Guidelines on Calibration and Measurement Capability (CMC) claims for Ozone

GAWG 2010_03 (Revised and re-issued January 2010)

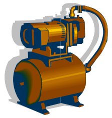
1. Matrix
2. Uncertainty of the ozone absorption cross-section
3. Dissemination range (specially the lower part)
4. Formulation of the CMC (equation)
5. Uncertainty of the calibrated instrument
6. Link with the performance in BIPM.QM-K1

1. THE MATRIX

	Range nmol/mol	Absolute uncertainty nmol/mol	Range nmol/mol	Relative uncertainty %(rel)	air / synth air
Exisiting EUROMET CMCs					
CHMI	10 to 100	2.3 to 2.4	100 to 1000	2.4 to 2.1	air
FMI	5 to 100	2.7			synth air
	100 to 500	2.7 to 12			synth air
INRIM	0 to 100	2	100 to 1000	2	synth air
LNE	0 to 100	2	100 to 1000	2	air
UBA(D)	3 to 100	1 to 2	100 to 1000	2	synth air
NPL	20 to 100	2	100 to 1000	2 to 1.5	synth air
Nmi	20 to 100	2	100 to 500	2.0 to 1.6	air
METAS	0 to 1000	Q[1.1, 0.017x(O3)], x(O3) in nmol/mol			air
Outside EUROMET					
NIST	10 to 100	2	100 to 1000	2	air
KRISS	1 to 100	2	100 to 1000	2	air
NMISA	1 to 100	3	100 to 1000	3	air
New claims (Cycle IX)					
ISCIII	1 to 100	0.8	100 to 500	1.2	air

Issue:

Air from outside ?



compressed and purified air?

Consensus:

synthetic air or **purified air**

2. Uncertainty of the ozone absorption cross-section

Issue:
there is a consensus on the value of ozone absorption cross-section used in ozone photometers, but not on its uncertainty

Suggestion in BIPM/NIST paper:
All photometers use the value measured by Hearn[1] => Hearn uncertainty budget revisited to comply with the GUM:

Standard deviation of the mean (%)	0.43
Tube length (%)	0.54
McLeod gauge (%)	0.81
Combined relative uncertainty (%)	1.06
Expanded relative uncertainty (k=2) (%)	2.12

Consensus on this value

[1]Hearn A G, "The absorption of ozone in the ultra-violet and visible regions of the spectrum", *Proc. Phys. Soc.*, **78,** 932-940, 1961

3. Lowest limit of the measurement range

Issue: how to define the lowest limit of the measurement range? Published CMCs show a variety of values : 0, 1, 5, 10, 20 nmol/mol….

debate : limit of quantification or zero

Consensus: Lowest limit = zero

4. Formulation of the CMC

Issue: how to write the CMC when the uncertainty varies with the measurand?

Suggestion:

With an ozone photometer, the uncertainty can be described as a combination of

- components which are constants over the range :
  combined uncertainty $\boldsymbol{u}_{\mathrm{a}}$

- components which are proportional with the ozone mole fraction x :
  combined uncertainty $\boldsymbol{u}_{\mathrm{b}}\,\boldsymbol{x}$

The formulation should thus be:

$$u(x) = \sqrt{u_{\mathrm{a}}^2 + (u_{\mathrm{b}} x)^2}$$

The Q notation will be used

$$\mathrm{Q}[u_{\mathrm{a}}, u_{\mathrm{b}} x] = \sqrt{u_{\mathrm{a}}^2 + (u_{\mathrm{b}} x)^2}$$

Consensus on this formulation

Inclusion of the "device under test" uncertainty in ozone CMC uncertainty statements

Extract from the CIPM (open access) document CIPM/2007-11 "Calibration and measurement capabilities - A paper by the joint BIPM/ILAC working group"
document GAWG/08-64 (http://www.bipm.org/wg/CCQM/GAWG/Restricted/welcome.jsp)

"N5. Contributions to the uncertainty stated on the calibration certificate and which are caused by the client's device before or after its calibration or measurement at a laboratory or NMI, and which would include transport uncertainties, should normally be excluded from the uncertainty statement. Contributions to the uncertainty stated on the calibration certificate include the measured performance of the device under test during its calibration at the NMI or accredited laboratory. CMC uncertainty statements anticipate this situation by incorporating agreed-upon values for the best existing devices. This includes the case in which one NMI provides traceability to the SI for another NMI, often using a device which is not commercially available."

Proposition to include *u*(calibrated instrument)

"Contributions to the uncertainty stated on the calibration certificate include the measured performance of the device under test during its calibration at the NMI or accredited laboratory"

device under test = ozone analyser

calibration = linear regression between reference instrument and calibrated instrument

Performance of the device during its calibration =

- **repeatability**: standard deviation on 10 (single) successive measurements
- **intermediate precision**: stability of the regression parameters assessed during a few days

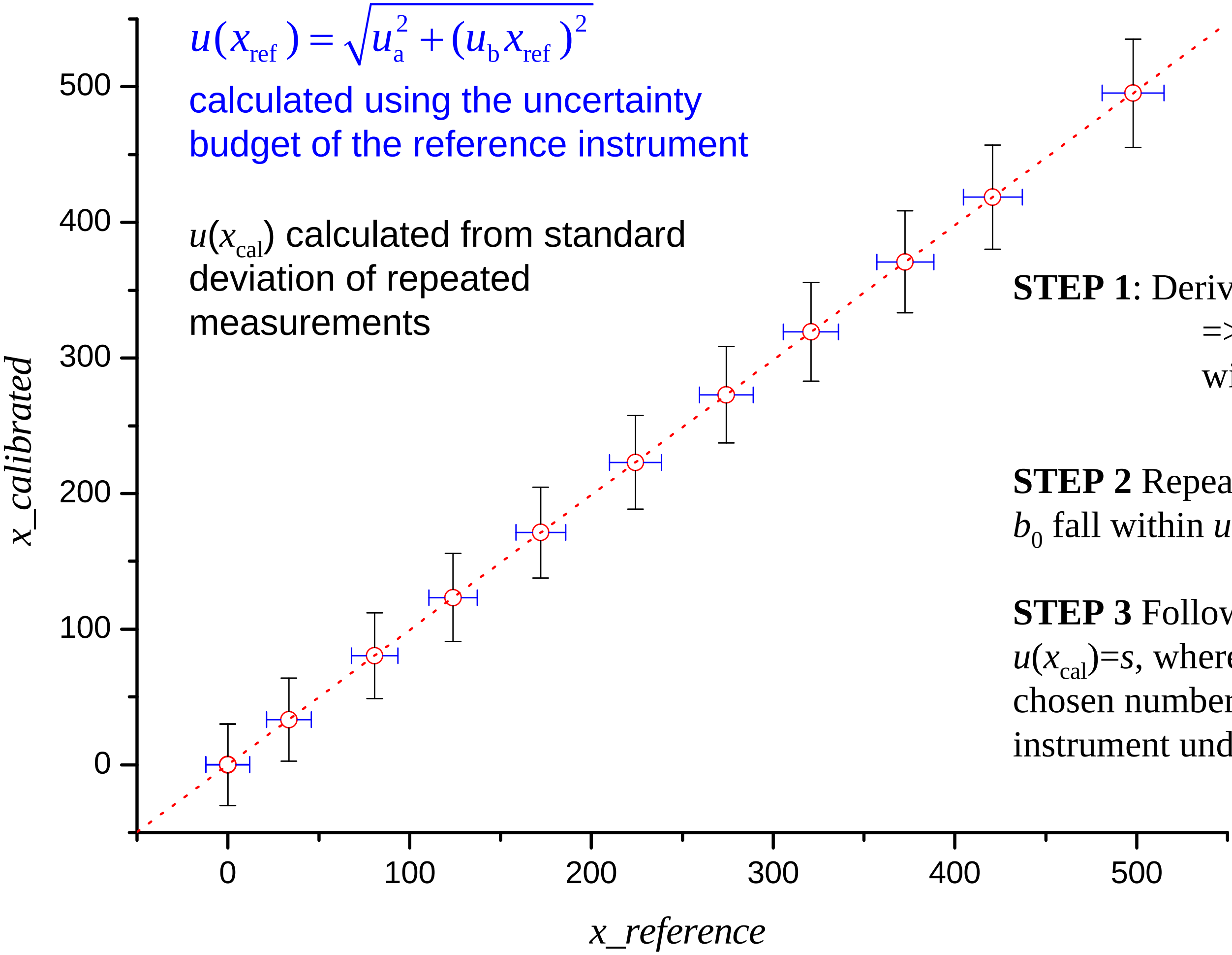
[1] The absorption cross-section uncertainty u_σ is not taken into account at that point for calculation reasons. It should be added and stated clearly in the CMC uncertainty statement.

Example of calculation to include *u*(calibrated instrument)

$u(x_{ref}) = \sqrt{u_a^2 + (u_b x_{ref})^2}$

calculated using the uncertainty budget of the reference instrument

$u(x_{cal})$ calculated from standard deviation of repeated measurements



STEP 1: Derive slope (b_1) and intercept (b_0) by GLS

=> $x_{ref} = b_0 + b_1\, x_{cal}$

with $u(b_0)$, $u(b_1)$ also given by GLS

STEP 2 Repeat calibration and ensure that values of b_0 fall within $u(b_0)$ and similarly for b_1 and $u(b_1)$.

STEP 3 Following STEP2, it is reasonable to set $u(x_{cal})=s$, where s is the standard deviation of the chosen number of repeat measurements by the instrument under calibration at each level.

Example of calculation to include *u*(calibrated instrument) (2)

STEP 4 prediction of the reference uncertainty

Applying Law of Propagation of Uncertainty to $x_{ref} = b_0 + b_1 x_{cal}$ gives

$$u(x_{ref}) = \sqrt{u^2(b_0) + b_1^2 u^2(x_{cal}) + x_{cal}^2 u^2(b_1) + 2x_{cal} \cdot u(b_0, b_1)}$$

Since b_1 is close to unity and b_0 close to zero, we can write $x_{ref} = x_{cal} = x$.
The correlation term is generally negligible and setting $u(x_{cal})=s_m$, the maximum standard deviation observed with the device under test, we arrive at

$$u(x) = \sqrt{u^2(b_0) + s_m^2 + x^2 u^2(b_1)}$$

Incorporating the uncertainty in the cross-section (u_σ) as agreed in Point 2 above leads to

$$u(x) = \sqrt{u^2(b_0) + s_m^2 + x^2 u^2(b_1) + x^2 u_\sigma^2}$$

Hence, using the Q notation, the uncertainty of the reference, <u>including the device under test and the absorption cross-section</u> is

$$\boxed{u(x) = Q\left[u_a', u_b' x\right]}$$

Where

$$u_a' = \sqrt{u^2(b_0) + s_m^2}$$

$$u_b' = \sqrt{u^2(b_1) + u_\sigma^2}$$

Are to be deduced from the calibration of the best device.

Example of BIPM-SRP27

Without DuT and without cross-section, uncertainty is Q[0.28 nmol/mol, 0.29%].
Including an uncertainty of the DuT (maximum standard deviation observed with the ozone analyser TEI49C maintained by the BIPM : 0.36 nmol/mol) and 1.06% for the cross-section would lead to an acceptable CMC of Q[0.52 nmol/mol, 1.11%].

6. Link between CMCs and performance in BIPM.QM-K1

Issue - Does the performance in BIPM.QM-K1 support the proposed CMC?

Answer - the following conditions must be met:

Condition 1: the laboratory result in BIPM.QM-K1 must "agree" with the reference value (easy to check in reports).

Condition 2: the part of the claimed uncertainty in the CMC coming from the standard must be >= the standard uncertainty reported in the key comparison.

Note: the declared absolute standard uncertainties for the ozone analysers calibration service at the BIPM, as stated on the BIPM website (http://www.bipm.org/en/bipm/calibrations/cms_qm.html), can be written as Q[0.52 nmol/mol, 1.11%] using the agreed notation. Those uncertainties are believed to be the lowest values achievable, and NMIs values are expected to be close or higher. Lower submitted values would need to be explained with a supporting documentation.