The role of the impurity component in the budgets of uncertainties

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I realize that to include a couple of new components to the budget of uncertainties is much easier than to remove one conventionally adopted component. Nevertheless, in this paper I will try to address some points against including the component coming from the impurity of metals in the full budget of uncertainties of the fixed point realizations.

The concentration of impurities is the main reason of the difference between fixed point cells. To reduce the non-uniqueness of the International Temperature Scale we have to put some correction to the value of the cell temperature with respect to the ideal purity cell. Since the value of the correction is very difficult to estimate accurately, it is usually set to zero, and the impurity uncertainty component is included in the budget of uncertainties of the fixed point realizations. Actually, it looks like we always make **an imaginary comparison with the ideal cell**. The role of the impurity component is to take into account the uncertainty of this imaginary comparison. Usually the impurity component is evaluated from the sample certificates or freezing curves as the value of possible change in the liquidus point temperature. Sometimes this value is divided by root three, sometimes not, but it does not matter considering a very low reliability of the evaluations.

The uncertainty budget of international comparisons

The impurity uncertainty component is usually included in the budgets of uncertainties submitted by the participants of international comparisons. At least, in CCT KC-3 and CCT KC-4 it was one of the components adopted by the coordinators and participating NMIs. The question is why each participant should make the imaginary comparison with the ideal cell, if the goal of the international key comparisons is to estimate the difference between the real fixed point cells of different countries? Why could not we manage without the imaginary intermediate cell? Obviously, the comparison with the ideal cell will increase the resulting uncertainty of the key comparisons. Probably it is better to exclude this component from the uncertainty budget?

The uncertainty budget of NMI reference cells

One can argue that sometimes we compare not only the fixed point cells, but the realizations of the temperature scale in different countries (as in CCT KC-3), and, so, we should compare the temperatures of the fixed points in association with the combined uncertainties which NMIs give to their customers. However, it seems that the including of the impurity component to the budget of uncertainties for a NMI reference cell, which the NMI reports to its customers, would not be justified also. The reference cell of a National Standard should bear the reference temperature, which is equal to that defined in the ITS-90, and the information about possible difference between this cell and the reference cells of other countries, obtained through key comparisons. It is really not necessary to know how this cell deviates from the ideal purity cell.

The other problem is how to choose the reference cell for a National Standard in order to ensure a small deviation from the KCRV and good consistency of the calibration results. No doubt, the reference cell has to be of the highest purity. However, everybody will agree, that is not easy to estimate the real impurity concentration in metals. Actually, only two methods are used at the present time for the estimation. The first is the analysis of the sample certificate, provided by the

manufacturer. The second is the analysis of the freezing and melting curves. Both methods are based on the Raoult's law of dilute solutions, both methods are not reliable. It is well known that there are a lot of limitations in using the Raoult's law of dilute solutions, the most serious ones are the conditions of the freeze and the segregation of impurities. As was shown in document CCT/03-12, the application of this law can sometimes results in a very significant underestimation.

Three methods were suggested in paper CCT/03-19 for the analysis of impurity concentrations besides the calculations using the sample certificate. The question is if these methods are really different methods to crosscheck the results? Obviously, the freezing curve method and the 1/F method should give identical results, since they are applied to the same freezing curve. The difference can occur only as a result of errors in the linear approximation. The direct comparison of fixed point cells in one laboratory may help to find out differences in the impurity concentrations of the cells. However, we can not be sure which cell is better. It is not only theoretical speculations, but it was observed several times at VNIIM, that a low-purity zinc can have a greater freezing temperature than the reference high-purity zinc. I should admit here that this phenomenon we saw only for zinc and for gallium. As a general rule, impurities really cause the freezing temperature to decrease. So, the methods based on the comparison of the freezing curves may be useful for choosing the best laboratory cell, especially if one has such excellent equipment as that at NIST and can obtain such perfect freezing plateaus. However, no impurity uncertainty component should be ascribed to the reference cell.

One useful method for choosing reference cells is to analyze the consistency of all set of the fixed point cells using redundant fixed points, overlapping ranges and alternative deviation functions. This method is used in VNIIM Standard and it really helps to reveal problems with some fixed point cells.

The uncertainty budget of a Secondary Standard

When the reference cell has been chosen we can compare this cell with the cells of Secondary Standards using for the realization of the ITS-90 all over the country. At this step, it seems justified to make corrections to the defined temperatures of the ITS-90 for the Secondary Standards in accordance with the results of this comparison, because it makes the temperature unit be traceable to the National Standard. Of course, the correction can be made only if the reproducibility of the comparison result is smaller than the correcting value.

Summarizing my considerations, I would like to suggest the following treatment to the problem of impurities in the fixed point cells:

- at a NMI try to choose the best cell by some methods, but **not** ascribe to this reference cell any uncertainty component coming from the impurities;
- compare the reference cell with the cells of other NMIs in the course of international comparisons, **not including** any impurity component in the reported budget of uncertainties;
- at the NMI make comparisons between the National Standard cell and Secondary Standard cells and **apply corrections** to the cells according to the results of these comparisons.