Comparison of Fixed Point Realisations between Inmetro and PTB

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Abstract. An interlaboratory comparison in the temperature range between –190 °C and 420 °C was organised between the National Institute of Quality, Normalisation and Industrial Quality (Inmetro), Brazil, and the Physikalisch Technische Bundesanstalt (PTB), Germany. This comparison followed the same protocol as the EUROMET project 552 comparison and was carried out in the years 2001-2002. A standard platinum resistance thermometer (SPRT) of 25 Ω was calibrated at the temperature fixed points of Ar, Hg, the triple point of water (TWP), Ga, In, Sn and Zn, with at least three realisations of each fixed point at both institutes. The uncertainty evaluation is given by Inmetro and some differences in the calibration procedures or in the measuring instruments used are described. The agreement between the results of laboratories was not in all cases within the combined uncertainties. Results of other comparisons are presented, which give additional information on the equivalence of the realised temperature scales.

INTRODUCTION

In the frame of the Mutual Recognition Arrangement (MRA) of the CIPM, interlaboratory comparisons are a procedure for demonstrating equivalence of measurement capabilities between National Metrology Institutes (NMIs). These comparisons are (usually) organised as multilateral key comparisons, either by the CIPM or by the Regional Metrology Organisations (RMOs). In the field of thermometry key comparison 3 (CCT-K3) covering the temperature between the triple point of argon and the freezing point of aluminium has been finished [1], and regional key comparisons in this temperature comparison have already been started. The regional key comparisons are linked together by joint participants in the CCT key comparisons. Supplementary comparisons between members of different RMOs will increase the reliability of the degrees of equivalence of measurement capabilities.

A bilateral comparison was organized between Inmetro and PTB in the temperature range –190 °C to 420 °C based on an SPRT. The comparison followed the protocol of EUROMET project 552, which is based on the protocol of CCT K3 [1]. The SPRT used in this comparison was a 25 Ω Rosemount model 162CE, s/n 4727. The SPRT was calibrated in both laboratories at temperature fixed points in the reported range. PTB served as the co-ordinating laboratory, so the SPRT was calibrated following the sequence: PTB – Inmetro – PTB. Initially, the results were compared using the normalised error ratio (NER) expression, considering the original results from the Inmetro's calibration and the PTB's calibration before and after the measurements at Inmetro. A table with NER for each fixed point is shown. The cell uncertainties from Inmetro are discussed based on previous bilateral cell comparisons performed between Inmetro and CENAM-Mexico (in 1997, range: –39 °C to 420 °C) and between Inmetro and NRC-Canada (in 2000, range: –190 °C to 962 °C). The fixed points were realised according to the procedures described in a CCT guideline [2, 3].

The aim of this bilateral comparison is to evaluate the degree of equivalence between the realisation of ITS-90 fixed points at both institutes when calibrating SPRTs in the temperature range –190 °C to 420 °C.

EQUIPMENT

The purity of the fixed-point cells at PTB and Inmetro is at least 99.999 % (5N). Furnaces with three heating zones were used for zinc, tin and indium fixed points. For the gallium melting point a single-zone furnace with temperature control based on Peltier elements was used.

TABLE 1. Details of Inmetro's fixed-point realisations used for the measurements.

Fixed point	Manufacturer of cell	Identification of Inmetro	Thermal environment
Zn	Engelhard Pyro-Control	sealed cell EPC 027	3 zone furnace
Sn	Engelhard Pyro-Control	sealed cell EPC 047	3 zone furnace
In	Engelhard Pyro-Control	sealed cell EPC 046	3 zone furnace
Ga	ISOTECH	sealed cell s/n 168	calibrator
TPW	CENAM	420-A-024	Dewar flask with crushed ice
Hg	ISOTECH	sealed cell M036	cryostat
Ar	BNM-INM	sealed cell INM-031	liquid N_2

TABLE 2. Details about PTB's fixed-point realisations used for the measurements.

Fixed point	manufacturer of cell	Standard of PTB	Thermal environment
Zn	PTB	group of cells, incl. open, home-made cells	3 zone furnace
Sn	ISOTECH	group of cells, incl. open, home-made cells	3 zone furnace
In	ISOTECH	open cell	3 zone furnace
Ga	ISOTECH	group of cells from different manufacturers	calibrator
TPW	FTG	group of cells	bath
Hg	YSI	group of cells from different manufacturers	bath
Ar	BNM-INM	group of cells	liquid N_2 bath

Mercury triple points were performed in cryostats designed specially for those cells. TPW cells were realised and kept in Dewar flasks with ice (Inmetro) or in a thermostatic bath (PTB). Argon triple points were performed in dedicated cryostats with liquid nitrogen. The realisation of the temperature scale at PTB is described in detail in [4].

Both laboratories used ASL F18 AC bridges with AC/DC standard resistors for resistance measurements. The standard resistors were kept in thermostatic controlled baths and temperature-controlled boxes (enclosures). The details for the instrumentation at Inmetro and PTB are given in Table 1 and Table 2.

INTERCOMPARISON PROCEDURE

The protocol of the intercomparison included the following procedure:

"The travelling SPRT is to pass through the following sequence:

1) a measurement at the triple point of water (TPW);

2) a stabilisation procedure;

3) a second measurement at the triple point of water;

4) measurements at metal fixed points in order of decreasing temperatures alternating with a measurement at the triple point of water.

"If no damage has been sustained and after reporting to the pilot laboratory, the host must measure the resistance of the travelling SPRT in a TPW cell at two measuring currents (in order to determine the zero-power value). The measurement current used must be such that the generated power does not exceed 250 µW. The 0 mA resistance values of the travelling SPRT at the TPW must be corrected for hydrostatic head to obtain R_{TPW}. The value of R_{TPW} must be communicated to the pilot laboratory. After receiving approval from the pilot laboratory to proceed with the comparison, the host laboratory can begin the SPRT stabilisation procedure:

The stabilisation of the thermometer is done by annealing the SPRT for two hours at 480 °C. The annealing procedure should result in a change of the resistance at the TPW equivalent to not more than 0.5 mK. Otherwise the procedure should be repeated, this time resulting in a change of the resistance at the TPW equivalent of not more than 0.2 mK. The measurements should be reported to the pilot laboratory. Alternative procedures should only be used after approval by the pilot laboratory."

At Inmetro the first annealing procedure resulted in a change at the TPW equivalent to 1.00 mK, the second annealing procedure in a change equivalent to 0.02 mK. PTB agreed to start the measurements.

Following the EUROMET protocol, the SPRT was calibrated at all of the fixed points in the range of comparison, i.e. measurements at TPW, Zn, TPW, Sn, TPW, In, TPW, Ga, TPW, Hg, TPW, Ar and TPW, in that order. Existing techniques as practised by the participating laboratory were used. For each metal fixed point, $W=R_T/R_{\text{TPW}}$ is calculated. R_{TPW} is the TPW resistance obtained immediately after the measurement of R_T. R_T and R_{TPW} were corrected for self-heating, hydrostatic head and, if applicable the pressure effect. At least three different phase transitions (three freezing plateaux for Zn, Sn, In, three melting plateaux for Ga, three triple points for Hg and Ar) were performed. The individual results were delivered together with the calculated mean value.

All data were reported to PTB, including graphs of the freezing / melting plateau and immersion curves of the thermometer in the fixed-point cells, which were compared with the expected theoretical curves.

RESULTS OF THE COMPARISON

All measurements at Inmetro were performed during July and August of 2001. The measurements at PTB were made in January 2001 and January 2002. The results are listed in Table 3. The standard deviation given for the measurements at PTB was calculated using measurements before and after the measurements at Inmetro. No significant change in the thermometer properties was found at PTB comparing the measurements before and after the calibrations at Inmetro.

TABLE 3 – Results of the intercomparison (*W* values are for zero power).

	***W* (Zn)**	***W* (Sn)**	***W* (In)**	***W* (Ga)**	***W* (Hg)**	***W* (Ar)**
Average of *W* (PTB)	2.568 658 6	1.892 655 5	1.609 702 5	1.118 121 3	0.844 163 60	0.215 970 6
St. Deviation (PTB)	0.46E−6	0.44E−6	0.64E−6	0.1E−6	0.02E−6	0.95E−6
St. Dev. /mK (PTB)	0.13	0.12	0.13	0.10	0.05	0.10
Average of *W* (Inmetro)	2.568 644 2	1.892 647 1	1.609 698 3	1.118 120 0	0.844 163 4	0.215 979 1
St. Deviation (Inmetro)	0.57E-6	0.38E−6	0.11E−6	0	0.34E−6	0.56E−6
St. Dev. /mK (Inmetro)	0.16	0.10	0.03	0.00	0.08	0.13
W (Inmetro) − *W* (PTB)	−14.43E−6	−8.39E−6	−4.16E−6	−1.25E−6	−0.23E−6	8.25E−6
T (Inmetro)−*T* (PTB) /mK	−4.13	−2.26	−1.09	−0.32	−0.06	1.90

UNCERTAINTIES

The methods used by EUROMET for estimating the uncertainty of the realisation of ITS-90 are described in [7]. PTB and Inmetro follow these methods, where the budget for estimating the uncertainties of both laboratories contains the same relevant components.

The details of the uncertainty budget for Inmetro are given in Table 4. For the Ar triple point, specifically, the uncertainty adopted by Inmetro is based on an INM (France) certificate. For PTB only the expanded combined uncertainties are given; details on the uncertainty budget are available in [7].

TABLE 4. Measurement uncertainties of Inmetro. All values in mK.

Fixed point	Ar	Hg	$H_2 0$	Ga	In	Sn	Zn
Highest purity	6N	5N		7N	5N	5N	5N
Type B uncertainty components							
1. Chemical impurities, isotopes	0.55	0.23	0.03	0.058	0.318	0.21	0.918
2. Hydrostatic head correction	0.033	0.012	0.008	0.012	0.038	0.025	0.031
3. Heat-flux immersion error		0.003	0.005	0.003	0.050	0.040	0.107
4. Self-heating error	0.006	0.024	0.02	0.032	0.047	0.055	0.08
5. Bridge measurement	0.003	0.001	0.015	0.002	0.002	0.003	0.004
6. Standard resistor	0.010	0.010	0.010	0.002	0.010	0.010	0.010
7. Uncertainty propagation from TPW	0.060	0.2		0.08	0.199	0.50	0.567
Type B combined	0.55	0.38	0.04	0.10	0.34	0.55	1.09
Type A uncertainty component	0.043	0.002	0.01	0.002	0.004	0.007	0.006
Standard combined uncertainty	0.56	0.38	0.04	0.10	0.34	0.55	1.09
Expanded uncertainty, $k = 2$	1.11	0.75	0.09	0.21	0.68	1.10	2.18
Expanded uncertainty, $k = 2$ for PTB	0.62	0.27	0.16	0.26	0.89	0.91	1.31

ANALYSIS OF THE RESULTS

The results (resistance ratios and uncertainties) of both NMIs (Inmetro and PTB) were compared using the Normalised Error Ratio (NER) (see Table 5). If NER ≤ 1, the measurements are compatible.

The NER expression is shown below:

$$\frac{\text{Abs}\left[\text{Meas1} - \text{Meas2}\right]}{\sqrt{u_1^2 + u_2^2}} = \text{NER} \qquad (1)$$

where: Abs = Absolute value,
Meas 1 = Average of the Lab1 measurements,
Meas 2 = Average of the Lab2 measurements,
u_1 = Expanded Uncertainty of Lab1 measurements,
u_2 = Expanded Uncertainty of Lab2 measurements.

The averages of resistance ratios (W) from Lab1 (PTB) and Lab2 (Inmetro) were compared for each fixed point with W values corrected to zero power. W_{Zn}, W_{Sn} and W_{Ar} are incompatible (NER > 1) and W_{In}, W_{Ga} and W_{Hg} are compatible (NER ≤1).

Inmetro could have applied corrections to W_{Zn}, adding 1.4 mK to the measured W_{Zn}, based on a systematic difference in the sealed zinc cell (see Table 7)—the zinc freezing point of Inmetro reference cell is approximately 1.4 mK (mean value between NRC and CENAM temperature differences) lower than the freezing points of the NRC and CENAM zinc reference cells.

NOTE: The original certificate of the cell (EPC027) issued by LNE-France shows that its temperature is 1.2 mK below the LNE Zn reference cell with an uncertainty of 7 mK (3σ).

This procedure would have reduced the difference between PTB and Inmetro W_{Zn} values to 2.73 mK. However, it was decided not to apply any corrections. There is still not enough information to find the magnitude of this systematic error; we are only sure of its negative value.

TABLE 5. Analysis of the SPRT Calibration Results from Inmetro and PTB.

Resistance Ratio	W(Zn)	W(Sn)	W(In)	W(Ga)	W(Hg)	W(Ar)
W difference / mK	–4.13	–2.26	–1.09	–0.32	–0.06	1.90
PTB Uncertainty ($k = 2$)/ mK	1.30	0.90	0.90	0.25	0.30	0.62
Inmetro Uncertainty ($k = 2$) / mK	2.18	1.10	0.68	0.21	0.75	1.11
NER (Normalised Error Ratio)	1.63	1.59	0.97	0.97	0.07	1.50

RESULTS OF OTHER INTERCOMPARISONS OF PTB AND INMETRO

In the last few years several intercomparisons between National Metrology Institutes have been organised. The combination of some of them allow an indirect comparison of the Inmetro and PTB temperature scales. Tables 6 and 7 show some relevant results of fixed-point cell comparisons between NMIs. The results of a comparison between CENAM (Mexico) and PTB is described in [8].

These comparisons were performed between PTB (Germany), NIST (USA) and NRC (Canada)—participants in CCT K3—and between Inmetro (Brasil), NRC and CENAM (Mexico)—SIM participants.

TABLE 6. Results from CCT key comparison 3: difference between PTB and SIM participants in CCT K3. Uncertainties are given for *k* = 2.

Fixed Point	*T* (PTB) – *T* (NIST) / mK	*T* (PTB) –*T* (NRC) / mK
Zn	−1.19 ± 1.29	− 0.03 ± 1.40
Sn	0.20 ± 0.86	1.55 ± 1.15
In	− 0.31 ± 1.12	0.72 ± 1.16
Ga	0.20 ± 0.24	0.34 ± 0.36
Hg	− 0.05 ± 0.28	− 0.27 ± 0.33
Ar	− 0.23 ± 0.55	− 0.33 ± 0.62

TABLE 7. Results from bilateral comparisons: Difference between Inmetro and CENAM (Mexico) in 1997 [5], Inmetro and NRC (Canada) in 2000 [6]. Uncertainties are given for *k* = 2.

Fixed Point	*T* (Inmetro)* – *T* (CENAM) / mK	*T* (Inmetro)* – *T* (NRC) / mK
Zn	−1.52 ± 0.52	−1.3 ± 1.2
Sn	−1.85 ± 0.21[a]	−1.9 ± 0.6[a]
		0.12 [b]
In	− 0.23 ± 0.18	− 0.3 ± 0.6
Ga	− 0.17 ± 0.06	− 0.1 ± 0.6
Hg	− 0.14 ± 0.18	− 0.4 ± 0.6
Ar		0.8 ± 1.0[c]

*See serial numbers of Inmetro cells in Table 1.
[a]Sn sealed cell s/n EPC 032
[b]Sn sealed cell s/n EPC 047 (This cell is not included in the average)
[c]The uncertainty is an estimate based on experience [6]

EVALUATION OF THE RESULTS

The Inmetro sealed cells used in this bilateral comparison with PTB were the same ones, except for Ga and Sn, used in the comparisons Inmetro and CENAM (1997), and Inmetro and NRC (2000). Inmetro decided to use the same sealed cells, when possible, to verify the temperature differences of the Inmetro reference sealed cells. In general, all temperatures of Inmetro cells (except for argon) are lower than the temperatures of PTB cells (see Table 5), confirming the results shown in Table 7.

In the Ar triple point (INM-031 cell), we are still investigating the reasons for the incompatible results found, despite the same type and model of cell used both in Inmetro and PTB.

At the tin fixed-point, the Sn cell temperature (EPC 047) is 0.12 mK higher than the Sn cell at NRC (see Table 7) and 1.6 mK higher than the Sn cell EPC 032 (cell used in the comparison with CENAM). Then, if EPC 032 cell was used in the comparison with PTB, the difference would be probably higher than 2.26 mK.

The main reason for the large magnitude of temperature differences can be the purity of Inmetro cells, which were only 99.999 %, while at PTB 99.9999 % pure cells were used. In addition to this, Inmetro cells were sealed ones, where a different pressure from one atmosphere can be present and it is not possible to measure. At PTB open cells were used whenever possible.

CONCLUSIONS

According to [1], "the best method for comparison of realisation of the ITS-90 by laboratories is to compare not only the temperatures of fixed-point cells by a direct comparison in each laboratory, but also to compare realisations of these fixed points through the calibrations of one or more SPRT's at these points in the respective laboratories... ;" this last possibility was the purpose of this comparison between Inmetro and PTB. This procedure may show systematic errors present in the measurements performed in both laboratories and compares results obtained by different methods. In the case of the Inmetro's Zn and Sn cells, the results confirm that the temperature of these cells is lower than the higher purity cells. However, the temperature differences were higher than the differences found in other international comparisons. It shows that not only the temperature differences are high, but also the cell uncertainties can be, when different procedures for fixed-point realisations are adopted .

As a final conclusion, the Thermal Metrology Division of Inmetro decided to build their own cells, starting with Sn and Zn. In this case, better results can be expected, due to higher purity reference materials that can be used and the knowledge of the real pressure inside the cells. In addition to this, new comparisons are also planned in order to give more consistency to these results.

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REFERENCES

1. Mangum, B. W., Strouse, G. F. and Guthrie, W. F., "Summary of comparison of realizations of the ITS-90 over the range 83.8058K to 933.473K: CCT Key Comparison CCT-K3," *Metrologia* **39**, 179-205 (2002).
2. Preston-Thomas, H., Bloembergen, B., Quinn, T. J., "Supplementary Information for the International Temperature Scale of 1990," 1990, Monograph CCT/WG1 – BIPM, pp. 29-78.
3. Preston-Thomas, H., "The International Temperature Scale of 1990 (ITS-90)," *Metrologia* **27**, 3-10 (1990).
4. Fellmuth, B. and Tegeler, E., "Realization and Dissemination of the ITS-90 in the Temperature Range from 0.65 K to 933 K (660 °C)," *Proceedings of TEMPERATUR '98*, VDI-Verlag, Duesseldorf 1984, pp. 3-12.
5. Valencia-Rodriguez, J., "Report on the Comparison of Thermometric Fixed-Point Cells of the Nations of the Americas," edited by CENAM-Mexico, March 1999 (unpublished SIM document).
6. Ancsin, J., Tischler, M., Petkovic. S. G., and Santiago, J. F. N., "Comparing Fixed Points of the ITS-90 as Realized in Canada, Argentina and Brazil," *Metrologia* **38**, 555-566 (2001).
7. Fellmuth, B., Fischer, J., and Tegeler, E., "PTB Comments on Uncertainty Budgets for Characteristics of SPRTs Calibrated According to the ITS-90" in *Workshop of the CCT and EUROMET*, Berlin, 2001, pp. 7-8 (unpublished EUROMET document).
8. Noatsch, U., Tegeler, E., and Méndez-Lango, E., "Intercomparison of the Realisation of the ITS-90 in the Temperature Range –40 °C to 420 °C," in *Temperature: Its Measurement and Control in Science and Industry*, Vol. 7, edited by D. C. Ripple et al., AIP Conference Proceedings, Melville, New York, 2003.