EURAMET.T-K3.5: Bilateral comparison of SPRT calibration at the ITS-90 Fixed Points of Ar, Hg, H₂O, Ga, In, Sn, Zn and Al

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FINAL REPORT Prepared in July 2014

1. Introduction

ROTH+CO. AG was recently designated by METAS for participation in the MRA in the field of thermometry. As VSL participated in both CCT-K3 and EUROMET.T-K3 and was thus able to provide direct link to both KCs, ROTH+CO. AG asked VSL to perform a bilateral comparison of calibration of SPRTs at the ITS-90 fixed points of Ar, Hg, H₂O, Ga, In, Sn, Zn and Al. The goals of such bilateral comparison were:

- Demonstrate the technical competence of ROTH+CO. AG in performing SPRT calibrations at the fixed points of Ar, Hg, H₂O,Ga, In, Sn, Zn and Al.
- Link ROTH+CO. AG to EUROMET.T-K3.
- Support the ROTH+CO.AG submission and publication of CMCs in the BIPM KCDB.

The technical protocol (see Appendix 1), describing the method of the comparison and the procedures to be followed by the participants, was drawn up in February 2013, was reviewed by the CCT-WG7 in April 2013 and was revised in April 2013.

2. Participant Laboratories

The participant laboratories with corresponding contact details are listed in Table 1:

Acronym	Institute	Address	Contact person and details
VSL	VSL, Dutch Metrology Institute	Thijsseweg 11 2629 JA DELFT The Netherlands	Andrea Peruzzi <u>aperuzzi@vsl.nl</u> +31 15 269 1519
ROTH+CO. AG	ROTH+CO. AG	Wiesentalstrasse 20 9242 Oberuzwil Switzerland	Remo Senn <u>r.senn@rothcoag.ch</u> +41 71 955 0202

 Table 1: Participants and contact details.

3. Transfer Standards and Comparison Scheme

The transfer standards used in this comparison were two long-stem SPRTs of ROTH+CO. AG property:

- Tinsley 5187, SN: 268755 for the range Ar to TPW
- Fluke 5681, SN: 1784 for the range TPW to Al

The comparison was divided in three parts:

- Part 1: the two SPRTs were calibrated at ROTH+CO. AG against ROTH+CO. AG fixed point cells (April 2013 to May 2013).
- Part 2: the two SPRTs were calibrated at VSL lab against VSL fixed point cells (June 2013 to September 2013)
- Part 3: the two SPRTs were calibrated again at ROTH+CO. AG against ROTH+CO. AG fixed point cells (December 2013 to January 2014)

4. Measurements at ROTH+CO. AG

4.1 Fixed Point Cells

The information concerning the fixed point cells used by ROTH+CO. AG is summarized in Table 2.

Fixed Point	Cell s/n	Manufacturer	Year	Immersion depth /cm	Pressure / Pa
AI	Al058	Pyro-Controle Chauvin Arnoux	1991	15.4	101325
Zn	Zn132	Pyro-Controle Chauvin Arnoux	1998	14.4	101325
Sn	Sn016	Engelhard	1989	14.6	101325
In	In131	Pyro-Controle Chauvin Arnoux	1998	14.5	101325
Ga	Ga25	Pyro-Controle Chauvin Arnoux	1994	17.8	101325
H ₂ O	NPL735	NPL	1994	23.3	Triple point
Hg	Hg98044	Hart Scientific	1998	17.8	Triple point
Ar	Ar14	BNM	1978	11.8	Triple point

Table 2: Fixed point cells used by ROTH+CO. AG.

4.2 Equipment

The resistance ratio, between the SPRT resistance and a 100 Ω standard resistor Tinsley 5685 A, was measured with an ASL resistance ratio bridge, model F-18. The standard resistor was enclosed in a Tinsley single enclosure box type 5648 with stability of 10 mK.

4.3. Uncertainty budget

The uncertainty budget for each fixed point is reported in Table 3.

Uncertainty component (k=1)	Ar	Hg	H ₂ O	Ga	In	Sn	Zn	AI
Repeatability readings	0.04	0.04	0.04	0.034	0.06	0.1	0.2	0.2
Plateau slope	0.02	0.02	0.00	0.02	0.02	0.04	0.03	0.13
Impurities	0.30	0.25	0.1	0.2	0.8	0.5	0.7	1.5
Hydrostatic head	0.03	0.06	0.01	0.01	0.03	0.02	0.02	0.01
Heat flux	0.15	0.05	0.05	0.05	0.08	0.2	0.14	0.24
SPRT self heating	0.05	0.05	0.017	0.01	0.003	0.04	0.08	0.07
Resistance bridge	0.18	0.20	0.20	0.20	0.20	0.21	0.21	0.23
Standard resistor stability	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Standard resistor change	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
in value								
Value standard resistor	0.06	0.06	0.06	0.07	0.11	0.13	0.18	0.26
AC/DC effect	0.10	0.10	0.05	0.1	0.1	0.1	0.1	0.1
Gas pressure	0.00	0.01	0.00	0.04	0.1	0.07	0.09	0.14
TPW propagation	0.07	0.22	0.00	0.28	0.42	0.61	0.64	1.42
W scatter	0.05	0.09	0.00	0.01	0.04	0.05	0.09	0.41
Standard uncertainty (k=1)	0.42	0.43	0.25	0.42	0.95	0.87	1.04	2.17

^{*}Including isotopic composition.

Table 3: Uncertainty budget for the measurements performed by ROTH+CO. AG (in mK).

4.4. Measurement results

The results of the measurements performed by ROTH+CO. AG are summarized in Table 4.

Average <i>W</i> (FP _i)	SPRT 268755	u(<i>W</i> (FP _i)) /mK	Number equilibria realized	SPRT 1784	u(<i>W</i> (FP _i)) /mK	Number equilibria realized
<i>W</i> (Ar)	0.21593145	0.42	3	-	-	-
W(Hg)	0.84415734	0.43	3	-	-	-
W(Ga)	-	-	-	1.11812883	0.42	3
W(In)	-	-	-	1.60973931	0.95	3
<i>W</i> (Sn)	-	-	-	1.89270173	0.87	4
W(Zn)	-	-	-	2.56873872	1.04	3
W(AI)	-	-	-	3.37571767	2.17	4
Final <i>R</i> (TPW)	25.1808844			25.2610766		

Table 4: The results of the measurements performed by ROTH+CO. AG.

4.5 Immersion profiles and realization curves

The immersion profiles and the realization curves performed at ROTH+CO. AG are reported in Appendix 2.

5. Measurements at VSL

5.1. Fixed Point Cells

The information concerning the fixed point cells used by VSL is summarized in Table 5.

Fixed Point	Cell s/n	Manufacturer (year)	Immersion depth /cm	Pressure / Pa
Al	VSL04T065(Al06)	VSL (2004)	12.4	P _{atm} + 10 KPa
Zn	VSL89T099(Zn02)	VSL (1989)	15.4	P _{atm} + 10 KPa
Sn	VSL04T104(Sn03)	VSL (2004)	17.4	P _{atm} + 10 KPa
In	VSL89T056(In1)	VSL (1989)	15.9	P _{atm} + 10 KPa
	VSL04T233(In3)	VSL (2004)	18.0	P _{atm} + 10 KPa
Ga	VSL89T020(Ga20)	VSL (1989)	24.8	Closed cell
04	VSL89T021(Ga21)	VSL (1989)	24.8	Closed cell
H ₂ O	VSL06T003	VSL (2006)	27.2	Triple point
1120	VSL08T005	VSL (2008)	25.8	Triple point
Hg	VSL89T009(Hg009)	VSL (1989)	14.5	Triple point
. 19	VSL89T010(Hg010)	VSL (1989)	14.5	Triple point
Ar	Ar01	LNE (1994)	12.1	Triple point

Table 5: Fixed point cells used by VSL. Note that P_{atm} is the atmospheric pressure of the day.

5.2. Uncertainty budget

The uncertainty budget for each fixed point is reported in Table 6.

Uncertainty component (k=1)	Ar	Hg	H ₂ O	Ga	In	Sn	Zn	AI
Realization repeatability	0.238	0.093	0.008	0.054	0.044	0.327	0.327	0.172
SPRT resistance	0.006	0.009		0.012	0.003	0.019	0.017	0.012
measurement								
Chemical impurities	0.032	0.012	0.020	0.079	0.027	0.175	0.312	0.387
Hydrostatic head	0.032	0.071	0.005	0.012	0.033	0.022	0.027	0.016
SPRT self heating (current)	0.026	0.006		0.004	0.006	0.006	0.006	0.005
SPRT self heating	0.001	0.021	0.005	0.022	0.009	0.009	0.010	0.011
(extrapolation)								
Standard resistor	0.007	0.021	0.015	0.042	0.064	0.076	0.110	0.158
Resistance ratio bridge	0.000	0.012	0.037	0.013	0.005	0.005	0.006	0.006
TPW propagation	0.009	0.039	0.000	0.053	0.079	0.095	0.137	0.196
Gas pressure	0.000	0.004	0.002	0.040	0.049	0.033	0.043	0.070
Heat flux	0.100	0.174	0.005	0.063	0.153	0.063	0.183	0.220
Standard uncertainty (k=1)	0.264	0.217	0.047	0.142	0.200	0.398	0.521	0.544

Table 6: Uncertainty budget for the measurements performed by VSL (in mK).

5.3. Equipment

The resistance ratio, between the SPRT resistance and a calibrated standard resistor, was measured with either 6010T or 6015T models of Measurement International Ltd. Depending on the value of the SPRT resistance used, different standard resistors were used: Tinsley type 5684 10 Ω , 25 Ω and 100 Ω , and Tinsley type 5685A 1 Ω , 10 Ω , 25 Ω and 100 Ω .

The standards resistors were maintained in a water bath at a controlled temperature of 27.837 $^{\circ}$ C (±2 mK).

5.4. Measurement results

The results of the measurements performed by VSL are summarized in Table 7.

Average <i>W</i> (FP _i)	SPRT 268755	u(<i>W</i> (FP _i)) /mK	Number equilibria realized	SPRT 1784	u(<i>W</i> (FP _i)) /mK	Number equilibria realized
W(Ar)	0.21592831	0.264	3	-	-	-
W(Hg)	0.84415579	0.217	6	-	-	-
W(Ga)	-	-	-	1.11812576	0.142	3
W(In)	-	-	-	1.60973373	0.200	4
W(Sn)	-	-	-	1.89269932	0.398	4
W(Zn)	-	-	-	2.56873018	0.521	3
W(AI)	-	-	-	3.37570263	0.544	4
Final <i>R</i> (TPW)	25.18101274			25.26119838		

Table 7: The results of the measurements performed by VSL.

6. Stability of circulating SPRTs

The standard uncertainty, expressed in terms of temperature, due to the stability of the circulating SPRTs during the period of measurements is:

$$u_{SPRT}(FP_i) = \frac{\left|W_{ROTHend}(FP_i) - W_{ROTHstart}(FP_i)\right|}{\sqrt{3}} \cdot \left(\frac{dT}{dW}\right)_{FPi}$$

where:

- *W*_{ROTHend}(FP_i) is the *W*(FP_i) value measured by ROTH+CO. AG at the fixed point FP_i in the part 3 measurements at ROTH+CO. AG
- $W_{\text{ROTHstart}}(\text{FP}_i)$ is the $W(\text{FP}_i)$ value measured by ROTH+CO. AG at the fixed point FP_i in the part 1 measurements at ROTH+CO. AG

Fixed point FP _i	W _{ROTHstart} (FP _i)	W _{ROTHend} (FP _i)	<i>∆W</i> (FP _i)	(<i>dT/dW</i>) _{FPi} /K	и _{sprt} (FP _i) /mK
Ar	0.21593145	0.21593235	0.00000090	230.33	0.120
Hg	0.84415734	0.84415732	-0.00000002	247.72	0.003
Ga	1.11812883	1.11812981	0.0000098	253.01	0.143
In	1.60973931	1.60973786	-0.00000145	263.09	0.220
Sn	1.89270173	1.89270122	-0.00000051	269.34	0.079
Zn	2.56873872	2.56873931	0.00000059	286.09	0.097
Al	3.37571767	3.37572259	0.00000492	312.02	0.886

Table 8: Uncertainty due to the stability of the circulating SPRTs during the period of measurements.

7. Comparison results

The comparison results can now be easily expressed in terms of degree of equivalence:

-
$$T_{ROTH} - T_{VSL} = (W_{ROTHstart} - W_{VSL}) \cdot \left(\frac{dT}{dW}\right)$$

- $U(T_{ROTH} - T_{VSL}) = 2 \cdot \sqrt{u_{VSL}^2 + u_{ROTH}^2 + u_{SPRT}^2}$

Fixed point FP _i	W _{ROTHstart} (FP _i)	W _{VSL} (FP _i)	(<i>dT/dW</i>) _{FPi} /K	T _{ROTH} – T _{VSL} /mK	U(T _{ROTH} – T _{VSL}) /mK
Ar	0.21593145	0.21592831	230.33	0.72	1.02
Hg	0.84415734	0.84415579	247.72	0.38	0.96
Ga	1.11812883	1.11812576	253.01	0.78	0.93
In	1.60973931	1.60973373	263.09	1.47	1.99
Sn	1.89270173	1.89269932	269.34	0.65	1.92
Zn	2.56873872	2.56873018	286.09	2.44	2.33
AI	3.37571767	3.37570263	312.02	4.69	4.81

Table 9: Degrees of equivalence and corresponding expanded uncertainty for this comparison.

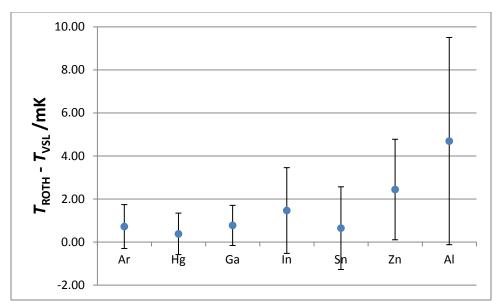


Figure 1: Degree of equivalence and corresponding expanded uncertainty (k=2) for each fixed point.

8. Link to CCT-K3

The link to CCT-K3 was obtained:

- through VSL participation in EUROMET.T-K3, for the fixed points from Ar to Zn
- through VSL participation in EUROMET.T-K4, for the Al fixed point

In the following two sections, we describe the linking mechanism for the two distinct cases.

8.1 Link to CCT-K3 for the fixed points from Ar to Zn

The formula for calculating the degree of equivalence $D_{\text{ROTH, LABi}}$ between ROTH+CO. AG and any CCT-K3 participant (LABi) is:

 $D_{\text{ROTH, LABi}} = (T_{\text{ROTH}} - T_{\text{VSL}})_{\text{EURAMET.T-K3.5}} + [(T_{\text{VSL}})_{\text{EURAMET.T-K3.5}} - (T_{\text{VSL}})_{\text{EUROMET.T-K3}}] + (T_{\text{VSL}} - T_{\text{wm552}})_{\text{EUROMET.T-K3}} + (T_{\text{wm552}} - T_{\text{P&CP}})_{\text{EUROMET.T-K3}} + (T_{\text{P&CP}} - T_{\text{LABi}})_{\text{CCT-K3}}$ Where:

- $(T_{\text{ROTH}} T_{\text{VSL}})_{\text{EURAMET.T-K3.5}}$ is the equivalence between ROTH+CO. AG and VSL established in this comparison and given in Table 9 above
- [(T_{VSL})_{EURAMET.T-K3.5} (T_{VSL})_{EUROMET.T-K3}] is the difference between VSL fixed point realization in this comparison (EURAMET.T-K3.5) and VSL fixed point realization in EUROMET.T-K3. Such difference is due to two effects: a) Different sets of fixed point cells used in the two comparisons and b) Redefinition of the VSL national reference for the TPW in 2006 after the 2005 CIPM clarification of the definition of the triple point of water. The impact of these two effects is summarized in Table 10.

	T _{VSL} (EURAMET.T-K3.5) – T _{VSL} (EUROMET.T-K3,K4) /mK							
Fixed point	Different set of cells /mK	TPW propagation /mK	Total effect /mK					
Ar	0	0.012	0.01					
Hg	-0.03	0.049	0.02					
H ₂ O	+0.06	-	0.06					
Ga	0	0.066	0.07					
In	-0.14	0.099	-0.04					
Sn	-0.02	0.120	0.10					
Zn	0	0.173	0.17					
Al*	0.14^{*}	0.247^{*}	0.39*					

* Relative to EUROMET.T-K4

Table 10: Difference between VSL fixed point realization in EURAMET.T-K3.5 and EUROMET.T-K3 (EUROMET.T-K4 for Al).

- $(T_{\text{VSL}} T_{\text{wm552}})_{\text{EUROMET.T-K3}}$ is the difference between VSL realization in EUROMET.T-K3 and the weighted mean of all participants in EUROMET.T-K3, T_{wm552} , and is given in Tables 16 to 20 of the EUROMET.T-K3 final report
- $(T_{wm552} T_{P\&CP})_{EUROMET.T-K3}$ is the difference between the weighted mean of all EUROMET.T-K3 participants and the mean of EUROMET.T-K3 pilot and copilot laboratories $T_{P\&CP}$ and is given in Tables 22 to 26 of EUROMET.T-K3 final report
- $(T_{P\&CP} T_{LABi})_{CCT-K3}$ is the difference between $T_{P\&CP}$ and any participant realization T_{LABi} , calculated from Tables 22, 24 to 28 of CCT-K3 as:

$$(T_{P\&CP} - T_{LABi})_{CCT-K3} = \frac{1}{n} \sum_{j=1}^{n} (T_{P\&CP_j} - T_{LABi})$$

The expanded uncertainty of the degree of equivalence between ROTH and CCT-K3 participant LABi is calculated as:

$$U(T_{ROTH} - T_{LABi}) = \sqrt{U^2(T_{ROTH} - T_{VSL}) + U^2(T_{VSL} - T_{wm552}) + U^2_{repr(P\&CP)_{mean}} + U^2(T_{P\&CP} - T_{LABi})}$$

Where:

 $U(T_{\text{ROTH}} - T_{\text{VSL}})$ is given in Table 9 above

 $U(T_{\rm VSL} - T_{\rm wm552})$ is given in Tables 16 to 20 of EUROMET.T-K3 final report

U_{repr(P&CP)mean} is given in Tables 28 of EUROMET.T-K3 final report

 $U(T_{P\&CP} - T_{LABi})_{CCT-K3}$ is calculated from Tables 22, 24 to 28 of CCT-K3 final report as:

$$U(T_{P\&CP} - T_{LABi}) = \frac{1}{n} \sqrt{\sum_{j=1}^{n} (U_{P\&CP_{j}, LABi})^{2}}$$

As worked out example, we show here how the equivalence between ROTH+CO. AG and NIST is obtained (Table 11).

Fixed Point	$T_{\rm ROTH} - T_{\rm VSL}$ in EUK3.5	$U(T_{ m ROTH}) - T_{ m VSL}$	$T_{\rm VSL}({\rm EUK3.5}) - T_{\rm VSL}({\rm EUK3})$	$\begin{array}{c} T_{\rm VSL} - \\ T_{\rm wm552} \text{ in} \\ {\rm EUK3} \end{array}$	$U(T_{\rm VSL} - T_{\rm wm552}) $ in EUK3	T _{wm552} - T _{P&CP} in EUK3	U _{repr(P&CP)} in EUK3	$T_{\text{P&CP}} - T_{\text{NIST}}$ in CCT-K3	$U(T_{P\&CP} - T_{NIST})$ in CCT-K3	D _{ROTH,NIST}	$U(D_{\rm ROTH,NIST})$
Ar	0.72	1.02	0.01	-0.01	0.52	-0.07	0.14	-0.18	0.27	0.47	1.18
Hg	0.38	0.96	0.02	0.11	0.45	-0.02	0.02	-0.07	0.18	0.42	1.08
Ga	0.78	0.93	0.06	-0.18	0.50	0.08	0.02	-0.02	0.12	0.72	1.06
In	1.47	1.99	0.07	-0.45	0.56	0.24	0.07	-0.62	0.34	0.71	2.10
Sn	0.65	1.92	-0.04	0.21	0.92	-0.11	0.05	-0.21	0.32	0.50	2.15
Zn	2.44	2.33	0.10	-0.82	1.58	0.17	0.16	-0.57	0.41	1.32	2.85

Table 11: Example of calculation of the equivalence between ROTH+CO. AG and NIST. All quantities are expressed in mK.

8.2 Link to CCT-K3 for the Al fixed point

The formula for calculating the DoE $D_{\text{ROTH, LABi}}$ between ROTH+CO. AG and any CCT-K3 participant (LABi) is:

 $D_{\text{ROTH, LABi}} = (T_{\text{ROTH}} - T_{\text{VSL}})_{\text{EURAMET.T-K3.5}} + [(T_{\text{VSL}})_{\text{EURAMET.T-K3.5}} - (T_{\text{VSL}})_{\text{EUROMET.T-K4}}] +$

 $(T_{\text{VSL}} - T_{\text{ERV}})_{\text{EUROMET.T-K4}} + [(T_{\text{ERV}})_{\text{EUROMET.T-K4}} - (T_{\text{ARV}})_{\text{CCT-K3}}] + (T_{\text{ARV}} - T_{\text{LABi}})_{\text{CCT-K3}}$

Where:

- $(T_{\text{ROTH}} T_{\text{VSL}})_{\text{EURAMET.T-K3.5}}$ is the equivalence between ROTH+CO. AG and VSL established in this comparison and is given in Table 9 above
- $[(T_{VSL})_{EURAMET.T-K3.5} (T_{VSL})_{EUROMET.T-K4}]$ is the difference between VSL fixed point realization in this comparison (EURAMET.T-K3.5) and VSL fixed point realization in EUROMET.T-K4. Such difference is given in the last row of Table 10.
- $(T_{VSL} T_{ERV})_{EUROMET.T-K4}$ is the difference between VSL realization in EUROMET.T-K4 and the simple mean of all participants in EUROMET.T-K4, T_{ERV} , and is given in Table 5.4 of the EUROMET.T-K4 final report
- $[(T_{\text{ERV}})_{\text{EUROMET.T-K4}} (T_{\text{ARV}})_{\text{CCT-K3}}]$ is the difference between the simple mean of all EUROMET.T-K4 participants and the average reference value (T_{ARV}) CCT-K3
- $(T_{ARV} T_{LABi})_{CCT-K3}$ is the difference between T_{ARV} and any participant realization T_{LABi}

The expanded uncertainty of the degree of equivalence between ROTH and CCT-K3 participant LABi is calculated as:

$$U(T_{ROTH} - T_{LABi}) = \sqrt{U^2(T_{ROTH} - T_{VSL}) + U^2(T_{VSL} - T_{ERV}) + U^2(T_{ERV} - T_{ARV}) + U^2(T_{ARV} - T_{LABi})}$$

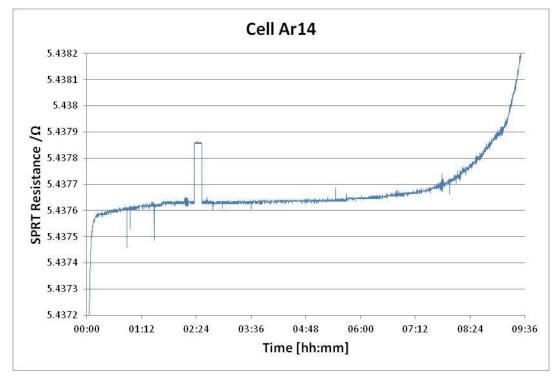
Where:

 $U(T_{\text{ROTH}} - T_{\text{VSL}})$ is given in Table 9 above $U(T_{\text{VSL}} - T_{\text{ERV}})$ is given in Table 5.4 of the EUROMET.T-K4 final report $U(T_{\text{ERV}} - T_{\text{ARV}})$ is given at page 17 of the EUROMET.T-K4 final report $U(T_{\text{ARV}} - T_{\text{LABi}})_{\text{CCT-K3}}$ is the uncertainty in $(T_{\text{ARV}} - T_{\text{LABi}})_{\text{CCT-K3}}$

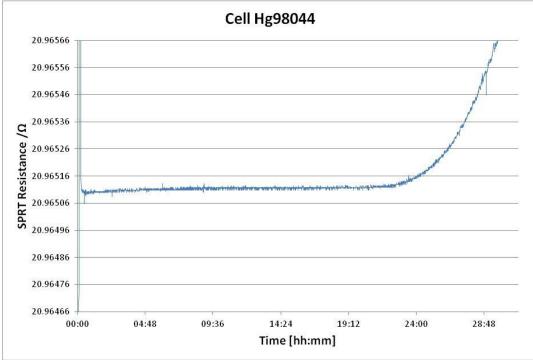
As worked out example, we show here how the equivalence between ROTH+CO. AG and NIST is obtained (Table 12).

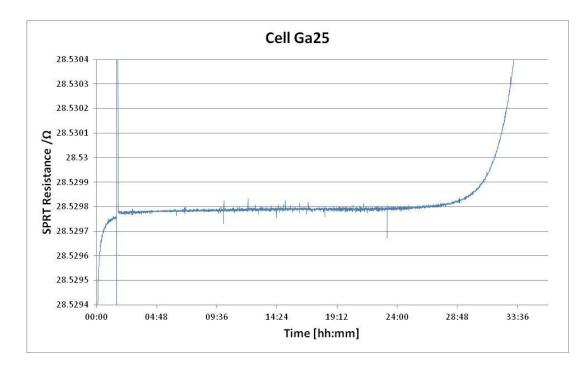
Fixed Point	$T_{\text{ROTH}} - T_{\text{VSL}}$ in EUK3.5	$\begin{array}{c} U(T_{\rm ROTH} \\ - T_{\rm VSL}) \end{array}$	$T_{\rm VSL}({\rm EUK3.5}) - T_{\rm VSL}({\rm EUK4})$	$\begin{array}{c} T_{\rm VSL} - T_{\rm ERV} \\ {\rm in \ EUK4} \end{array}$	$U(T_{\rm VSL} - T_{\rm ERV})$ in EUK4	$T_{\rm ERV} - T_{\rm ARV}$	$U(T_{\rm ERV} - T_{\rm ARV})$	$T_{ARV} - T_{NIST}$ in CCT-K3	$U(T_{ARV} - T_{NIST})$ in CCT-K3	D _{ROTH,NIST}	$U(D_{\rm ROTH,NIST})$
Al	4.69	4.81	0.39	0.71	4.51	0.54	1.96	-0.31	1.26	6.02	7.38

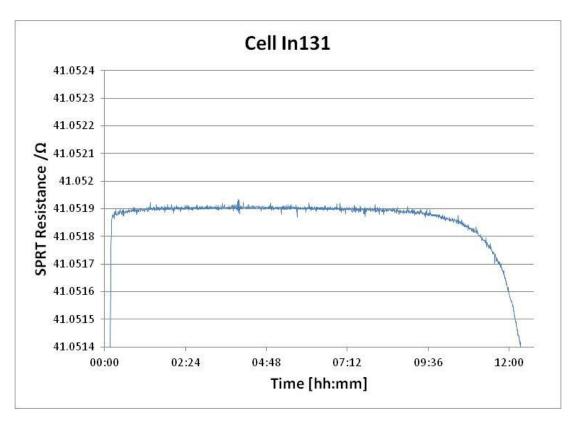
Table 12: Example of calculation of the equivalence between ROTH+CO. AG and NIST for Al. All quantities are expressed in mK.

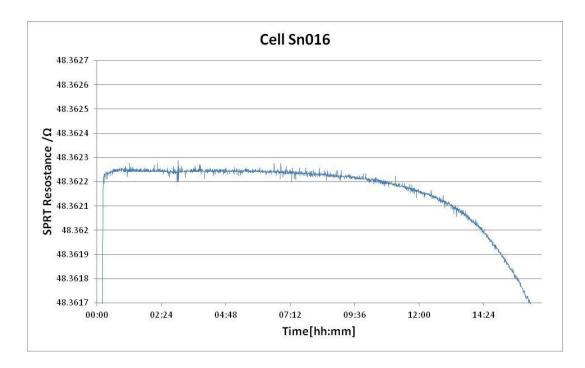


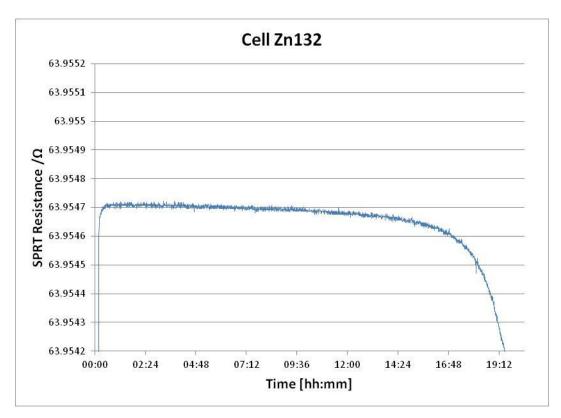
9 Examples of ROTH+CO. AG realization curves

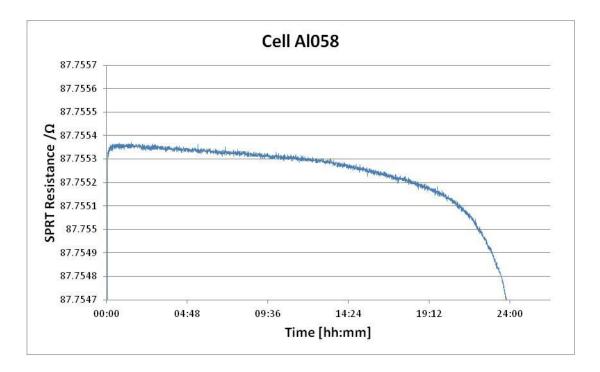












10 Immersion profiles

