Report of Working Group 3 to the Comité Consultatif de Thermomètrie : May 2003

This report has been prepared by the following WG3 members (or associate members) :
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Present members are from AIST, BIPM, BNM, CSIRO, IMGC, NIST, MSL, NMi-VSL, PTB, SMU, VNIIM.

As a result of deliberations of the Comité Consultatif de Thermométrie (CCT), the mandate of Working Group 3 (WG3) is defined as to be concerned with : "*Uncertainties in Temperature Measurements* " . The WG3 activity is aiming to produce a document, accompanying the Supplementary Information Document and intending to be a guide for expressing the uncertainties in Temperature Measurements.

Taking the opportunity of the 8th Symposium on Temperature, its Measurement and Control in Science and Industry, WG3 had a meeting in Chicago on October 2002. As an output of this meeting an amended document has been established and many pending questions has been asked to be further discussed by the WG3 members.

In return WG3 chairman got some further material. On the 12th of May 2003 a meeting will be held to decide on the way for processing the received information.
Today some information was already able to be incorporated, as improvement of the document, out of any meeting and the corresponding document is presented below.
Several CCT (2003) documents will have to be taken in account and specifically the report of WG1.
A large part of the uncertainty budget is due to the impurities content of the substances used to realize temperature fixed points. In turn the corresponding uncertainty component is linked to the practical definition of temperature fixed point value.

The document proposed below is, so far, uniquely intended to be considered as draft working document requiring many improvements.

Georges Bonnier
Chairman of WG3

WG3 Draft (2003) (proposed to the CCT members)

Dear colleagues,

During the last WG3 Workshop (Chicago on October 2003) the last draft established by WG3 was presented and debated.

In the appendix it's possible to find :
1- a copy of the corresponding transparencies presented during this Chicago workshop
2- the outcome of the debate.
3-in red colour the questions whereby we need your answer

After the workshop we received further comments. Sometime these comments are inconsistent and we would like knowing your point of view about.

- 1) Do we use the same presentation than the document of the WG5 "uncertainty budget for realization of ITS-90 by Radiation thermometry"? Do you prefer that we quote the Supplementary Information as reference when it is possible?
- 2) Do we need to give numerical values for the component? If your answer is "yes", could you send to BNM-INM your uncertainty budget associated to the determination of the W at the zinc point (Zn fixed point and TPW). We will be establishing a synthesis using all the uncertainty budgets with numerical received.
- 3) Do you think that we must debate of the uncertainty propagation during the next CCT meeting? If your answer is "yes" do we take in account of the correlation coefficients? How determine the values of these coefficients?
-

Answers

from MSL :

Q1a: Yes I do like the WG5 approach, with one exception :Repeatability: The one feature of the WG5 approach is the inclusion of the term repeatability. The non-repeatability of fixed points for example arises from identifiable physical causes including impurities and strain in SPRT for example.
To include a term for repeatability is to count these terms twice.

Q1b: Yes we should exploit references to redbook where practical. However we should consider what will happen with the revision of redbook.

Q2a: 2 numerical values would be useful, as with WG5; typical and state of the art.

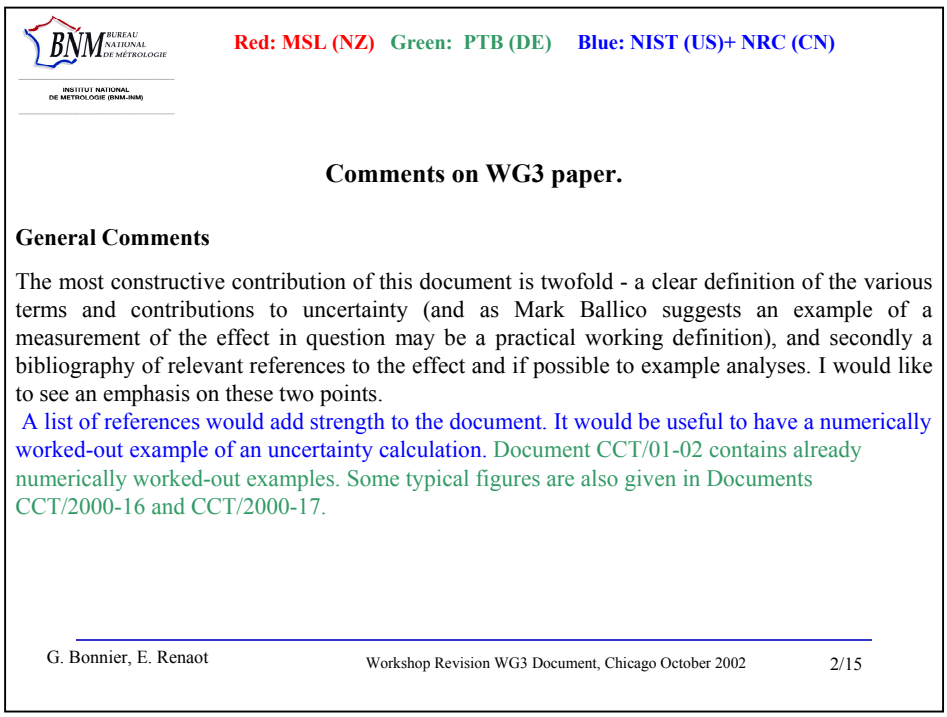
Q3a: Yes we should mention propagation (note in last version of the document the equations were wrong), but briefly. I would hope that the revised red book should cover propagation in proper detail (we need to check).

Q3b: Correlation: highlight possibility/probability, very uneasy about using numerical values other than zero

from NMi: NMi sent an uncertainty budget for W determination at the Zinc FP

Appendix

Transparency 1



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INSTITUT NATIONAL DE METROLOGIE (BNM-INM)

Red: MSL (NZ) Green: PTB (DE) Blue: NIST (US)+ NRC (CN)

Comments on WG3 paper.

General Comments

The most constructive contribution of this document is twofold - a clear definition of the various terms and contributions to uncertainty (and as Mark Ballico suggests an example of a measurement of the effect in question may be a practical working definition), and secondly a bibliography of relevant references to the effect and if possible to example analyses. I would like to see an emphasis on these two points.

A list of references would add strength to the document. It would be useful to have a numerically worked-out example of an uncertainty calculation. Document CCT/01-02 contains already numerically worked-out examples. Some typical figures are also given in Documents CCT/2000-16 and CCT/2000-17.

G. Bonnier, E. Renaot Workshop Revision WG3 Document, Chicago October 2002 2/15

Outcome

It is not required to add an example but a list of communications given an example must be included in the document. BNM-INM collects these communications and transfer them to all the WG3 members.

Could you send to BNM-INM your own method for quoting the different uncertainty budget components, for SPRT calibrations at the defining fixed points?At least the two or three major contributions

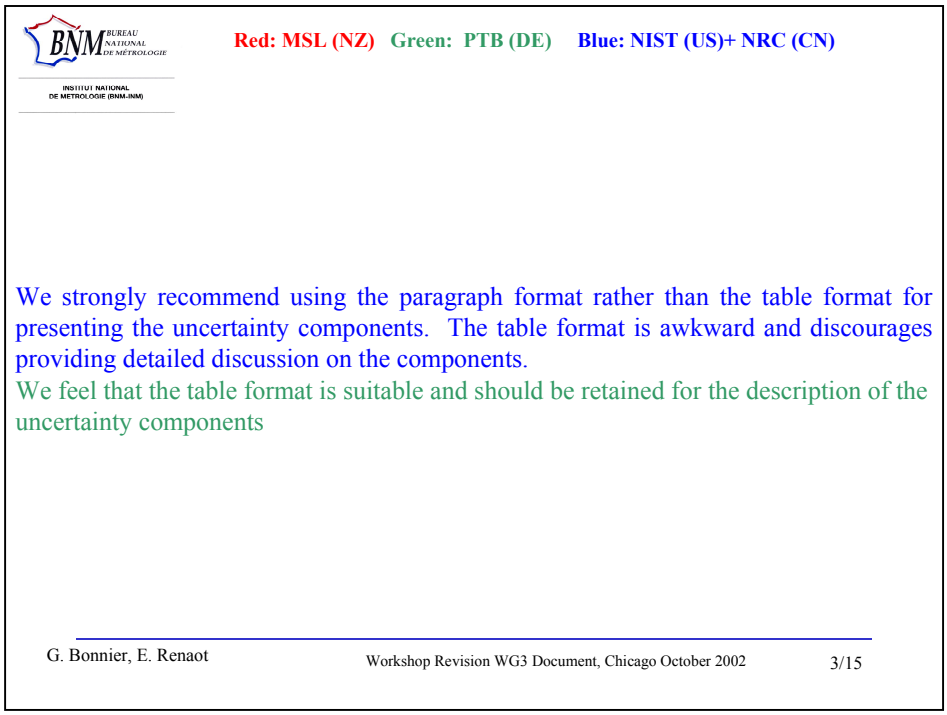
Answer from MSL:

The main purposes of this uncertainty document is to harmonise. To that end we need to

(1) identify and define all influence variables
(2) indicate how the variables influence the measurements
(3) provide references to detailed studies and models of the effects) (4) provide indicative magnitudes for effects
(5) provide references to detailed uncertainty assessments of the effects (6) provide an outline of propagation to temperature
(7) provide references to detailed studies on propagation.

In general it should not be the complete 'textbook' but provide an overview and point to detailed references

Transparency 2



Outcome

The table format seems to be more useful; nevertheless this table could be completed with some paragraphs given more detail on some components.

Transparency 3

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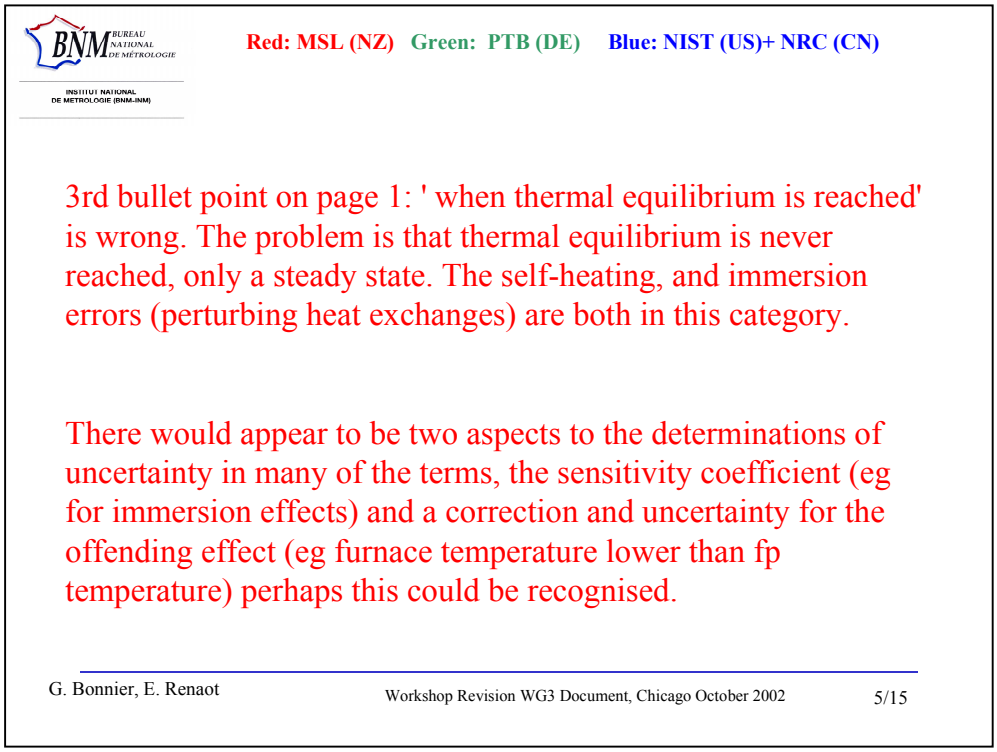
The document should clearly state that it pertains only to those fixed points that do not involve vapor-pressure measurements.

The equations in the document should be numbered. The notation, in particular the subscripts, should be changed to make it more less confusing. For example, $C_{X0.01,i}$ can be confused as a matrix element. We recommend changing "$X_{0.01}$" to "TPW" and making use of superscripts. For example, $C_{X0.01,i}$ could be written as C_i^{TPW}. We all feel that the final equations for W and σ in the document should be made as simple and as unintimidating as possible. For this, we should mention all terms that we know are always negligible and present a final equation without them. It is fine to list these terms at first for the sake of completeness

Outcome

The document will be amended in this meaning.

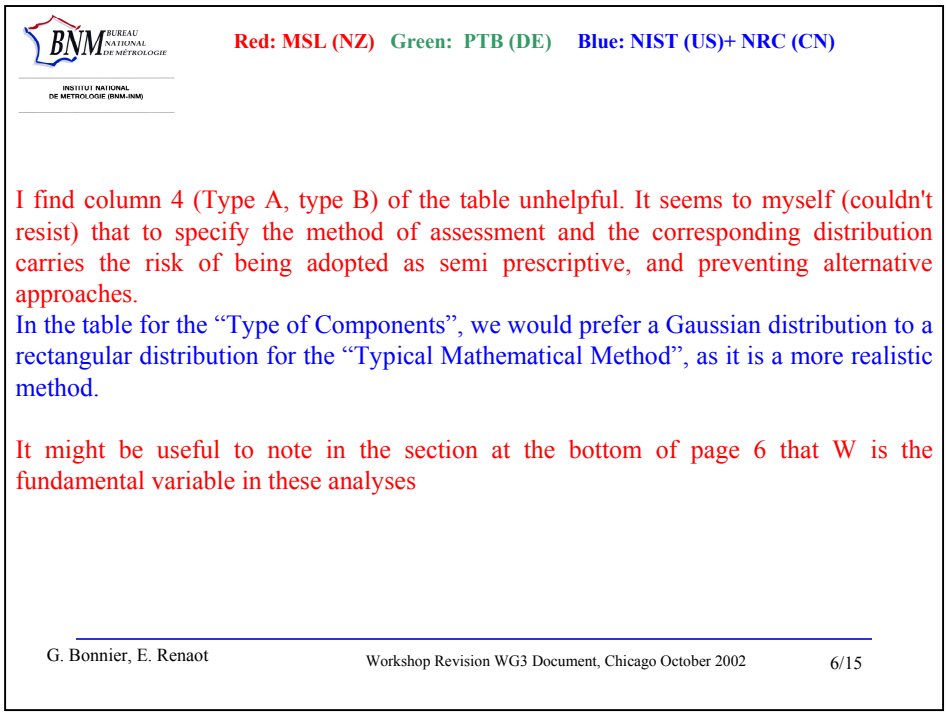
Transparency 4



Outcome

“Thermal equilibrium” must be replaced by ”steady state”

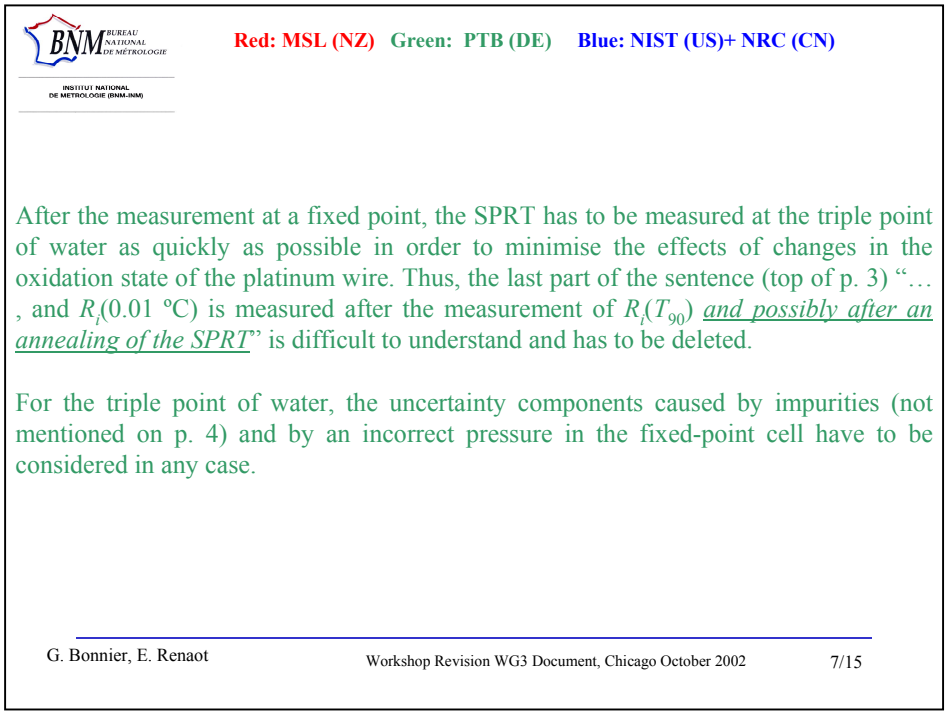
Transparency 5



Outcome

The laboratory must be able to justify the choice of the probability law.
If the law is known without an unambiguous it can be include in the document.
Do you think that for a specific component, determined with a type B method, the associated law is known without ambiguity ? Could you send us some example?
Answer from NMi:
The Probability Distribution Function (PDF) assigned to a Type B uncertainty component will never describe exactly the uncertainty component itself.

Transparency 6



Outcome

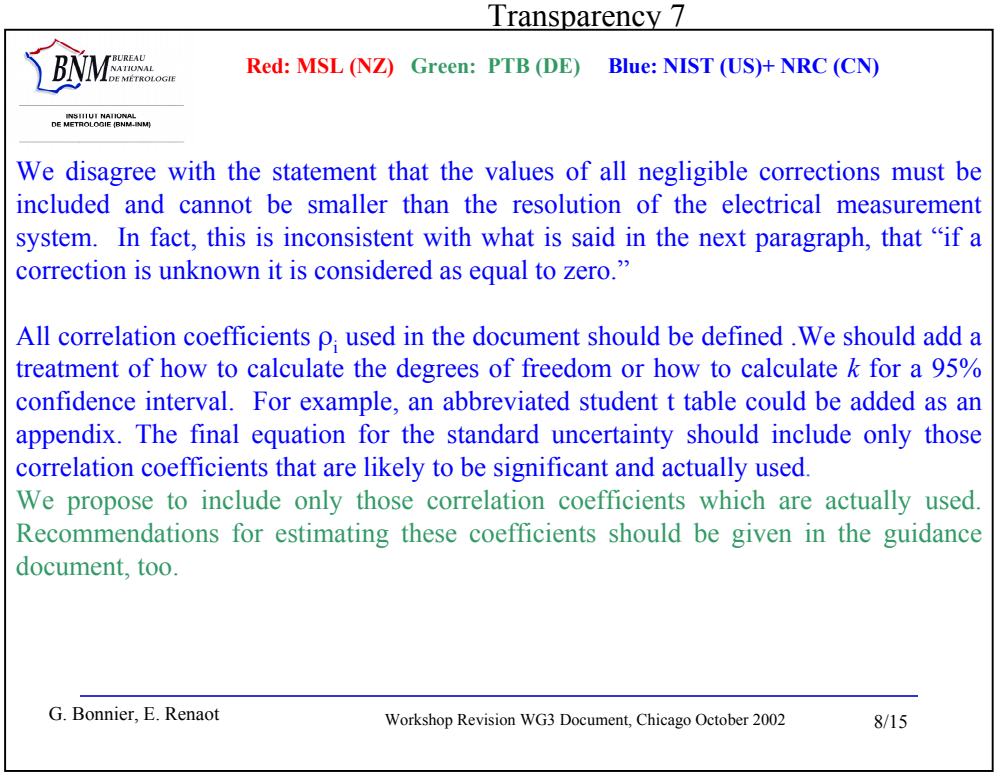
It must be write that the annealing concerns only the HTPRTs

The component $C_{X0.01\text{-}1}$ must be divided on 3 components: Impurities, isotopic composition, and incorrect pressure. These 3 components can be determined globally (by comparing different cells) or separately.

The WG1 must define in which state (annealed, oxided,…) the R(TPW) must be measured

After this workshop we received more comments and we need your point of view on the following questions:

Transparency 7



Outcome

It is necessary to have more debate about the correlation coefficients

What are the correlation coefficients likely to be significant and actually used in your laboratory? How do you determine the value of these coefficients? Do you use an experimental method?

Answer from NMi:

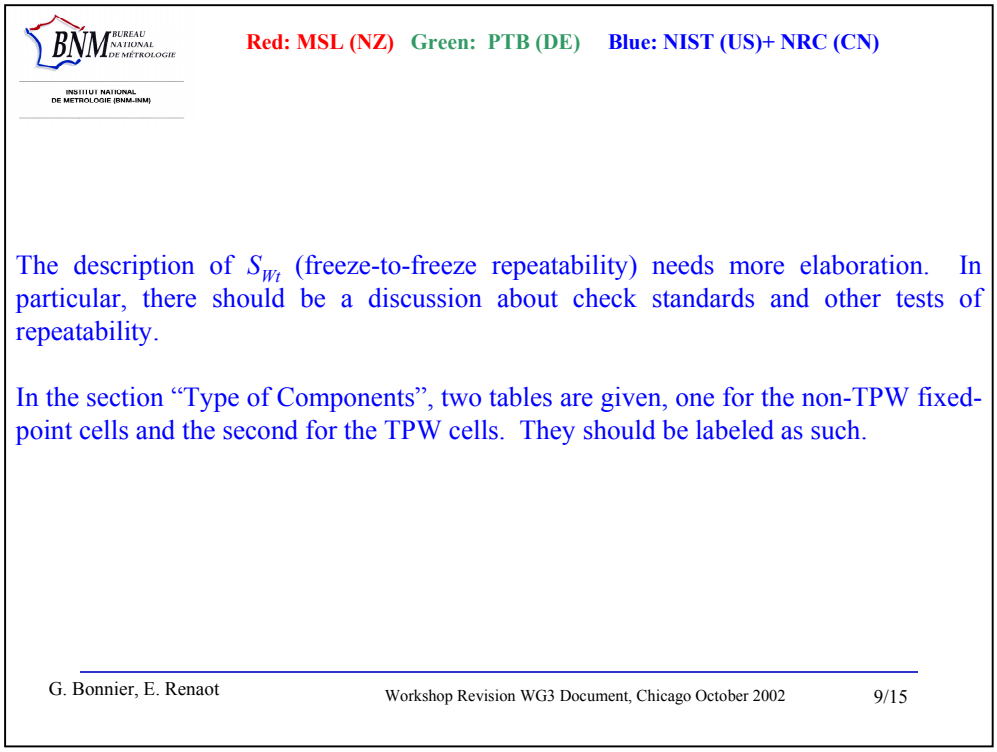
In our laboratory we do not determine any correlation coefficient. As the uncertainty contributions for the bridge are heavily correlated, in the actual calculation we only include the largest contribution.

When the same standard resistor is used for the FP and the WTP, the uncertainty of the standard resistance is cancelled out.

Answer from MSL:

At present the only serious correlation in fixed point work arise because we do not apply corrections for impurities. If corrections were applied then we would eliminate bias and need for inclusion of correlations.

Transparency 8



Outcome

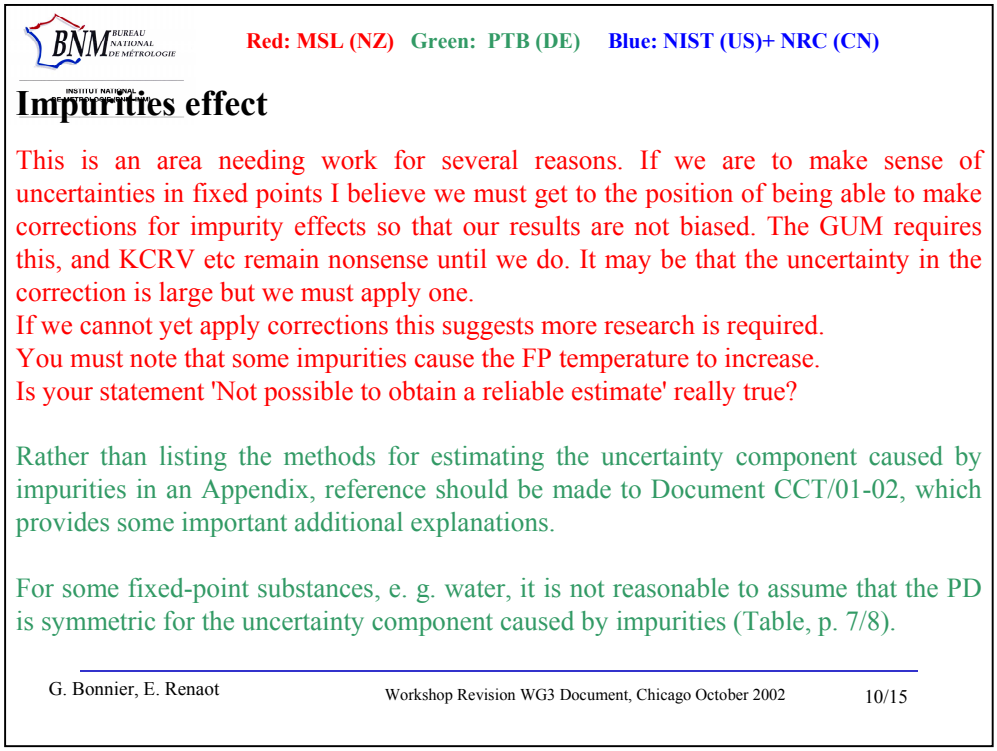
Do you think that freeze-to-freeze repeatability could be determined by check standards or does you think that the measurement conditions during the calibration must be taken into account?

Answer from NMi:

We determine the freeze-to-freeze repeatability from 3 independent realizations of WTP and FP:

Measure FP(1), measure WTP(1), find W(1).
Measure FP(2), measure WTP(2), find W(2).
Measure FP(3), measure WTP(3), find W(3).
Freeze-to-freeze repeatability is the experimental standard deviation of W(1), W(2) and W(3).

Transparency 9



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Impurities effect

This is an area needing work for several reasons. If we are to make sense of uncertainties in fixed points I believe we must get to the position of being able to make corrections for impurity effects so that our results are not biased. The GUM requires this, and KCRV etc remain nonsense until we do. It may be that the uncertainty in the correction is large but we must apply one.
If we cannot yet apply corrections this suggests more research is required.
You must note that some impurities cause the FP temperature to increase.
Is your statement 'Not possible to obtain a reliable estimate' really true?

Rather than listing the methods for estimating the uncertainty component caused by impurities in an Appendix, reference should be made to Document CCT/01-02, which provides some important additional explanations.

For some fixed-point substances, e. g. water, it is not reasonable to assume that the PD is symmetric for the uncertainty component caused by impurities (Table, p. 7/8).

G. Bonnier, E. Renaot Workshop Revision WG3 Document, Chicago October 2002 10/15

Outcome

The WG3 asks to the president of the CCT and to the WG1 to deal with the point of the impurities effect (more precise definition of the fixed points?).

Answer from MSL

Isotopic composition of water

The composition of MSL five cells has been determined and isotopic corrections are applied as suggested. The propagated uncertainties in the corrections are less than 1 µK.

Isotopic fractionation during use

During use of a triple point of water cell, isotope fractionation occurs. For frozen fractions between 10% and 40% the temperature realised is reduced by between 1 µK and 5 µK below that of a cell with a uniform distribution of the isotopes. It is assumed that the definition of the water triple point is for a cell with the equilibrium fractionation so that the fractionation introduces uncertainty but no bias. A standard uncertainty of 1 µK has been assigned.

Impurity due to dissolved gasses

Approximately one quarter of the difference between the temperature of the ice point and the triple point of water is due to dissolved gasses. Thus, any impurity effect due to dissolved gasses is likely to be smaller than the pressure effect due to residual gasses. The assigned uncertainty is zero

Impurity due to dissolved glass

It is known that the borosilicate glass of the triple point cell is weakly soluble in water. Also Hill has suggested that cells deteriorate at a rate of perhaps 4 µK/yr due to this effect, although the variation between cells is very large. When glass dissolves some of the solutes (e.g. sodium) ionize and contribute to conductivity while others do not. Hill also observed that the impurities in old cells are consistent with the composition of the glass, suggesting nearly uniform dissolution of the glass. If it is assumed that the glass dissolves uniformly then the effective conductivity of glass as a solute is about 1.43 mS.m2 per mole of impurity per litre of water.

Ballico describes a method for measuring the conductivity of the water in triple-point cells and hence to infer the concentration of ionic impurities in the water. The conductivity is

measured as the turnover frequency in the cell capacitance versus frequency. For pure water the turnover frequency is about 0.9 kHz. Using the conductivity given above it can be inferred that a correction of 5.6 μK/kHz should be applied to account for dissolved glass. Measurements of the turnover frequency of all of MSL cells (some >20 yrs old) are consistent with Hill drift figure of 4 μ/yr. Also the turnover frequency of cells when freshly sealed is about 1 kHz, indicating that the conductivity is very close to that for pure water. In practice the glass is unlikely to dissolve uniformly so the standard uncertainty in the correction is assigned the relatively large value of 2 μK/kHz. The corrections applied to the five MSL cells included in the comparison range from about 3 μK to 35 μK.

Impurities due to crystal defects, strain, interfacial curvature
When the cell is frozen it is done under non-equilibrium conditions. Initially the distribution of vacancies and other crystal defects will not be at the equilibrium concentration, especially when the mantle is frozen fast enough to cause cracking. Experience has shown that, depending on the freezing method, it may take between 3 days and 2 weeks for the mantle to anneal. In this comparison a heat-pipe cooling stick was used to freeze the mantle very slowly so that no cracks were formed so a 3-day annealing period should be sufficient. It was noted also that during the few days after the mantle was frozen, crystal boundaries had migrated through most of the ice, suggesting equilibrium conditions were reached quite quickly. In practice the annealing period was generally 7 days or more.
A related effect is the change in melting point due to the curvature of the ice crystals. It is assumed that this effect reaches an equilibrium state during the annealing of the cell and that it varies little once the ice is annealed because the radius of curvature of the ice is largely determined by the diameter of the thermometer well.

It is assumed that over repeated measurements and different mantle freezes, any variations in the annealed state will contribute only random error to the measurement of differences. The standard uncertainty in a single measurement is assigned a value of 5 μK, being close to the limit of detection.

Other impurity effects
The other main source of impurity is low-volatility compounds in the source water. For example, light hydrocarbon compounds have a similar boiling point to water so distillation may not remove them. The absolute magnitude of the possible effects is unknown, however the results of this comparison are suggestive. Two of the five cells, MSL 01/02 (the transfer cell) and MSL 96/1, were subjected to a much prolonged degassing period during manufacture (approx. 2 days) and these two cells appear to be some 20 μK higher than the other three cells after all other corrections have been applied. If this difference is taken to be indicative of these impurities then the distribution of the impurity error can be modelled by a rectangular distribution between 0 μK and 20 μK, suggesting a correction of 10 μK and an expanded uncertainty of 10 μK.

Answer from NIST
NIST PRT Laboratory Methods of Estimating the Impurity Uncertainty Component for ITS-90 Fixed Point Cells from Ar TP to the Ag FP (G. Strouse)

Answer from MSL :

Hydrostatic pressure effects

Hydrostatic pressure corrections are applied. The uncertainty is dominated by the uncertainty in the knowledge of the thermal centre of the SPRT and fluctuations in the pressure due to changes with the redistribution of ice with time. Because the same SPRT is used for in each measurement of difference the uncertainties are expected to be highly correlated, and any fluctuations will contribute to the Type A uncertainty.

Residual gas pressure

Bubble compression tests of MSL cells show that the vapour pressure of residual gasses has effects well below 1 μK. The uncertainty is assigned a value of zero.

Buoyancy pressure

The lower density of ice compared to that of water, causes the ice mantle to float and to push against the end of the thermometer well. The pressure on the ice-water interface at the end of the well causes a reduction in temperature. The magnitude of the effect depends on many factors: the frozen fraction, the fraction of ice above the surface of the water, the area of contact between the ice and the well, the thermal connection between the area of contact and the SPRT, the curvature of the end of the thermometer well. For flat bottomed thermometer wells the effect is about 8 μK , but can be amplified considerably for wells with tapered orspherical ends. However the use of a thermally insulating sponge in the thermometer well will insulate the SPRT from this effect. When a sponge is used the assigned uncertainty is zero.

For the comparison carried out here, a sponge was not used. This was done to help locate the SPRT in the centre of the thermometer well in order to reduce possible variations due to changes in the thermal resistance between the SPRT and triple point that would results in variable self-heating corrections. However it is suspected that most of the observed variations in temperature difference were due to variations in the buoyancy pressure effect. Because all five cells are of the same design, the variations introduced are expected to be random and contribute to the Type A uncertainty derived from repeated measurements.

Instrumental effect: Self heating

Self heating corrections are applied by extrapolating to zero current. The correction equation used for the comparison is the usual one based on three measurements at currents of 1mA, √2 mA, and 1 mA. The magnitude of the corrections varies according to the dimensions of the thermometer well in the triple point cells and the construction of the SPRT sensor. The two thermometers used by MSL in this comparison are of the L&N 8163 and L&N 8167 models. The 8167 model has the lower self heating of about 430 μK compared to 1500 μK for the 8163 model. The correction varies due to slight changes in the immersion conditions and position of the SPRT affecting the thermal resistance, however this is assumed to be random over averaged measurements, and contribute to the Type A uncertainty.

A second possible error arises if the ratio of the two sensing currents is in error. For a nominal current ratio of √2 and a self heating correction of 1500 μK, the current ratio must be accurate to 0.025% to ensure the error is less than 1 μK. This is so for MSL F18 bridge. The uncertainty due to this effect is below 1 μK and assigned a value of zero.

Bridge noise and non-linearity

For absolute measurements where the water triple point is used for calibrating SPRTs the standard uncertainty in averaged bridge readings is determined using a resistance bridge calibrator to be about 2.5 10^{-8}. With a standard resistor of 100 ohms and a 25 ohms SPRT this corresponds to an uncertainty of about 25 μK. The uncertainty is due to a combination of noise, which is random over time and bridge reading, and differential non-linearities, which are random only with bridge reading.

For the differential measurements employed in the comparison, a 25 ohms standard resistor was used so the effect of uncertainty in bridge readings is reduced to about 6 μK. Further, the measurements are made over a very narrow range of resistance ratios so correlation is expected to reduce the effect of the largest differential non-linearities. For the comparison, separate uncertainty terms for bridge noise and remnant non-linearity are not required since they contribute to the contribute to the Type A uncertainty in repeated measurements.

Perturbing heat exchanges
There are three tests we have carried out for perturbing heat influences.

The immersion profile for the SPRT, as it is increasingly immersed in the cell,should show a slope corresponding to the hydrostatic pressure correction. With MSL cells, which are larger than most, there appears to be at least 50 mm of excess immersion suggesting that heat leaks up the stem of the thermometer are negligible.

Routinely the triple point cells are maintained in self draining dewars containing shaved ice. The lid to the dewar has a hole slightly larger than the SPRT handle to allow the lid to be in place when the cell is in use. A black velvet cloth is used to cover the handle to prevent light from penetrating the cell. No change in temperature is observed when the cloth is removed, or when the depth of the layer of ice over the cell is increased.

The uncertainty due to perturbing heat exchanges is assumed to be zero.