

CCT Workshop on Uncertainty in Temperature Fixed Points

Organised by Georges Bonnier (BNM-INM) and Richard Rusby (NPL)

Tempmeko 2004, Cavtat, Croatia

26 June 2004, from 9h00 to 12h30

Programme

1. Introduction and purpose of the workshop *Georges Bonnier, (BNM-INM), and Richard Rusby, (NPL)*
2. Definition of the national temperature standard for a given fixed point? *Dean Ripple (NIST)*
What are the possible differences coming from different approaches: best cell or group of cells?
3. Uncertainty budgets for calibrating fixed point cells? *Eliane Renaot (BNM-INM)*
4. Effect of the impurities. *Bernd Fellmuth (PTB)*
How to define the temperature value from a plateau observation?
Use of the liquidus point to define the temperature fixed point
5. Effects of isotopic composition. *Franco Pavese (IMGC)*
6. Effects of heating method. *Ken Hill (NRC)*
Comparison between permanent heat flux and calorimetric method
7. Thermal drain along the thermometer well. *Valentin Batagelj (FE-LMK)*
Is the hydrostatic effect a relevant criterion for assuming the absence of thermal drain?

Notes from the proceedings

1. GB introduced the workshop, saying that uncertainty estimation in temperature fixed points is a topic of continuing importance and debate within the CCT and regional metrology groups. It had been decided that a workshop should be held following Tempmeko, to provide the opportunity for a discussion open to all.

He was grateful to the speakers for agreeing to introduce the six topics and lead the discussion.

RR agreed to take notes and prepare a short record of the workshop for electronic distribution to participants, with the slides presented.

2. Definition of the national temperature standard for a given fixed point? *Dean Ripple (NIST)*
What are the possible differences coming from different approaches: best cell or group of cells?

DR showed 7 slides (attached) identifying the sources of differences between cells, how the best fixed point value might be chosen, difficulties with the statistics, and the analysis of uncertainty budgets. Known differences, eg due to isotopic effects in the water triple point, can be corrected for, following the GUM; the choice of the 'best cell' is not necessarily in the realm of statistics. He cautioned against the view that it doesn't matter how the average is defined as long as international equivalence of that average is established by key comparisons

Points of discussion:

- Should one take the standard deviation of a group of cells? The standard deviation of the mean is not appropriate. If (eg) contamination is suspected the 'best cell' may be on the edge of the distribution.
- We should make appropriate use of measurements of sets of cells, even if the statistical average is not too meaningful - DR's main concern was that we not take the statistical uncertainty of the mean as having a clear interpretation. Use of the total variance of the cells, or computing the variance with respect to a cell that is plausibly the best of the lot, is potentially useful for assigning uncertainties.
- Concern about the use of statistics for a necessarily small number of cells, and the arbitrary exclusion of outliers. From the quality point of view, it avoids the problem of blunders
- But only a few laboratories have large numbers of cells
- Variance can be found from a hierarchical model (see Paper 276) - DR agrees, not done at NIST.
- ITS-90 specifies the ideal case: how to comply? can apply corrections, but what is the meaning of differences between cells? - no problem if cells agree!
- Failure to make corrections (for impurities for example) creates the illusion of correlations between uncertainties at the different fixed points.
- One can't just rely on statistics: need physics or physical chemistry.
- We have a population, but no idea what it is.
- Analogy with Weston cells, standard resistors, etc: what is the effect of the size of the sample?
- How does one know if the results are in the same population? Can consider as the same population – all are realisations of the ITS-90. Need not treat as a hierarchy, but obtain a value representative of the sample.
- Correct for known biases, reduce to a common physical state (WG1 is producing guidance).
- What about the use of one cell only? - generalise to an international distribution, through key comparisons? But these do not determine national offsets and are not calibrations. Rather they are used to confirm estimates of uncertainty.

3. Uncertainty budgets for calibrating fixed point cells? *Eliane Renaot (BNM-INM)*

ER considered a national standard consisting of a group of cells and reviewed how the differences are determined. Three stages of uncertainty were identified: those in the comparisons, those in establishing the national group of cells, and those relating the group to the ITS-90. The basic model was set up, and the components of uncertainty were listed. She gave an example of a group of water triple-point cells, where the range of temperatures was 0.17 mK leading to a standard uncertainty for the national reference of $\pm 50 \mu\text{K}$.

Points of discussion:

- How many cells are used to make up a group (at BNM-INM): are they open or closed? – typically 5 or 6, measured open, then sealed.
- Are there enough degrees of freedom to use statistics?
- Difference between repeatability and reproducibility: GUM and 17025 lead to two different approaches. The selection of the batch must not be biased.
- Difference between TPW and FP Al or Ag: due the heat flux in the thermometers. Problems in CCT K3 and K4 were due to the thermometers, eg SPRT properties and drift
- Ideally need adiabatic measurement.
- Impurities are mobile, and the highest temperature is not necessarily correct.
- Analysis and comparisons of cells improves harmonisation: can we use a SRM approach? - as in mass and pressure: need harmony rather than truth. In CCT is this not enough?
- Leave flexibility in following the definition – use WG1 document, but how to establish reliable uncertainty quotations? Harmonisation is not as important as reliable uncertainties. It leads to a 'wire scale', with ambiguity. Try to make ITS accessible.
- 'Truth' is thermodynamic; ITS is practical. Are open and sealed cells weighted the same? ER: don't distinguish. GB: decided to seal to avoid pollution. The problem comes from use: does the pressure change or depend on the temperature profile?

-What if a cell 'goes bad' – can continue to use with a correction? Depends on reproducibility and duty cycle. Need to do a consistency test at the end of a calibration.

4. Effect of the impurities. *Bernd Fellmuth (PTB)*

How to define the temperature value from a plateau observation?

Use of the liquidus point to define the temperature fixed point

BF considered the connection between applicability of Raoult's law and the distribution coefficient k_0 , and the effect of the freezing conditions (complete mixing, partial mixing and no mixing). He then discussed three methods for estimating uncertainties due to impurities (SIE: sum of the individual estimates, OME: overall maximum estimate, and ERC: estimate based on representative comparisons). He looked forward to recommended values for k_0 from WG1, better uncertainty assessments from impurity analyses, and improved estimates of $(T_{\text{obs}} - T_{\text{pure}})$ and of the liquidus point.

Points of discussion:

- Does the analysis assume no diffusion in the solid? – yes, even at high temperatures.
- Determination of the liquidus-point temperature. Freezing curves: the maximum gives the best estimate. Melting curves: can the results for $F > 70\%$ yield reasonable estimates? - depends on the experimental conditions as well as the effects and parameters influencing the curve shape, e.g. k_0 .
- Use k_0 values to determine which impurities are problematic. Not all important impurities decrease the transition temperature T : e.g. in Al, for several impurities $k_0 > 1$ and T is increased.
- Zone refining can leave problematic impurities with $k_0 \ll 1$. For Ti in Al ($k_0 \gg 1$), analysis shows that it is important to know when a supplier changed from zone refining to fractionation.
- Can the plot T versus $1/F$ be useful? Most of the impurities are poorly or even not soluble in the solid phase ($k_0 \ll 1$). The influence of these impurities can be estimated from the plot.
- "Zero-point systems": $k_0 \ll 1$, i.e. no solubility? The combined SIE/OME method can be used.

5. Effects of isotopic composition. *Franco Pavese (IMGC)*

FP pointed out that the ITS-90 specifies only 'naturally occurring' isotopic composition, but how much variation is there, and how significant is it? He reviewed the various cases, starting with water, then the cryogenic gases and finally the metals. He asked if the guidance in the Supplementary Information is enough – but this is not supposed to provide additional *definition*: it requires an amendment to the ITS-90 itself. If defined compositions are to be produced, who should do it? - CCQM? - IUPAC? – or CCT? CCT should be careful not to conflict with other definitions. For practical purposes we need better assays and data to convert these to uncertainties. A laboratory which cannot do the analysis will not be able to achieve the smallest uncertainties: the requirements are stringent. Should we refer to a batch of the best reference materials?

Discussion was taken privately over the coffee break

6. Effects of heating method. *Ken Hill (NRC)*

Comparison between permanent heat flux and calorimetric method

In his presentation, KH compared and contrasted the continuous heat flux and adiabatic methods for realising fixed points, with reference to work on Al and Ag by Ancsin (1992, 2001) and Renaot et al (1996, 1999). He concluded with four questions:

What do we mean by equilibrium?

Do temperatures realised by the adiabatic and continuous heat flux methods differ in principle?

Are solid/liquid interfacial temperatures a function of interfacial velocity?

Can diffusion in the solid state be a factor?

Points of discussion:

-Equilibrium implies no concentration gradients: we can have only thermal, not thermodynamic, equilibrium in the short time of the experiments.

- Analysis of Jimeno-Largo et al (Paper 236): the distribution coefficients do not achieve their equilibrium values for Ancsin's adiabatic calorimetry, so it is not equilibrium melting
- Can consider either melt or freeze. Future definition should not refer to direction, but 'thermodynamic equilibrium'.
- Case of Hg: excellent agreement was achieved at NRC between dynamic melting and an adiabatic pulse-heating method for a sealed cell in a calorimeter (with high purity sample)
- Rate of freezing: (In?) varied by factor 3, with no measurable difference.
- Experience from metal carbides: freeze rates and heat treatments – but diffusivity is worse.
- Adiabatic method is used in cryogenics because conductivity is poor and enthalpy is low.
- Rate dependence depends on whether there is an inner interface.
- Why does the 'run-off' happen when there is so much solid left? $1/F$ may be 3, not 1.
- Is a uniform furnace correct? Need a gradient to drive the interface.
- McLaren 'morphology': where is interface? Can have small samples for adiabatic method, but must manage the surrounds well. Large sample provides thermal stability.
- McLaren found dendrites in the sample, but later they disappear.
- Can investigate by non-destructive evaluation? Old data is in danger of being lost.

7. Thermal drain along the thermometer well. *Valentin Batagelj (FE-LMK)*

Is the hydrostatic effect a relevant criterion for assuming the absence of thermal drain?

VB identified several methods for evaluating the thermal conditions in a fixed-point cell: immersion profiles, use of different bushes, different enclosures and modelling. He showed isotherms in his thermal model of an indium cell, and data obtained with a Rosemount thermometer with and without a glass tube bush. He concluded that in this case the immersion error was about 220 μK . He concluded by asking three questions:

Is immersion profile a reliable measure for the estimation of the immersion error?

Is it possible, that even with excellent immersion profile immersion error is significant?

If we have a reasonably accurate (numerical?) estimation of the temperature difference ΔT , how do we use it?

Points of discussion:

- Could the difference in self-heating be due to Joule heating?
- Furnace heat leak has overwhelming effect: 10 times bigger than hydrostatic effect (except for Hg, H_2O , Ga).
- Is the profile correct? Can we assume that the SPRT is in equilibrium? Or should we add an uncertainty or correction?
- Marcarino: measured the hydrostatic effect in a furnace with a metal block and the top of the crucible at a slightly higher temperature. Now uses a heat-pipe, but sometimes the interface is at the top. Is the profile then correct?
- NIST requires a match to hydrostatic effect, even for Al, Ag. The profiles depend on the SPRT, but as immersion increases all approach the expected behaviour. The model shows that this is not fortuitous.
- Is measurement at $\sqrt{2}$ mA as well as 1 mA in the same profile? Can this be detected?
- Should use 0 mA values.
- Effect of touching the bottom – best to raise the SPRT a little – but at the bottom the SPRT is centralised and touches the well only at a small point. When raised, it can touch the sides over a larger area.
- Does the weight of the SPRT affect the cell?
- Is 20 cm immersion enough to ensure good conditions? – it depends on the SPRT design.
- The gap is the most problematical part.
- How to explain the uniform flat profile in the case where the error was 220 μK ?
- Can the modelling result for In be extrapolated to other points? - no, it depends on the properties.
- SPRT integrates over ~ 50 mm
- Does model include radiation? - Yes, done at Zn but not yet tried at Al.
- Is the interface considered as a heat-sink? - Yes