Thermometry

EUROMET Project No.778

Comparison of realizations of aluminium and silver freezing point temperatures

Final report

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1. Introduction

The comparison was organised according to a protocol, that was agreed between both participants. This protocol follows the same principles as most EUROMET intercomparisons, for instance EUROMET 552. The aim of the comparison was to compare the realizations of Al (660,323°C) and Ag (961,78 °C) freezing-point temperatures at VMT/PFI with the realizations of Al and Ag freezing-point temperatures at PTB.
PTB was the pilot laboratory in this comparison. Two thermometers were calibrated first at PTB, then at VMT/PFI and finally again at PTB. The SPRT was calibrated only the Al freezing point, the HTSPRT at the Al and Ag freezing points. For all measurements the uncertainty were carefully determined. The resistances of the thermometers at the triple point of water are around 25 Ω for SPRT and around 0,6 Ω for HTSPRT.

2. Participating laboratories

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3. Comparison programme

At the beginning of the comparison, PTB calibrated the HTSPRT at Al and Ag freezing points, and the SPRT at Al freezing point. Then the thermometers were hand carried to VMT/PFI. After the reception of the thermometers, VMT/PFI laboratory calibrated them at Al and Ag freezing points in the same sequence as in PTB. The calibration report was established and sent to PTB immediately after the calibration was finished. Then the thermometers were hand carried to PTB, where they were recalibrated.

The comparison programme is given in table 1.

Table 1. Comparison programme

Task	Laboratory
Selection and calibration of the thermometers at Al and Ag freezing points	PTB
Carriage of the thermometers to VMT/PFI	VMT/PFI
Calibration of the thermometers at Al and Ag freezing points	VMT/PFI
Carriage of the thermometers to PTB	PTB
Recalibration of the thermometers at Al and Ag freezing points	PTB

4. Procedures

PTB selected and calibrated one SPRT at Al freezing point and one HTSPRT at Al and Ag freezing points. The HTSPRT is quartz sheathed Long-Stem High Temperature Standard Platinum Resistance Thermometer with the resistance of 0,6 Ohms at the triple point of water. The SPRT is metal-sheathed Long-Stem Standard Platinum Resistance Thermometer with the resistance of 25 Ohms at the triple point of water.
After reception of the thermometers from VMT/PFI, PTB recalibrated the thermometers at Al and Ag freezing points, and established the difference with the associated uncertainty between PTB and VMT/PFI laboratories.

Following procedure of the stabilization of the thermometers used:

- For the HTSPRT:
  - Carefully insert the HTSPRT into an annealing furnace at 450 °C;
  - Heat the HTSPRT to 975 °C with maximum heating rate of 200 °C/hour;
  - Anneal the HTSPRT for 4 hours at 975 °C;
  - Cool down the HTSPRT in the furnace to 450 ^{o}C with a cooling rate 60 ^{o}C/hour;
  - Carefully remove the HTSPRT from the furnace directly to the room environment;
  - Re-determine the value of R_{TPW}.

- For the SPRT:
  - Carefully insert the SPRT into an annealing furnace at 450 °C;
  - Heat the SPRT to 675 °C with maximum heating rate of 200 °C/hour;
  - Anneal the SPRT for 4 hours at 675 °C;
  - Cool down the SPRT in the furnace to 450 ^{o}C with a cooling rate 60 ^{o}C/hour;
  - Carefully remove the SPRT from the furnace directly to the room environment;
  - Re-determine the value of R_{TPW}.

Stabilization procedure was repeated until the decrease or increase in the calculated TPW resistance of the HTSPRT and SPRT before and after the annealing is less than equivalent of 0.5 mK. When the procedure of annealing is finished, calibration of the HTSPRT at Ag and Al freezing points as well as of the SPRT at Al fixed point performed. The thermometers were preheated before they are placed into the freezing point cell. The preheating is done following the procedure given below:

- Ag fixed-point cell:
  - Carefully insert the thermometer into an annealing furnace at 450 °C;
  - Heat the thermometer to 962 °C with maximum heating rate of 200 °C/hour;
  - Remove the thermometer from the annealing furnace and insert it into Ag fixed-point cell.

- at Al fixed-point:
  - Carefully insert the thermometer into an annealing furnace at 450 °C;
  - Heat the thermometer to 661 °C with maximum heating rate of 200 °C/hour;
  - Remove the thermometer from the annealing furnace and insert it into Al fixed-point cell.

For each metal fixed point the $W=R_T/R_{TPW}$ calculated. R_{TPW} is the TPW resistance obtained immediately after the measurement of R_T followed by appropriate annealing procedure.

The annealing procedures for HTSPRT was following:

- After Ag fixed-point measurement:
  - remove the HTSPRT from Ag cell and insert it into the annealing furnace at 975 ^{o}C;
  - anneal the HTSPRT for 30 minutes at 975 °C;
  - cool down the annealing furnace with the HTSPRT to 450 ^{o}C with a cooling rate 60^{o}C/hour;
  - carefully remove the HTSPRT from the annealing furnace directly to the room environment.

- After Al fixed-point measurement:
  - remove the HTSPRT from Al cell and insert it into the annealing furnace at 675 ^{o}C;
  - anneal the HTSPRT for 30 minutes at 675 °C;
  - cool down the annealing furnace with the HTSPRT to 450 ^{o}C with a cooling rate 60^{o}C/hour;
  - carefully remove the HTSPRT from the annealing furnace directly to the room environment.

R_T and R_{TPW} were corrected for self-heating, hydrostatic head and, if any, the pressure effect. At least 3 different phase transitions were be performed.
The measurement sequence for calibration of the HTSPRT at Ag and Al fixed points is given in table 2. The measurement sequence for calibration of the SPRT at Al fixed point is given in table 3.

Table 2. Measurement sequence of the HTSPRT at Ag and Al fixed points

Ag fixed point	
Measurement at TPW	
Measurement at Ag fixed point	W_{Ag} *1*
HTSPRT annealing procedure for Ag	
Measurement at TPW	
Measurement at Ag fixed point	W_{Ag} *2*
HTSPRT annealing procedure for Ag	
Measurement at TPW	
Measurement at Ag fixed point	W_{Ag} *3*
HTSPRT annealing procedure for Ag	
Measurement at TPW	
Al fixed point	
Measurement at TPW	
Measurement at Al fixed point	W_{Al} *1*
HTSPRT annealing procedure for Al	
Measurement at TPW	
Measurement at Al fixed point	W_{Al} *2*
HTSPRT annealing procedure for Al	
Measurement at TPW	
Measurement at Al fixed point	W_{Al} *3*
HTSPRT annealing procedure for Al	
Measurement at TPW	

Table 3. Measurement sequence of the SPRT at Al fixed point

Al fixed point	
Measurement at TPW	
Measurement at Al fixed point	W_{Al} *1*
SPRT annealing procedure for Al	
Measurement at TPW	
Measurement at Al fixed point	W_{Al} *2*
SPRT annealing procedure for Al	
Measurement at TPW	
Measurement at Al fixed point	W_{Al} *3*
SPRT annealing procedure for Al	
Measurement at TPW	

5. Results

The differences between PTB and VMT/PFI calibrations are presented in the Tables 4 to 5 and Figures 1 to 3.

Table 4. The differences between HTSPRT calibrations performed by PTB and VMT/PFI at Ag and Al freezing points

Freezing point	Laboratory	ΔT in mK	$U(\Delta T)$ mK
Ag	PTB	-9.06	3
	VMT/PFI	-6.96	8.3
	PTB	5.51	3
Al	PTB	0	2.5
	VMT/PFI	6.19	3.25
	PTB	10.11	2.5

Table 5. The differences between SPRT calibrations performed by PTB and VMT/PFI at Al freezing point

Freezing point	Laboratory	ΔT in mK	$U(\Delta T)$ mK
Al	PTB	0	2
	VMT/PFI	1.37	3.6
	PTB	3.42	2

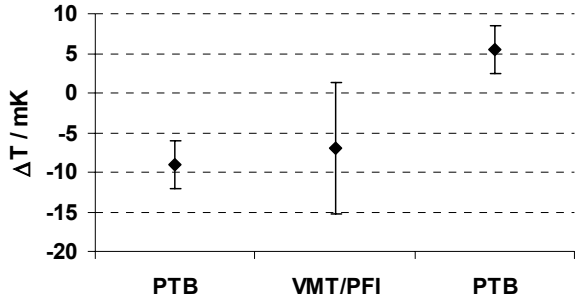

Figure 1. HTSPRT at Ag freezing point

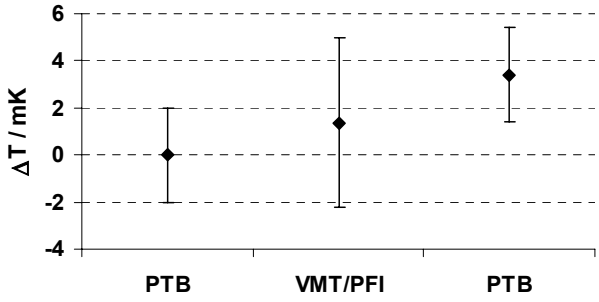

Figure 2. HTSPRT at Al freezing point

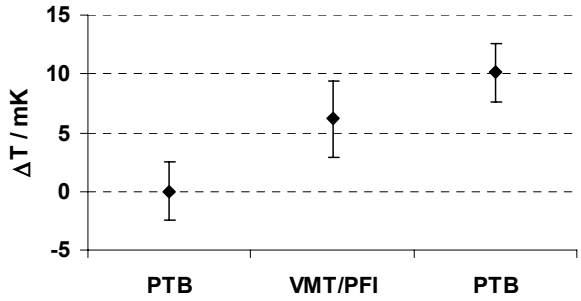

Figure 3. SPRT at Al freezing point

For all measurements the uncertainty were carefully determined. Examples of an uncertainty budgets of VMT/PFI calibrations of HTSPRT at Ag and of SPRT at Al freezing points are shown in Tables 6 to 7.

Table 6. VMT/PFI uncertainty budget of HTSPRT calibration at Ag freezing point

Quantity Q_i	Components	Standard uncertainty $u_{(Qi)}$	Degrees of freedom components evaluated by a type A method * n_i	Sensibility coefficient	Uncertainty contribution u_i in mK
X_t	Repeatability of readings	0.1 mK	19	1	0.100
$C_{Xt/1}$	Uncertainty linked with purity	4 mK	infinite	1	4.000
$C_{Xt/2}$	Uncertainty linked Hydrostatic pressure correction	0.016 mK	infinite	1	0.016
$C_{Xt/3}$	Uncertainty linked with perturbing heat exchanges	0.732 mK	infinite	1	0.732
$C_{Xt/4}$	Uncertainty linked with self-heating correction	0.029 mK	infinite	1	0.029
$C_{Xt/5}$	Uncertainty linked with bridge linearity	0.094 mK	infinite	1	0.094
$C_{Xt/6}$	Uncertainty linked with AC/DC current	negligible			
$C_{Xt/7}$	Uncertainty linked with gas pressure	0.3 mK	infinite	1	0.300
$C_{Xt/8}$	Uncertainty linked with choice of fixed-point value	0.242 mK	infinite	1	0.242
$X_{0.01\ °C}$	Repeatability of readings	0.03 mK	19	4.286	0.129
	Repeatability of temperature realized by cell	0.06 mK	infinite	4.286	0.257
	Short repeatability of calibrated HTSPRT	0.127 mK	infinite	4.286	0.544
$C_{0.01°C/1}$	Uncertainty linked with purity and isotopic composition	0.1 mK	infinite	4.286	0.429
$C_{0.01°C/2}$	Uncertainty linked Hydrostatic pressure correction	0.001 mK	infinite	4.286	0.005
$C_{0.01°C/3}$	Uncertainty linked with perturbing heat exchanges	0.007 mK	infinite	4.286	0.030
$C_{0.01°C/4}$	Uncertainty linked with self-heating correction	0.089 mK	infinite	4.286	0.384
$C_{0.01°C/5}$	Uncertainty linked with bridge linearity	0.012 mK	infinite	4.286	0.052
$C_{0.01°C/6}$	Uncertainty linked with AC/DC current	negligible			
$D_{RS/1}$	Uncertainty linked with stability of RS	negligible			
$D_{RS/2}$	Uncertainty linked with temperature of RS	0.00000002	infinite	1508763 mK	0.035
S_{Wt}	Wt scatter	0.234 mK	infinite	1	0.234
Combined uncertainty					4.180
Coverage factor					2
Expanded uncertainty					8.36

*** for type B method the number of degres of freedom is considered as being infinite**

Table 7. VMT/PFI uncertainty budget of SPRT calibration at Al freezing point

Quantity Q_i	Components	Standard uncertainty $u_{(Qi)}$	Degrees of freedom components evaluated by a type A method * n_i	Sensibility coefficient	Uncertainty contribution u_i in mK
X_t	Repeatability of readings	0.02 mK	19	1	0.020
$C_{Xt/1}$	Uncertainty linked with purity	1.5 mK	infinite	1	1.500
$C_{Xt/2}$	Uncertainty linked Hydrostatic pressure correction	0.005 mK	infinite	1	0.005
$C_{Xt/3}$	Uncertainty linked with perturbing heat exchanges	0.084 mK	infinite	1	0.084
$C_{Xt/4}$	Uncertainty linked with self-heating correction	0.035 mK	infinite	1	0.035
$C_{Xt/5}$	Uncertainty linked with bridge linearity	0.05 mK	infinite	1	0.050
$C_{Xt/6}$	Uncertainty linked with AC/DC current	negligible			
$C_{Xt/7}$	Uncertainty linked with gas pressure	0.035 mK	infinite	1	0.035
$C_{Xt/8}$	Uncertainty linked with choice of fixed-point value	0.179 mK	infinite	1	0.217
$X_{0.01\ °C}$	Repeatability of readings	0.02 mK	19	3.376	0.068
	Repeatability of temperature realized by cell	0.06 mK	infinite	3.376	0.203
	Short repeatability of calibrated SPRT	0.208 mK	infinite	3.376	0.702
$C_{0.01°C/1}$	Uncertainty linked with purity and isotopic composition	0.1 mK	infinite	3.376	0.338
$C_{0.01°C/2}$	Uncertainty linked Hydrostatic pressure correction	0.001 mK	infinite	3.376	0.004
$C_{0.01°C/3}$	Uncertainty linked with perturbing heat exchanges	0.006 mK	infinite	3.376	0.019
$C_{0.01°C/4}$	Uncertainty linked with self-heating correction	0.015 mK	infinite	3.376	0.052
$C_{0.01°C/5}$	Uncertainty linked with bridge linearity	0.007 mK	infinite	3.376	0.024
$C_{0.01°C/6}$	Uncertainty linked with AC/DC current	negligible			
$D_{RS/1}$	Uncertainty linked with stability of RS	negligible			
$D_{RS/2}$	Uncertainty linked with temperature of RS	0.00000002	infinite	1053202 mK	0.024
S_{Wt}	Wt scatter	0.574 mK	infinite	1	0.574
Combined uncertainty					1.815
Coverage factor					2
Expanded uncertainty					3.63

*** for type B method the number of degres of freedom is considered as being infinite**

6. Conclusions

For two adjacent measurements in all cases an agreement within the combined uncertainty was found. Unfortunately the HTSPRT was found to be unstable: The first and final measurements at PTB do not agree within the uncertainties. Therefore this intercomparison is only of limited value for evaluation of the CMC values.
It can be concluded from the results that EUROMET T-K4 must be organised in such a way that there is some redundancy in the measurements