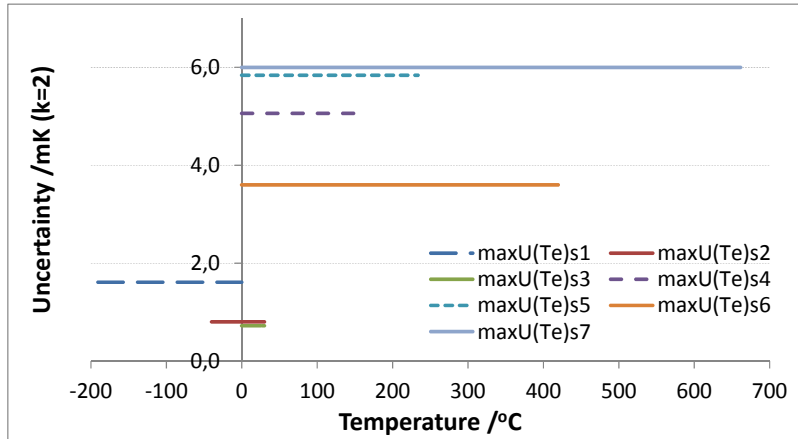


Fig. 2b. The graphical representation of the expanded uncertainties ($k=2$) for the 7 subintervals: the maximum uncertainties from figure 2a.

6. Conclusions

The realization of the International Kelvin Temperature T_{90} with the Romanian Temperature National Measurement Standard was made using the description of ITS-90 from [1] and the evolved significance of some relevant metrological concepts [8]. It has been taken into account that T_{90} is a “practical

temperature” [15,16] and for one thermodynamic equilibrium state corresponds not one but a set of temperature values that can be assigned to the true value with different probabilities.

The main sources of this plurality of values are or come from:

- (i) SPRT calibration: the uncertainties generated at the SPRT fixed point calibration and the uncertainty generated by the non-uniqueness. The second one can be considered *definitional uncertainty* ([8], 2.27).
- (ii) SPRT use: SPRT indication uncertainty. The uncertainties presented in this paper contain only the propagation of uncertainty $u_{R_{H_2O}} \cong 0,15$ mK and do not contain other effects produced by uncertainties introduced by the end user, the SPRT behavior in time or transportation and maintenance of SPRT after calibration.

A tool was created that allows a better way of reporting the calibration results of a SPRT with the *national standard* intended to realize T_{90} for all the interpolation variable W values in the respective temperature subinterval in the national laboratory from BRML-INM and in an external ones as well. This also allows the correlation effect estimation (e.g. “u(T+)” in figure 1). The study of correlations was not included in the present paper and a way of their estimations can use the results of the study presented in paper [17].

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