CCT Workshop: Toward the ITS-XX
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Summary of the proceedings

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Introduction

The following is a brief record of the workshop, produced using notes taken. It includes almost all issues raised, but it does not include all points made in the discussion. Overheads used by the presenters are listed in the Annex.

At the opening of the meeting the workshop objectives were stated as:

- to review current and future needs in respect of the ITS
- to review the limitations of the ITS-90
- to identify possible alternatives or solutions to problems
- to identify areas in need of further research.

It was pointed out that there is no CCT WG tasked with producing a new scale.

The program was organized in four sessions, each with a chairman and two or three discussion leaders who introduced particular topics as indicated in the report. The sessions were:

1. Thermodynamic aspects
2. SPRT sub-ranges, Ar-Ag
3. Radiation thermometry
4. Low temperatures.

1. Thermodynamic aspects (Chair: Rod White, MSL)

1a. Triple point of water: a tighter definition? (Wes Tew, NIST)

After an introduction concerning the history of the triple point of water and the definition of the kelvin, WT summarized what is and what is not discussed in the Supplementary Information for the ITS-90, and raised a number of questions, as follows:

•Included Now
–Isotopic composition
–Chemical purity (qualitative)
–Hydrostatic pressure correction
–Mantle preparation technique
–Recommended use
–Cell and mantle maintenance
–Metal cell alternatives

•Not Included Now
–SMOW or similar IRMs
–Quantitative purity examples
–Residual gas pressure
–Dissolved gas
–Dissolution of impurities from container
–Buoyancy induced pressure
–Ortho-para equilibrium

1.Should the SI definition of the kelvin be consistent with the TPW fixed point definition in the ITS [Supplementary Information]?
2.Does the word "substantially" introduce an unacceptable degree of ambiguity in the ITS?
3.Is the amount of detailed information on TPW realization now found in the ITS-90 supplement sufficient for most purposes?
4.What is of greater importance to ITS TPW and kelvin definitions:
a)The current best practice of TPW cell realization OR
b)The strict adherence to a SMOW (Standard Mean Ocean Water) interpretation.
5.What are the costs versus the benefits of modifying the TPW definition to one with greater precision?

Points raised in discussion:
Referring to CCT Recommendation T2 of 1993, what is the status of cell comparisons?
How thick should the inner layer of water be, how effective is the hydrostatic head correction, what is the effect of the curvature of the water surface (under gravity)?
What is the practicality of analysis?
What is the effect of the container, and the procedure for cleaning?
How much should be specified in the definition? What is the cost/benefit of a new definition? [Can't improve without it; …but if it meets the needs…? ..ITS should have practical guidelines.. ..the definition is simple, leave details to the Supplementary Information…]
Other points have isotope effects
Other effects are also important – eg dissolved air
Need flexibility: can't perform complete plateau? - it has been done.

1b. Thermodynamic accuracy (Richard Rusby, NPL)

The current status of thermodynamic temperature determinations was reviewed by reference to a graph by J Nicholas, and an up-date including the PTB and NIST data above 0 °C presented at the Symposium.

The ITS-90 temperature values up to 460 °C were mainly based on an average of the Guildner-Edsinger-Schooley constant-volume gas thermometry at NBS (approximately 1960 to 1985), and an extrapolation of them to the gold point, using the blackbody radiance ratio measurements of Fischer and Jung at PTB. Acoustic gas thermometry and absolute spectral radiometry now seem to support the later (Edsinger-Schooley) results, the temperatures being consistently higher than in the ITS-90, by about the 1 standard uncertainty estimated in 1990.

Below 0 °C, recent acoustic thermometry and the revised VNIIFTRI constant-volume gas thermometry suggest a 0.01 °C dip in differences ($T - T_{90}$), contrary to the CVGT work of Kemp *et al* and absolute total radiometry of Quinn and Martin. The apparent recovery of the VNIIFTRI results to the ITS-90 values near 100 K is hard to understand.

A significant body of experiments is in progress to add new information:

Acoustic	NIST: 273 K to 800 K
	IEN-IMGC (Italy): 234 K to 400 K
Dielectric constant	PTB: below 273 K
Rayleigh scattering	NPL: 200 K to 300 K
Noise	PTB: FP Cu, MP Pd
	NIST: 273 K to 933 K
	MSL: 430 K
Radiometry	NPL: total radiometry, 234 K to 302 K
	PTB: absolute spectral, 690 K to 933 K
	NIST, NPL: absolute spectral, at various fixed points
	NRC: Fourier Transform Spectroscopy, 800 K to 1250 K.

Points of discussion:
Can one use the slope of the acoustic thermometry differences near 150 K? – No
Accuracy is mostly good below 100 K – data are needed above this.
Is thermodynamic accuracy important? – one requirement is in thermo-chemistry, where accuracy can be important (spherical acoustic resonators were developed for work on PVT-data, not thermometry).
Scale changes annoy customers: one can always provide 'accuracy up-dates' to those who need them. (Scales revisions are done for practical reasons, but these provide rare opportunities to improve accuracy and self-consistency).
The ITS is an intermediary for *T*; one should aim to keep it thermodynamic.

2. SPRT sub-ranges, Ar-Ag (Chair: Georges Bonnier, BNM-INM)

2a. Fixed points: status and requirements (Greg Strouse, NIST)

Five main issues were raised for discussion:

1. Impurities
Raoult's law is in most cases not applicable because impurities are soluble in the solid phase.
It tends to underestimate uncertainties, sometimes by a factor of 5 – Recommendations for estimating the influence of impurities are under discussion in WG1.
Assays tend not to give uncertainties
Are independent assays essential? What is the effect of the crucible?
Aluminium or graphite can 'absorb' argon: can use nitrogen instead.

2. New fixed points
Xe TP (~160 K) still does not look good – need information on isotope effects
It is difficult to enrich in sufficient quantity
CO_2 TP (~215 K) is also problematical, and close to Hg TP
N_2 TP (63 K) is first quality – but not included in ITS-90 as O_2 TP is better located

3. Availability of 6N materials
6N Al was not available – but is again
'6N' does not always mean 6N – analysis is needed
Melting range is about 1 mK/ppm
Oxygen is never included in analysis

4. Alternative definitions to the silver point
Concern about HTSPRT range – is the scale transferable, or does it sit on the shelf?
NRC suggests alternatives to customers, and replaced a broken HTSPRT with a Au/Pt thermocouple
Not much commercial demand – Au/Pt and Type S thermocouples are more popular
HTSPRT s replaced Type S thermocouples in the ITS after much work – they are more accurate, and avoid a junction at Al FP
Can allow overlap with radiation thermometry? HTSPRTs are needed for cell comparisons.
Need HTSPRTs in the lab [NMI], but Au/Pt is better at keeping uncertainty outside
HTSPRT quality depends on workmanship – eg flame polishing of silica

P Marcarino outlined the IMGC 'temperature amplifier' in which a temperature-controlled mercury heat-pipe between 240 °C and 400 °C generates a stable pressure in an inert gas. This then controls the temperature of a sodium heat-pipe between 660 °C and 962 °C (Metrologia **39,** 395-398, 2002). Once the relationship between the two temperatures is established, a scale can be set up with very low non-uniqueness between the Al and Ag

freezing points. The relationship must not depend on the heat-pipe design, only on the material purity. IMGC has made a system (with 7N Hg, 3N5 Na), and offers a collaboration.

Points of discussion:
Can an artefact like this be adopted for the definition of the ITS?
What is the effect of impurity in the sodium?
What is the pressure drop across the interface between the vapour and the inert gas?
How could a heat-pipe scale be linked to lower and higher ITS ranges?
Are the impurities segregated? (not a problem at dew point)
Uses sodium vapour pressure: ITS-XX should give (p, Txx) relation, to permit other solutions (but the pressure measurement is less precise than using the temperature amplifier)
ITS is usually thermometer-based, but a heat-pipe is a source/generator. It could equally be used for SPRT/thermocouple calibration or a blackbody, with no inherent preference.
It could be used to control a fixed point cell.

2b. SPRTs: performance and limitations (Ken Hill, NRC)

A number of limitations were identified:

•Reversible changes of the sensing element
– Oxidation (W is affected, but less dramatically than R. Can be 10's mK)
– Point vacancies caused by quenching (equilibrated by annealing)
•Irreversible changes of the sensing element (drift)
– Chemical changes (contamination, permeability of sheath to Ag, Cu, Ni – use Pt sleeve?)
– Mechanical changes (can be positive or negative)
•Dimensional changes
– grain growth
– changes in cross-sectional area
•Strains, eg in shipping (often partially removed by annealing)
•Electrical leakage: low temperature (humidity), high temperature (ions, impurities)
•Sheath failure (devitrification of silica, catalysed by impurities
– alternatives: alumina, platinum, sapphire

Three questions:
•Could the upper limit be > 962 °C ?
– Platinum melts at 1768 °C
– some SPRTs already tested to 1500 °C
– Pt resistance thermometry to the Pd point (1550 °C)?
•Do we understand the effects of applying a bias voltage and the influence on electrical leakage?
•Should high temperature PRTs incorporate guard electrodes?

Points of discussion:
What about SPRT orientation? – vertical, horizontal, upside-down. Effects are variable.
What is the justification of the W(Ga) and W(Ag) requirements in the ITS-90? N Moiseeva showed two slides, see also Tempmeko 2001, pp91-96. Some SPRTs of low W(Ga) can be OK, but for HTSPRTs W(Ga) should be > 1.11810. For W(Ag), a leakage effect of 0.21 K can be allowed!
ITS-90 requirement is optimistic: the leakage effect is exponential. A guard electrode is needed to control it.
Different quench anneal procedures are needed for HTSPRTs of different quality.
200 – 400 hours at Ag point is enough, but the cycling effect is problematical.
W values are not so useful at low temperatures because of the very small sensitivity. A

Z-function is better: $Z(T) = (R_T - R_{4\,K})/(R_{tpw} - R_{4\,K})$
SPRT has potential for development – increase the range, rather than decrease it
Take advantage of high resolution.

Should the triple point of gallium point be used in place of the TPW? (for SPRT interpolation and/or the kelvin)?
Experience in CCT-K3 was not encouraging. The gallium point needs to be further tested
Discussion about convenience and cost: preference seems not to change (?)
Water isotope variability in wine is apparently smaller than in ocean water!

2c. SPRT interpolation and structure (Rod White, MSL)

Factors affecting choice of structure:
Convenience in use
-Does not require extended temperature range or many fixed points
-Mathematical simplicity
-Ease of uncertainty analysis
Immunity to uncertainties in the realisation of the ohm
-e.g. $W = R(T)/R(0.01\ °C)$
Highly reproducible (low uncertainty):
-Immunity to variations in R(T), oxidation, strain, impurities, etc
-Low sensitivity to fixed point uncertainties
-Low sensitivity to uncertainty in R measurements
Thermodynamic accuracy, smoothness
Ease of design of scale
Uncertainty analysis is increasingly important

Questions to address before changing
-Are there alternative scale structures with better properties?
-Are there better models of an SPRT? e.g $R(T) = R(T)_{ideal} + DR + f(T)$
-Are there alternative interpolation schemes with reduced non-uniqueness? e.g. cubic splines do not propagate uncertainty backwards so would eliminate sub-range inconsistency problems
-Is linear interpolation (to first order) OK?
-Do we need to specify the interpolation?
-Allow the user to trade-off non-uniqueness and simplicity?
-Allow other, simpler, interpolations as approximations to the ITS-XX ?

Points of discussion:
How accurately can W(Zn) be correlated with W(Sn)? – to 10-20 mK? A group of 120 SPRTs correlated to about 4 mK: interesting as a check, but not usable for calibration.
More and more possible alternatives – no convergence!
- but could have been more complicated – Ga point is not needed.
No redundancy in the ITS-90: include additional points for checks, and use least-squares fitting
More points is better: Least Squares shows up odd points, eg could identify a leaky fixed point cell
Chebyshev fits allow truncation of coefficients if not required
In and Cd are available – now used as check points.

3. Radiation thermometry (Chair: Joachim Fischer, PTB)

3a. Fixed points (Fumihiro Sakuma, NMIJ)

The presentation included a table of 'best uncertainty' at the Ag, Au and Cu freezing points and their influence at 3000 K (8 mK and 38 mK, respectively), and recent fixed point comparisons (uncertainties typically 20-60 mK). Better results could be obtained if fixed points were available at higher temperatures. Difficulties include impurities, radiation heat losses, emissivity, size-of-source, reproducibility, international confirmation.

Points of discussion:
Are the carbide fixed points suitable for (eg) Pt/Pd thermocouples? – should be
They are also required in photometry and radiometry
Can one be confident that a eutectic is produced? – it precipitates out in that way
The phase diagrams are complex, one can be led to the wrong place? - It comes down as a carbide, the problem is impurity.

3b. ITS-XX and *T*: source-based and detector-based solutions (Pieter Bloembergen)

Radiation thermometry is needed for measurements ranging from furnaces to the universe. Laboratory sources are artefacts with assigned temperatures T_{90}: detectors can lead directly to temperature T – pragmatism versus fundamentalism. For sources the traceability chain is short: measure a freeze as defined in the scale. In future one could take points at the high and low extremes (eg Cu and TiC) and interpolate. Both absolute (detector-based) and source-based schemes can give non-uniqueness uncertainties < 0.15 K, better than the ITS-90. If this is shown to be realistic in practice, one should take advantage of it.

Points of discussion:
Are these uncertainties of comparison or scale? - ITS-90 is also affected by uncertainties in wavelength, but with interpolation using eutectics the robustness of the interpolation would be much better.
The uncertainties in the fixed points are not stated in the ITS-90 – but they are given, and belong, in the Supplementary Information.
Can clean graphite be used as a fixed point? The sublimation point – the 'carbon arc' – at 3600 °C has been used, but not melting or freezing points.
The choice is whether to forget T_{XX} altogether, and measure T directly. T_{90} is a construct for practical convenience. If T can be measured directly there is no need for a scale (revision) – but is the detector-based alternative available? will all laboratories be able to do it?
The differences in uncertainty may be significant: with a detector-based method, one can improve procedures, but for practical measurements it is more convenient to have a defined scale.
Can a detector-based scale be made useful to users?
One must also consider contact-thermometer users
The Al-Ag range can be done by contact or non-contact methods
Given fixed-point temperatures, one can then use conventional techniques

4. Low temperatures (Chair: Richard Rusby, NPL)

4a. Cryogenic fixed points, limits of realization (Bernd Fellmuth, PTB)

For the range below 1 K, there are several intrinsic fixed points on the ^{3}He melting curve: further experience in realising them at the highest level of accuracy is needed. Also, superconductive reference points are becoming available again.

Above 1 K first-quality points are available in the lambda point and the ITS-90 points, but differences larger than expected (standard deviation 0.34 mK) are found for hydrogen in international intercomparisons, due to variability of deuterium content and the effect of the spin-conversion catalyst. A better definition is needed (SLAP is more representative than VSMOW). A proposal is to be made to the CCT.
Static and dynamic temperature-measurement errors (gradients, heat leaks, thermal recovery after heat pulses) have to be estimated reliably using appropriate parameters for describing the thermal properties of the fixed-point cells.
The crystal quality of the solid phase and segregation of impurities influence the shape of the melting curves measured to determine the fixed-point temperature. Isotope effects are a concern in Ne, the relatively large temperature width of melting curves for Ne and Ar need investigation, and a comparison of lambda cells is needed. A definition of the fixed-point temperature is also needed.

Points of discussion:
Does the use of 1/F (F = melted fraction) also apply at high temperatures? – in most cases it is not justified because it requires that Raoult's law is obeyed.
Can one use SLAP and SMOW as reference materials and eliminate mass spectrometer non-linearity? (only ratios of isotopes are required)
In the long term, can one consider using the deuterium triple point (in place of the hydrogen vapour-pressure points), if it can be contained without contamination? But in that case there would also be fewer points for interpolation.
The range to 25 K needs the hydrogen triple point, and is not as well-behaved as the full range: it would be nice to have a 'triple-points only' scale, including both hydrogen and deuterium.

4b. Interpolation and structure (Peter Steur, IMGC)

Can new fixed points be used: lambda point, deuterium point, solid-solid transitions?
Given some redundancy, can a least-squares interpolation be applied?
ITS-90 non-uniqueness:

- SPRT: various overlapping sub-ranges
- Interpolating CVGT, with ^{3}He or ^{4}He
- ^{3}He and ^{4}He vapour pressure scales
- ^{3}He melting pressure (PLTS-2000)

How much inter-realisation non-uniqueness can be tolerated, with the definition of the fixed points tending to 0.1 mK? Is the figure ~0.5 mK in the ITS-90 too large now?
Non-uniqueness in SPRTs has been considered earlier. For capsule SPRTs, the residual resistance (at ~4.2 K) can be used to correct for resistance changes with time: ie, Matthiessen's rule can be applied, Z-functions can be used.

Points of discussion:
The use of Z-functions is equivalent to the lnW terms in the deviation equations
Solid-solid transitions are a problem thermally, with poor contact to the transition
Overlapping sub-ranges lead to inconsistencies – a single full-range SPRT definition is preferable
– ie include the hydrogen vapour-pressure points? (at NIST the CVGT uncertainties were slightly larger).
Would like to have flexibility. He vapour pressure consistency is adequate.
Is the ICVGT to stay? What about the deadspace effect and the e-H_2 fixed point values?
Can't do without the ICVGT. The treatment of the dead volume is not specified, but must be considered by the experimenter.
There has been no comparison of ICVGTs yet – but some information may become available from Key Comparison CCT-K1.

The ITS-90 reference function is based on a single thermometer – but several thermometers could be averaged using modern mathematical methods.
A problem arose with the ITS-90 mismatch at 273.16 K, where the derivatives were forced to agree.

Concluding points

A workshop on ITS-XX for industrial instruments (IPRTs, thermocouples) would be useful.
The opportunity for industry to take part in this workshop was appreciated.

Annex: Overheads presented at the workshop

The following overheads were shown at the workshop and circulated with the report to all participants in December 2002:

1. W Tew: file *TPW_ITS-XX_Workshop.ppt*

2. R Rusby: file *CCT WG4 TC Graphs DRW.xls*

3. G Strouse: files *Acoustic T-T90 Ripple and Strouse* and *ITS-XX-Strouse.ppt*

4. K Hill: file SPRT Limitations.ppt

5. D R White: files *pres0.ppz* and *Pngsetup.exe*

6. P Marcarino: files *Workshop.ppt* and *Pressure drop.jpg*

7. M Arai: file HTPRT at *Cu FP.ppt* and *PRT-guard.ppt*

8. N Moiseeva: files *Slide-1.doc* and *Slide-2.doc*

9. F Sakuma: file *Fixed points2.ppt*

10. P Bloembergen: files *TS8-207_o.pdf, CCT Workshop5.doc, CCT-title1.doc, CCTWSA6.doc, Scientist2.doc, CCTWS3a.doc, CCTWSB3.doc, CCTWSC3.doc, CCTWSD2.doc*

11. B Fellmuth: file *CCT_Workshop_Fellmuth.ZIP*

11. P Steur: file *CCT wkshp Steur Dec02.doc*