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WORKING GROUP 4 REPORT TO CCT

25 June 2008

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Terms of reference : thermodynamic temperature determinations and extension of the ITS-90 to lower temperatures

New measurements of T-T_{90} :

The following recent measurements presented at TEMPMEKO 2007 were included into the data collection of WG4: acoustic gas thermometry at NIST [Ripple, Strouse, Moldover: Int. J. Thermophys. **28**, 1789–1799, 2007], dielectric constant gas thermometry at PTB [Gaiser, Fellmuth, Haft: Int. J. Thermophys. **29**, 18–30, 2008], noise thermometry at NIST [Labenski, Tew, Benz, Nam, Dresselhaus: Int. J. Thermophys. **29**, 1–17, 2008], spectral radiation thermometry at PTB [Noulkhow, Taubert, Meindl, Hollandt: Int. J. Thermophys. **29**, 2008], and constant volume gas thermometry at NMIJ [Tamura, Takasu, Nakano, Sakurai: Int. J. Thermophys. **29**, 31–41, 2008].

During the meeting at CCT-24, members of the working group and of the task group TG-SI announced that several new measurements are planned for the near future: At NIST, acoustic gas thermometry will be extended to the range between 550 K and 700 K. In addition, noise thermometry at 77 K and between 700 K and 930 K is planned for the first half of 2009 and dielectric constant gas thermometry at the Hg and Ga fixed points. LNE-INM will repeat acoustic gas thermometry between 77 K and the triple point of water (TPW) in 2008 and in the first half of 2009 extend the temperature range from 77 K down to 4 K. PTB will measure with dielectric constant gas thermometry in the framework of the Boltzmann project around the TPW. Related to the Boltzmann project NPL and INRIM will employ acoustic gas thermometry and measure thermodynamic temperatures, NPL around the TPW, INRIM only at the TPW. At NIM measurements are under way with noise thermometry at the Ar point and with acoustic gas thermometry at the TPW. Absolute radiation thermometry will be performed at NPL to measure the Au and Cu fixed points and at LNE-INM to measure the Cu point. The same method is used at PTB in 2009 between the Zn and Al fixed points, for the Au and Cu fixed points and later also at lower temperatures.

Extension of the ITS-90 to lower temperatures:

The document 'Supplementary Information for the realization of the PLTS-2000' has been prepared by a task group of Working Group 4. The document has been accepted by CCT WG's 1 and 4 for inclusion in the CCT pages of the BIPM website.

The CCT formally approved the document in 2007 by e-mail, and it was posted on the BIPM web-site in the public area of CCT. With the authorisation of the CCT in 2005, the group has also prepared a paper 'Realization of the ^{3}He Melting Pressure Scale, PLTS-2000' for wider circulation, and this has now been published by the Journal of Low Temperature Physics, **149**, 156-175, 2007. The members of the task group and the authors of the paper are R. L. Rusby, B. Fellmuth, J. Engert, W. E. Fogle, E. D. Adams, L. Pitre and M. Durieux.

WG4 spreadsheets on T-T_{90} :

The main field of work was the update and critical review of the data collection on measurements of T-T_{90}. This task was given priority in view of the envisaged inclusion of corresponding data in the Mise en pratique for the definition of the kelvin. We note that no data have so far been reported for measurements of T with respect to the ITS-90 as interpolated by SPRTs at any temperature below 77 K. Some constant volume gas thermometry data which originally provided values of (T-T_{68}) have been converted to (T-T_{90}). For all of the following entries in the data collection the uncertainties were reviewed and the conversion of older data to ITS-90 was documented.

The list below is ordered along the employed methods and summarizes all experiments taken into consideration including the covered temperature ranges or fixed points. In parentheses the data files with the conversion calculations are given for reference.

Constant Volume Gas Thermometry:

Berry: Metrologia **15,** 89-115, 1979	4.2 K to 24.6 K
(converted in *CCT WG4 Berry T75-T90(ICVGT)rev2a*)	
Kemp, Kemp and Besley: Metrologia **23**, 61-86, 1986	14 K to 287 K
Steur and Durieux: Metrologia **23**, 1-18, 1986	4.2 K to 24 K
(converted in *KOL gas thermometry*)	24.5 K to 100 K
Guildner and Edsinger: J Res Nat Bur Stands **80A**, 703-738, 1976	273 K to 730 K
	not used for mean
Edsinger and Schooley: Metrologia **26**, 95-106, 1989	505 K to 904 K
(converted in *CVGT Results and Uncertainties Version 1*)	Al
Astrov, Belyansky and Dedikov: Metrologia **32**, 393-395, 1995/96	4.2 K to 24.4 K
(converted in *Astrov Gas Thermometry_to_VNIIFTRI*)	24.5 K to 309 K
Tamura, Takasu, Nakano, Sakurai: Int. J. Thermophys. **29**, 31–41, 2008	4.2 K to 22.5 K

Acoustic Gas Thermometry:

Ewing and Trusler: J. Chem. Thermodynamics **32**, 1229-1255, 2000	90 K to 301 K
Moldover, Boyes, Meyer and Goodwin: J. Res. Natl. Inst. Stand. Technol. **104**, 11-46, 1999	
Ripple, Strouse, Moldover: Int. J. Thermophys. **28**, 1789–1799, 2007	217 K to TPW
	TPW to 552 K
Strouse, Defibaugh, Moldover and Ripple: TMCSI, vol. 7, 2003, 31-36	Ga, In, Sn
Benedetto, Gavioso, Spagnolo, Marcarino and Merlone: Metrologia **41**, 74-98, 2004	234 K to 380 K
Pitre, Moldover, and Tew: Metrologia **43**, 142-162, 2006	7 K to 24.6 K
	77.7 K to TPW

Spectral Radiation Thermometry:

Fischer, Jung: Metrologia **26**, 245-252, 1989	Al, Ag, Au
Fox, Martin and Nettleton: Metrologia **28**, 357-374, 1991	Al, Ag, Au
Stock, Fischer, Friedrich, Jung and Wende: Metrologia **32**, 441-444, 1995/96	
Taubert, Hartmann, Hollandt and Fischer: TMCSI, vol. 7, 2003, 7-12	
Noulkhow, Taubert, Meindl, Hollandt: Int. J. Thermophys. **29**, 2008	692 K to 1235 K

Yoon, Gibson, Allen, Saunders, Litorja, Brown, Eppeldauer and Lykke: TEMPMEKO 2004, 59-70	Ag, Au
Goebel, Yamada, Stock: TEMPMEKO 2004, 91-99	Cu
Various other sources: Report to WG4 prepared by Rusby 2008	Cu

Total Radiation Thermometry:

Martin, Quinn, Chu: Metrologia **25**, 107-112, 1988 (converted in *CCT WG4 QM data MdP*)	144 K to 375 K not used for mean

Noise Thermometry:

Edler, Tegeler and Zimmermann: TMCSI, vol. 7, 2003, 13-18	Cu presently not used for mean
Labenski, Tew, Benz, Nam, Dresselhaus: Int. J. Thermophys. **29**, 1–17, 2008	Zn

Dielectric Constant Gas Thermometry:

Luther, Grohmann, Fellmuth: Metrologia **33**, 341-352, 1996	
Gaiser, Fellmuth, Haft: Int. J. Thermophys. **29**, 18–30, 2008	4.2 K to 24.6 K

Special attention was given to the following problems:

Low Temperature Constant Volume Gas Thermometry

Results from Acoustic Gas Thermometry (AGT) suggest deviations of the ITS-90 from thermodynamic temperature in the range below 273 K, with absolute values that rise to a maximum of almost 10 mK at 150 K. These values seem to corroborate (revised) results from Astrov´s Constant Volume Gas Thermometry (CVGT), initially indicating such deviations. Two other CVGT experiments in the range (Steur, up to 100 K and Kemp, up to 287 K), together with the unrevised Astrov CVGT and Quinn and Martin´s total radiation thermometry, constituted important ingredients for the construction of the ITS-90. Leaving aside the puzzle about the reason for Astrov's change in his thermal expansion coefficient, the principle problem is caused by the disagreement between the gas thermometry work of Astrov and of Kemp. WG4 examined several effects that could have contributed to the difference:

a) Virial coefficients:
In the **absolute** pV-isotherm CVGT method, the gas bulb at a constant but unknown temperature T is filled with a series of increasing amounts of gas to obtain a series of pressures p. The quantity pV/NR may be plotted as a function of N/V. The intercept of the resulting isotherm is the temperature T. For this method, it is not necessary to know the virial coefficients because the extrapolation to zero pressure is made by fitting a virial expansion to the experimental data. The usual method used to determine the amount of gas is to set up a bulb at a known reference temperature T_r, e.g. 273.16 K, and to calculate the amount of gas in the bulb of volume V_r at initial pressure p_r, which requires knowing the virial coefficients at T_r. More accurate is the method applied by Berry in 1979 to determine only the ratios of pressure p/p_r and volume V/V_r, where p is the pressure after connecting the evacuated measuring bulb to the reference bulb.

Relative pV-isotherm CVGT is performed by measuring the pressures p_r and p of the same gas sample in the thermometer bulb at a known thermodynamic reference temperature T_r and the unknown temperature T. In carrying out pV-isotherm CVGT at low temperatures, it is cumbersome to have to determine the amount of gas always with reference to the triple point of water. Instead, once a single temperature T_r has been established in the low-temperature range, the quantity of gas at neighbouring temperatures can be established by reference to the known quantity at T_r. Extrapolation of isotherms to zero molar density is very time consuming as the measurements have to be carried out at quite a large number of densities. If the virial coefficients $B(T)$ and $C(T)$ are known as accurately as necessary at T_r and in the temperature range of interest, it is easier to perform CVGT along an isochore (V=const.) and to calculate the temperature applying the virial expansion for $T = T_r\, p/p_r$.

Often, several methods are combined to cover a sufficiently large temperature range. The following methods were applied: Berry (1979, absolute and relative isotherms, isochores), Kemp *et al* (1986, relative isotherms, isochores), Steur and Durieux (1986), and Astrov *et al* (1989) (both isochores). This explains that the uncertainty contributions to thermodynamic temperature arising from the virial coefficients can be very different. Therefore, the question of recalculating the results by using recent values of virial coefficients was put aside. It would be very difficult to change the original values of the uncertainties for the virial coefficients with convincing justification.

b) Cold work:
The effect of cold work on the linear thermal expansion coefficient ought to apply to all (low-temperature) gas thermometry experiments, since all used (OFHC) copper bulbs. It is therefore unclear why some experiments should be more subject to this effect than others. It is reasonable to expect that other gas thermometers (with a bulb of the same material) are affected in a similar way, in the same direction, thus diminishing its effect on the differences between gas thermometers. It was concluded that the effect of cold work could contribute to the uncertainty in the linear thermal expansion coefficient by 0.3%, which equals about 1% in the change of volume. This would be equivalent to about 1 mK only at 150 K. Thus, the differences between the data of Astrov and of Kemp remain significant.

c) Gold layer:
Starting with the NPL gas thermometry of Berry, bulbs to be used at low temperatures (< 30 K) have been gold-plated in order to reduce adsorption effects, occurring at the lowest temperatures, as much as possible. This procedure has been followed by both Steur and Kemp, but ***not*** by Astrov. Although very little is known about the thermal expansion coefficient of gold-plated copper, it may well be possible that the gold-plating somehow inhibits the natural expansion of copper, resulting in a smaller volume than assumed by the experimenter, who then calculates a too high temperature for his gas thermometer. Such an effect ought then to result in a linear deviation (expressed in mK) with temperature, but due to the presence of two fixed points, at 0 K and at 273.16 K, this behaviour changes into a quadratic one, which is roughly the observed tendency, assuming that AGT represents thermodynamic temperature better (although AGT already returns into agreement with ITS-90 at about 25 K, unlike the supposed quadratic tendency).

In this context, it might be worthwhile to reconsider the CVGT isotherm data of Weber [PTB Bericht PTB-W-47, 1991], which were not officially published because of the apparent conflict with other data available at the time (at 90 K, 8 mK below Kemp and Steur, from his Table 7). His bulb was ***not*** gold-plated [Anderson and Neubert, Inst. Phys. Conf. Ser. No. **26**, 38-43, 1975], so following the reasoning about the gold-plating effect one would expect agreement with the (revised) VNIIFTRI data, but Weber’s value at 90 K falls actually well below those of VNIIFTRI, and agree surprisingly well with the acoustic data.

The gold layer of Kemp's bulb has a thickness of 0.05 mm. Both the Berry, NPL and Steur, KOL gas thermometers mention exactly the same thickness for the gold layer. With the dimensions taken from the KOL paper, a total enclosed volume of 1000 cm^3 is estimated. The gold layer amounts to about 1% of the total solid. Applying the dimensions of Kemp's bulb, however, an amount that is about half of that, 0.5% is calculated. It is noted here that the outer surface of Kemp´s bulb was also coated with a very thin layer of gold. As to Steur´s KOL gas thermometry (which traces Kemp´s NML gas thermometry rather closely), there is a detail related to the gold-plating that has never been written down in any publication. The KOL bulb has been gold-plated twice, since after the first time the bulb had been heated, for baking purposes, to a too high temperature, with the result that nearly all the gold was absorbed inside the copper main body. Therefore, a second gold-plating was applied, with the same thickness. If it would be reasonable to assume that the first and second gold 'layers' maintained some kind of continuity, the question is whether a bi-metallic construction still describes the situation in the sense of two layers of different metals. With the KOL gas thermometer having double the amount of gold as the NML gas thermometer, this fact was applied to estimate an upper limit for the effect of gold-plating, amounting to no more than 2 mK at 100 K.

A look into the data collected by Touloukian regarding the thermal expansion of copper and of gold gives further insight. These tables report recommended values for a limited set of temperatures. From these, one finds a $\Delta L/L_0$ value at 100 K of -0.282 % for Copper and of -0.260 % for gold, where L_0 denotes the length at 293 K. The *difference* between the two is 0.022 % or 220 ppm, or roughly 660 ppm in $\Delta V/V$. At 100 K, the volume would have shrunk more if all the bulb were made of copper. Therefore, the gold-plating would have hindered the natural shrinking of the copper bulk, especially since it was applied to the inside surface. The maximum effect would of course be obtained if one assumes a copper bulb while it really is a gold one. The difference in volume shrinkage, $\Delta V/V(\mathrm{Cu})-\Delta V/V(\mathrm{Au})$ of 660 ppm translates into a temperature equivalent of 66 mK at 100 K. However, only a tiny part of the wall is made of gold, actually a volume fraction of 0.5 % to 1 %, leading to a temperature effect between 0.33 mK and 0.66 mK. In order to arrive at the effect that we are looking for of about 8 mK at 100 K, the influence of this tiny fraction has to increase by some process by a factor of 12 to 24 which seems to be not reasonable.

It is concluded that the error for Kemp´s bulb would be a maximum around 150 K of about 2 mK to 3 mK which leads to an increase of the original uncertainties by about 50%. Although this shows that the effect cannot explain the larger difference between Kemp and Astrov, it is significant in the context of the work of WG4. Therefore, WG4 remains concerned about the effect of the alloy layer at the interface between the copper and gold; it could well be a lot stiffer and have a very different expansion coefficient. This might be a major problem if the bulb was annealed with the gold plate so the gold diffused into the copper. However, there was agreement that for the exclusion of data-sets WG4 must adhere to published data where possible. Consequently, the data-sets of VNIIFTRI, NML and KOL cannot be excluded from consideration, on the basis that no published data is available on the gold-plating effect on thermal expansion.

NBS/NIST Constant Volume Gas Thermometry from 0 °C to 660 °C

In his 1990 publication [1, Schooley, J. F., J. Res. Natl. Inst. Stand. Technol. **95**, 255 (1990)], Schooley reviewed the history and the results of CVGT at NBS/NIST. Schooley reports that CVGT was a continuing activity at NBS/NIST that began in 1928 and concluded in 1990. The earliest NBS CVGT is documented only in internal NBS reports. Later, significant publications in the archival literature include those of Stimson, Guildner and Edsinger [2, Stimson, H. F., "Precision resistance thermometry and fixed points," Temperature, Its Measurement and Control in Science and Industry, 2, Wolfe, H. C., Ed., Reinhold Pub. Corp., New York (1955) pp. 141-168] and [3, Guildner, L. A. and Edsinger, R. E., J. Res. Natl. Bur. Stand. (U.S.) **77A**, 383 (1973)], Edsinger and Schooley [4, Guildner, L. A. and Edsinger, R. E., J. Res. Natl. Bur. Stand. (U.S.) **80A**, 703 (1976)] and Schooley [5, Edsinger, R. E. and Schooley, J. F., Metrologia, **26,** 95 (1989)]. Schooley's review [1] shows that the NBS/NIST gas thermometer underwent several stages of improvements, particularly as problems were discovered when the thermometer was operated at the higher temperatures. This point of view is evident in Schooley's section heading "8. Most Recent Version of the NBS/NIST Gas Thermometer". Although Schooley [1] *does not say so explicitly*, the most recently published results [1] must be regarded as superseding earlier results including Guildner and Edsinger [3,4] and Edsinger and Schooley [5].

Schooley [1] states that many components of the NBS/NIST gas thermometer where changed between the publication by Edsinger and Schooley [5] and the earlier publications. Eight of these changes are: (1) replacing the very homogeneous thermal environment of the gas bulb from immersion in thermostated baths of salt solutions to the less-homogenous environment of a multi-shell thermostat in an oven that could operate at higher temperatures than the salt baths, (2) altering the system for purifying the helium, (3) improving the platinum resistance thermometry, (4) replacing the gas bulb (twice), (5) altering the data acquisition procedure, (6) improving the data-acquisition software (7) improving the technique for balancing the pressure inside the gas bulb with a counter-pressure outside the bulb, and (8) improving the measurements of the thermal expansion of the alloys used to manufacture the gas bulb.

Schooley [1] does not state which, if any, of the eight changes enumerated above explains the inconsistencies between the 1989 data of Edsinger and Schooley [5] and the 1976 data of Guildner and Edsinger [4]. A careful reading of all publications concerning the NBS/NIST gas thermometry indicates that the gas bulb was the source of particularly vexing problems. After completing their measurements, Guildner and Edsinger discovered that the top of their cylindrical gas bulb had been accidentally fabricated from the alloy 80 Wt% Pt and 20 Wt% Rh, while the sides and the bottom of the bulb had been fabricated from the alloy 88 Wt% Pt and 12 Wt% Rh alloy. Guildner and Edsinger [4], and later Edsinger and Schooley [5] measured the thermal expansions of samples of these two alloys along single directions and showed they differed by only small amounts. Guildner and Edsinger [4] asserted, without details, that the small differences of the thermal expansions did not affect their measurements. Schooley [5] emphasized: (1) CVGT results are very sensitive to the thermal expansion of the bulb, (2) a bulb constructed out of two alloys changes its shape as it expands, and (3) a spherical bulb has advantages compared with the cylindrical bulbs that were actually used. Because of time limits, Edsinger and Schooley could not incorporate a spherical bulb into the NBS/NIST gas thermometer. They constructed two cylindrical bulbs entirely out of the alloy 80 Wt% Pt + 20 Wt% Rh. In the range 230 °C to 660 °C, Edsinger and Schooley discovered a temperature-dependent drift in the apparent volume of their first gas bulb [1, Fig. 19]. They cut the drift rate in half by replacing the 1 mm thick lower end cap of the gas bulb with a 2.5 mm thick cap. Edsinger and Schooley compensated for the remaining drift by measuring the apparent volume as a function of time at each test temperature and then extrapolating the data back to the time when the bulb was first heated to the test temperature. Because they were aware of drifts, Edsinger and Schooley returned the gas thermometer to 0 °C after each test temperature. In contrast, Guildner and Edsinger detected no drift up to 457 °C and they measured successively higher test temperatures without returning to 0 °C.

In the region of overlap (230 °C to 457 °C), the more recent NBS/NIST gas thermometry results [1,5] are not consistent with the earlier results [3,4] within their combined uncertainties. Because of the continuity of the NBS/NIST program and because of the progressive discovery and mitigation of gas-bulb-related problems, the most recently published results [1,5] must be regarded as superseding earlier results [3,4]. Because the earlier data [3,4] below 230 °C were acquired with apparatus and procedures similar to those that led to the inconsistent results at 230 °C, the uncertainties claimed for the NBS/NIST gas thermometry results below 230 °C are not reliable.

Total radiation thermometry of Quinn and Martin

Here, a summary of e-mails with Terry Quinn prepared by Michael DePodesta is reported. In the original Quinn and Martin (QM) paper and the subsequent Martin, Quinn and Chu (MQC) paper, errors were made in determining some of the factors that enter into the calculation of σ, the Stefan Boltzmann constant. Knowing what Terry Quinn knows now, he would revise his estimate for σ. The revised value is some 3.5 parts in 10^4 below the CODATA value. This underestimate can be explained in several ways that fall into two categories:

Error type 1: QM could have made a mistake in the estimation of the **coupling of the calorimeter and the radiator**. Suppose the calorimeter measured 1 mW of radiant power with the radiator at the triple point of water. If they estimated that the effective emissivity/absorptivity factor was 0.9999 and the actual factor was 0.9998, then they would infer that a perfect blackbody would emit 1.0001 mW, but in fact a perfect black body would emit 1.0002 mW. By using their incorrect estimation, they would infer a value of σ that would be too small.
Error type 2: One of QM's errors appears to have been overestimating the **efficiency of the light trap**. Suppose the calorimeter measured 1 mW of radiant power with the radiator at the triple point of water. If they estimated that the light trap was perfect, then they would infer that the emitted power from the radiator into the relevant solid angle was 1 mW. However, if the light trap was not 100% efficient, some of the power emitted outside the relevant solid angle would additionally reach the calorimeter. This would cause QM to infer a value of σ that would be too large.

In retrospect, QM appears definitely to have errors of the second kind, and since their estimate for σ is low, (if we assume for the moment the CODATA value is correct), we can infer that they must also have had other errors that have an effect similar to the errors of the first kind described above. This is the situation with regard to estimation of σ, but Terry Quinn pointed out that it is difficult to understand how these errors can have an effect on the thermometry experiments. When used as a primary thermometer, the cryogenic calorimeter is essentially a comparator between emitted power at an unknown temperature and emitted power at 273.16 K. These power ratios should be robust against a wide class of errors affecting absolute power measurements. To produce significant systematic errors requires a dependence of the corrections on temperature, and this probably implies a rather striking dependence on wavelength, which seems at first sight implausible. WG4 asked whether the described errors could change the slope of the data (T-T_{90}) versus T. The answer of NPL was 'Yes, it could change the slope, but whether the circumstances in which it could change the slope (strong wavelength-dependence of certain retro-reflection terms) apply is simply not known'.

To bring the QM and MQC temperature estimates into line with the more recent acoustic data would require a correction to their data that is outside any known error. This is not to say that the data must be correct, but it does mean that neither Terry Quinn nor Nigel Fox can give a plausible explanation for how the temperature estimates could be so far out, and although with hindsight they might enlarge their uncertainties, they would not enlarge them so greatly as to agree with current acoustic data.

NPL thinks in all probability that the acoustic data is basically correct, but it is a concern that all the data that indicates the QM and MQC work is in error rest only on a single technique (albeit with different implementations and gases and many internal consistency checks). NPL suggests that in surveys of experiments, the total radiation thermometry data should be retained with uncertainties as published, even if we now believe that either the data or the uncertainty estimates are unreliable. However, because we lack a reliable estimate for the uncertainty of the data, NPL suggests the QM and MQC data should be excluded from calculations of a consensus estimate of $T - T_{90}$.

Converting of temperatures measured in terms of NPL-75

Conversion will be needed to calculate (T_{gas} - T_{90}) for Astrov's, Berry´s and Steur´s gas thermometry data points where they give ($T_{\text{gas}} - T_{\text{NPL-75}}$), unless they have data relating their rhodium-iron thermometers to the ITS-90 fixed points. There are two main routes for the conversion, which differ mainly according to which sub-range of the ITS-90 is used. Both routes make use of the long-term stability of thermometers calibrated against different temperature scales. The first uses **SPRTs above 13.8 K**, which is called $T_{\text{NPL-75}}$ - T_{90} via IPTS-68. The second uses **rhodium-iron thermometers**, in principle applicable over the full range of the NPL-75, **2.6 K to 27.1 K**. In effect, the latter leads to differences $T_{\text{NPL-75}}$ - T_{90}(ICVGT).

In the **first route,** one can access the T_{68} calibration values from the Ward and Compton comparison [Ward and Compton, Metrologia **15**, 31-46, 1979] and the T_{90} ones from key comparison CCT-K2. Rusby used Berry's data for $T_{\text{NPL-75}}$ - T_{68}(213865) above 13.8 K [Berry, Metrologia **15**, 89-115, 1979, Tables 12, 13 and 14], and calculated ($T_{\text{NPL-75}}$ - T_{68}) - (T_{90} - T_{68}), for SPRT 213865 (which Berry used in his experiments) and also 1728839 (which is the NPL reference thermometer for the IPTS-68). To calculate (T_{90} - T_{68}) for 213865, Ward and Compton's comparison calibration data were used to calculate W_{90} at the fixed points (with interpolation to obtain the values at the Ne and Hg points), and so the ITS-90 coefficients were generated (fig. 1).

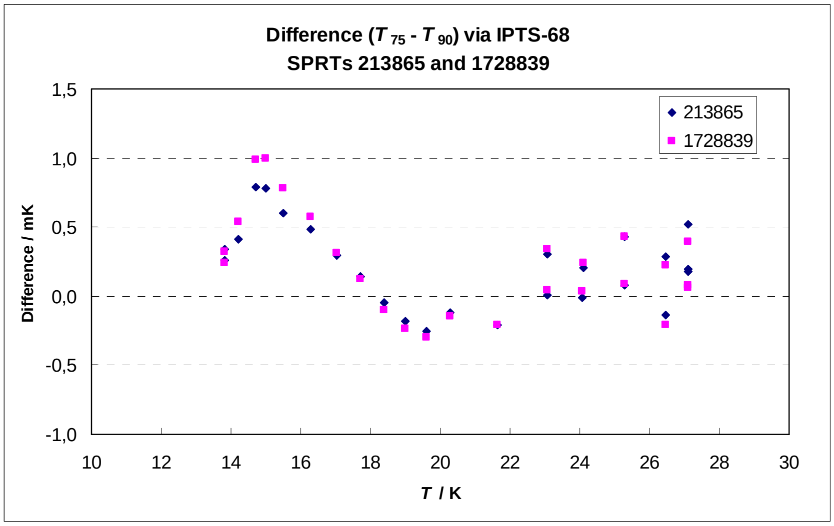

Figure 1: The graph shows the results of the calculations of ($T_{NPL\text{-}75}$ - T_{90}) **via IPTS-68**. The non-uniqueness effect is small, being only that due to the ITS-90. It is noted that the overall pattern is reminiscent of the ITS-90 sub-range differences (SPRT versus ICVGT) published by Meyer, Strouse and Tew in Tempmeko 1999, p. 93.

There is bound to be a certain level of ambiguity in the differences for temperatures that are not defining fixed points for both scales due to the non-uniqueness of the respective temperature scales, with the non-uniqueness of the IPTS-68 being substantial between the fixed points. At the common defining fixed points (hydrogen triple and boiling points, oxygen triple point), the values ought to agree fairly well with the defined differences from [Rusby, Metrologia, **28**, 9-18, 1991]. For the fixed points that are not common defining fixed points of both scales (triple point of neon, triple point of argon, triple point of mercury), the tabulated scale differences for T_{68} temperatures of 24.5616 K, 83.798 K, 234.3082 K agreed within 0.9 mK with the present calculation.

In the **second route,** the differences were deduced between NPL-75 and the ITS-90 (ICVGT), i.e. ITS-90 as interpolated using a CVGT. To do this, one has to find the differences at the three fixed points, and then deduce a quadratic correction equation. Contemporary (1970s) information at the triple points of hydrogen and neon comes from comparisons of NPL-75 with calibrated SPRTs. What we can use is the differences between the NPL-75 values of the fixed points and those specified in the ITS-90. Thus, Berry's data can be used to see how NPL-75 differed from what we now call the ITS-90 (in the ICVGT sub-range). Berry gave data at the boiling point of He and the triple point of H_2, but we still have to interpolate a value of $T_{NPL\text{-}75}$ - T_{68} at the triple point of Ne, using his Table 12, and then apply differences for T_{90} - T_{68}, deduced as above. The triple point of neon had not been realised in 1975 and Berry did not make measurements at that specific temperature.

Method 1 deduces $T_{NPL\text{-}75}$-T_{90}(ICVGT) using Berry's documented data at the helium and hydrogen fixed points, and near the neon point. **Method 2** uses the comparison that Ward and Rusby did in February 1977, including all of Berry's thermometers and Ward's master cSPRT 1728839. This provides a more direct link between NPL-75 and IPTS-68(NPL), and was also more precise because Ward used a Guildline bridge rather than a dc potentiometer. The differences used in Methods 1 and 2 at the triple point of H_2 come from the data and at the triple point of Ne from interpolation. These, together with the zero at 4.2221 K, are then used to generate quadratic equations for $T_{NPL\text{-}75}$ - T_{90}(ICVGT). Both methods give similar results, but interpolation using Ward's data is more reliable.

There is another possibility, **Method 3**. Although the triple point of Ne was not available at the time, Ward did realise it in 1978-79 (see CCT/80-51). The result was T_{68}(1728839) = 24.56188 K. From this, $T_{NPL\text{-}75}$ is derived and hence $T_{NPL\text{-}75}$ - T_{90} = 0.49 mK (Method 3.1). Later, about 1980-81, Rusby measured four neon cells in the CCT comparison of cells, and found an average value of T_{68} = 24.56160 K (BIPM Monograph 84/4, p. 201), which leads to $T_{NPL\text{-}75}$ - T_{90} = 0.21 mK (Method 3.2). Methods 3.1 and 3.2 have the virtue of **using direct measurements at the triple point of Ne**, though from slightly later experiments. Note that if everything is completely consistent, adding T_{90} - T_{68} to the T_{68} value would give 24.5561 K, Method 3 would be equivalent to Method 2, and the circle would be closed. Neither of the two triple point realisations leads to this result, though the second is similar to what NPL has subsequently found. If it is representative, then the mismatch may indicate a real offset in the ITS-90 value, or otherwise just experimental differences due to isotope effects, etc. All three methods are shown in fig. 2.

For the present purpose, Rusby recommended that WG4 adopt the following:

T_{90} = 4.2221 K : $T_{\text{NPL-75}} - T_{90}$ = 0.00 mK
T_{90} = 13.8033 K : $T_{\text{NPL-75}} - T_{90}$ = 0.33 mK (using the comparison data point)
T_{90} = 24.5561 K : $T_{\text{NPL-75}} - T_{90}$ = 0.21 mK (based on comparison of Ne TP cells, Method 3.2) .

The equation for this is $(T_{\text{NPL-75}} - T_{90})$ / mK = $- 2.241\times10^{-3}\times T_{90}^{2} + 7.466\times10^{-2}\times T_{90} - 2.753\times10^{-1}$. Regarding data from other authors who reference their results to NPL-75 (Astrov, Steur), WG4 decided that the above equation is added to their differences $(T_x - T_{\text{NPL-75}})$ to obtain $(T_x - T_{90})$, unless they have their own (contemporary) information about $T_{\text{NPL-75}} - T_{90}$ at the defining points.

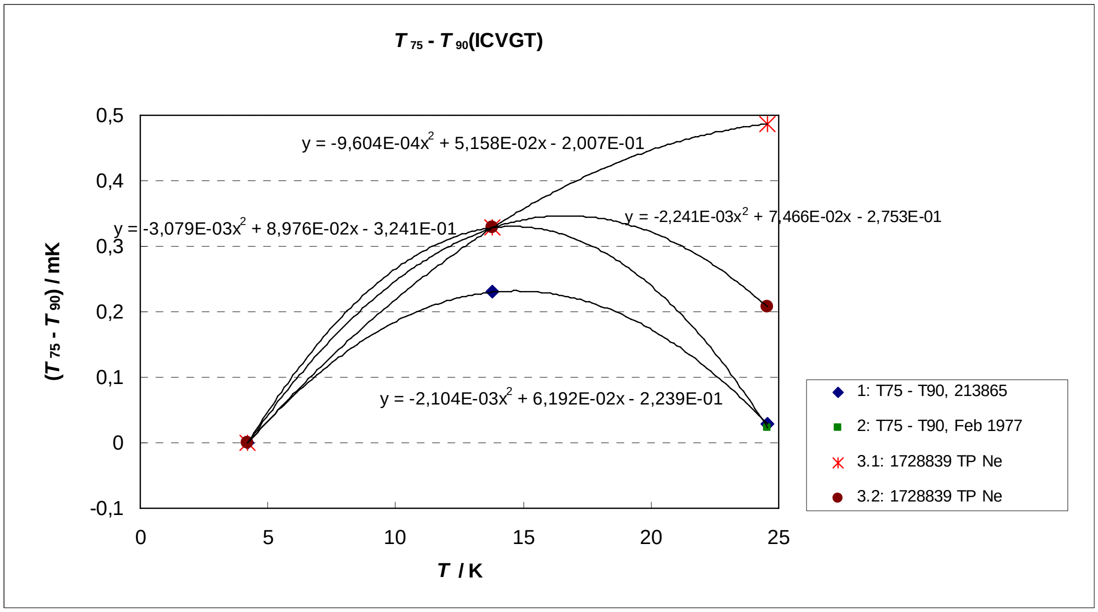

Figure 2: Comparison of different methods for converting NPL-75 to ITS-90 following the second route.

As indicated above, there is some subjectivity in this choice. However, Rusby believes it gives a reasonable representation of the situation as Berry left it, which is of course a retrospective calculation of T_{90}. However, we ought also to check how some of the available copies of NPL-75 compare with ITS-90 realizations, and the suggested differences are significantly different from the 'correction equation' NPL derived in the mid-1990s for Thermometer 221481 (one of the three used in the NPL-75 experiments) following its calibration at the triple points of hydrogen and neon (see CCT/93-15). While the difference at the triple point of Ne is similar to what NPL found in their Ne cells around 1990, their cell H2-1 gave $(T_{\text{NPL-75}} - T_{90}) \sim 0.6$ mK, see [Head and Rusby, TMCSI 1992, pp. 161-163]. As it seems that the Rh-Fe thermometer 221481 has been stable, one can only suppose that the change is due to the use of different hydrogen samples; new gas was certainly obtained for the later work. This conclusion is consistent with the observation by Fellmuth et al., Metrologia **42**, 171-193, 2005, that the NPL cell is on the low side, compared with the average of cells they measured. Other thermometers, and other ITS-90 realizations, would of course lead to different results, and it would be interesting to know how typical the result for 221481 is. Recalibration at the fixed points would be advantageous.

Rusby included estimates of the uncertainties in $(T - T_{90})$ as determined using NPL-75, i.e. including the thermodynamic uncertainties in the NPL-75 as well as in the resistance thermometer comparisons and in the fixed point realizations. The four components are as follows:

(i) Type A uncertainties in the Rh-Fe curve-fits [Berry, Figure 20], which are represented by (0.08 - 0.0018T) mK below 20.3 K and (0.16/12) × (T-16) mK above 20.3 K, at $k = 1$,
(ii) Type B uncertainties [Berry, Figure 21], which are represented by (0.2 + 0.044T)/3 mK,
(iii) the comparison uncertainties adapted from Ward and Compton 1979, Fig 3: a constant of 0.15 mK ($k = 3$) was taken, which allows for the decrease in uncertainties in cSPRT measurements as the temperature increases being offset by increased uncertainties with Rh-Fe thermometers, and
(iv) the uncertainties in the realisations of the IPTS-68, for which was taken 0.14 mK at the triple point of H_2 and 0.2 mK at the H_2 boiling points and at 24.5 K. It is noted that the uncertainty in the scale differences ($T_{\mathrm{NPL\text{-}75}}$ - T_{90}) to be used for conversion of other data excludes the systematic uncertainties in NPL-75, and is about half that in (T - T_{90}).

Employing the first route of conversion based on cSPRTs down to 13.8 K, artefacts of IPTS-68 and non-uniqueness effects can be seen around the hydrogen triple point, especially in Astrov´s data (see fig. 4). In the absence of new data with respect to SPRTs, all data presented for T-T_{90} below 24.5561 K are based on the ITS-90 interpolated by ICVGTs and Rh-Fe thermometers following the second route. As shown in fig. 3, with this choice a smooth interpolation function could be applied. For some data sets, two different individual interpolation functions are used to cover the whole temperature range.

Consensus estimate of $T – T_{90}$ by averaging of data

The conversion of the differences relating them to T_{90} is completed now for all measurements above 4.2 K. The upper end of the averaging process is the copper point. The treatment of T-T_{90} below 4.2 K must wait as WG4 wanted to finish first the higher temperature ranges.

It was decided to exclude the Quinn and Martin total radiation measurements from the averaging procedure as explained above. Following the investigations of Moldover, WG4 decided to exclude the measurements of Guildner and Edsinger from the averaging process. The gas thermometry results of Astrov, Steur, and Kemp are retained for the averaging using the recent uncertainty re-calculations. The relative radiation thermometry of Jung and Fischer at the Al, Ag, and Au points and of various other sources at the Cu point (Righini et al, 1972, Coates and Andrews, 1978, Ricolfi and Lanza, 1977, Jones and Tapping, 1982) are included to benefit from their low uncertainties.

For the averaging process, it was decided to construct first smooth interpolating functions for each of the different data sets. These functions will allow us to easily average the values of T-T_{90} at a pre-defined set of temperature points including the fixed points of ITS-90. The concept of individual interpolation functions avoided also the over-estimation of a measurement that was made at narrowly–spaced temperatures. Concerning the number of temperature points forming the mean, it started with the defining fixed points of ITS-90 and then additional points were selected. The additional points are often secondary reference points; where such points are not available the temperatures have been arranged to cover the scale in approximately equidistant steps, these intervals being more narrow in the low temperature range to prevent the smooth curve from oscillating (see table). Several arrangements have been tested but, in general, more points do not increase significantly the content of information compared to the required effort.

The following members of WG4 prepared the respective interpolating functions and for reference in parentheses the names of the data files including the functions and coefficients are given:

Steur : Steur and Durieux; Benedetto et al. (Fits to KOL and INRIM AGT, 12 Nov 2007)
Moldover: Edsinger and Schooley; Moldover, Ripple et al. (WG4 T-T90 Ripple, Strouse, Moldover, 10 Oct 2007)
Hill: Astrov et al.; Kemp et al. (Astrov and Kemp Interpolations, 24 Aug 2007)
Fischer: Stock, Taubert, Noulkhow et al. (mean_u_T-T90_PTB, 12 Dec 2007); Luther, Gaiser et al. (DCGT_ITS-90_1996_2007, 03 Dec 2007)
DePodesta: Ewing and Trusler (CCT WG4 Report on Ewing and Trusler, 20 Nov 2007)
Rusby: Berry (CCT WG4 Berry T75-T90(ICVGT) rev2a, 13 Nov 2007)
Pitre: Pitre et al. (WG4 T-T90 Pitre, Tew, Moldover_ver3, 05 Feb 2008)
Tamura: Tamura et al. (TT90NMIJ_WG4_2, 29 Feb 2008)

In principle, there are two approaches to calculate the uncertainties associated with the averaging process. One described e.g. in Stock, Metrologia **43**, 03001, 2006 (Key comparison CCT K7) is simply the use of the standard deviation of the mean without any reference to the experimental measurement uncertainties. If individual uncertainties are available, one may propagate those according to eq. (2) in the paper of Cox, Metrologia **39**, 589-595, 2002. Of course, consistent input data were required to apply this calculus and this was checked with the chi-squared test. As WG4 has spent considerable efforts to update the uncertainties of the measurements, there is now confidence that these are (as much as possible) reliable and scientifically justified. Therefore, the resulting uncertainties for the mean of T-T_{90} were calculated using the formalism of Cox as displayed in figs. 3-5 as error bars of the points denoted "mean". The mean was formed using the uncertainties as identified by WG4 as weighing factors.

The inconsistency between the CVGT and AGT results below the triple point of water and the lack of recent measurements in the region between the neon point and 77 K required some additional considerations. It was consensus that there should not appear kinks (except at the triple point of water) in a smooth interpolation function of T-T_{90} representing the consensus estimate as this does not reflect properly nature. In this respect, a piecewise interpolation as considered earlier is not helpful. The problem is highlighted by the fact that, in the region between the neon point and 77 K, only older CVGT data are available that seem to be inconsistent with recent acoustic results. It would be misleading to force a curve to cross over from the CVGT data to the new acoustic data. On the other hand, the uncertainties of the CVGT data have been carefully re-analyzed and WG4 decided to use all of the remaining data sets.

The evident fact that there is an unknown bias due to uncorrected systematic effects is mitigated in the following way: The problem was treated in the paper "An approach to combining results from multiple methods motivated by the ISO GUM" by M. S. Levenson et al. in J. Res. Natl. Inst. Stand. Technol. **105**, 571-579, 2000 by introducing a type B on bias (BOB) uncertainty. This method is an advanced, more modern follow-up of the well-known Paule-Mandel formalism [J. Res. NBS **87**, 377-385, 1982] successfully used by CCT WG2 to calculate the temperature values for the supplementary fixed points of ITS-90. With the BOB method it should be possible to average across the old and new data and it was applied to the points from 35 K to 70 K where CVGT and acoustic measurements seem to be significantly inconsistent. As WG4 has decided to consider all of the remaining data sets with the best estimates of their uncertainties, there is no other way as the mathematics has to dictate the averaging result. WG4 could not wait for new data as was tasked to present a snapshot of the current situation.

To guide the interpolation process between 35 K and 100 K, WG4 discussed how to employ the available measurements. It was deemed unacceptable to adjust constant volume gas thermometry referenced to the triple point of water (Kemp, Astrov), as there is no change in this point and we have no better estimate for the thermal expansion error propagation. In contrast, **CVGT referenced to a low temperature point** (Tamura, Steur) could be renormalized as long as there is a significant change in that reference temperature value. It was found that the data of Steur between 4 K and 100 K are well suited to form a basis of a thermodynamically sound interpolation. Only for that purpose, they were renormalized to a reference temperature of 100 K, well apart from the lower end at 77 K of the recent acoustic gas thermometry. In this way, by using the BOB method the gap between the neon point and 77 K was bridged. Above 77 K, again the weighted mean was used, however, to account for some remaining discrepancy to Kemp´s constant volume gas thermometry, the uncertainties where expanded according to the limited degrees of freedom for the averaging process up to 255 K.

The low temperature data of Tamura were renormalized, referenced to the mean value obtained for the neon point.

It is noted that there must be an uncertainty in establishing the reference temperature in primary thermometry, such as CVGT or AGT, because one relies on an SPRT to transfer the value from a physical realisation of the reference (triple point of water cell) to the environment of the gas thermometer bulb or resonator. All the uncertainties in this process lead to components of uncertainty in measured values of T/T_r and hence T, but they do not affect the uncertainty of the reference temperature itself (which is zero in the case of the triple point of water, by definition). In a similar way, the uncertainty of the calibration of the SPRT is identically zero at $W = 1$. Hence there is no uncertainty in stating that $T-T_{90} = 0$ at the triple point of water.

Conclusions

Comparing the uncertainty of the mean of $T-T_{90}$ with the thermodynamic uncertainty of ITS-90, there is significant progress in the low temperature range from 4.2 K to the neon point (see fig.3). There are a lot of recent and consistent measurements available. This is not the case say, between 35 K and 77 K, where we still rely on Astrov, Kemp and Steur. Therefore, WG4 found presently no other solution as to apply the described BOB formalism to account for this leading to considerably higher uncertainties of the mean between 35 K and 70 K. Above, there is again considerable progress as Pitre et al., Ewing and Trusler, and others at higher temperatures contributed with new results of acoustic gas thermometry (fig. 4). These results confirm the discontinuity in the slope of $T-T_{90}$ at the triple point of water. However, there is the unexplained inconsistency to the CVGT of Kemp which was accounted for by expanding the uncertainties of the mean. Clearly, the temperature range between the neon point and the triple point of water needs further consideration before any recommendation towards a new temperature scale can be made. WG4 is strongly encouraging researchers to undertake additional high-precision measurements of thermodynamic temperatures in this range.

Another gap is between 550 K and the zinc point, where we have only Schooley´s CVGT results (fig. 5). This gap should be closed by acoustic gas thermometry, radiation thermometry or even by advanced noise thermometry. There have been only two recent measurements at the copper point, Goebel´s absolute radiation thermometry being 148 mK above ITS-90 and Edler´s noise thermometry, 80 mK below . This is the only point where originally the chi-squared test failed.

Therefore, "various" other data (Righini et al, 1972, Coates and Andrews, 1978, Ricolfi and Lanza, 1977, Jones and Tapping, 1982) have been included to take into account the older relative radiation thermometry. Presently, the result of Edler is excluded from the averaging process as a correction due to a recently detected statistical bias is pending. Again, more measurements are urgently required here.

The following table summarizes the result of the averaging process for measurements of T-T_{90} and represents the present best estimate of the experts in working group 4. Clearly, considering the various weaknesses discussed above, it would be premature to base a new temperature scale on these results.

Table: Current best estimates of T-T_{90} between 4.2 K and the copper point. The uncertainties are representing the k=1 level.

T_{90} K	T-T_{90} mK	u mK	T_{90} K	T-T_{90} mK	u mK
4.2	-0.02	0.12	161.405	-8.43	1.8
5	0.11	0.12	195	-6.97	1.8
6	0.05	0.13	234.3156	-3.25	1.0
7	-0.08	0.10	255	-1.64	0.9
8	0.02	0.10	273.16	0	0
9.288	0.13	0.11	290	2.19	0.4
11	0.28	0.12	302.9146	4.38	0.4
13.8033	0.44	0.14	335	7.62	0.5
17.035	0.51	0.16	373.124	9.74	0.6
20.27	0.32	0.17	429.7485	10.1	0.8
22.5	0.10	0.18	505.078	11.5	1.3
24.5561	-0.23	0.20	600.612	9.21	6.1
35	-0.53	1.0	692.677	13.8	6.9
45	-0.75	1.4	800	22.4	6.4
54.3584	-1.06	1.6	903.778	27.6	7.6
70	-1.57	1.9	933.473	28.7	6.6
77.657	-3.80	1.2	1052.78	40.9	26
83.8058	-4.38	1.3	1150	46.3	20
90	-5.30	1.1	1234.93	46.2	14
100	-6.19	1.2	1337.33	39.9	20
130	-8.07	1.6	1357.77	52.1	20

Analytical smooth interpolation functions:

Finally, it is discussed here how to disseminate the differences T-T_{90} via the Mise en pratique. It may be convenient to form simple analytic expressions. The general idea is to approximate the differences in two temperature intervals with different functions.

Having prepared a consensus estimate for the weighted mean, an attempt was made to interpolate the full range from 4.2 K to 273 K with one unique function. The trial with a linear temperature scale failed as polynomials of high order were required to fit the low temperature part below 24 K, which resulted in oscillations at higher temperatures. In addition, weighted fits were tried but they oscillated even more at low temperatures. WG4 then tried a fitting with a logarithmic temperature scale $x=\log_{10}(T)$, similar to the SPRT reference function in the ITS-90 below the triple point of water (see figs. 3 and 4):

$$(T\text{-}T_{90}) \,/\, \text{mK} = \Sigma_{i=0..7}\, b_i \,(\log_{10}(T_{90}/T_{\text{TPW}}))^{i+1} \qquad (1)$$

with the coefficients b_i:

$b_0 = 4.42457\ 10^{1}$ $\quad b_1 = -1.76311\ 10^{2}$ $\quad b_2 = -1.53985\ 10^{3}$ $\quad b_3 = -3.63685\ 10^{3}$
$b_4 = -4.19898\ 10^{3}$ $\quad b_5 = -2.61319\ 10^{3}$ $\quad b_6 = -8.41922\ 10^{2}$ $\quad b_7 = -1.10322\ 10^{2}$

By forming the ratio to the temperature of the triple point of water T_{TPW} in the argument of the logarithm, the function is forced to go through the definition point of the kelvin. It is noted that the current derivative at the triple point of water is 7 10^{-5} (K/K). Of course, these fits reflect work in progress and need to be updated as new measurements become available.

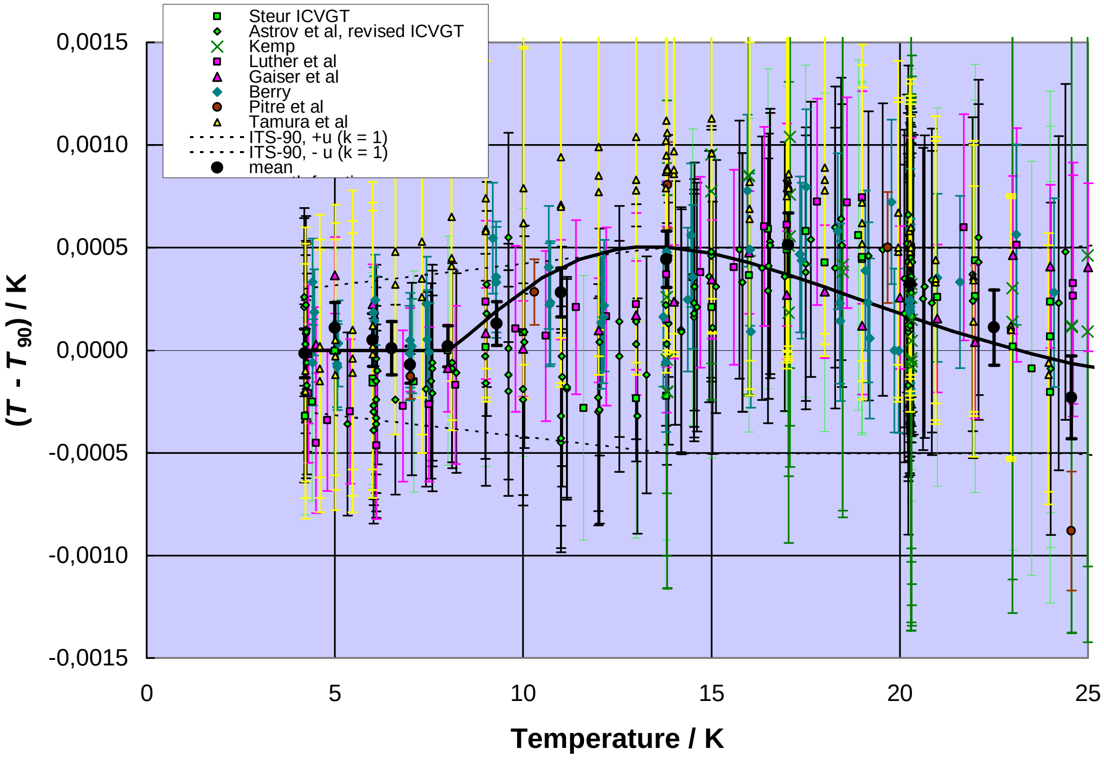

Figure 3: Measurements of $T\text{-}T_{90}$ in the low temperature range below the neon point. Data in terms of NPL-75 have been converted to ITS-90 using stable Rh-Fe thermometers. The smooth function (eq. (1), solid black line) interpolating the mean values (bold black dots) is set identically zero below 8 K. All error bars represent uncertainties with k=1.

From the triple point of water to the copper point, a fifth order polynomial with the coefficient c_0 slightly adjusted to go through the triple point of water is recommended (fig. 5). The derivative at the triple point of water is 1.83 10^{-4} (K/K). The discontinuity of the slope is 1.1 10^{-4} (K/K), the value being higher than the result of 4 10^{-5} (K/K) of recent acoustic gas thermometry [Pitre et al., Metrologia **43**, 142-162, 2006]. On the other hand, the accumulated discrepancy $T\text{-}T_{90}$ between the

Hg and Ga points is 1.1 mK, where experiments based on the resistance ratios of platinum resistance thermometers [Singh et al., Metrologia **31**, 49-50, 1994] suggested 1.5 mK.

The function has the form

$$(T\text{-}T_{90}) / \mathrm{mK} = \Sigma_{i=0..5}\, c_i\, T_{90}^{\,i} \qquad (2)$$

with the coefficients c_i:

$c_0 = -1.9492\ 10^{2}$ $c_1 = 1.5439\ 10^{0}$ $c_2 = -4.3630\ 10^{-3}$ $c_3 = 5.7328\ 10^{-6}$
$c_4 = -3.4666\ 10^{-9}$ $c_5 = 7.8472\ 10^{-13}$

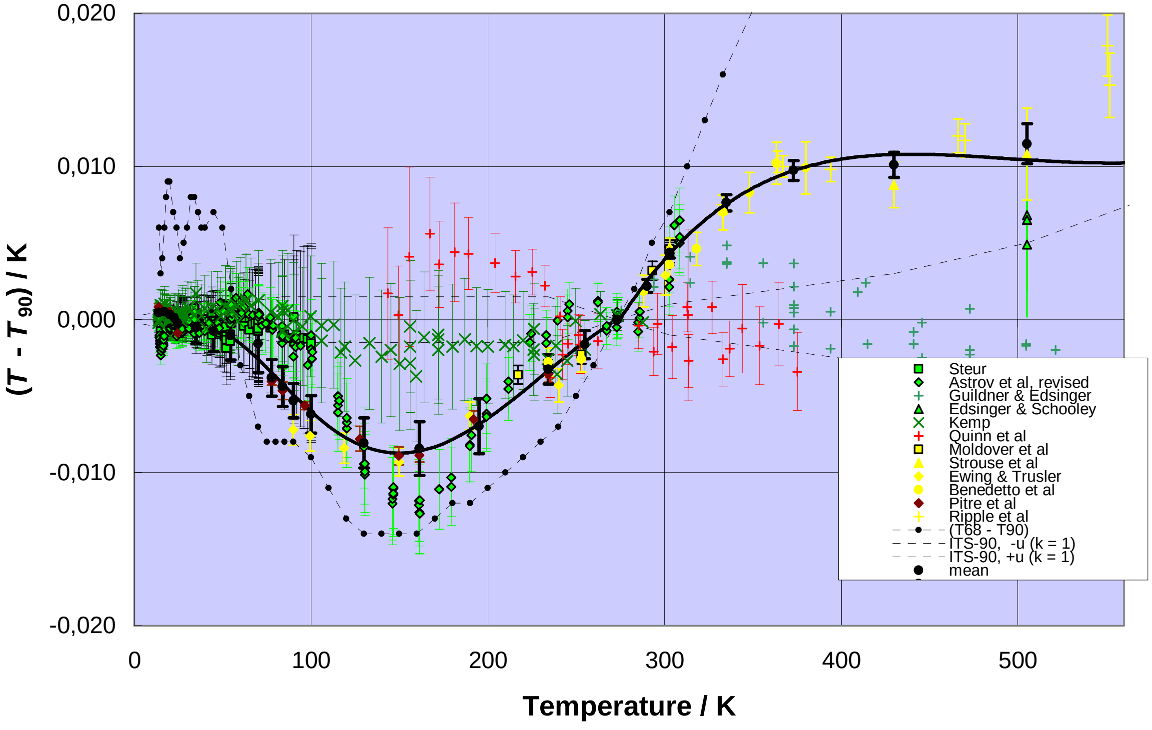

Figure 4: Measurements of $T\text{-}T_{90}$ in the temperature range above the hydrogen point to 550 K. Data in terms of IPTS-68 have been converted to ITS-90 using stable cSPRTs. The smooth function (eq. (1), solid black line) is interpolating the mean values (bold black dots) below the triple point of water. Above, shown by the same symbols, the polynomial of eq. (2) is recommended. All error bars represent uncertainties with k=1.

WG4 recommends that, after approval by the CCT, in the mise en pratique for the definition of the kelvin, the differences $T\text{-}T_{90}$ and the corresponding uncertainties as stated in the table of this report are listed. In addition, the smooth interpolation functions eqs. (1) and (2) with the coefficients should be included for convenience of the user.

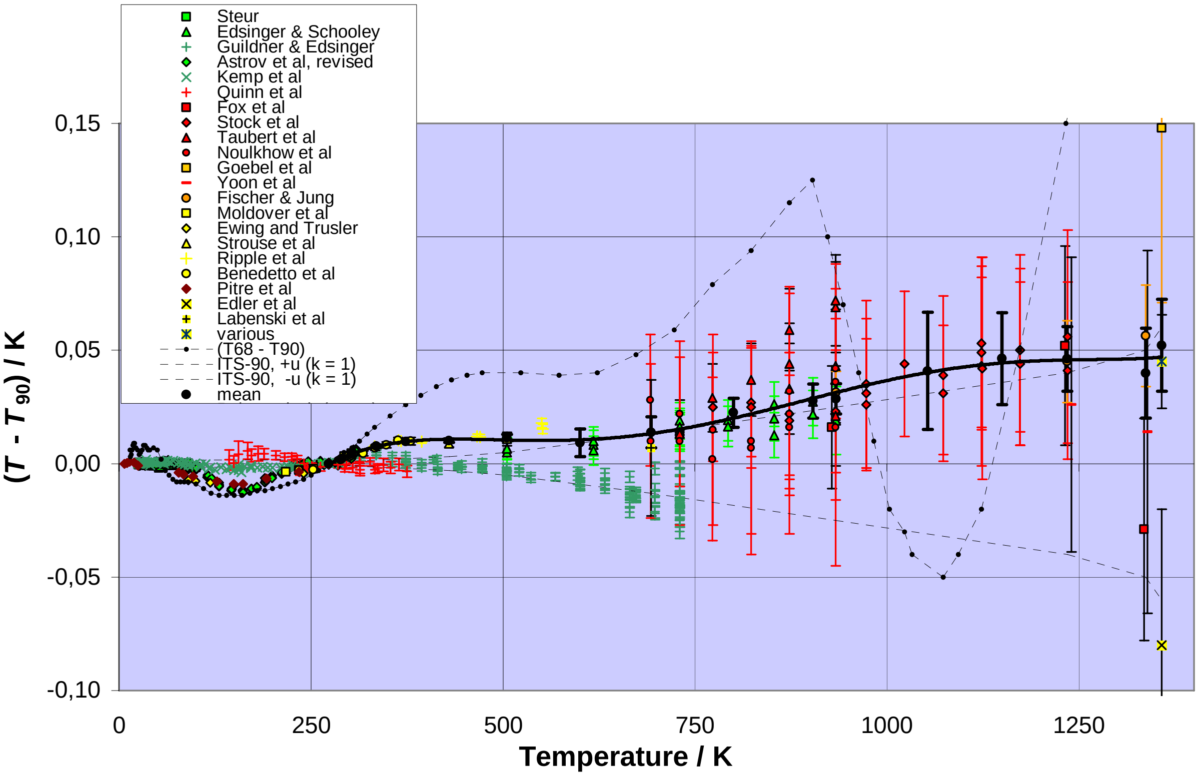

Figure 5: Overview of measurements of T-T_{90} with emphasis on the range above the triple point of water. The smooth function (eq. (2), solid black line) interpolating the mean values (bold black dots) is recommended above the triple point of water. All error bars represent uncertainties with k=1.