WORKING GROUP 3 REPORT TO CCT: May 2014

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Terms of reference:

To review and recommend methods for evaluating, combining and reporting uncertainties in temperature, humidity, and thermophysical properties measurements and to ensure consistency of CCT advice in matters related to uncertainty.

Working Group 3 is tasked with continuing the production of documents on uncertainty budgets for contact thermometry, and to act in an oversight role for similar documents produced by other working groups.

1. Introduction

During this term, the attention of WG3 has been focussed on two tasks; preparing an uncertainty guide for noble-metal thermocouples, and a review of the uncertainty guide on SPRTs (CCT/08-19rev, *Uncertainties in the Realisation of the SPRT subranges of ITS-90*). Otherwise, the Working Group's activities have been light with a major commitment of members (especially Chairman) to the TEMPMEKO 2013 conference, and to other working groups. During the term, WG3 received a request from WG7 to develop a guide for the uncertainty analyses of sealed metal fixed-point cells.

The current activities on WG3 task list include, in order of priority

- Review of CCT/08-19rev.
- The uncertainty guides for noble-metal thermocouples.
- Guide on sealed metal fixed-point cells
- Uncertainty in the extrapolation of long-stem SPRT calibrations to liquid nitrogen temperatures
- A better understanding of non-uniqueness in the SPRT sub-ranges of ITS-90.
- A watch on the development of the GUM revision.

These issues are discussed in more detail below.

2. Membership

During the term:
Vito Fernicola replaced Franco Pavese as the INRIM representative.
Dr Pavese stays on as an independent expert
Murat Kalemci (UME) replaced Aliye Kartal Dogan
Ronan Maurice (LNE-CNAM) resigned, and
Jonathan Pearce (NPL) joined the group.

For the purposes of the preparation of the uncertainty guide for noble-metal thermocouples, the working group has also co-opted expert members:

Ferdouse Jahan (NMIA)
Frank Edler (PTB)
Karen Garrity (NIST)
Hideki Ogura (NMIJ)

3. Issues

3.1 Review of CCT/08-19rev

The review of the SPRT uncertainty guide was prompted by a letter from Ms Sonia Gaiță (Romania, received 6 Jan. 2014) advising Dr Duan of problems with the Guide. The letter was accompanied by two supporting documents. The first document discussed the method by which uncertainty is propagated in the guide, while the second listed a number of errors in the guide. Around the same time, WG1 was preparing the revised Chapter 5 on SPRTs for the *Supplementary Information on the ITS-90*, and some of the text on the sources of uncertainty and uncertainty analysis was being abstracted from sections of CCT/08-19rev. It was clear during the process of preparing the chapter that there were a number of sections of the CCT/08-19rev that were now well out of date. It seemed timely to expand the evaluation of Ms Gaiță's critique to a more thorough review of the guide.

The first response to Ms Gaiță's concerns was to quickly review the supporting documents to determine the seriousness of the issues raised and the immediate response required. The following email was sent to Ms Gaiță.

> You will be glad to know that as a result of your email we have decided to review the document in its entirety, in part to address your concerns, and in part because in the five years since the document was presented to the CCT, significant advances have occurred in some areas of our science and the document may longer be providing the most up-to-date advice to users of SPRTs. The task group assigned to the review comprises half a dozen members of CCT-WG3 (Uncertainties) representing several key NMIs and includes the best experts in this area. They expect to complete their review in time for the scheduled CCT meeting this May. You will receive a copy of the report.
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> After some discussion we decided not to withdraw the document from the public domain. Despite possible errors, it remains the best guidance available for users of SPRTs – there is currently no other document that collates all of the sources of uncertainty, nor provides such complete advice on how to calculate and propagate uncertainty. Another working group is currently working on a revision of the SPRT chapter for the Supplementary Information for the ITS-90, and it may be that some of the information will be included there. In the meantime, we will include a warning to users, on the cover of CCT/08-19rev, to advise that it is under review. This decision will be reviewed at the time of the CCT meeting once the document review is complete and a draft of the Supplementary Information chapter is available.

The detailed review has now been completed. With respect to Ms Gaiță's first document on methods for propagating uncertainty, her suggestion for propagating uncertainty is mathematically equivalent to that currently used in CCT/08-19rev. Indeed there are three equivalent approaches known, each with advantages in different situations. Her preference most closely reflects the formulation of the ITS-90 equations in terms of deviations. The approach adopted in the guide, although not expressed in terms of deviations, is marginally simpler and is most like the algebra in mathematical texts on interpolation, which aids in the understanding of interpolation process and in the origin interpolation errors (the various forms of non-uniqueness). This discussion echoes a similar discussion between authors involved of the revised SPRT chapter of the *Supplementary Information*. It may be that there should be some discussion in the guide of the alternative propagation methods.

Most of the errors identified in Ms Gaiță's second document can be classified into three main groups (i) typographical errors in equations (some repeated several times due to the different variations in the equations), (ii) errors of omission where definitions are incomplete or imprecise, and (iii) a lack of clarity linked to our failure to give an explicit statement of the measurement model. The first two groups of errors are minor and simple to correct, but correcting the third group is not so simple. While it is obvious where a statement of the measurement model should be included in the guide (Section 9), it is not obvious how to include it. The complexity arising from several layers of calculation (SPRT and standard-resistor resistance models, bridge ratios, self-heating correction, temperature related corrections, then interpolation), the variations due to different calibration methods, variations between different fixed points, and variations in the choice of interpolating equation, was the very reason such as statement was not included in the first place. However, we concluded there should be some sort of summary collating all of the mathematical models.

The review of the scientific content of the guide identified several areas requiring major revisions or additions:

- A more complete and definitive statement on the uncertainties associated with sealed metal fixed-point cells.
- Expansion of the discussion on impurities in fixed points
  - Emphasise that the number of impurity particles dissolved in the solid/liquid determines the temperature elevation/depression. Account must be made of chemical reactions causing precipitation of impurities, or changes to different species.
  - Methods for correcting for impurities and their limitations.
  - Tabulation of the distribution coefficients
  - Where distribution coefficients with $k > 1$are known to be rare (e.g., with tin), use a single-sided OME method
- Isotope effects for neon
- New section on interface curvature and initiation effects in metal fixed points (Gibbs-Thomson effect) and conclusions from numerical models
- Update isotopic correction constants for water triple point
- New data on drift rates of TPW cells, and dilution effects
- Update information on use of bushings in fixed points
- Update information on impurity and drift effects in SPRTs
- Update information on non-uniqueness, including the discontinuity at TPW
- Optimal measurement strategies for self-heating correction in SPRTs
- Anomalous self-heating in C-SPRTs
- Use of Alan variance to investigate resistance bridge performance

After some discussion, the working group has decided that we should make a minimal and quick revision to CCT/08-19rev addressing as many of Ms Gaiță's concerns as is practical. The revised document should retain the Working Document number CCT/08-19rev so it is clear to users that it represents a snapshot of the science circa 2008. Then at some time in the future a full revision addressing, the problem with the measurement model, correlations (also raised by Ms Gaiță), and updated for scientific content can be completed. This cannot occur immediately because of members' commitments to other projects, and is probably best left until sometime well after the SPRT chapter of the Supplementary information has been published.

3.2 Uncertainty guide for noble-metal thermocouples

The group has commenced the development of an uncertainty guide for noble-metal thermocouples (Types R, S, B, Au/Pt, and Pt/Pd). The need for a guide was discussed at the last CCT meeting and prompted by concerns, raised initially by Dr Ballico (NMIA), about uncertainties associated with the use of calibrated Type R and Type S thermocouples when the calibration state of the thermocouple was not defined. The situation is made worse by different NMIs using different anneal states for the calibration conditions.

For the most part much of the material required for the guide is well known and readily accessible. However there are several points where the information is less well-known, fragmented, or lacking:

- Calibration state and hysteresis: In order for thermocouple users to gain the lowest uncertainties, it is essential that the thermocouples are calibrated in a well-defined state, and that state is reported on the calibration certificate. The guide should provide estimates of uncertainties due to hysteresis when thermocouples are not used in the nominal calibration state. This information is known for Types R and S, but may require further research for the other noble-metal thermocouples.
- Inhomogeneities: One of the largest sources of uncertainty in the use of thermocouples is inhomogeneities in the Seebeck coefficient along the length of the thermocouple. Some laboratories measure the inhomogeneity and include an uncertainty term but as yet there is no guidance on the resolution required of the homogeneity scanner, or how such data should be interpreted in the uncertainty analysis. Guidance is necessary because most industrial furnaces employing these thermocouples have sharper gradients than the calibration furnaces and oil baths typically used to measure inhomogeneity.

- Extrapolation: A number of laboratories commonly extrapolate calibrations above the silver or copper points, but the uncertainties associated with these procedures have not been investigated.

In order to address these points and help develop the guide, WG3 has co-opted expert members Frank Edler (PTB), Ferdouse Jahan (NMIA) and Karen Garrity (NIST).

3.3 Uncertainty guidance for sealed fixed point cells

Working Group 7 (comparisons) has asked WG3 to consider and advise on the uncertainty to be assigned to sealed metal fixed point cells used for long-stem SPRTs (excluding mercury). The issue was considered briefly in CCT/08-19rev, but firm guidance was not provided. Since the SPRT uncertainty guide was published, it has become apparent that manufacturers of the cells may be unable to seal the cells (while they are at the fixed point temperature) at the standard pressure, 101 325 Pa due to the altitude and low ambient pressure at the manufacturing site. This combined with other technical limitations may lead to a wider dispersion of realised temperatures than previously expected.

Working Group 3 has concluded that sealed cells should ideally be calibrated as for a secondary standard, in which case the uncertainty will be reported on the calibration certificate. Guidance should be given for uncertainty calculation in the absence of a calibration, which takes account of the very wide range of internal pressures that can occur through a range of mechanisms.

3.4 Extrapolation of long-stem SPRTs to liquid nitrogen temperatures

As mentioned at the previous CCT meeting, Dr Rusby (NPL) raised concerns about the uncertainties associated with the extrapolation of calibrated long-stem SPRTs below the triple point of argon. A recently published EURAMET Technical Guide tg-1 specifically addresses this issue and has provided appropriate authority to support the practice. However, WG3 believes an archival paper presenting supporting mathematics to the empirical evidence given in the EURAMET guide would be of value to the community. We are hopeful that this might be undertaken in the near future.

3.5 Sub-range inconsistency in the SPRT sub-ranges of ITS-90

Sub-range inconsistency (SRI or Type 1 non-uniqueness) has three main causes (i) variations in the $R(T)$ of different SPRTs, (ii) inconsistency amongst the W_r values assigned to the fixed points by ITS-90, and (iii) variations in the fixed point realisations. SRI is a major contributor to uncertainty in the realisation of the SPRT sub-ranges of ITS-90, and, at present, the uncertainty guide prepared by the Working Group has simply adopted a single uncertainty to characterise all SPRTs. Although no progress has been made, we have a group of members interested in studying SRI, with a view to assigning an SRI uncertainty to specific SPRTs. The same study would also provide information on the inconsistency of the W_r values assigned by ITS-90, and may also provide insight into possible correlations between Type 1 and Type 3 non-uniqueness. Such a study has gathered increased importance with the exposure of the discontinuity in ITS-90 at the triple point of water, which is an artefact of SRI. No progress has been made since the last CCT meeting.

3.6 The GUM revision

The JCGM has announced their intention to revise the GUM, and that the GUM revision will be based on Bayesian statistics. There is still too little known about the revision to provide informed comment, but concerns remain about the consequences of a change from frequentist to Bayesian statistics. Working Document CCT/12-07, outlining some of the concerns, was presented at the last CCT and a copy was forwarded to the JCGM working group, but no feedback has been provided.