CCQM-GAWG strategy for comparisons and CMC claims

Preamble

This document describes a strategy for broader application of key comparisons and their results in the gas analysis area. For a selected number of components, matrices and amount-of-substance fraction ranges, a more flexible approach to supporting claims of calibration and measurement capabilities (CMCs) was established in April 2010. Based on the experience gained so far, the strategy is revisited and elaborated to address the needs of members of the CCQM Gas Analysis Working Group (GAWG) as well as those from members from similar working groups in the Regional Metrology Organisations (RMOs).

One of the extensions concerns claims for purity analysis. Notwithstanding the fact that a number of comparisons have been organised to assess measurement capabilities for purity analysis, there is a need to come up with an approach for supporting CMC claims based on existing key comparisons, irrespective of whether these are preparative or analytical.

Scope

This strategy applies to CMC claims that are submitted under the "How far the light shines statement" (HFTLS), without further evidence.

Key comparisons in the gas analysis area

Key comparisons in the gas analysis area focus on demonstrating competence with respect to

- The preparation of static and dynamic reference standards for gas analysis
- Purity analysis
- Analytical verification of composition
- The services provided

The services provided can be distinguished between the measurement of the composition of a gas mixture (e.g., CCQM-K46, CCQM-K77), or the provision of a gas mixture with a fully characterised composition (e.g. CCQM-K53, CCQM-K82). A third type of service concerns the purity analysis (e.g., CCQM-K66).

In some key comparisons, a specific challenge is the main subject, which can be analytical (natural gas, refinery gas, low levels of sulphur dioxide), reactive components (ammonia, ethanol), or a combination of such challenges.

The GAWG shall agree for what CMCs a key comparison provides support. Such a “HFTLS”-statement shall consider the relevance of the demonstrated competence for:

a) Other ranges for the component(s) and matrix being subject of the key comparison;
b) Other components in the same matrix;
c) Other matrices with the same component(s);
d) Purity analysis;
e) Other competences.

Strategy for selecting comparison studies for the GAWG work programme

To align with the strategy of the CCQM, comparisons are divided into four classes. In alignment with other CCQM working groups, these are referred to as track A, C and D comparisons. A description of each is provided below and figure 1 illustrates these with a Venn diagram.

Track A - Compliance with the objectives of the CIPM-MRA requires key comparisons to underpin the competencies claimed by an NMI/DI. This aims to support demonstration of equivalence of CMC claims of the various services that an NMI/DI provides. Comparisons are designed to test the core skills and competencies required in gravimetric preparation, analytical certification and purity analysis of the gas mixtures in Table 1, where a number of NMIs/DIs have consistently demonstrated equivalence since the GAWG was established. Track A key comparisons are intended to assess the basic capabilities of NMIs active in gas analysis.

Components and matrix	**Amount-of-substance fraction range**
CO, CO_2, O_2, CH_4, C_2H_6 or C_3H_8 in N_2 or air	10 µmol/mol – 500 mmol/mol
CO, CO_2, C_3H_8 and O_2 in N_2	10 µmol/mol – 500 mmol/mol
SO_2 in N_2 or air	100 µmol/mol – 500 mmol/mol

Table 1 Components and amount-of-substance fraction ranges to assess core competences

Track C – Verification of the equivalence of measurement services provided by NMI/DIs is one objective of the CIPM-MRA. Comparisons in Track C are designed to support CMC claims for components which present an analytical challenge and are prepared and analysed using competencies beyond those required for track A. Track C key comparisons address issues such as unstable and reactive gas mixtures. Examples are CH_4 at an amount-of-substance fraction below 10 µmol/mol (e.g. CCQM-K82 with CH_4 in air at 1.8 µmol/mol), NO_2, NH_3 and ethanol.

Track D – Includes all other studies (stand-alone studies and studies run in parallel to key comparisons). These studies are not intended to lead to CMCs or to support CMC claims in the KCDB.

In the report of track A key comparisons, there shall be a "HFTLS"-statement for use of the key comparison as a track C key comparison (the *default* scheme), complementary to the statement for use as track A key comparison (the *flexible* scheme) as detailed later in the document.

Strategy for CMC claims

Guidance for the *default* scheme to support CMCs (Track A and C)

1. CMCs for individual components shall be evidenced by a dedicated key comparison for the component being claimed.
2. The uncertainty that can be claimed cannot be less than the submitted expanded uncertainty by the participant (assuming that equivalence is demonstrated with the Key Comparison Reference Value (KCRV)). Otherwise, the uncertainty cannot be less than the submitted standard uncertainty added in quadrature to the difference between the submitted value and the KCRV, multiplied with an appropriate coverage factor.

   Example
   Suppose a laboratory states an amount-of-substance fraction propane of 993.0 µmol/mol ± 0.7 µmol/mol (k = 2). Let the key comparison reference value for the transfer standard be 993.1 µmol/mol ± 0.6 µmol/mol (k = 2).

   The difference d_i is computed as
   $d_i = x_i - x_{\mathrm{KCRV}} = 993.0 - 993.1 = -0.1$ µmol/mol
   The standard uncertainty associated with d_i is obtained by combining the standard uncertainties of the laboratory result and the key comparison reference value.
   $u(d_i) = \sqrt{u^2(x_i) + u^2(x_{\mathrm{KCRV}})} = \sqrt{0.35^2 + 0.30^2} = 0.46$ µmol/mol
   Using a coverage factor k = 2, the expanded uncertainty associated with the difference is 0.92 µmol/mol. As the absolute value of the difference d_i is less than its expanded uncertainty, the laboratory result is consistent with the reference value. Hence, the laboratory can support its reported measurement uncertainty by its participation in the key comparison and may use their reported measurement uncertainty to underpin appropriate CMC claims.

   Suppose now that another laboratory reports in the same key comparison for the same transfer standard a result of 992.0 µmol/mol ± 0.7 µmol/mol (k = 2). The difference with respect for this laboratory is
   $d_i = x_i - x_{\mathrm{KCRV}} = 992.0 - 993.1 = -1.1$ µmol/mol
   As this laboratory also states an expanded uncertainty of 0.7 µmol/mol, the expanded uncertainty associated with d_i does not change. As in this case
   $|d_i| > U(d_i)$
   the result is inconsistent with the reference value. Hence, the laboratory cannot support its claimed measurement uncertainty with this key comparison. Instead, the laboratory can claim an uncertainty that takes into account the observed bias d_i = –1.1 µmol/mol. The performance of the laboratory in the key comparison is good enough to support an expanded uncertainty of
   $U_{\mathrm{CMC}} = k \cdot \sqrt{d_i^2 + u^2(x_i)} = 2 \cdot \sqrt{(-1.1)^2 + 0.35^2} = 2 \cdot 1.15 = 2.3$ µmol/mol

3. The HFTLS statement contains an amount fraction range defined by a lower amount fraction boundary (LB) and an upper amount fraction boundary (UB). LB is equal to the smallest absolute expanded uncertainty that can be claimed on the basis of a participant's result in the key comparison. The UB is usually 500 mmol/mol (the transition point where a component becomes the matrix). When the physical properties of the component prevent mixtures being prepared at 500 mmol/mol (e.g., because of condensation issues), an alternative UB shall be agreed by the GAWG and stated in the key comparison report.

4. The minimum absolute expanded uncertainties that can be claimed over the amount fraction range in the HFTLS statement are as follows:

    a) If the key comparison reference value (x_{KCRV}) ≥ 10 µmol/mol:

    For amount fractions *y* between LB and 10 µmol/mol, CMCs are acceptable that are equal to or greater than the absolute expanded uncertainty calculated at 10 µmol/mol (from the participant's relative uncertainty in the key comparison (LB/ x_{KCRV} x 10)).
    For $y \geq 10$ µmol/mol, CMCs are acceptable that are equal to or greater than the participant's relative expanded uncertainty.

    Example:
    If x_{KCRV} = 1000 µmol/mol and U = 1 µmol/mol, the best CMCs claims are:
    From 1 (LB) to 10 µmol/mol (0.01 µmol/mol)
    From 10 µmol/mol to UB (0.1 % relative)

    b) If 1 µmol/mol ≤ x_{KCRV} < 10 µmol/mol:

    For amount fractions *y* between LB and 10 µmol/mol, CMCs are acceptable that are equal to or greater than LB.
    For $y \geq 10$ µmol/mol, CMCs are acceptable that are equal to or greater than the relative uncertainty calculated at 10 µmol/mol from the participant's absolute uncertainty in the key comparison (LB/ 10 x 100).

    Example:
    If x_{KCRV} = 2 µmol/mol and U = 0.02 µmol/mol, the best CMCs claims are:
    From 0.02 (LB) to 10 µmol/mol (0.02 µmol/mol)
    From 10 µmol/mol to UB (0.2 % relative)

    c) If x_{KCRV} < 1 µmol/mol:

    For amount fractions *y* between LB and x_{KCRV}, CMCs are acceptable that are equal to or greater than the absolute expanded uncertainty (LB).
    For $y \geq x_{KCRV}$, CMCs are acceptable that are equal to or greater than the participant's relative expanded uncertainty in the key comparison.

    Example:
    If x_{KCRV} = 0.8 µmol/mol and U = 0.08 µmol/mol, the best CMCs claims are:
    From 0.08 (LB) to 0.8 µmol/mol (0.08 µmol/mol)
    From 0.8 µmol/mol to UB (10 % relative)

    In each case LB corresponds to the expanded uncertainty reported by the participant (*U*). This extrapolation scheme is valid for all track A and C comparisons when approved by the GAWG and published in the key comparison report.

5. The GAWG maintains lists of key comparisons that can be used as evidence to support submitted CMC claims. The list of key comparisons that can be used as evidence is reviewed every year by the GAWG and made available to the NMIs in a timely manner. Key comparisons that were published more than ten years ago can only be used to support CMC claims where no replacement exists. Key comparisons published more than fifteen years ago cannot be used to support CMC claims.

Guidance for the *flexible* scheme to support CMCs (Track A)

- Guidelines from the previous section apply, with the exception of number 1.
- CMC claims for all core competencies are evidenced by the last **three** key comparisons in track A. Previous track A key comparisons include CCQM-K1(a-d), CCQM-K3, CCQM-K52, CCQM-K53, CCQM-K76, CCQM-K111 and CCQM-K120b.
- Future track A key comparisons shall involve a simple mixture (one or a few non-interfering components in air or nitrogen) at a nominal amount fraction > 10 µmol/mol. Air is defined as a mixture of approximately 21 cmol/mol of oxygen and 79 cmol/mol of nitrogen.
- The list key comparisons in track A that are eligible for supporting CMC claims shall be reviewed and updated by the GAWG every year.

NMIs can choose to adopt the flexible CMC scheme if they meet the following 4 criteria:

1. An NMI shall have participated in at least **three** key comparisons in track A organised by the GAWG. *The same criterion applies to any new NMI*
2. An NMI shall continue to participate in at least **one** key comparison in track A every **three years**, when available through the GAWG. *This includes RMO linked key comparisons. In some cases, the GAWG may not organise a suitable comparison every 3 years. NMIs will not be penalised as a result of this.*
3. It shall establish a link between CMCs and performance in track A key comparison in accordance with GAWG/09-07. *A quantitative link like the one proposed by Maurice Cox (GAWG/09-07) is essential for an efficient process.*
4. It shall have a quality system in accordance with ISO/IEC 17025 and ISO 17034 and a measurement capability that covers all CMCs.

If an NMI ceases to meet these criteria for submitting flexible CMCs, it shall resubmit all CMCs for track A within established HFTLS statements under the default scheme in the upcoming cycle for submitting CMCs. NMIs that do not meet these criteria shall use the default scheme.

Implementation of the flexible scheme to support CMCs

- Track A key comparisons shall be organised by the GAWG.
- Any impurities in a mixture in a track A key comparison shall not present any additional measurement challenge, as agreed by the GAWG.
- Track A key comparisons shall have two statements of HFTLS: a dedicated statement that can be used for supporting CMC claims under the default scheme and a broad statement for use under the flexible CMC scheme.
- NMIs adopting the flexible CMC scheme shall have CMC claims for any track A components in the KCDB, judged by their pooled performance in the last three track A key comparisons.
- If an NMI does not demonstrate equivalence with the KCRV in a track A comparison and is using the flexible scheme, the value of the uncertainty used for the pooled uncertainty is the submitted uncertainty added in quadrature to the difference between the submitted value and the KCRV.
- For components in track A that have featured in a key comparison in the last **ten** years, NMIs can select to support CMCs for that particular component by either the dedicated key comparison or their pooled performance in the last three key comparisons in track A (whichever is the best reflection of their current capabilities).
- For NMIs adopting the flexible CMC scheme, an onsite-visit by peers is required to ensure that CMCs for **all track A gas mixtures in the KCDB** can be demonstrated. This should take place within the first **two** years of an NMI adopting the scheme and at least once every **five** years thereafter. This can include surveillance visits from national accreditation bodies auditing ISO/IEC 17025 and ISO 17034.

Guidance for CMC claims for purity analysis

- Future purity CMCs will be evidenced by the HFTLS statement in all key comparisons, without the requirement for dedicated purity comparisons.
- Purity CMCs for individual components can either be evidenced by a dedicated key comparison for the component and matrix being claimed (default scheme described earlier) or by a flexible approach if eligible (flexible scheme described earlier).
- The claimed uncertainties for purity for any track A components in the KCDB shall be compatible with the approach described under “Implementation of the flexible scheme to support CMCs”.
- Participating NMIs in key comparisons are required to report the results of their purity analysis with uncertainties, as far as these are relevant for the CMCs claims to be supported.

Guidance for applying excess variance to CMC claims

- Laboratories that demonstrate equivalence with the KCRV without the inclusion of the excess variance calculated from the submitted data can use their stated uncertainty as basis for supporting CMCs. The excess variance is explicitly tabled in the comparison report.
- Laboratories that can only demonstrate equivalence including the excess variance calculated for the dataset, should combine their stated uncertainty with the excess variance as basis for supporting CMCs.

If no excess variance is computed, the bias with respect to the key comparison reference value shall be combined with the stated standard uncertainty as described for the *default scheme*, item 2.

Guidance for linking RMO comparisons to track A key comparisons

Procedure

1. Comparisons can be organised by an RMO as a satellite to a track A key comparison organised by the GAWG for acceptance in the flexible CMC scheme.
2. The GAWG shall decide on the coordinating laboratories for future RMO comparisons during the planning stage of a track A key comparison (a minimum of 2 laboratories per RMO shall be involved in the track A key comparison organised by the GAWG).
3. The coordinating laboratory of an RMO linked comparison shall:
    a. preferably be a participant in the track A key comparison organised by the GAWG (i.e. one of the linking laboratories);
    b. have demonstrated equivalence with one or more laboratories having participated in the key comparison organised by the GAWG;
    c. avoid collusion through, e.g., the use of the same set of transfer standards in the CCQM and RMO key comparisons (for example by advising the participants in the first key comparison confidentially in the draft A stage of the comparison).
    d. submit prior to the track A key comparison a protocol to the GAWG for approval;
    e. submit a Key comparison report, to the RMO and then to the GAWG for approval.
4. The linking between the RMO comparison and GAWG track A key comparison shall be performed as described below.
5. NMIs, wishing to have a subsequent bilateral key comparison should seek a coordinating laboratory willing to provide such a comparison. Such a key comparison can however only be used in the track B scheme (direct support to CMCs), and not to replace a degree-of-equivalence obtained in the track A key comparison.

Linking

1. A link is only possible if
    a. the artefact(s) used have the same nominal composition;
    b. the linking comparison takes place within 2 years of publication of the CCQM track A key comparison;
    c. a link is demonstrable between the coordinating laboratories, if there is more than one.
2. For linking comparisons operated with a KCRV calculated from gravimetric gas mixture preparation, the procedure described in Metrologia **40** (2003) pp. 18–23 shall be followed.
3. An RMO comparison cannot be linked if the results from the linking laboratories are not equivalent in both comparisons (i.e., their results differ more than the expanded uncertainty expressed at a coverage level of 95%). In that case, the RMO comparison cannot be used under the flexible scheme.

Approval of the protocols of RMO track A key comparisons

1. The protocol shall contain all sections of the agreed protocol for the GAWG key comparison, amended as appropriate;
2. The protocol shall contain a section as to how the results of the RMO key comparison can be linked to the GAWG key comparison, including a proposal for the evaluation of the measurement uncertainty;
3. The GAWG shall identify a coordinator overseeing the RMO key comparisons; this coordinator shall report on the progress and any issues arising in due course of the set of track A key comparisons.

Annex A: Example calculations for track A (K52, K53 and K76) and track C (K82, K46 and K93)

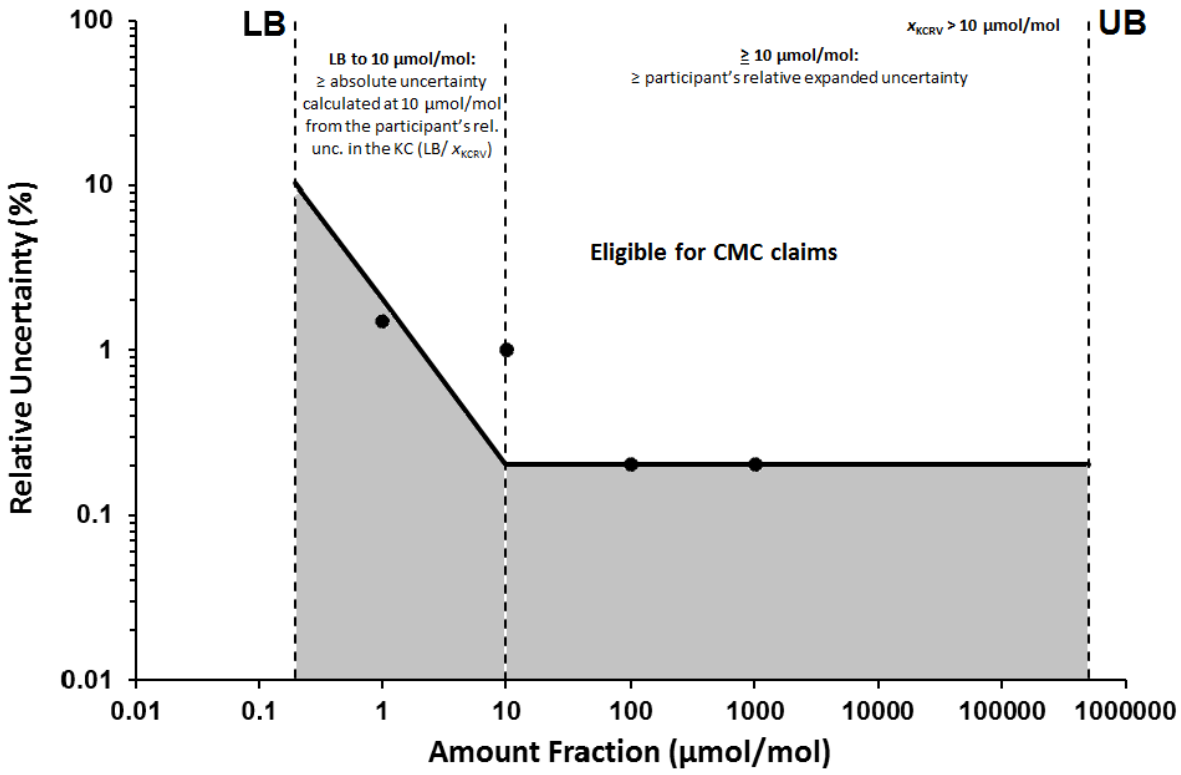

Figure 2 Illustration of the minimum expanded uncertainties that can be claimed vs amount fraction for K76 (SO_2 in nitrogen at (100.23 ± 0.34) µmol/mol), where NPL has submitted (100.13 ± 0.20) µmol/mol and demonstrated equivalence with the KCRV. The solid line show calculations using the model proposed in this document. Circles show actual CMCs. The unshaded region shows the eligible CMC claims (> 10 % at 0.2 µmol/mol, > 0.2 % for 10 µmol/mol and above)

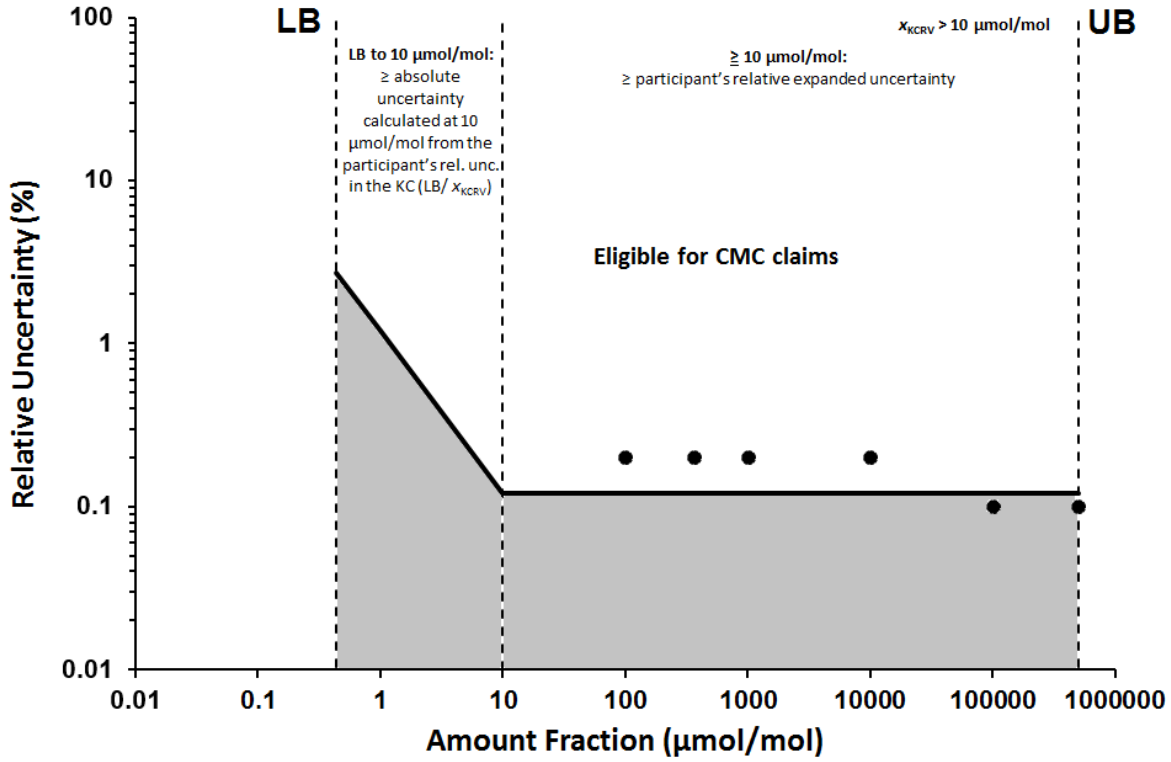

Figure 3 Illustration of the minimum expanded uncertainties that can be claimed vs amount fraction for K52 (CO_2 in nitrogen at (364.15 ± 0.59) µmol/mol), where NPL has submitted (364.39 ± 0.44) µmol/mol and demonstrated equivalence with the KCRV. Solid lines show calculations using the model proposed in this document. Circles show actual CMCs. The unshaded region shows the eligible CMC claims (> 2.72 % at 0.44 µmol/mol, > 0.12 % for 10 µmol/mol and above).

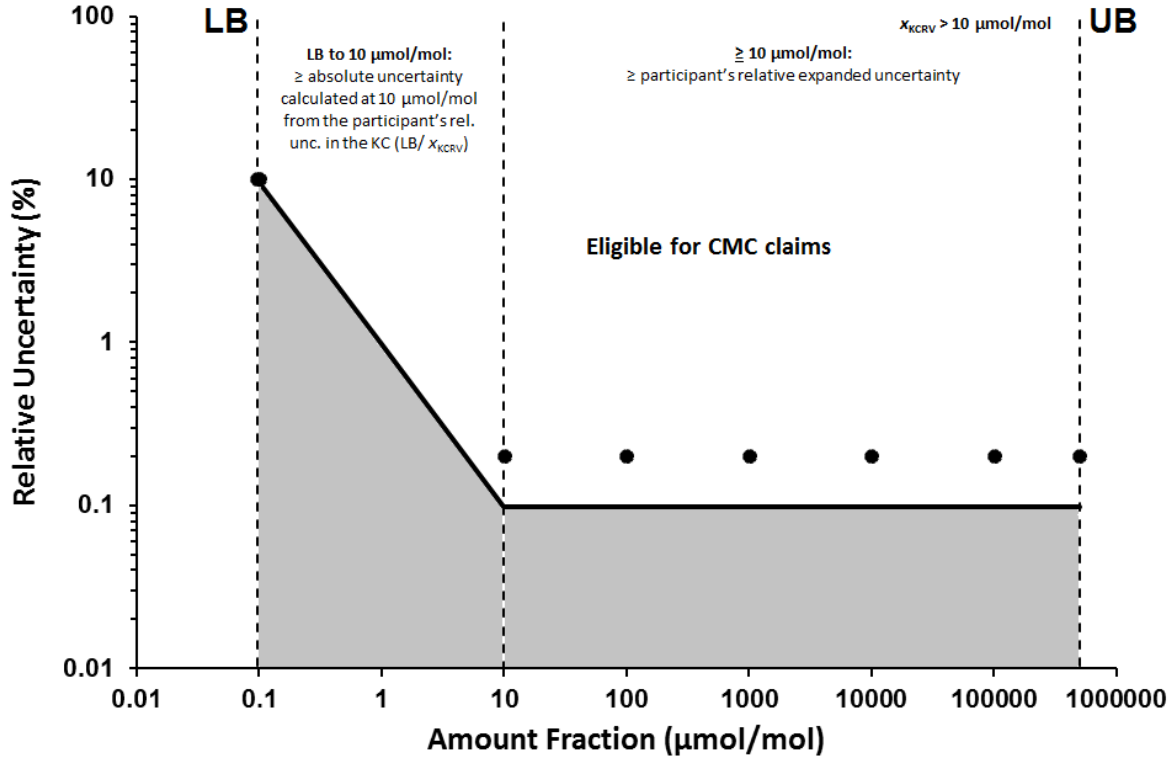

Figure 4 Illustration of the minimum expanded uncertainties that can be claimed vs amount fraction for a K53 (O_2 in nitrogen at (99.045 ± 0.056) µmol/mol), where NPL has submitted (99.002 ± 0.096) µmol/mol and demonstrated equivalence with the KCRV. Solid lines show calculations using the model proposed in this document. Circles show actual CMCs. The black circles show actual purity CMCs. The unshaded region shows the eligible CMC claims (> 9.7 % at 0.1 µmol/mol, > 0.097 % for 10 µmol/mol and above).

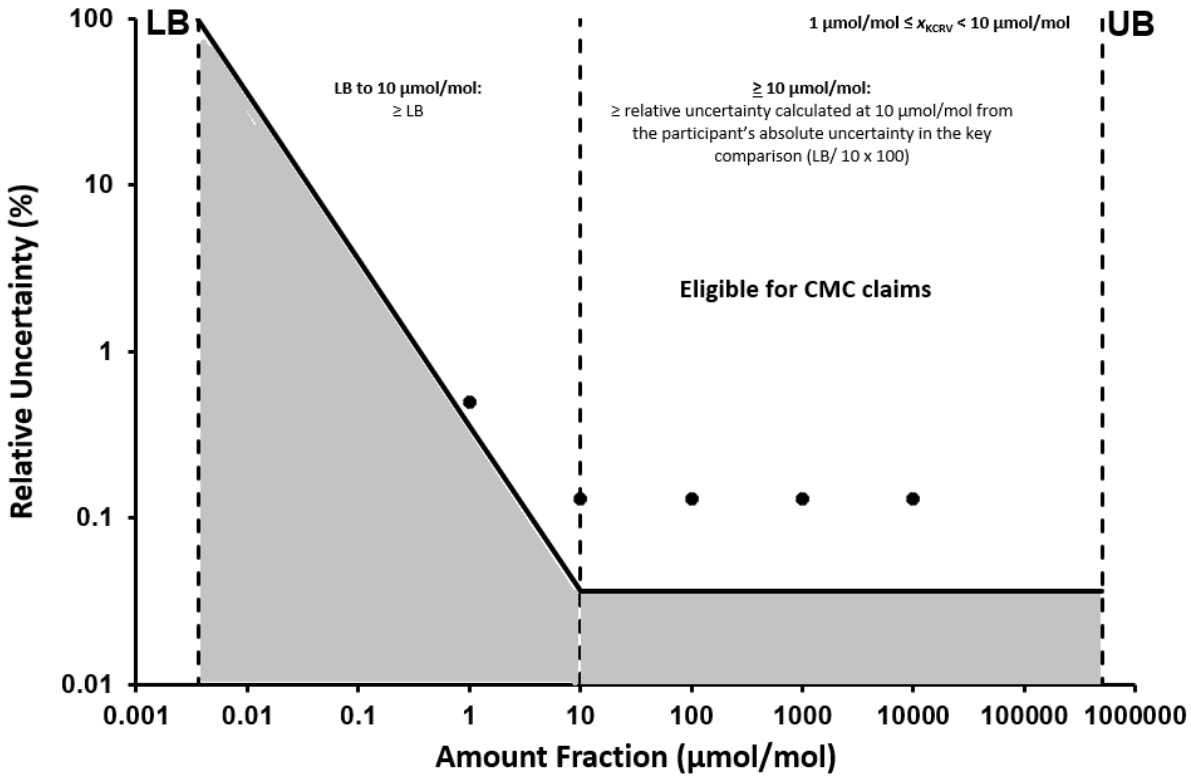

Figure 5 Illustration of the minimum expanded uncertainties that can be claimed vs amount fraction for K82 (CH_4 in air at (1.8006 ± 0.0014) µmol/mol), where NPL has submitted (1.7994 ± 0.0036) µmol/mol and demonstrated equivalence with the KCRV. Solid lines show calculations using the model proposed in this document. Circles show actual CMCs. The unshaded region shows the eligible CMC claims (> 100 % at 0.0036 µmol/mol, 0.036 % for 10 µmol/mol and above).

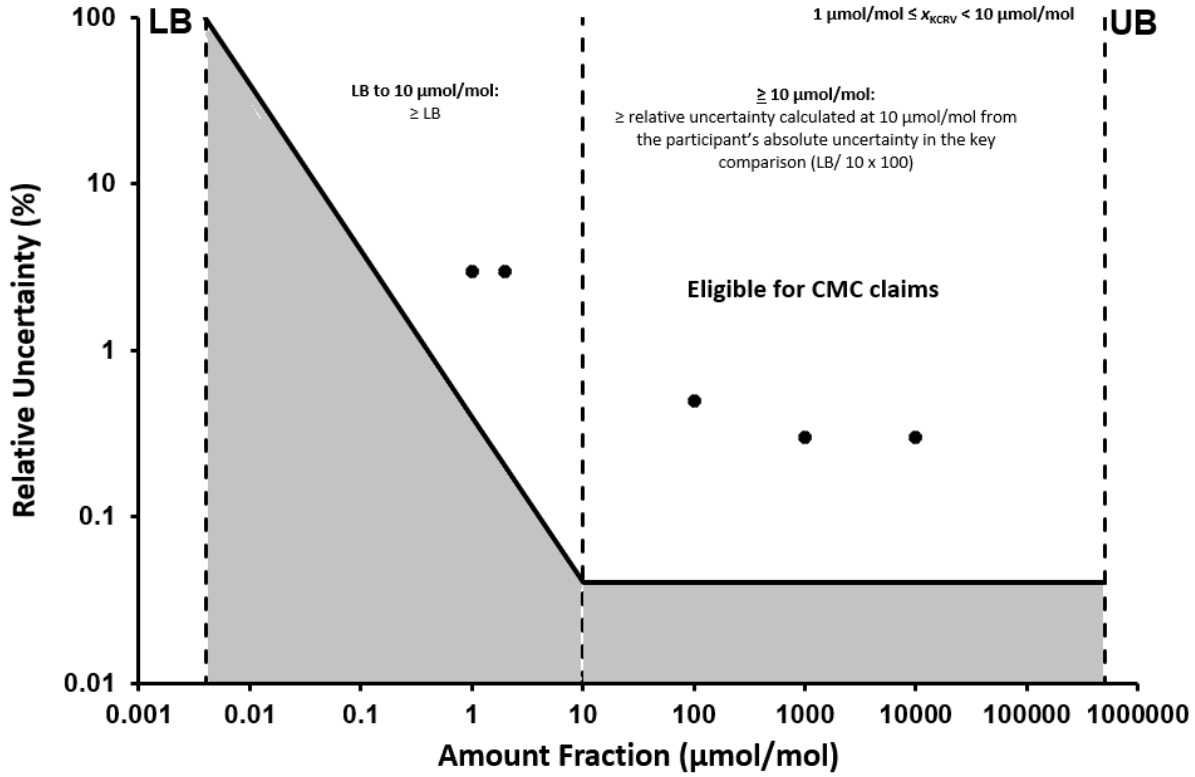

Figure 6 Illustration of the minimum expanded uncertainties that can be claimed vs amount fraction for K82 (CH_4 in air at (1.7978 ± 0.0014) µmol/mol), where VSL has submitted (1. 7983 ± 0.0040) µmol/mol and demonstrated equivalence with the KCRV. Solid lines show calculations using the model proposed in this document. Circles show actual CMCs. The unshaded region shows the eligible CMC claims (> 100 % at 0.004 µmol/mol, 0.04 % for 10 µmol/mol and above).

Example calculations for reactive gases (K46 and K93)

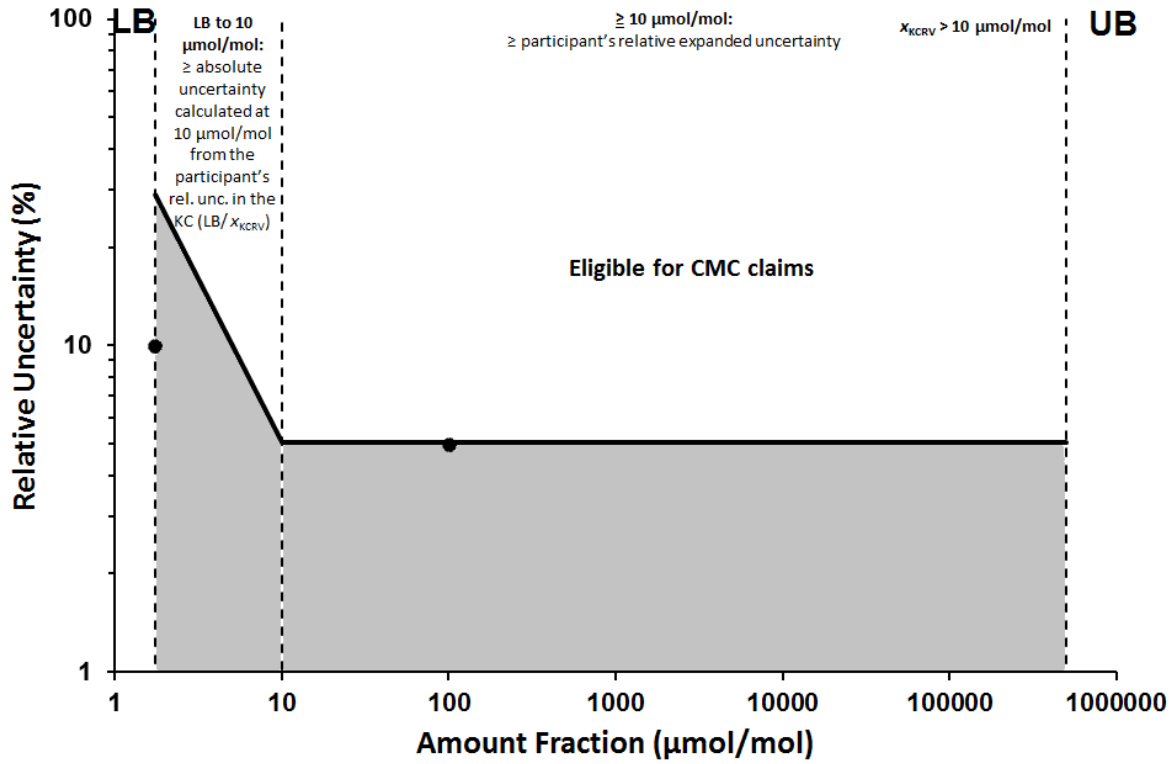

Figure 7 Illustration of the minimum expanded uncertainties that can be claimed vs amount fraction for K46 (NH_3 in nitrogen at (33.09 ± 1.03) µmol/mol), where NPL has submitted (34.52 ± 0.99) µmol/mol. Solid lines show calculations using the model proposed in this document. Circles show actual CMCs. The unshaded region shows the eligible CMC claims (> 28.97 % at 1.74 µmol/mol, 5.05 % for 10 µmol/mol and above).

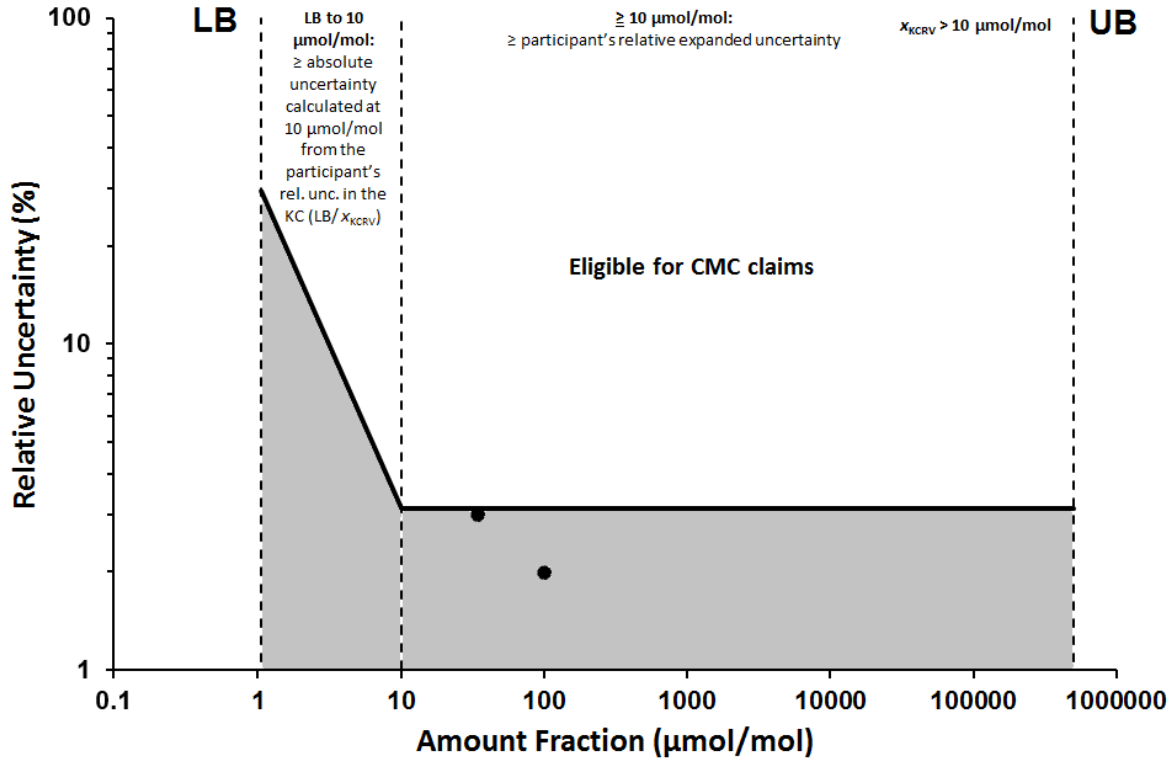

Figure 8 Illustration of the minimum expanded uncertainties that can be claimed vs amount fraction for K46 (NH_3 in nitrogen at (33.01 ± 0.76) µmol/mol), where VSL has submitted (33.8 ± 0.70) µmol/mol. Solid lines show calculations using the model proposed in this document. Circles show actual CMCs. The unshaded region shows the eligible CMC claims (> 28.59 % at 1.06 µmol/mol, 3.12 % for 10 µmol/mol and above).

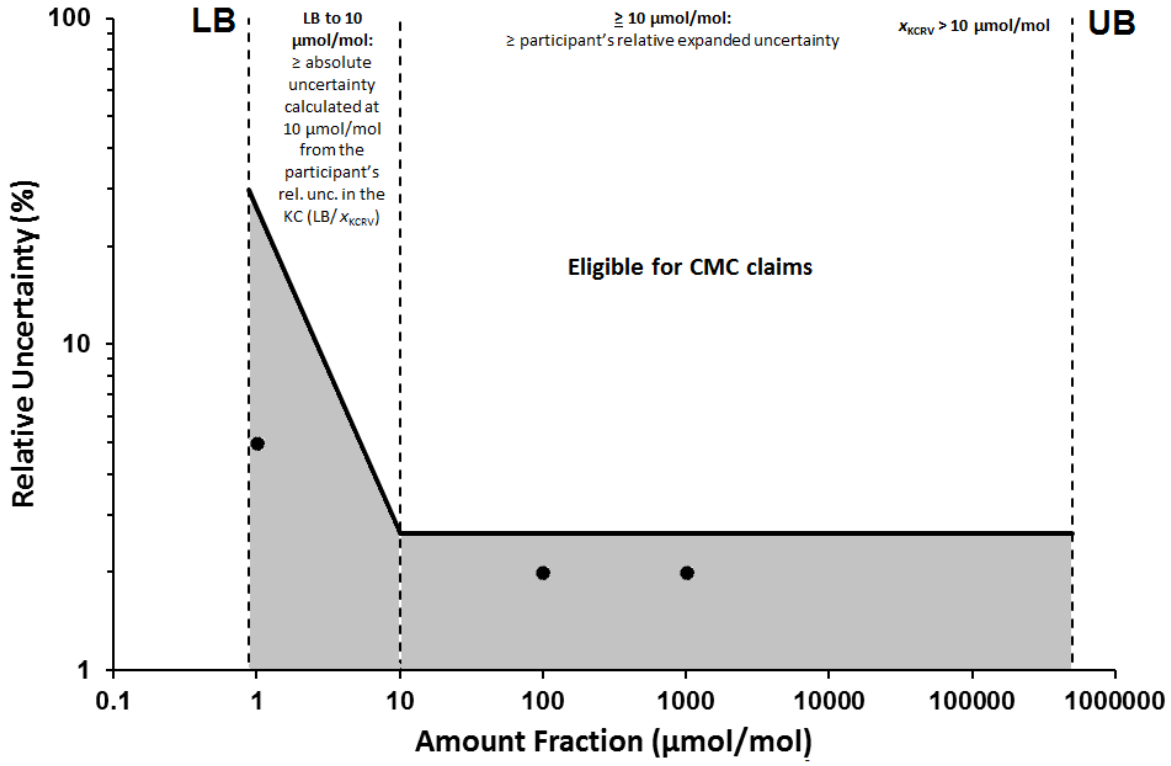

Figure 9 Illustration of the minimum expanded uncertainties that can be claimed vs amount fraction for K46 (NH_3 in nitrogen at (32.965 ± 0.577) µmol/mol), where VNIIM has submitted (33.7 ± 0.5) µmol/mol. Solid lines show calculations using the model proposed in this document. Circles show actual CMCs. The unshaded region shows the eligible CMC claims (> 29.67 % at 0.89 µmol/mol, 2.64 % for 10 µmol/mol and above).

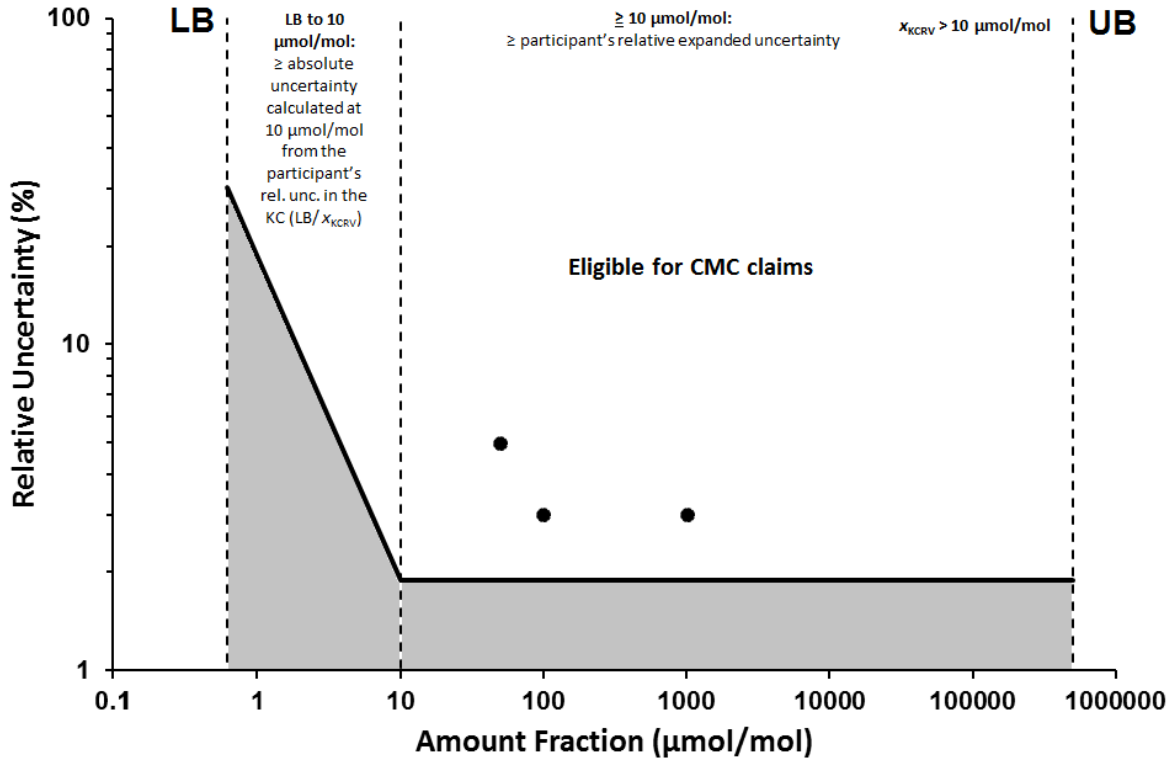

Figure 10 Illustration of the minimum expanded uncertainties that can be claimed vs amount fraction for K46 (NH_3 in nitrogen at (33.095 ± 0.689) µmol/mol), where KRISS has submitted (32.91 ± 0.62) µmol/mol. Solid lines show calculations using the model proposed in this document. Circles show actual CMCs. The unshaded region shows the eligible CMC claims (> 30.39 % at 0.62 µmol/mol, 1.88 % for 10 µmol/mol and above).

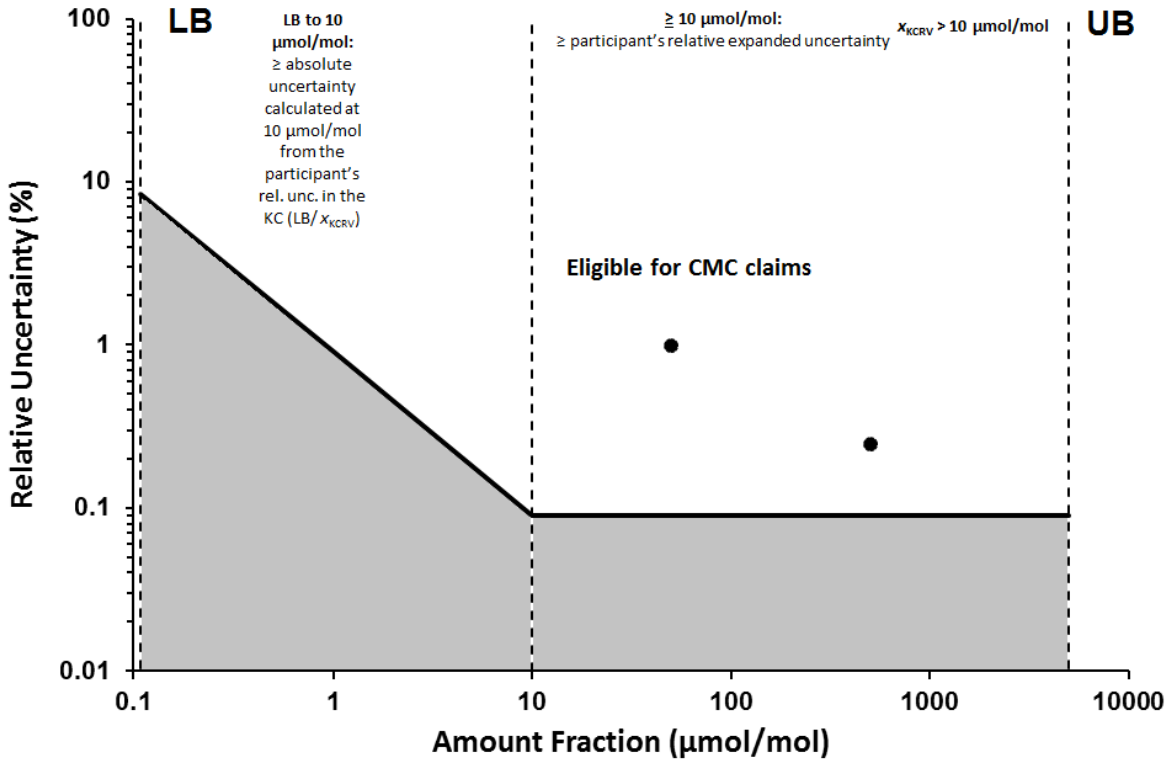

Figure 11 Illustration of the minimum expanded uncertainties that can be claimed vs amount fraction for K93 (ethanol in air at (120.04 ± 0.13) µmol/mol), where NPL has submitted (120.03 ± 0.11) µmol/mol. Solid lines show calculations using the model proposed in this document. Circles show actual CMCs. The unshaded region shows the eligible CMC claims (> 8.33 % at 0.11 µmol/mol, 0.09 % for 10 µmol/mol and above).

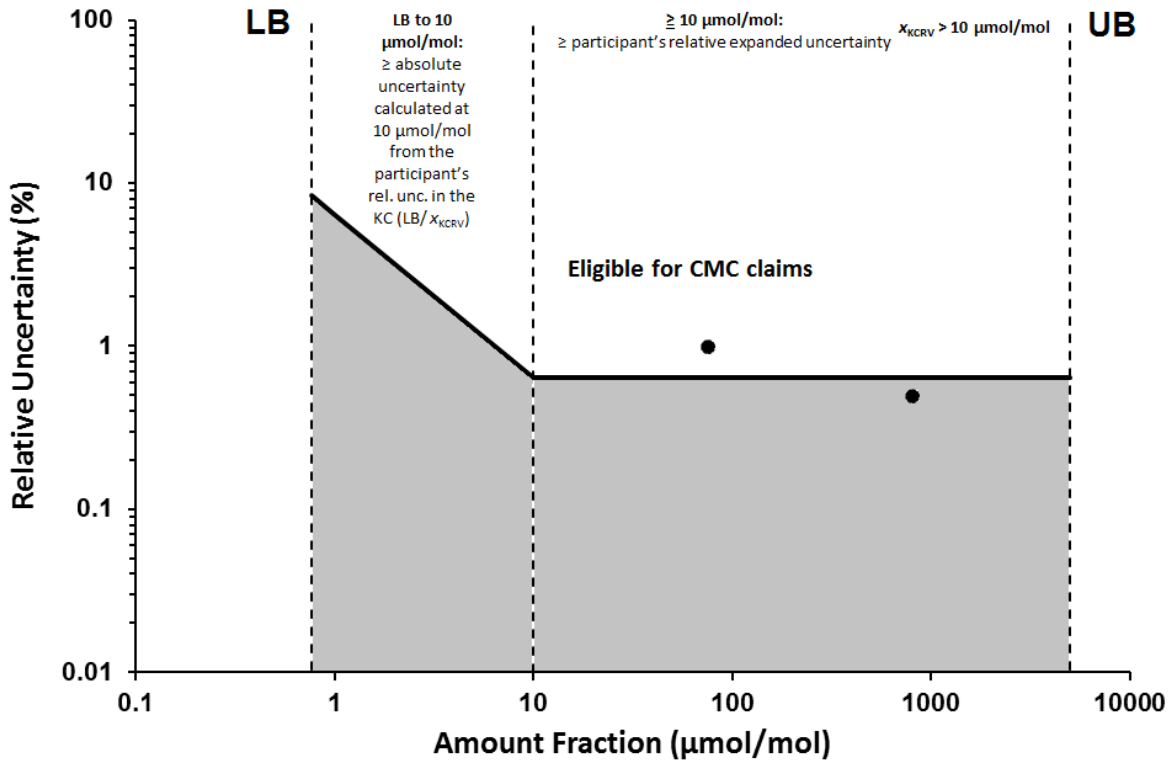

Figure 12 Illustration of the minimum expanded uncertainties that can be claimed vs amount fraction for K93 (ethanol in air at (118.85 ± 0.41) µmol/mol), where VSL has submitted (119.5 ± 0.4) µmol/mol. Solid lines show calculations using the model proposed in this document. Circles show actual CMCs. The unshaded region shows the eligible CMC claims (> 8.33 % at 0.76 µmol/mol, 0.64 % for 10 µmol/mol and above).

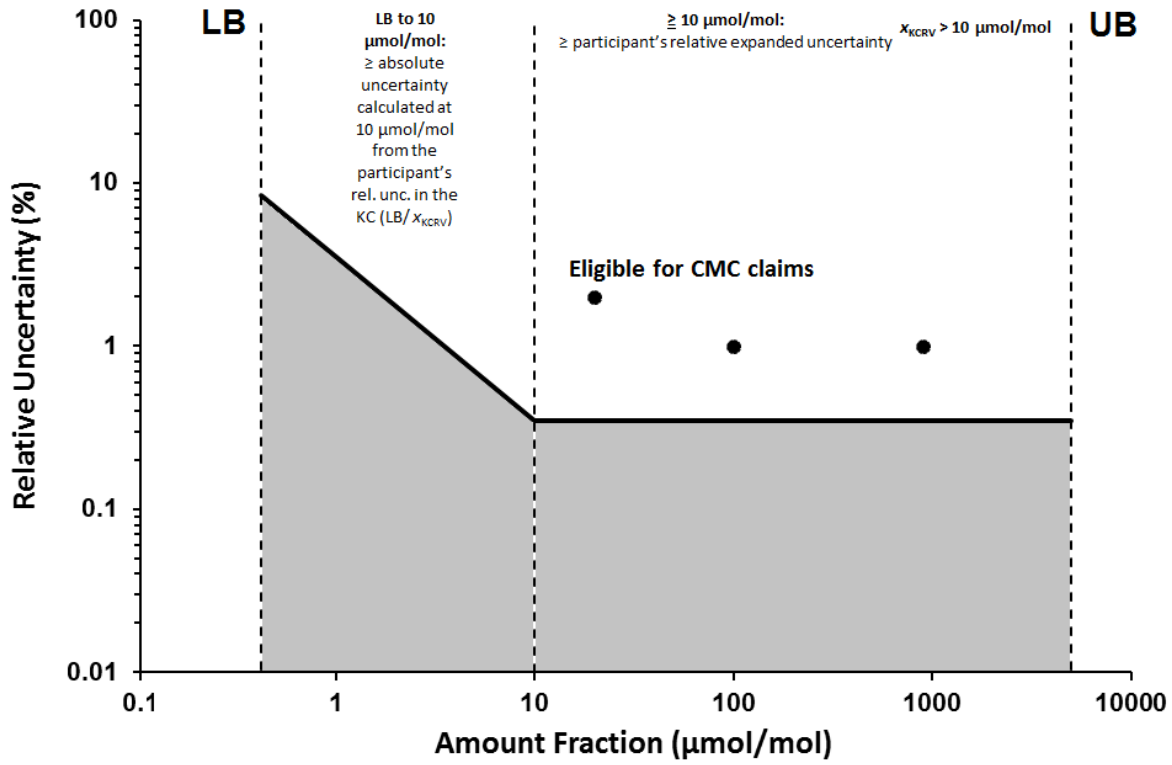

Figure 13 Illustration of the minimum expanded uncertainties that can be claimed vs amount fraction for K93 (ethanol in air at (120.03 ± 0.52) µmol/mol), where VNIIM has submitted (120.3 ± 0.4) µmol/mol. Solid lines show calculations using the model proposed in this document. Circles show actual CMCs. The unshaded region shows the eligible CMC claims (> 8.33 % at 0.42 µmol/mol, 0.35 % for 10 µmol/mol and above).

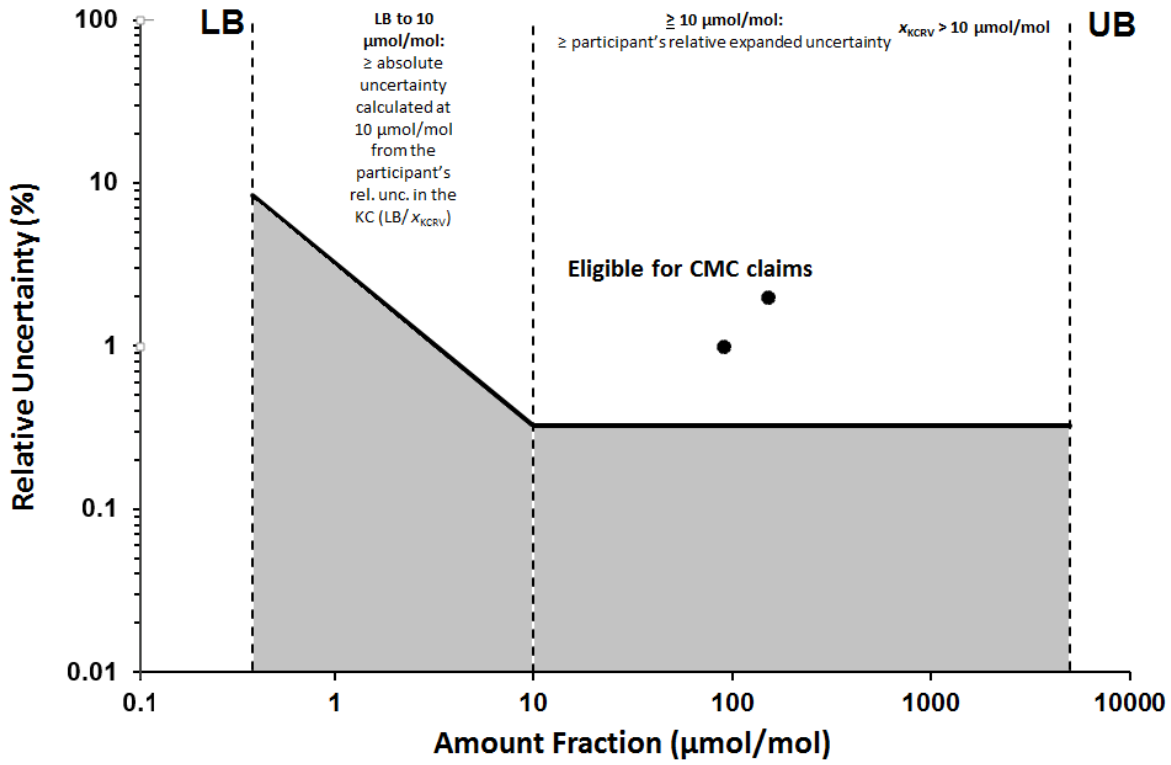

Figure 14 Illustration of the minimum expanded uncertainties that can be claimed vs amount fraction for K93 (ethanol in air at (120.16 ± 0.27) µmol/mol) where KRISS has submitted (119.87 ± 0.26) µmol/mol. Solid lines show calculations using the model proposed in this document. Circles show actual CMCs. The unshaded region shows the eligible CMC claims (> 8.33 % at 0.39 µmol/mol, 0.32 % for 10 µmol/mol and above).

Example calculations for pooling data under the flexible scheme

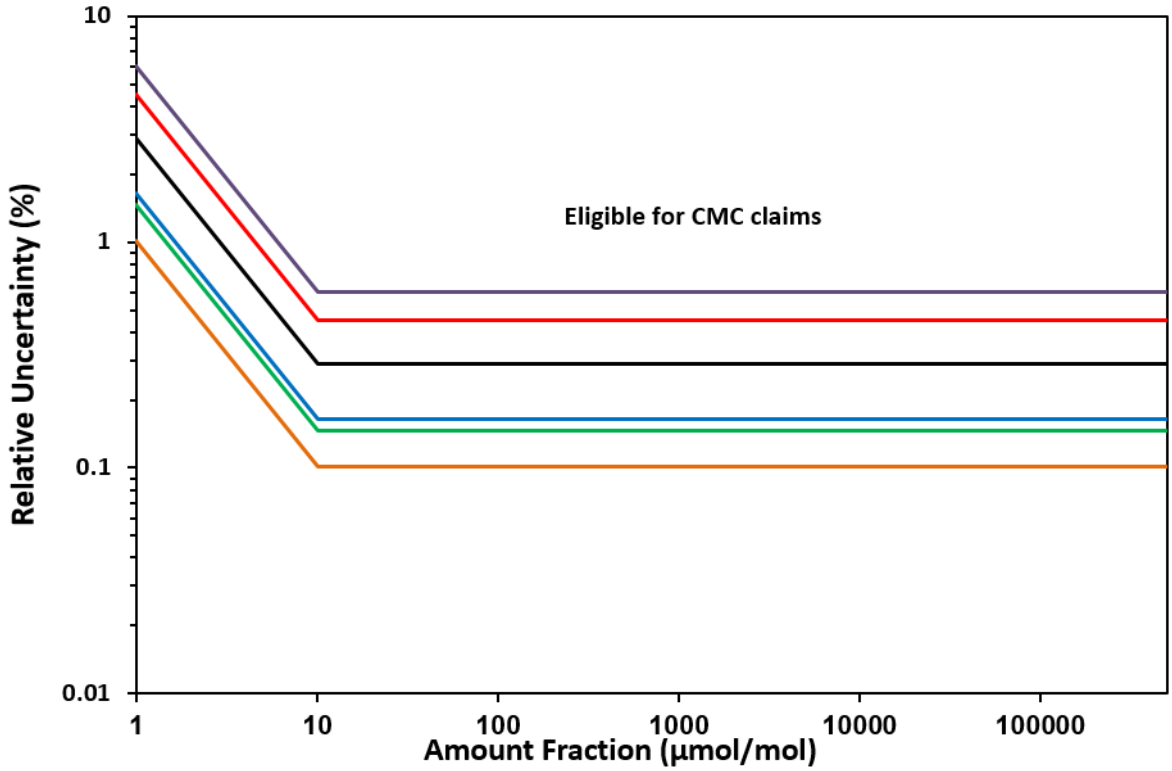

Figure 15 Illustration of the minimum expanded relative uncertainties that can be claimed vs amount fraction for NPL (blue), VSL (orange), VNIIM (red), NIST (green), LNE (purple) and KRISS (black) based on pooled data from the last 3 track A comparisons (K52, K53 and K76).

Example

NPL's relative expanded uncertainties from three track A comparisons (K52, K53 and K76) were 0.122 %, 0.096 % and 0.200 % respectively.

$$\text{The pooled relative expanded uncertainty} = \sqrt{\frac{0.122^2 + 0.096^2 + 0.200^2}{3}} = 0.146 \ \%$$

As all track A comparisons have a nominal amount fraction greater than 10 µmol/mol, for amount fractions *y* between LB and 10 µmol/mol, CMCs are acceptable that are equal to or greater than the absolute uncertainty calculated at 10 µmol/mol from the participant's pooled relative expanded uncertainty (in this case 0.146 %, hence 0.0146 µmol/mol) which equates to 1.46 % at 1 µmol/mol (as shown in figure 15).

For $y \geq 10$ µmol/mol, CMCs are acceptable that are equal to or greater than the participant's pooled relative expanded uncertainty, in this case 0.146 %.