

Method for determining acceptable CMCs to ensure consistency with KC results

Maurice Cox, Peter Harris and Martin Milton
National Physical Laboratory, Teddington, Middlesex, TW11 0LW, UK
maurice.cox@npl.co.uk

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Abstract

We propose an approach for determining minimum acceptable CMCs for laboratories that participate in a KC. It applies when the CMCs and the KC refer to the same measurand (that is the same species, the same matrix and the same amount fraction) with the same measurement procedure. Our approach is based on ensuring that the CMCs are consistent with the results of the KC.

1 The proposed approach

Paragraph T.7 of the MRA states that

“... calibration and measurement capabilities ... listed for each participating institute in Appendix C ... must be consistent with the results given in Appendix B, derived from the key comparisons ...”

It is general practice to interpret the consistency of results by the use of the following criterion:

the interval relating to a 95 % level of confidence for the DoE contains zero.

Subject to meeting this criterion, it is generally accepted that

the minimum acceptable CMC (in terms of a standard uncertainty), $u_m(\text{cmc}_i)$, should be the standard uncertainty $u(x_i)$ associated with the participant's measured value x_i in the KC, i.e. $u_m(\text{cmc}_i) = u(x_i)$.

For a participant that is not consistent with the KCRV, it is necessary to determine a justifiable value for $u_m(\text{cmc}_i)$, which must be larger than $u(x_i)$. This may arise as a result of a genuinely

overlooked effect or a consequence of statistical variability. Since, in general, it is not straightforward to distinguish between these two possibilities, they are placed on an equal footing.

We propose that $u_m(\text{cmc}_i)$ should be determined by $u(x_i)$ combined in quadrature with $u(b_i)$:

$$u_m^2(\text{cmc}_i) = u^2(x_i) + u^2(b_i). \quad (1)$$

where the standard uncertainty $u(b_i)$ relates to the performance of participant i in the KC as follows:

$$u^2(b_i) = \frac{d_i^2}{k^2} - u^2(d_i).$$

with

$$d_i = x_i - x_{\text{ref}}$$

and x_{ref} is the KCRV. It is shown in Annex B that the right-hand side of expression (1) is the smallest value for $u_m(\text{cmc}_i)$ giving consistency for participant i .

Some examples showing the results of using expression (1) are presented in Annex A. There are two particular cases of expression (1). When a KCRV is formed independently of x_i .

$$u^2(d_i) = u^2(x_i) + u^2(x_{\text{ref}}).$$

giving

$$u_m^2(\text{cmc}_i) = \frac{d_i^2}{k^2} - u^2(x_{\text{ref}}). \quad (2)$$

When a KCRV is formed as the weighted mean of the x_i .

$$u^2(d_i) = u^2(x_i) - u^2(x_{\text{ref}}).$$

giving

$$u_m^2(\text{cmc}_i) = \frac{d_i^2}{k^2} + u^2(x_{\text{ref}}). \quad (3)$$

These results also apply when the KCRV is formed as the weighted mean of the largest consistent subset, expression (2) when participant i is not in the subset and expression (3) when it is.

References

- [1] BIPM, IEC, IFCC, ISO, IUPAC, IUPAP and OIML. Evaluation of measurement data — Guide to the expression of uncertainty in measurement. Joint Committee for Guides in Metrology, JCGM 100:2008 (GUM 1995 with minor corrections). http://www.bipm.org/utils/common/documents/jcgm/JCGM_100_2008_E.pdf

A Examples

The proposed approach is illustrated using the following examples:

- CCQM K-16, natural gas (nitrogen, high calorific value): figure 1;
- CCQM K-16, natural gas (neo-pentane, high calorific value): figure 2;
- CCQM K53, oxygen in nitrogen: figures 3 and 4 (data extracted from Draft A report);
- CCQM P73, nitrogen oxide in nitrogen: figure 5.

In each case two graphs are presented. The first shows the DoEs for the participants as the 'error bars' $[d_i - U(d_i), d_i + U(d_i)]$ with $U(d_i) = 2u(d_i)$. The second shows the expanded uncertainties $U(x_i) = 2u(x_i)$ (left, open bars) and $U(\text{cmc}_i) = 2u(\text{cmc}_i)$ (right, closed bars) with $u(\text{cmc}_i)$ calculated using expression (1) for participants that are not consistent. For those participants that are consistent, $U(\text{cmc}_i)$ is taken as $U(x_i)$.

For CCQM K16 the reference values $x_{\text{ref},i}$ and the associated standard uncertainties $u(x_{\text{ref},i})$ are formed independently of the results provided by the participants. For CCQM K53 and CCQM P73 the results provided by a subset of the participants are used to form the values $x_{\text{ref},i}$ and $u(x_{\text{ref},i})$. For CCQM K53 the proposed approach is applied for different choices of the participants used to form $x_{\text{ref},i}$ and $u(x_{\text{ref},i})$.

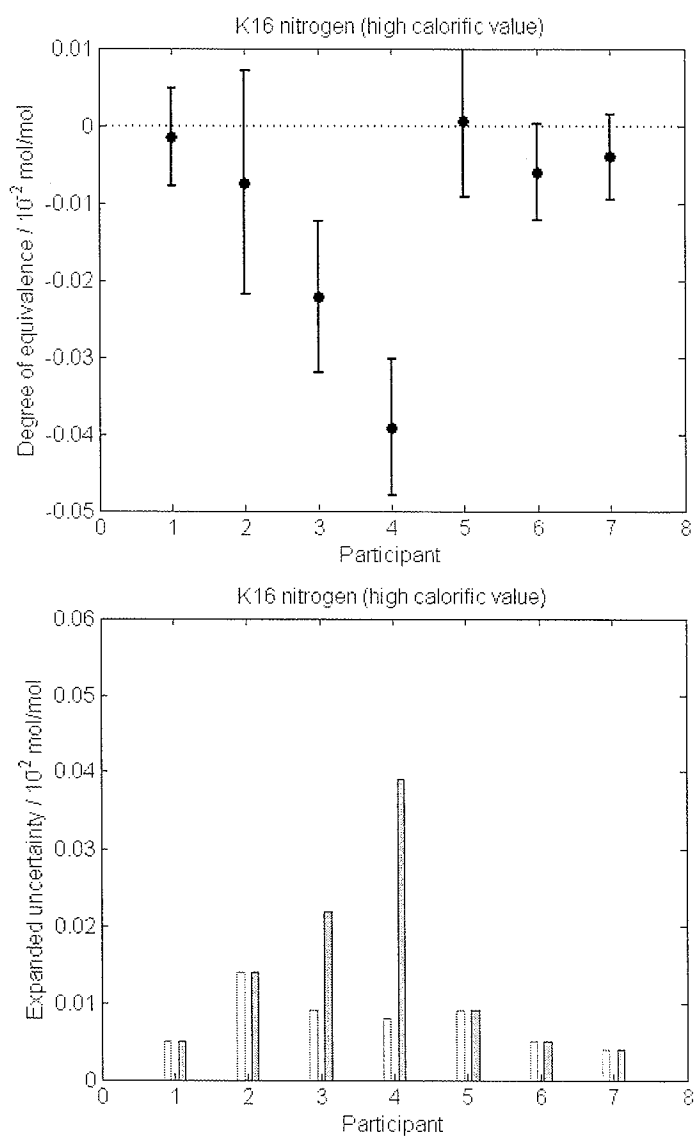


Figure 1: DoEs depicted as 'error bars' $[d_i - U(d_i), d_i + U(d_i)]$ for the participants (top), and expanded uncertainties $U(x_i)$ and proposed $U(\text{enc}_i)$ (bottom) for the species nitrogen (high calorific value) in CCQM-K16.

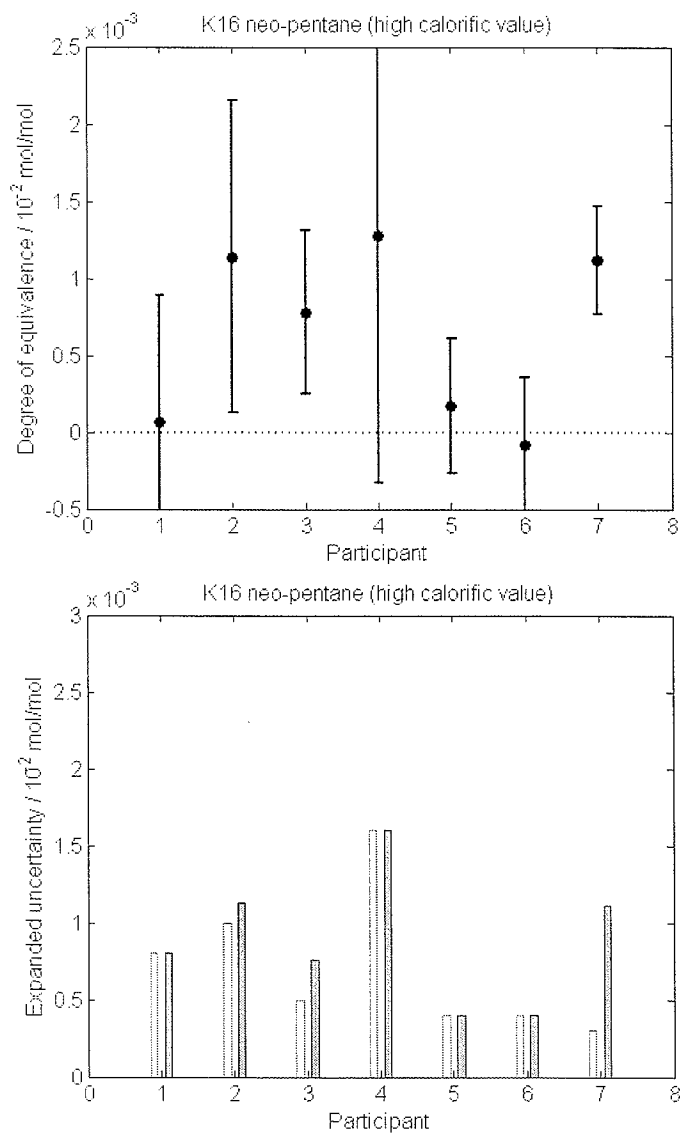


Figure 2: As Figure 1 except the species is neo-pentane (high calorific value).

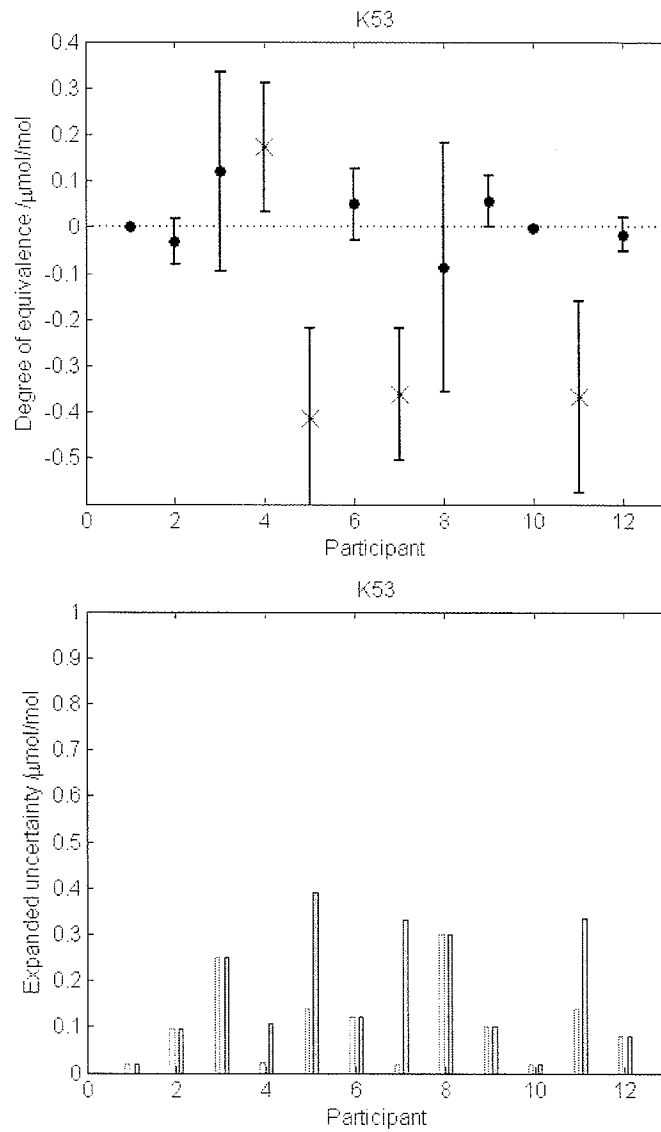


Figure 3: As Figure 1 except for CCQM-K53. Participants 4, 5, 7 and 11 do not contribute to the determination of the estimates $x_{ref,i}$ and the associated standard uncertainties $u(x_{ref,i})$.

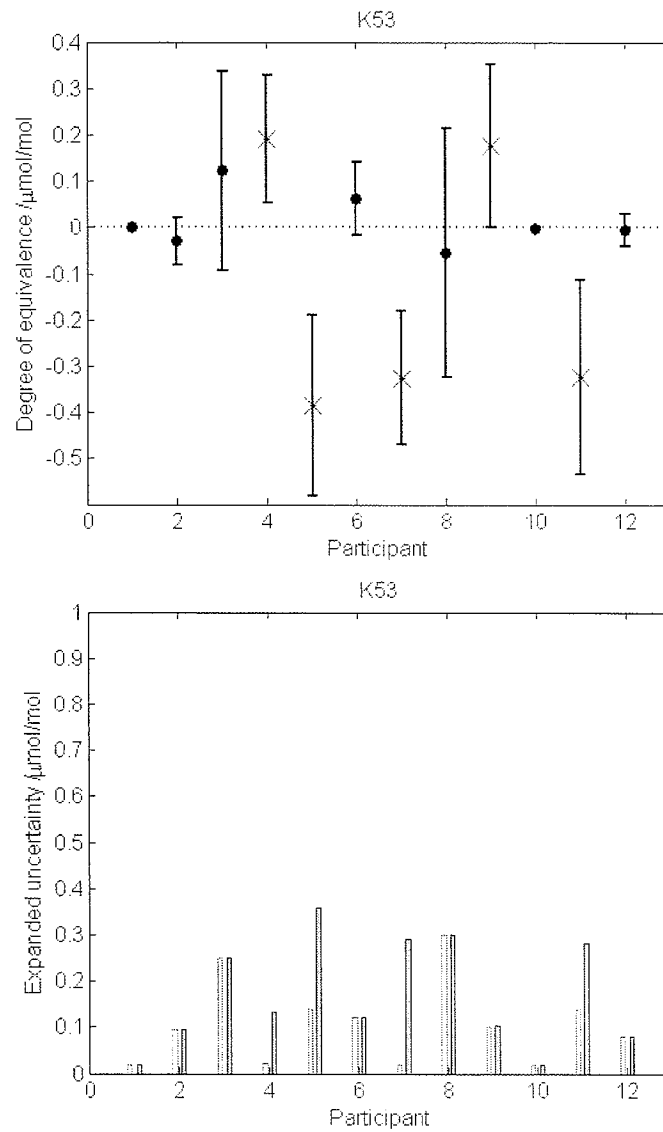


Figure 4: As Figure 3 except participants 4, 5, 7, 9 and 11 do not contribute to the determination of the estimates $x_{\text{ref},i}$ and the associated standard uncertainties $u(x_{\text{ref},i})$.

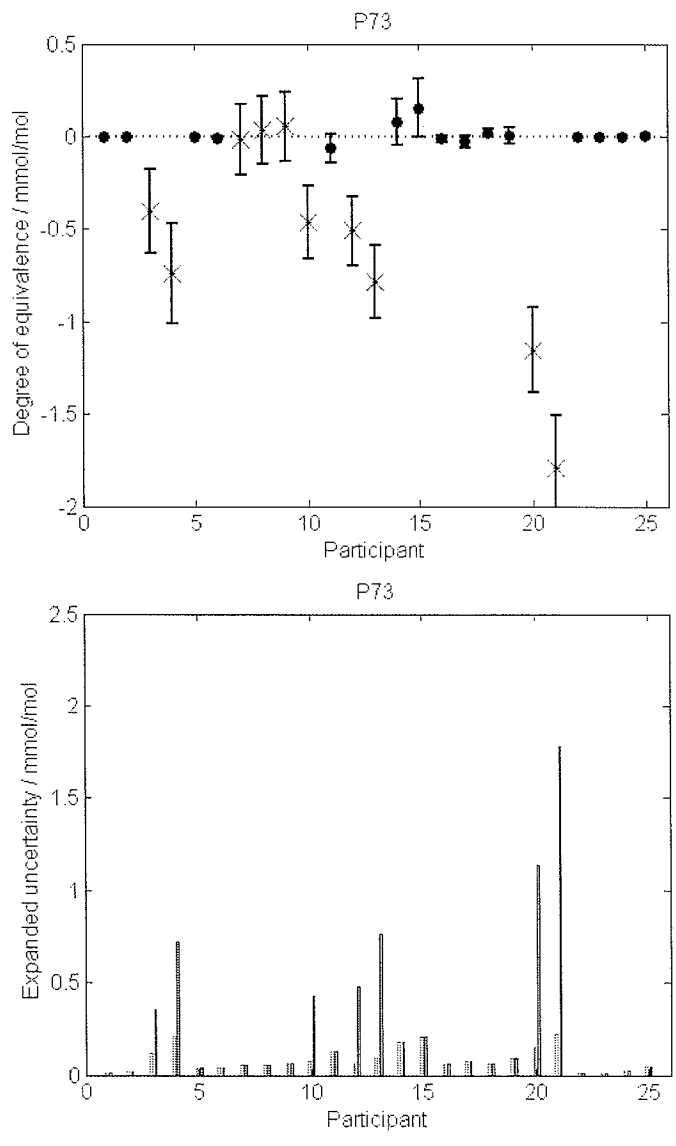


Figure 5: As Figure 1 but for CCQM-P73. Participants 3, 4, 7, 8, 9, 10, 12, 13, 20 and 21 do not contribute to the determination of the estimates $x_{ref,i}$ and the associated standard uncertainties $u(x_{ref,i})$.

B Technical basis

The technical basis for the above proposed approach is given using simple models of measurement in the sense of the GUM [1]). Quantities (such as Q) are generally denoted by upper case letters and values by the corresponding lower case letters (such as q). The standard uncertainty associated with a value q is denoted by $u(q)$.

The DoE (as a quantity) for participant i is expressed as

$$D_i = X_i - X_{\text{ref}}, \quad (4)$$

where X_i is a quantity of which x_i is a best estimate, and X_{ref} denotes a key comparison reference quantity.

For a completed KC, a best estimate x_{ref} (KCRV) of X_{ref} and the standard uncertainty $u(x_{\text{ref}})$ associated with x_{ref} are available. The corresponding DoE is $(d_i, U(d_i))$ with value component

$$d_i = x_i - x_{\text{ref}} \quad (5)$$

and $U(d_i)$ the uncertainty component for a 95 % level of confidence. $U(d_i)$ is given by

$$U(d_i) = ku(d_i), \quad (6)$$

where $u(d_i)$ is the standard uncertainty associated with d_i and k is the coverage factor (often taken as 2).

The case is considered when the DoE for participant i is inconsistent in that the magnitude of its value component exceeds the uncertainty component (figure 6):

$$|d_i| > U(d_i). \quad (7)$$

This case is addressed using a model of the form

$$X'_i = X_i + B_i \quad (8)$$

where B_i denotes an unknown effect, and X'_i denotes X_i modified by that effect. Take the best estimate of B_i as $b_i = 0$ and, as in section 1, denote the standard uncertainty associated with b_i by $u(b_i)$. We can consider a DoE D'_i for participant i that would have been obtained had we used X'_i in place of X_i (although we have no intention of making any explicit change). This DoE is based on the model

$$D'_i = X'_i - X_{\text{ref}} = X_i + B_i - X_{\text{ref}} = D_i + B_i,$$

using expressions (4) and (8). Hence the best estimate of D'_i is

$$d'_i = d_i + b_i = d_i. \quad (9)$$

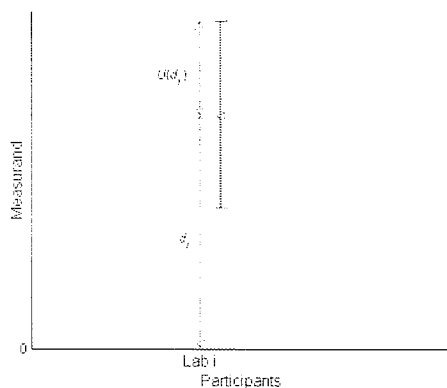


Figure 6: Magnitude of the value component d_i of the DoE exceeds the uncertainty component $U(d_i)$: participant i is not consistent.

since $b_i = 0$, with associated standard uncertainty $u(d'_i)$ given by

$$u^2(d'_i) = u^2(d_i) + u^2(b_i). \quad (10)$$

The CMC declared by participant i should have a standard uncertainty $u(\text{cmc}_i)$ that is no smaller than the standard uncertainty associated with its modified value of x_i , that is

$$u(\text{cmc}_i) \geq u(x'_i). \quad (11)$$

From expression (8), the standard uncertainty $u(x'_i)$ associated with x'_i is given by

$$u^2(x'_i) = u^2(x_i) + u^2(b_i). \quad (12)$$

For participant i to be consistent, we need to choose a standard uncertainty $u(b_i)$ associated with b_i such that

$$|d'_i| \leq U(d'_i). \quad (13)$$

It follows from inequality (13) and expressions (6), (9) and (10) that

$$d_i^2 \leq k^2 u^2(d'_i) = k^2 [u^2(d_i) + u^2(b_i)],$$

which implies that

$$u^2(b_i) \geq \frac{d_i^2}{k^2} - u^2(d_i).$$

Hence, expression (12) gives

$$u^2(x'_i) \geq u^2(x_i) + \frac{d_i^2}{k^2} - u^2(d_i),$$

which together with inequality (11) and expression (5) establishes inequality (1).