On the need to tackle GUM requirement to perform the corrections for recognised systematic effects: the effects of chemical impurities on the realisations of fixed points of the ITS-90.

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The expression of uncertainty in the field of metrology is based on the *Guide to the expression of uncertainty in measurement* (GUM) [GUM 1999]. According to the GUM (3.2.4), "it is assumed that the results of a measurement have been corrected for all recognised significant systematic effects".
The International Temperature Scale of 1990 (ITS-90) specifies that the substances used for the realisation of the 'fixed points' must be "ideally pure". However, an analytical assay of any fixed-point material will necessarily find various chemical impurities to be present, or will report that they may be present at concentrations below the detection limit of the method used. Some of them are "significant". Thermometry is therefore becoming dependent on chemical metrology, as discussed in [Hill and Rudtsch 2005], similarly to what is also happening for isotopic composition [Pavese 2005].

To fully implement the intent of the GUM, corrections should be applied for all chemical impurities that significantly affect the value of the measurand.
This dependence is becoming more important with the decrease in magnitude of the other components of the fixed-point uncertainty budgets that have come about as the result of improvements in the experimental techniques and instruments and improvements in our understanding of the thermal and physical-chemical parameters involved in the temperature scale realisation.

As a result, the contribution from chemical impurities can today easily *dominate the uncertainty budget*, so the normal practice, of omitting any correction for this effect and expressing the resulting bias in the realized temperature as an uncertainty to be added to the uncertainty budget of the fixed point realisations, assuming that the mean effect is zero, so being the correction.
This approach has two main problems: i) there is no evidence that the assumption of the mean effect of impurities being zero is true, on the contrary for some substances there is evidence that is never zero; ii) it can limit the obtainable accuracy of the best realisations and can render irrelevant the reduction in the uncertainty that can be achieved by taking into account the effect of the isotopic composition of certain substances.

On the other hand, the problem cannot be solved only by requiring the use of the purest available substances available, since some specific thermometric needs are not relevant to the market of common use of many of the 'pure' substances used in thermometry. E.g., some impurities are irrelevant to other purposes, so that sufficiently accurate analytical assays for some impurities relevant only to thermometry are presently not readily –or at all– available.
In addition, obtaining a value for a correction sufficiently reliable and with a sufficiently low uncertainty is not only a matter of reliable and traceable analytical assays, but is also connected to the state-of-knowledge of the physical-chemical conditions of the substances inside the thermometric cells, including the spatial distribution of the impurity amount concentrations (however, the latter problem can be a minor issue in very small cells, to be used with small-size thermometers).

These issues are addressed by Working Group 1 [WG1 2005] of the Consultative Committee for Thermometry (CCT) and, for the implications on uncertainty, by its Working Group 3 [WG3 2005, White *et al.* 2007]. In principle, also other CCT Working Groups are interested in this subject matter, namely WG2, WG4 and WG8 are supposed to make use of the corrections after they are established, for recommending them, e.g., when performing KCs or in the process of evaluating the CMCs; or, WG9 on thermophysical properties can act as a direct promoter of some of the needed activities.

In fact, a choice is now needed *for each specific substance* among the developed methodologies.
Thanks to the work performed by WG1 and WG3 on this subject matter, we already have a valuable starting point, the identified methodologies SIE and OME, which appear to be sound and well based.
In this respect, also the outcomes in the near future of activities like the EUROMET Project 732 from the triple point of water up and of the iMERA Project on neon (see other CCT document) can be a good starting point.

What is now needed is a work of synthesis allowing to identify which method will result to be the most appropriate for each substance of interest.

For this purpose, a broader range of the competences and synergies is necessary, and links may become necessary with frames competent in chemical assays: CCQM and IUPAC are two of those potential frames.

Having considered the literature information, the state-of-the-art and the undergoing experimental activities and studies, I am convinced that *there are already some substances for which a solution is close* and a CCT decision is at hand to be adopted for inclusion in the Technical Annex of the ‘mise en pratique’ in a 2-years time span (e.g., tin [Fellmuth and Hill 2006], e-hydrogen, neon, oxygen, argon). For other substances, a solution can require more effort and time.

This is prompting this proposal to the 2008 CCT Meeting.

The field of testing is presently accelerating in moving toward a solution of similar problems that often need be tackled in order to perform reliable corrections for bias and to estimate the residual uncertainty.

It seems to me that is the time now also in calibration to start a specific action concerning formally agreed recommendations about the correction for the effect of chemical impurities, *probably specific and different for each substance*, especially considering that sufficient interaction has also to be found outside thermometry fields, namely with chemical metrology, a certainly slow process. If CCT never starts, it will never succeed, so limiting the best accuracy that can be achieved for several reference points and keeping to the status of a theoretical exercise the excellent work already done by WG1 and WG3.

On the other hand, it is necessary to facilitate the documentation, research and assay activities necessary to move toward the finalisation of recommendations for the substances still suffering of incomplete knowledge, by identifying on a *progressive time scale* the ones that are closer to a solution, requiring less work to complete the necessary knowledge, and in promoting the relevant activities in the laboratories, NMIs or others.

Clearly this work is better done by an *ad hoc* group than by WG1 and WG3 (or WG9) alone, not only because they are overloaded by many other tasks or because they have already produced the necessary documents about methodologies, but also because *finalising the issue for each substance is a different broader task*. I do not see any conflict in respect to the terms of reference of these or other present WGs.

Therefore, the best way to proceed should comprise two actions:

a) to form an *ad hoc* CCT Task Group, in order to have a sufficiently comprehensive group of experts to tackle the issue and to work toward a *progressive* solution of the problem for the substances of use in thermal metrology (*a draft proposal is attached as Appendix A to this document*).
b) to issue at the 2008 meeting a CCT Resolution to promote further activities in this field where they are still needed (*a draft proposal is attached as Appendix B to this document*)

By starting now, there is a good chance that by the time of the foreseen revision of some SI units in 2011 proposals will also be finalised for a number of thermometric substances.

References

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Appendix A

Proposal fo the **Term of reference of a Task Group (TG-QCI)**
“**Quantification of the effect of chemical impurities in substances used in thermal metrology**”

The remit of the new Task Group CI is to study the problems and the limits connected with the application of the GUM statement “it is assumed that the results of a measurement have been corrected for all recognised significant systematic effects”. They concern both the way a numerical correction can be obtained and the degree of its reliability in view of the correction, and the way the uncertainty component of the uncertainty budget due to this effect is estimated.

Terms of reference:

- *to gather information from the relevant Working Groups and directly from the literature* dealing with evaluation of information about the effect of chemical impurities in substances relevant to thermal metrology;
- *to gather information from the relevant Working Groups and directly from the literature* dealing with evaluation of information about the uncertainty that is associated to data on diluted mixtures of chemicals in substances relevant to thermal metrology;
- *to gather additional information from external bodies and groups*, in both metrology and testing areas, about the statistical treatment of bias in methods and in data;
- *to identify the best procedure, among those identified by WG1, that can bring, for each specific substance of interest in thermal metrology*, to the effect of chemical impurities being quantified and taken into account correctly, effectively and consistently;
- *to identify the best method, among those identified by WG3, to estimate the uncertainty arising from the above effect that should be included, for each specific substance of interest in thermal metrology*, in the uncertainty budget of metrological experimental realisations in a correct, effective and consistent way;
- *to identify the issues that should be dealt in co-operation with external bodies, namely CIPM CCQM and IUPAC,* to obtain from chemical metrology the necessary integration of tools bringing, in particular, to sufficiently sensitive, accurate and traceable analytical assays of chemical impurities in substances relevant to thermal metrology.

TG-QCI is tasked with producing *a set of subsequent documents, one for each specific substance or, when possible, group of substances,* illustrating in details the rational for the recommended procedure and method, together with a recommendation to the CCT concerning its adoption for each particular substance, for inclusion in the Technical Annex to the ‘mise en pratique’ of the kelvin and for consideration of WG4, WG5, WG7, WG8 and WG9 for the parts concerning their respective competences.
Secondarily, to produce additional recommendations on the same subject concerning substances not presently used in formal temperature scales but useful to work in thermal metrology and of interest of WG2 and WG9.

Appendix B

Proposal for a **CCT 2008 Resolution N. …**
"Need for an increase of the investigations concerning the effects of chemical impurities in pure substances of use in thermal metrology"

The CCT,

having become aware of the present difficulties to obtain for several substances of interest in thermal metrology the necessary information, the production of new data and the setup of new techniques and facilities that can solve specific problems needed for the full evaluation of the effect of chemical impurities in pure substances of interest of thermal metrology, then allowing the metrologist to chose the best-suited methodology to take this effect into account in a GUM-compliant way among the already identified ones,

invites

the National Metrological Institutes and all kind of Institutions working in this field to intensify their activities in order to provide the needed experimental data and chemical-physical studies, and

the funding bodies to take in due consideration these themes that are critical to the improvement of the quality of the contribution of thermal metrology to the progress of science and of the entreprise and societal needs.